[illegible] T NO. 20

Scientific Assessment of Stratospheric Ozone: 1989

Volume II

Appendix: AFEAS Report

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION U.S.A.

UNITED KINGDOM DEPARTMENT OF THE ENVIRONMENT

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION U.S. DEPARTMENT OF COMMERCE

(NASA-TM-105443) SCIENTIFIC ASSESSMENT OF STRATOSPHERIC OZONE: 1989, VOLUME 2. APPENDIX: AFEAS REPORT (NASA) 478 p
CSCL 13B
G3/45
N92-15435
--THRU--
N92-15451
Unclas
0053035

WORLD METEOROLOGICAL ORGANIZATION
GLOBAL OZONE RESEARCH AND MONITORING PROJECT – REPORT NO. 20

Scientific Assessment of Stratospheric Ozone: 1989

Volume II
Appendix: AFEAS Report

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
UNITED KINGDOM - DEPARTMENT OF THE ENVIRONMENT
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
UNITED NATIONS ENVIRONMENT PROGRAM
WORLD METEOROLOGICAL ORGANIZATION
ALTERNATIVE FLUOROCARBON ENVIRONMENTAL ACCEPTABILITY STUDY (AFEAS)

TABLE OF CONTENTS

VII. LIQUID PHASE PROCESSES

VIII. OZONE DEPLETION POTENTIALS

IX. HALOCARBON GLOBAL WARMING POTENTIALS

X. IMPACT ON PHOTOCHEMICAL OXIDANTS INCLUDING TROPOSPHERIC OZONE

XI. NATURAL SOURCES

XII. BIOLOGICAL AND HEALTH EFFECTS

ANNEXES:

I. INTRODUCTION

Introduction

INTRODUCTION

This report is the outcome of the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS). AFEAS was organized to evaluate the potential effects on the environment of alternative compounds targeted to replace fully halogenated chlorofluorocarbons (CFCs). The objective was to:

Evaluate all relevant current scientific information to determine the environmental acceptability of the alternative fluorocarbons with special emphasis on:

- the potential of the compounds to affect stratospheric ozone,
- their potential to affect tropospheric ozone,
- their potential to contribute to model calculated global warming,
- the atmospheric degradation mechanisms of the compounds, in order to identify their products and hence,
- the potential environmental effects of the decomposition products.

The alternative compounds to be studied were hydrofluorocarborns (HFCs) with one or two carbon atoms and one or more each of fluorine and hydrogen and hydrochlorofluorocarbons (HCFCs) with one or two carbon atoms and one or more each of fluorine, chlorine and hydrogen. Because they contain hydrogen atoms, HFCs and HCFCs are less stable in the atmosphere than CFCs and thus have greatly reduced ozone depletion potentials. Additionally, HFCs do not contain chlorine atoms which are the key factor in ozone depletion. All compounds meeting the above criteria were evaluated where data exists but emphasis was placed on evaluating the following.

HCFC 123	CCl_2HCF_3
HCFC 141b	CCl_2FCH_3
HCFC 142b	$CClF_2CH_3$
HCFC 22	$CClF_2H$
HCFC 124	$CClFHCF_3$
HFC 134a	CF_3CFH_2
HFC 152a	CF_2HCH_3
HFC 125	CF_3CF_2H

The 52 scientists worldwide who were involved in AFEAS are listed in at the end of this report in Annex A. Experts prepared review papers on all aspects of the topic and each paper was reviewed by one or more scientists. In addition, model calculations were carried out on ozone depletion and halocarbon global warming potentials. A meeting was held in Boulder, Colorado in May 1989 under the chairmanship of Dr. R. T. Watson of the National Aeronautics and Space Administration (NASA) for experts and reviewers to discuss and reach a consensus. The papers in this report are the outcome of that meeting. Summaries of these papers form part of the August 1989 UNEP Science Assessment.

AFEAS was conducted by independent scientists but was organized and sponsored by fifteen CFC producers from around the world as part of cooperative industry efforts to study the safety and environmental acceptability of CFC alternatives. Companies participating in AFEAS are listed in Annex B.

INTRODUCTION

The statement of work used to initiate this project and the work assignments are given in Annex C.

This report consists of the individual papers prepared for the Boulder meeting, revised to take account of reviewers' opinions and discussion. They are arranged in sections according to subject matter. Where there is more than one paper on a topic, a combined summary and conclusions was prepared to introduce the papers in that section.

II. PHYSICAL PROPERTIES

Physical Properties of Alternatives to the Fully Halogenated Chlorofluorocarbons

Mark O. McLinden
Thermophysics Division
National Institute of Standards and Technology
Boulder, Colorado 80303

EXECUTIVE SUMMARY

This report is concerned with physical properties of possible alternatives to the fully halogenated chlorofluorcarbons (CFCs) used as refrigerants, solvents, and foam blowing agents. Specifically considered are the fixed points of the fluids (triple point and boiling point temperatures, and critical temperature, pressure, and density), vapor pressure, saturated liquid density, solubility in water, and hydrolysis rates. These properties directly or indirectly influence the fate of a chemical in the environment and also include the key thermophysical data necessary to estimate other properties. The fluids considered are hydrogen-containing halogenated methanes and ethanes. Included are R125, R22, R134a, R152a, R124, R142b, R123, R141b, and methyl chloroform.

A wide variety of data sources have been considered including published data, surveys and compilations of properties, and unpublished data provided by several of the companies which are members of the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) consortium. These data have been compiled and evaluated. Recommended values are tabulated for the fluid fixed points. The temperature dependencies of vapor pressure, saturated liquid density and solubility in pure water are presented in terms of correlations and as a tabulation of values calculated from these correlations.

The data vary greatly in quality and reliability, and are sometimes conflicting. At least limited data were available for the fixed points, vapor pressure and liquid density of all of the compounds. The values presented here are felt to be reasonable, although the lack of documentation in many cases makes an objective assessment of accuracy impossible, and revisions will certainly be necessary as additional data become available. Identified as high priority needs are improved vapor pressure data for R124, R142b, and, especially, R141b, and improved liquid density data for R142b.

For solubility in water, the data were much more limited. Published, fully documented data were available only for R22. For the other fluids, unpublished data provided by the chemical manufacturers were used; again, while these data may be reliable, an assessment of their accuracy was not possible. The solubility information was correlated in terms of the Henry's law constant. The use of Henry's law in extrapolating from the saturation vapor pressure conditions employed in most of the measurements to the extremely low partial pressures that can be expected in the atmosphere is a source of uncertainty. For solubility in salt water, only data for R22 and methyl chloroform were found; an empirical 'salting parameter' evaluated from data for these two fluids can be applied to the other fluids in the absence of data.

Finally, hydrolysis is considered. Hydrolysis represents one possible mechanism for the environmental decomposition of a compound dissolved in the oceans or in cloud water. The data for hydrolysis rates were quite sparse; except for R22 and methyl chloroform, recommended values could not be developed. In view of the very limited solubilities of these compounds, even the order of magnitude-type information that can be estimated or extrapolated from the available data may be sufficient to determine whether dissolution in water and subsequent hydrolysis is a significant destruction mechanism for these compounds. Thus, complete data on solubility and hydrolysis may be needed only for methyl chloroform. This point is considered in detail in a study by Wine and Chameides presented elsewhere in this volume.

PHYSICAL PROPERTIES OF ALTERNATIVES TO THE FULLY HALOGENATED CHLOROFLUOROCARBONS

Mark O. McLinden
Thermophysics Division
National Institute of Standards and Technology
Boulder, Colorado 80303

1. INTRODUCTION

The physical properties of a fluid largely determine its suitability for use in a given application. The present study is concerned with properties of possible alternatives to the fully halogenated chlorofluorcarbons, a class of compounds widely used as working fluids (refrigerants) in refrigeration and air-conditioning equipment, as solvents and foam blowing agents, and in a wide variety of other applications. As examples, the thermophysical properties such as enthalpy, the pressure-volume-temperature (PVT) behavior, and viscosity are necessary to predict the performance of a fluid in refrigeration equipment. The thermal conductivity of the blowing agent has a large effect on the insulating value of a foam. The normal boiling point is important for solvent uses.

This paper, as part of the larger Alternative Fluorocarbon Environmental Assessment Study (AFEAS), focuses on those properties that influence the environmental acceptability of alternative fluorocarbon fluids. Specifically considered are the fluid fixed point parameters (triple point, normal boiling point, and critical point parameters), vapor pressure, saturated liquid density, solubility in water, and hydrolysis rates. The environmental implications of the first five properties listed are indirect. These properties are, however, often required as inputs for various models and estimation techniques. The last two properties can directly affect the fate of a fluorocarbon once it is emitted to the environment. One possible mechanism for the removal of a fluorocarbon from the environment is its dissolution in the ocean or in water droplets in clouds and subsequent reaction of the fluorocarbon with water (hydrolysis). This paper addresses the basic data associated with this mechanism of decomposition in the environment; the effectiveness of this mechanism is assessed by Wine and Chameides (1989).

The fluids to be considered in this report are the leading candidates to replace the fully halogenated CFCs such as R12 (CCl_2F_2) and R11 (CCl_3F). All are hydrogen-containing halogenated methanes and ethanes. The range of normal boiling points for these candidate fluids is similar to the range seen with the fully halogenated compounds.

In many cases, the fluids considered here have never been commercially produced and as a consequence, the data for many of them are sparse; thus, all possible sources of data have been utilized. These include the published literature (as revealed by a search of Chemical Abstracts and surveys such as that by Stewart, et al. (1981)), compilations such as that by the Japanese Association of Refrigeration (1975), unpublished data provided by several chemical manufacturers which are members of the AFEAS group, and, finally, experimental work in progress at the National Institute of Standards and Technology (NIST). Where available, preference is generally given to published over unpublished sources and to actual experimental values over information presented graphically or in terms of a correlation. The data differ greatly in quality and reliability and, as will be seen, are sometimes conflicting.

To be of maximum and immediate utility to the other AFEAS groups which may need to make use of this information, all data are fit with standard forms and presented primarily in terms of the resulting correlations. In this report a summary section containing coefficients to the correlations, etc. precedes a detailed discussion of the data themselves.

2. SUMMARY

Fluid Fixed Points

The triple point, normal boiling point, and critical point parameters are fundamental characteristics of a fluid. The triple point is the state at which three phases (solid, liquid and vapor) coexist; it is virtually identical with the more often reported freezing point. The normal boiling point is simply the temperature at which the vapor pressure of a fluid is one standard atmosphere (101.325 kPa). Since the vapor pressures of nearly all fluids are approximately parallel when plotted as the logarithm of pressure versus inverse temperature, the normal boiling point is a rough predictor of the vapor pressure at all temperatures. The critical point is the state at which the properties of the saturated liquid and vapor become indistinguishable; coexisting liquid and vapor are possible only at temperatures and pressures below the critical point values.

These parameters, often in the absence of any other information, are frequently used in screening among many different compounds to select a more limited set for further study. For many applications they define the temperature limits for the use of a particular fluid. Clearly a solvent or refrigerant cannot be used below the triple point temperature. For many refrigeration applications, operation at sub-atmospheric pressures is avoided and, thus, the normal boiling point is a more practical lower limit. Vapor compression refrigeration equipment transports heat through condensation and evaporation (i.e. two-phase) processes and thus the critical point represents an upper temperature and pressure limit. The critical point parameters are the essential inputs to estimation techniques based on the law of corresponding states, which is the observation that, when scaled by the critical parameters, the properties of nearly all fluids are similar.

The triple point, normal boiling point, and critical point parameters are given in Table 1. (In this table, and all subsequent tables, the fluids are listed in order of increasing normal boiling point temperature.) The selection of these values is discussed in detail in the Discussion section.

Vapor Pressure

The experimental vapor pressure data were fit to the following equation, which is a modification of a form suggested by Goodwin & Haynes (1982):

$$\ln p = a_1/T + a_2 + a_3T + a_4(1 - T/T_c)^{1.5} \qquad (1)$$

where p is pressure, T is absolute temperature (kelvins) and T_c is the critical temperature. Theories for asymptotic critical behavior predict a value of approximately 1.9 for the exponent in the last term in Equation (1); a value of 1.5, however, was empirically found to yield a better fit over a wide temperature range for R134a and R123 (Weber 1989). The coefficients for each of the fluids considered, along with the temperature range of the data, are given in Table 2. Modest extrapolations outside this range should yield fairly accurate results. This table also gives the RMS deviations between Equation (1) and the input data. These RMS values serve as indications of the precision of the data and the agreement between different sources. Particularly for those fluids with only one data source, the method of computing RMS deviations cannot detect any systematic errors in the data, and thus RMS values provide little information on the accuracy of the data and the resulting correlation. In most cases the accuracy of the correlation cannot be stated because of insufficient documentation; this is considered in more detail in the Discussion section. The vapor pressures as functions of temperature are also tabulated along with the other properties in the Appendix.

Saturated Liquid Density

Liquid densities along the saturation line, ϱ, were fit to the commonly used form:

$$\varrho/\varrho_c = 1 + d_1\tau^{\beta} + d_2\tau^{2/3} + d_3\tau + d_4\tau^{4/3} \qquad (2)$$

where $\tau = (1 - T/T_c$ and ϱ_c is the critical density. The critical exponent, β, is properly evaluated from experimental measurements near the critical point. For most of the fluids considered here a value of 1/3 is assumed because of the lack of data. Equation (2) is well-grounded in theory, has the proper form over a wide range of temperature including the vicinity of the critical point, and is often used in the correlation of saturated liquid densities. The fit of density data to Equation (2) is summarized in Table 3. As with vapor pressure, the temperature range of the data and the RMS deviation are also given. The critical temperature and density required in Equation (2) may be found in Table 1.

Solubility in Water

The fluids considered in this report are all highly volatile (most have normal boiling points well below typical ambient temperatures) and thus their presence in the environment will be predominantly as trace gases in the atmosphere. Atmospheric gases will, however, dissolve to some extent into the oceans and into water droplets in clouds. The magnitude of this solubility will influence the importance of hydrolysis as a degradation mechanism. The dissolution of trace gases into water is well-represented by Henry's law:

$$x_a = p_a/H_a \qquad (3)$$

which states that the concentration of substance "a" dissolved in a solvent, x_a, is proportional to the partial pressure of substance "a" over the solution, p_a. Henry's law strictly applies only in the limit of x_a approaching zero but in practice holds very well for gas partial pressures up to a few hundred kPa and even higher for gases of low solubility (such as the fluorocarbons). The proportionality factor in Equation (3), H_a, is called the Henry's law constant. The units of H_a are pressure divided by a concentration (e.g. kPa/mass % or atm/ppm). The Henry's law constant is not constant but is a function of temperature which can be well represented by:

$$\ln (1/H_a) = h_1 + h_2/(T + h_3) \qquad (4)$$

Solubility data have been used to evaluate the coefficients in Equation 4; they are given in Table 4. Note that the term h_3 is used only for R22. Equation 4 has been used to calculate solubilities in water at the commonly referenced conditions of 298.15 K (25°C) and a fluorocarbon partial pressure of one standard atmosphere. (While this is an unrealistically large partial pressure for gases in the environment, it is useful for comparisons between compounds.) For several of the fluids there was considerable disagreement (as much as a factor of two) in measured solubility from different sources; these are flagged by comments in Table 4.

PHYSICAL PROPERTIES

At least limited solubility data were obtained (mostly from unpublished sources) for all of the compounds considered as part of AFEAS. For other fluids which may be of interest and for which data may not exist, the method of Irmann (1965) (as reported by Lyman, et al. 1982) can be used to estimate the solubilities of the halogenated hydrocarbons. This method requires only the molecular structure and vapor pressure at 298.15 K (25°C) of the compound in question and yields the solubility in water at 298.15 K. The results of applying this estimation technique to the nine compounds considered here are given in Table 5. For most of the fluids the agreement is very good (within 15%), validating this method. The estimated values for R125 and R141b, however, differ by factors of two and five, respectively from the reported values. In view of the good agreement for the other fluids, this discrepancy casts some doubt on the reported values for R125 and certainly for R141b.

The above results are for solubilities in pure water. The solubilities in saline solutions can be represented by the following form reported by Lyman, et al. (1982):

$$\ln (x_a/x_{a,s}) = K_s C_s \qquad (5)$$

where x_a is the solubility in pure water and $x_{a,s}$ is the solubility in a saline solution of concentration C_s. The term K_s is an empirical salting parameter. Values of K_s are positive, so solubilities in salt water are lower than those in pure water. For the compounds of interest here, data were found only for R22 and methyl chloroform. Zhang, et al. (1985) report R22 solubilities in sodium chloride solutions over the temperature range 283-323 K. Their data confirm Equation (5) and can be used to compute values of K_s ranging from 0.0060 L/g at 283 K to 0.0082 L/g at 333 K. These correspond to solubilities in sea water which are 81-75% of those in pure water. Walraevens, et al. (1974) report a salting parameter of 0.0073 L/g for methyl chloroform corresponding to a solubility in sea water which is 78% of that in pure water.

Limited data for the solubility of other fluorocarbons in salt solutions were also found. Data for R21 ($CHCl_2F$) (Downing 1988) and R114 ($CClF_2CClF_2$) (Stepakoff and Modica 1973) give values of K_s of 0.0061 and 0.029 L/g respectively; these correspond to solubilities in sea water which are 81 and 36% of those in pure water. This range for the ratio of sea water to pure water solubilities is similar to those observed with other classes of fluids (Lyman, et al. 1982). The polar, hydrogen-containing R22, R21, and methyl chloroform are better analogues to the full set of fluids considered here than the weakly polar, fully halogenated R114. The effect of salt on the solubilities of the fluids considered in this report is, thus, probably closer to those observed with R22 and R21 than with R114. Considering the similarity of salting parameters for R22, R21, and methyl chloroform, a salting parameter of 0.007 L/g is recommended for the other fluids in the absence of data. This corresponds to a solubility in sea water which is 78% of that in pure water.

Hydrolysis Rates

Hydrolysis refers to the reaction of a compound in aqueous solution. For the fluorocarbons, two mechanisms are possible (Ellenrieder and Reinhard 1988). In nucleophilic substitution, or hydrolysis proper, the fluorocarbon reacts with water or the hydroxide ion (OH-) to form an alcohol plus an acid:

$$\text{R-C-R'X} + H_2O/OH^- \rightarrow \text{R-C-R'OH} + HX \qquad (6)$$

where X represents a halogen (F or Cl) and R and R' are nonreacting groups. In the second mechanism, known as elimination or dehydrohalogenation, water or hydroxide catalyzes the reaction to form an alkene plus acid:

$$\text{R-CH-CR'X} + \text{H}_2\text{O/OH}^- \rightarrow \text{RC=CR'} + \text{H}_2\text{O/OH}^- + \text{HX} \tag{7}$$

In this work, the term "hydrolysis" will refer to the general reaction in aqueous solution; the terms "substitution" and "elimination" will be used when it is necessary to distinguish between the different mechanisms. A single-carbon compound (such as R22) can obviously undergo only the substitution process. Other mechanisms occur for the fully halogenated compounds (Downing 1988) but will not be considered here.

The elimination process becomes more important as the number of halogens in the molecule increases (Vogel, et al. 1987). Either process may be neutral (reaction primarily with water) or base-promoted (reaction primarily with hydroxyl). A third possibility, acid promotion by the hydronium ion, H^+, does not occur (Mabey and Mill 1978).

The rate of reaction, expressed in terms of the disappearance of fluorocarbon, is proportional to the fluorocarbon concentration. Thus the solubility of the compound will have an influence on its reaction rates. For base-promoted processes, the reaction rate is also proportional to the hydroxyl concentration, which in turn is related to the pH. Where the neutral process dominates, the rate is independent of pH. For the general case of base-promoted and neutral processes occurring simultaneously, the reaction rate can be expressed as:

$$-d[RX]/dt = [RX](k_B[OH^-] + k_N) \tag{8}$$

where square brackets denote a concentration in moles/liter, RX is the reacting fluorocarbon, and k_B and k_N are the rate constants for the base-promoted and neutral processes, respectively. Both k_B and k_N may be further broken down into additive contributions from the substitution and elimination mechanisms. Each of the rate constants are functions of temperature, typically expressed in terms of an Arrhenius expression:

$$k = A \exp(-E/RT) \tag{9}$$

where E is the activation energy of the reaction and R is the gas constant.

The hydrolysis of a fluorocarbon is thus seen to be a rather complex process with several possible mechanisms. To fully describe the temperature and pH dependence of a reaction requires up to eight parameters. To further complicate the situation, metals can catalyze hydrolysis and increase reaction rates by an order of magnitude or more (Downing 1988). The information located for the hydrolysis rates of the fluorocarbons considered here was limited.

Downing 1988 gives information on both the temperature and pH dependence of R22 hydrolysis rates:

$$-d[R22]/dt = k[R22][OH^-] \tag{10}$$

The temperature dependence of k is given by Equation (9) with:

$$A = 1.87 \times 10^{8}\ \mathrm{L/(mol{\cdot}s)}$$

$$-E/R = -7692.\ \mathrm{K}$$

One must infer from Equation (10) that either the neutral and base-promoted processes have been lumped together into a single rate constant or that the former process is insignificant, i.e. k_N is small.

At a temperature of 298 K and a concentration of hydroxide of 1 x 10^{-7} mol/L (corresponding to pure water of pH = 7) the above expression yields an overall rate constant (i.e. $k_B[OH^-] + k_N$) of 1.15 x 10^{-10} s^{-1}; at an R22 concentration of 0.033 mol/L (the solubility of R22 at a partial pressure of 101.3 kPa) the corresponding hydrolysis rate is 3.8 x 10^{-12} mol/(L·s). This is in reasonable agreement with the value of 4.5 x 10^{-12} mol/(L·s) given by DuPont (1989) at the same conditions.

Ellenreider and Reinhard (1988) have developed an interactive, computerized data base for the calculation of hydrolysis rates as functions of temperature and pH. While this would be an ideal method of presenting hydrolysis data, of the compounds of interest here, only methyl chloroform is presently included in this data base. In the paper by Ellenreider and Reinhard, methyl chloroform is presented as an example. At 293 K in pure water (pH = 7) the rate constant for the substitution reaction is 8.1 x 10^{-9} s^{-1} with the neutral process dominant by several orders of magnitude over the base-promoted process; for the elimination mechanism the rate constant is 2.0 x 10^{-9} s^{-1} for the neutral process (no data are given for the base-promoted elimination process). The overall rate constant is 1.0 x 10^{-8} s^{-1}. For a concentration of 0.033 mol/L (the saturation concentration of methyl chloroform) the hydrolysis rate is 3.3 x 10^{-10} mol/(L·s). The temperature dependence is also given by Ellenreider and Reinhard. The overall rate constant can be expressed in terms of Equation (9) with:

$$A = 1.28 \times 10^{13}\ \mathrm{s^{-1}}$$

$$-E/R = -14244.\ \mathrm{K}$$

This implies that the hydrolysis reaction is a factor of five faster at 303 K than at a temperature of 293 K.

Perhaps a more convenient means of expressing the rate of a first order reaction is in terms of the half-life of the reacting species. The half-life is independent of reactant composition. Ellenreider and Reinhard report a half-life of 0.96 year for methyl chloroform at 298 K and pH = 7. The hydrolysis rate constant for R22 yields a half-life of 191 years at the same conditions. Thus, there is a vast difference in the effectiveness of hydrolysis in breaking down a compound in the environment.

For R123, DuPont (1989) reports a hydrolysis rate approximately 4.3 times that for R22 for a test of 100 days at 328 K. A series of 3-day tests at 358 K indicated that R141b is less stable than R123 but considerably more stable than methyl chloroform. In these short-term test the amount of decomposition was less than 5 ppm for R123 and R141b and 0.006% for methly chloroform. "Stability" data of Allied (1989), however, report that the production of acid from R123 in aqueous solution is 38% of that with R22. The Allied information also indicates that the acid production rates with R124 and R142b are, respectively, 1.35 and 1.65 times that observed with R22. The Allied data are for tests at 314 K and result from measurements of the decomposition of fluorocarbon over a period of three months. The differences in the DuPont and Allied results suggest caution in the use of any hydrolysis rate data.

The database of Ellenreider and Reinhard, along with a survey by Mabey and Mill (1978), unfortunately, do not contain information on any of the other compounds of interest here. In general terms, chlorine is much more reactive than fluorine (Hine, et al. 1961) so the chlorine-free compounds (R125, R134a, R152a) will probably have lower hydrolysis rates than those reported for R22 or R123. The data for the relative reaction rates of R22, R142b, R124, R123, and R141b suggest that the hydrolysis rates for all of these chloroflouro compounds will be of the same order of magnitude. Thus, for the nine fluids considered here, only methyl chloroform is likely to have a hydrolytic half-life on the order of a year; all the others will likely have half-lives on the order of a century or more.

3. DISCUSSION

R125

The data for R125 (pentafluoroethane) are limited. Both Allied (1989) and DuPont (1989) report a critical temperature of 339.4 K. DuPont also gives a freezing point temperature and critical density. None of these values are documented, but they are adopted here in the absence of any other data.

The saturated liquid density and vapor pressure data reported by Allied were selected over the single liquid density value and graphical presentation of vapor pressure given by DuPont in fitting the coefficients to Equations (1) and (2). A comparison of these data with the correlations is presented in Figure 1. The critical pressure (reported in Table 1) was calculated by an extrapolation of Equation (1) to the

Table 1. Fluid Fixed Points

Fluid	Chemical formula	Mol. mass (g/mol)	Tr. Pt. temp. (K)	Norm. Boiling Pt. temp. (K)	Norm. Boiling Pt. liq. den. (kg/m^3)	Critical Point temp. (K)	Critical Point pres. (kPa)	Critical Point density (kg/m^3)
R125	CF_3CHF_2	120.020	170.	224.6	1515.	339.4	3631.	571.5
R22	$CHClF_2$	86.468	113.	232.4	1409.	369.30	4990.	513.0
R134a	CF_3CH_2F	102.030	172.	247.1	1373.	374.21	4056.	515.3
R152a	CHF_2CH_3	66.050	156.	249.0	1011.	386.44	4520.	368.0
R124	$CHClFCF_3$	136.475	74.	261.2	1472.	395.65	3640.	560.0
R142b	CH_3CClF_2	100.495	142.	264.0	1193.	410.25	4246.	435.0
R123	$CHCl_2CF_3$	152.930	166.	301.0	1456.	456.94	3674.	549.9
R141b	CH_3CCl_2F	116.950	170.	305.3	1216.	481.5	4540.	464.1
methyl chlr.	CH_3CCl_3	133.405	243.	347.3	1250.	545.	4300.	470.0

*Note: None of the critical densities are known to four significant figures; they are given to this level for consistency with Eqn (2).

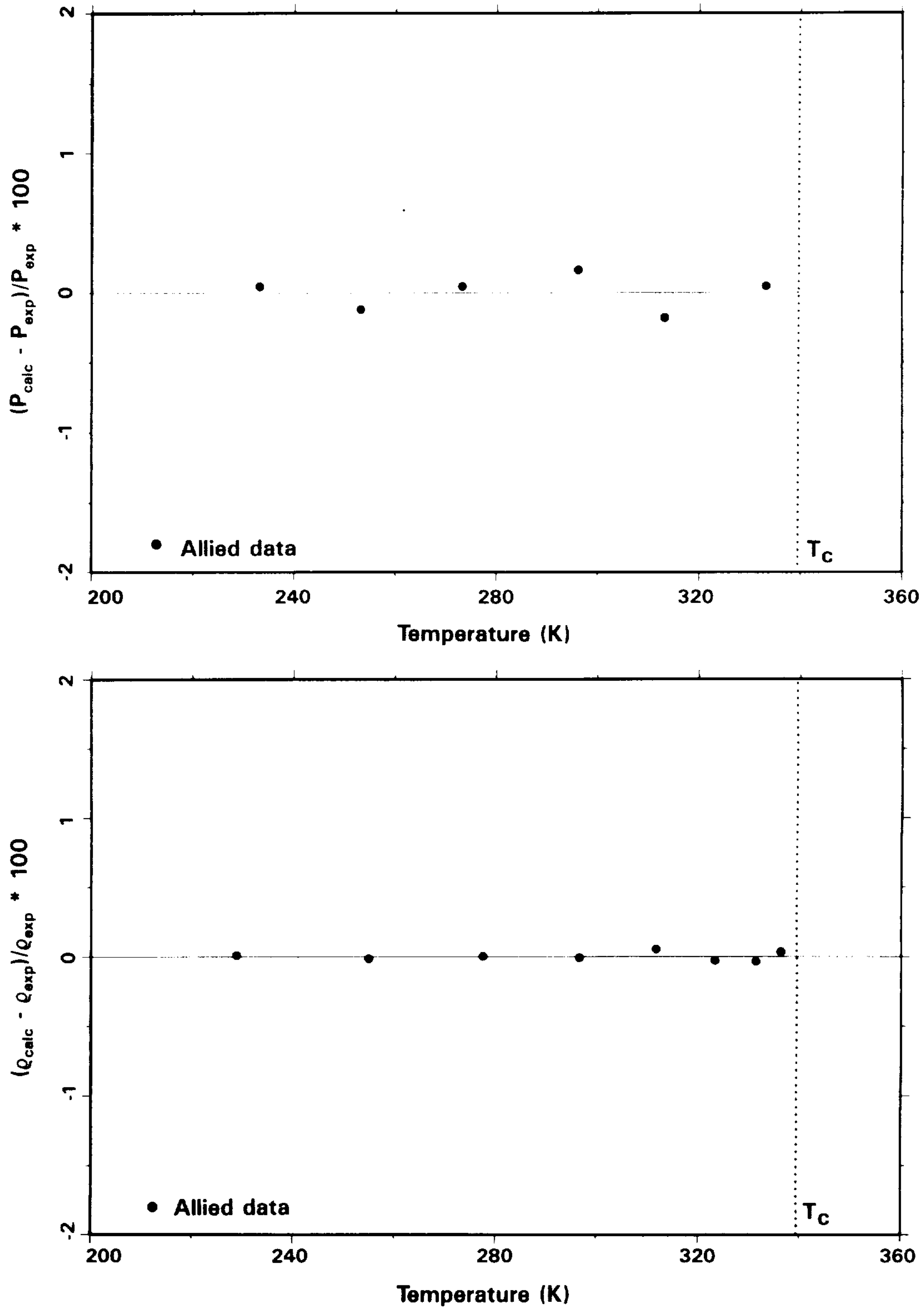


Figure 1. Comparison of correlations with data for R125; a) vapor pressure; b) saturated liquid density.

critical temperature (an extrapolation of only 6.3 K) rather than the value of 3520 kPa reported by DuPont, (1989). As with all the fluids in this report, the normal boiling point temperature reported in Table 1 is obtained by finding the temperature at which Equation (1) yields a pressure of one standard atmosphere (101.325 kPa).

The eight liquid densities reported by Allied were measured over the temperature range 228.7-336.3 K using glass flotation beads of known density. In this technique, the temperature of the fluid is adjusted so that the density of the fluid matches that of one of the beads. In another work by the same group (Wilson and Basu 1988), the accuracy of this method is claimed to be 0.2 kg/m^3. The values for R125 were apparently not corrected for the effects of temperature on the densities of the glass beads. Judging by other results by this method, these corrections should be less than 0.1 kg/m^3 for the temperature range of the measurements for R125. The excellent fit of Equation (2) to within 6 K of the critical temperature gives some credence to the critical density of DuPont used in the correlation.

The only information on solubility in water were coefficients to a correlation similar in form to Equation (4) reported by DuPont (1989). The experimental technique was similar to that employed by Parmalee (1953). No data were given but an "experimental data range" of 298-333 K was indicated. These coefficients are reported in Table 4 after the appropriate conversion of units.

R22

The extensive body of data on R22 (chlorodifluoromethane) is summarized, evaluated, and correlated in the treatise by the Japanese Association of Refrigeration (1975). Although additional data have been meas-

Table 2. Vapor Pressure

Fluid	Temperature low (K)	limits high (K)	Coefficients to Equation (1) a_1	a_2 (p in kPa, T in K)	a_3	a_4	RMS error (%)
R125	233.	T_C	-2678.571	16.63306	-0.001602304	1.390420	0.12
R22	223.	T_C	-2907.443	17.05244	-0.001796055	2.204052	0.09
R134a	210.	T_C	-3353.464	18.36056	-0.002908044	2.783663	0.19
R152a	273.	T_C	-3110.511	17.02405	-0.001445740	2.105154	0.05
R124	222.	T_C	-3471.946	18.16083	-0.002997217	2.703744	0.35
R142b	233.	369.	-3382.422	17.01384	-0.001012149	3.224924	0.30
R123	243.	T_C	-4060.080	18.20783	-0.002426370	3.164297	0.17
R141b	243.	475.	-4388.810	18.40668	-0.001808752	5.149630	2.20
methyl chlr.	295.	371.	-4809.873	17.93429	-0.001362322	4.617096	0.02

TABULATED VALUES OF VAPOR PRESSURE, LIQUID DENSITY AND SOLUBILITY IN WATER

Properties of R125

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m^3)	Henry's const. (kPa/Mass%)
-40.0	150.6	1484.0	
-35.0	186.9	1465.4	
-30.0	229.8	1446.3	
-25.0	280.1	1426.8	
-20.0	338.5	1406.8	
-15.0	406.0	1386.2	
-10.0	483.3	1365.0	
-5.0	571.4	1343.1	
0.0	671.2	1320.4	(242.)
5.0	783.7	1296.8	(331.)
10.0	909.8	1272.2	(448.)
15.0	1050.7	1246.4	(599.)
20.0	1207.2	1219.3	(794.)
25.0	1380.6	1190.4	1042.
30.0	1571.9	1159.6	1355.
35.0	1782.4	1126.2	1747.
40.0	2013.4	1089.7	2234.
45.0	2266.2	1048.8	2835.
50.0	2542.5	1001.8	3572.
55.0	2844.1	945.3	4469.
60.0	3173.5	870.5	(5553.)
65.0	3534.4	735.8	(6857.)
NBP: -48.6	(101.3)	(1515.2)	
T_c: 66.3	(3630.6)	(571.5)	

Properties of R22

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m^3)	Henry's const. (kPa/Mass^7)
-40.0	105.3	1406.5	
-35.0	132.0	1391.8	
-30.0	163.8	1376.9	
-25.0	201.2	1361.8	
-20.0	245.1	1346.4	
-15.0	295.9	1330.6	
-10.0	354.5	1314.6	
-5.0	421.6	1298.2	
0.0	498.0	1281.5	(82.)
5.0	584.3	1264.3	(122.)
10.0	681.3	1246.7	171.
15.0	789.9	1228.6	227.
20.0	910.8	1210.0	288.
25.0	1044.9	1190.7	354.
30.0	1193.1	1170.8	425.
35.0	1356.1	1150.1	498.
40.0	1534.8	1128.6	573.
45.0	1730.3	1106.0	650.
50.0	1943.4	1082.3	727.
55.0	2175.3	1057.1	805.
60.0	2427.1	1030.3	883.
65.0	2700.0	1001.3	961.
70.0	2995.4	969.7	1038.
75.0	3315.1	934.4	1114.
80.0	3660.8	893.9	(1189.)
85.0	4035.1	845.2	(1263.)
90.0	4441.6	780.6	(1336.)
95.0	4886.2	660.9	(1408.)
NBP: -40.8	101.3	(1408.9)	
T_c: 96.2	(4995.6)	(513.0)	

ured since the publication of this work, the recommendations of the JAR were adopted here so that the limited time available for this project could be better expended on other fluids for which no such compilations exist.

The triple point and critical point values of the JAR are adopted here. The saturated-liquid densities were fit by the JAR based largely on the data of Zander (1968) to the same form used here (Equation (2)) and thus the coefficients given in Table 3 are those reported by the JAR. This correlation is valid from 204 K to the critical temperature with an RMS deviation of approximately 0.1%.

The vapor pressure data of Kletskii (1964), Kohlen (1985), and Zander (1968) were fit to Equation (1); the residuals are shown in Figure 2. The three lowest temperature (203.3-211.3 K) points of Zander and his point at 366.1 K were excluded from the fit. The high temperature point appeared to be anomalously high compared to the other data sets while the three low temperature points could not be fit without seriously affecting the correlation at higher temperatures. (In Figure 2 and all similar residual plots, points used in the correlation are shown as filled-in symbols; points excluded from the fit are shown as open symbols.)

R22 solubility data are reported by Parmelee (1953). Fourteen data points at three temperatures were measured with an estimated accuracy of 5% using a gas volumetric technique. Parmelee correlated his data to a form similar to Equation (4) and his coefficients are reported in Table 4 after the appropriate conversion of units.

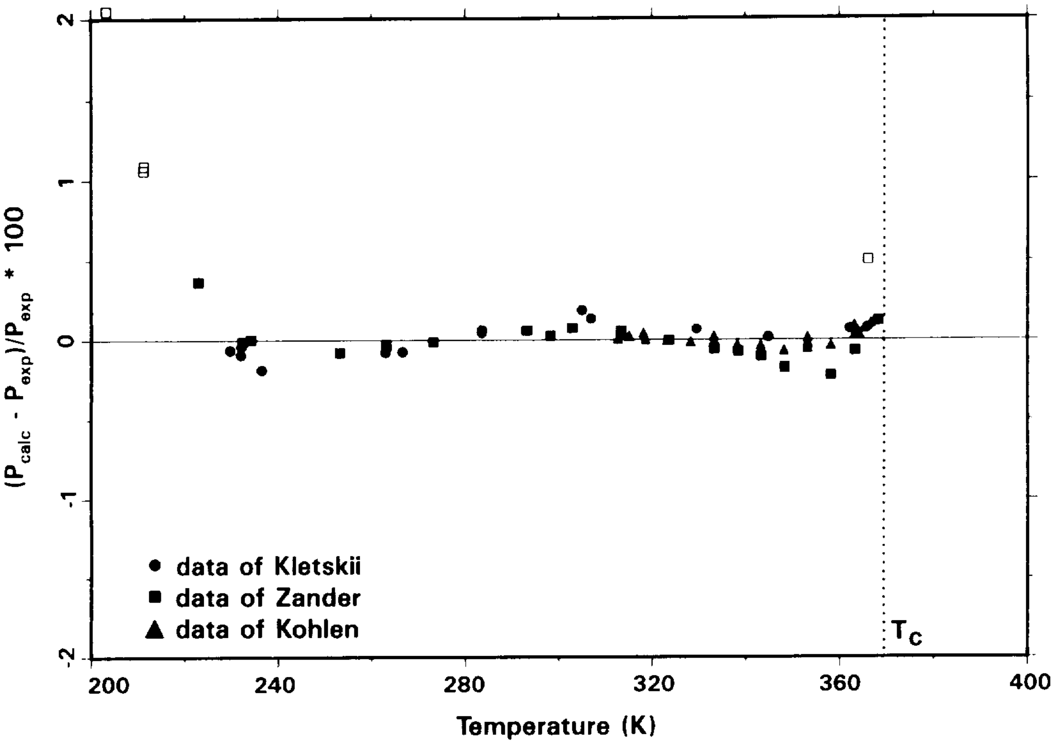


Figure 2. Comparison of vapor pressure correlation with data for R22; filled-in and open symbols indicate points used and not used, respectively, in fitting correlation.

PHYSICAL PROPERTIES

R134a

Refrigerant 134a (1,1,1,2-tetrafluoroethane) has been the focus of considerable attention in the fluid property community recently, and considerable data have become available. The critical point has been measured by Kabata, et al. (1988), Wilson and Basu (1988), and Morrison (1989). Morrison's determination, carried out at NIST, is adopted here, although all three sets of critical parameters are in excellent agreement. DuPont (1989) and Daikin (1989) both report freezing temperatures of 172 K.

Two reliable sources of vapor pressure data are available; together they span the temperature range from 211.0 K to within 1 K of the critical temperature. Weber (1989) measured 22 values with an estimated accuracy of 0.2 kPa. Wilson and Basu (1988) report 32 values with an accuracy of 0.7-7. kPa (depending on the pressure). As shown in Figure 3, the two data sets are in excellent agreement over the temperature range of overlap. The correlation presented here is identical with that presented in McLinden, et al. (1989). Yamashita, et al. (1988) have measured the vapor pressure of R134a at 25 temperatures from 253-371 K. Unfortunately, their paper does not give the experimental points. Saturated liquid densities have been reported by three independent groups. Wilson and Basu (1988) report nine measurements over a fairly wide range of temperature (238.9-371.6 K) using the floating bead technique. Kabata, et al. (1988) report six measurements in the vicinity of the critical point. Morrison (1989) has measured 11 values from 268.2-368.2 K with a variable-volume, mercury-displacement apparatus. These three data sets were used in fitting Equation (2); the residuals are shown in Figure 3. (Further measurements by Morrison using a vibrating tube densimeter were not available in time to include in this work.) The different data sets are in reasonable agreement, although differences of as much as 1.5% exist, especially near the critical point.

The solubility of R134a in water has been measured by DuPont (1989) at 298 and 353 K. These two points were read off their graphical presentation and used to fit the coefficients in Equation (4).

R152a

The primary source of data for R152a (1,1-difluoroethane) was the work of Higashi, et al. (1987). Their critical point determination is consistent with the earlier determination by Mears, et al. (1955), which is the basis of the critical parameters listed on many manufacturer's data sheets. The determination by Higashi, et al. is, however, of much higher accuracy (0.01 K for temperature, 1.0 kPa for pressure, and 2 kg/m^3 for density) and is adopted here. The freezing point reported by DuPont (1989) is used here.

Higashi, et al. report 44 vapor pressure measurements from 273.1 K to within 0.4 K of the critical temperature with a precision better than 0.17%. Additional data, of lower accuracy but covering a wider temperature range (203.7 K and above), are reported by Mears, et al. The data sets of Higashi, et al. and Mears, et al. are in reasonable agreement above 290 K but diverge rapidly at lower temperatures; see Figure 4. (In Figure 4 and all similar figures, points drawn just outside the frame of the plot indicate residuals greater than the limits of the ordinate and are not to scale.) All attempts to extend the range of Equation (1) to lower temperatures by including selected low temperature points of Mears resulted in a much poorer fit at the higher temperatures. The accuracy of the data by Mears, et al. is difficult to ascertain but is probably no better than 5-10 kPa; this uncertainty would be equivalent to an error of as much as 10% at the lowest temperatures. Thus, only the vapor pressure data of Higashi, et al. were used in fitting Equation (1).

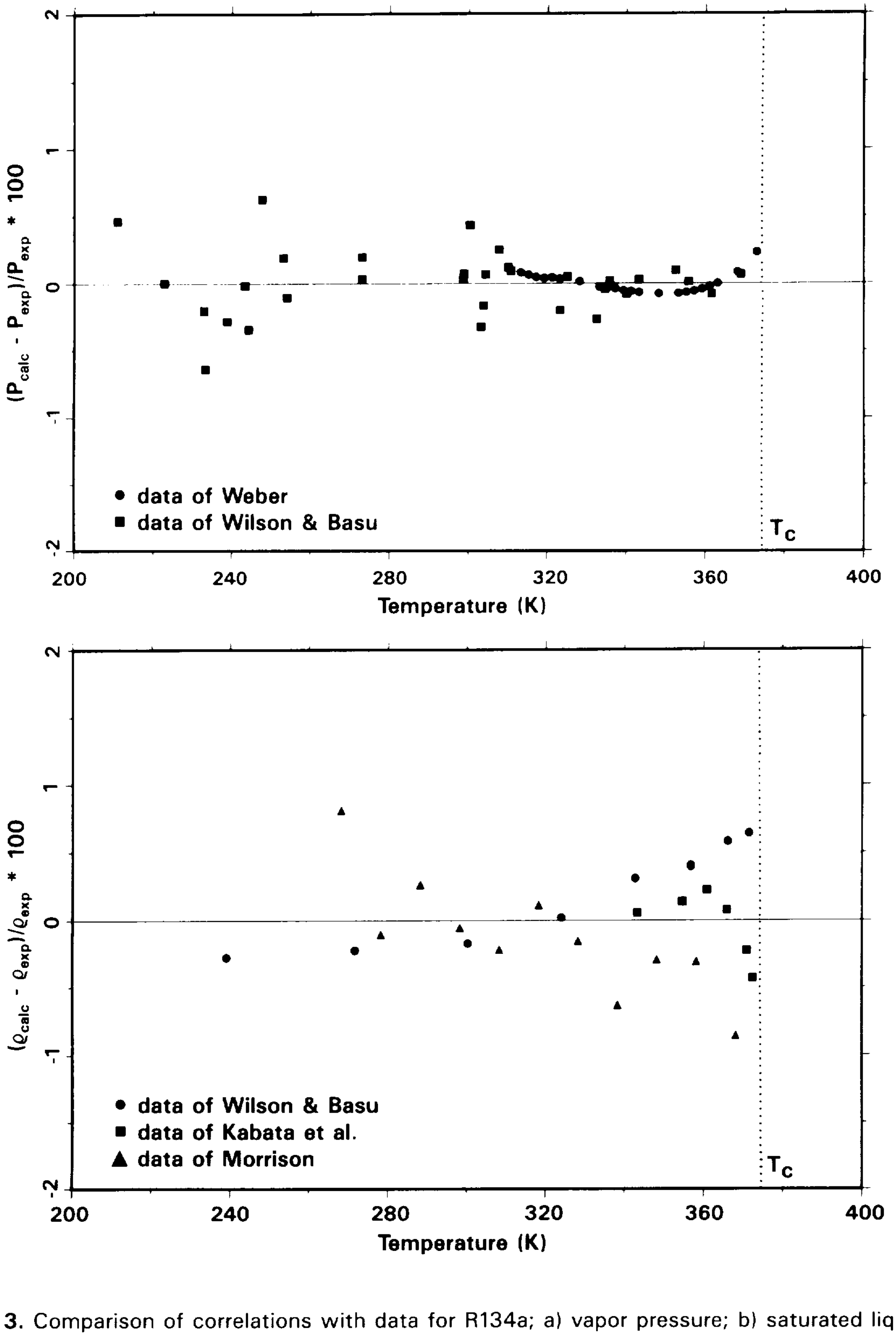


Figure 3. Comparison of correlations with data for R134a; a) vapor pressure; b) saturated liquid density.

Properties of R134a

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	51.6	(1413.5)	
-35.0	66.5	(1399.2)	
-30.0	84.7	1384.6	
-25.0	106.6	1369.8	
-20.0	132.9	1354.8	
-15.0	164.1	1339.5	
-10.0	200.7	1324.0	
-5.0	243.4	1308.2	
0.0	292.9	1292.1	(302.)
5.0	349.8	1275.7	(359.)
10.0	414.8	1258.8	(425.)
15.0	488.7	1241.5	(499.)
20.0	572.1	1223.8	(583.)
25.0	665.8	1205.5	678.
30.0	770.7	1186.7	784.
35.0	887.4	1167.1	903.
40.0	1017.0	1146.8	1035.
45.0	1160.1	1125.7	1181.
50.0	1317.8	1103.4	1342.
55.0	1491.0	1080.0	1520.
60.0	1680.7	1055.1	1714.
65.0	1888.2	1028.5	1927.
70.0	2114.6	999.6	2158.
75.0	2361.5	967.9	2409.
80.0	2630.4	932.4	(2682.)
85.0	2923.4	891.4	(2976.)
90.0	3243.1	841.7	(3293.)
95.0	3593.0	775.3	(3634.)
100.0	3979.6	650.9	(3999.)
NBP:-26.1	101.3	1373.1	
T_C: 101.1	4067.9	515.3	

Properties of R152a

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(48.0)	1043.0	
-35.0	(61.5)	1033.2	
-30.0	(77.9)	1023.1	
-25.0	(97.6)	1013.0	
-20.0	(121.2)	1002.6	
-15.0	(149.0)	992.1	
-10.0	(181.8)	981.3	
-5.0	(219.9)	970.3	
0.0	263.9	959.1	178.
5.0	314.6	947.7	207.
10.0	372.5	936.0	239.
15.0	438.2	924.0	275.
20.0	512.5	911.7	316.
25.0	596.0	899.0	360.
30.0	689.4	886.0	409.
35.0	793.4	872.6	462.
40.0	908.9	858.8	521.
45.0	1036.5	844.5	584.
50.0	1177.1	829.7	654.
55.0	1331.5	814.2	729.
60.0	1500.5	798.1	809.
65.0	1685.1	781.1	896.
70.0	1886.2	763.2	990.
75.0	2104.8	744.2	(1090.)
80.0	2342.1	723.9	(1197.)
85.0	2599.3	701.8	(1310.)
90.0	2877.9	677.5	(1432.)
95.0	3179.4	650.1	(1560.)
100.0	3505.8	618.1	(1696.)
NBP: -24.2	101.3	1011.2	
T_C: 113.3	4519.8	368.0	

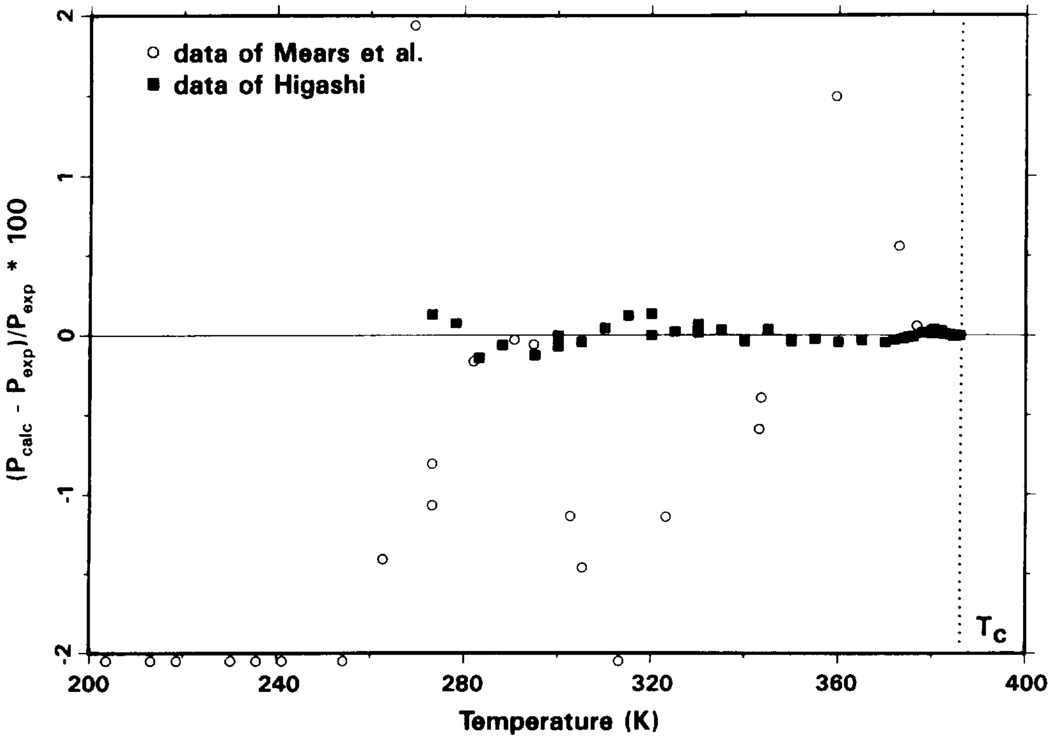


Figure 4. Comparison of vapor pressure correlation with data for R152a.

Higashi, et al. give a correlation of the saturation density based on a total of 48 measurements including their own work, the data of Mears, et al. and the 23 values of Kanome and Fujita (1986). Because of the unavailability of this last reference (published only in a thesis of Keio University), 12 densities from 220-385 K were calculated with Higashi's correlation and used as input data to fit Equation (2). The correlation of Higashi represented the experimental data with an RMS deviation of 0.21% over the temperature range 221.0-386.4 K. The RMS deviation between Equation (2) and Higashi's correlation was 0.001% implying that Equation (2) would also fit the data to 0.21%.

The solubility data of DuPont (1989) were again the basis of fitting the coefficients to Equation (4). They report three measurements by a technique similar to Parmalee (1953) over the temperature range 298-353 K as well as four additional measurements from unspecified other sources from 273-303 K. A single value at 294 K reported by Allied (1989) is in excellent agreement with the DuPont values.

R124

Measurements of the thermodynamic properties of R124 (1-chloro-1,2,2,2-tetrafluoroethane) have been published by Kubota, et al. (1988). Their measurements include a critical point determination which is in excellent agreement with the parameters reported by Allied (1989) and DuPont (1989). The values of Kubota, et al. are used here because of the preference for published, documented measurements over unpublished values. Again, the only information on the triple point was an undocumented value reported by DuPont.

Although fairly comprehensive, the measurements of Kubota, et al. have two weaknesses. The first is a lower temperature limit of only 278 K. The second, more serious problem, is the fairly poor precision of the pressure measurements. An accuracy of 12 kPa is claimed for the vapor pressure measurements; this is equivalent to an error of 6% at the lowest temperature. The relative error would be smaller at higher temperatures and pressures, yet for temperatures between 300 and 350 K there are serious discrepancies between the data of Kubota, et al. and the 17 vapor pressure points reported by Allied (1989) (see Figure 5). The boiling point temperature given by DuPont (1989) is also significantly different. Because of the wider temperature range of the Allied data (222.3-389.8 K) and the good accuracy for other fluids measured by this group (e.g. Wilson and Basu 1988), only these data were used in fitting Equation (1). Further measurements on this fluid will be required to ascertain whether this was the proper choice.

For liquid density, the situation is considerably better. The three available data sources are in good agreement, as shown in Figure 5. The saturated liquid densities reported by Kubota, et al. were obtained by extrapolating compressed liquid measurements to the saturation pressure. The stated accuracy of the density measurements is 0.09% with the extrapolation adding perhaps a comparable uncertainty. The point at 323.2 K appeared to be an outlier and was excluded from the fit. Saturated liquid densities have been measured by Allied (1989) from 216-391 K using a vibrating tube densimeter. These results were available only as a correlation, and, thus, the points shown in Figure 5 have been calculated from this correlation for use in fitting Equation (2). The precision of measurements made with this type of device is very high, although the accuracy is dependent on calibration of the instrument. The two liquid density values reported by DuPont are also consistent with the other sources.

As with R125, the correlation coefficients presented by DuPont (1989) are the basis for the solubility of R124 in water. The applicable temperature range is stated as 313-348 K.

R142b

The long-standing reference for the thermodynamic properties of R142b (1-chloro-1,1-difluoroethane) has been Mears, et al. (1955); for example, the thermodynamic data of ASHRAE (1985 and 1987) are taken directly from Mears. A second source is that of Cherneeva (1958). Although the data of Cherneeva are claimed to be more accurate than those of Mears, et al., there is some reason to doubt Cherneeva's data (as discussed below) and thus the critical parameters of Mears were selected for this work. The freezing temperatures reported by DuPont (1989) and Solvay (1989) for Refrigerant 142b are consistent.

The vapor pressure data of Cherneeva and Mears, et al. are fairly consistent, although both exhibit considerable scatter as shown in Figure 6. The data of Cherneeva extended over a wider temperature range and gave a slightly better fit to Equation (1) and were thus selected over the data of Mears. A substantially improved correlation was obtained by omitting the points at 213, 218 and 284 K.

At temperatures above 320 K, the saturated liquid densities from Mears et al. and Cherneeva exhibit serious differences (see Figure 6). These differences are at least an order of magnitude larger than can be explained by the accuracies of 0.1 and 0.2% claimed by Cherneeva and Mears, respectively. A third

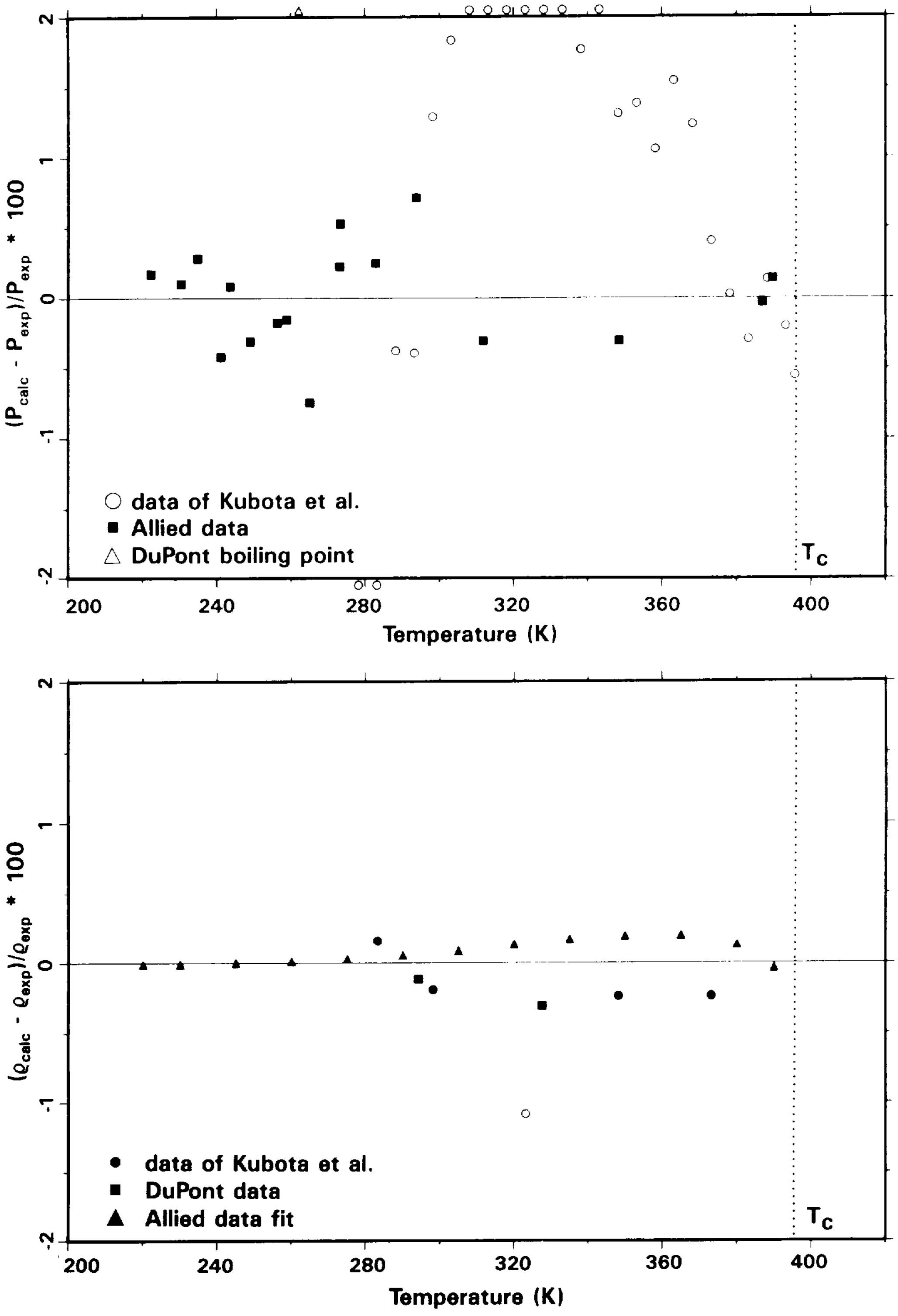
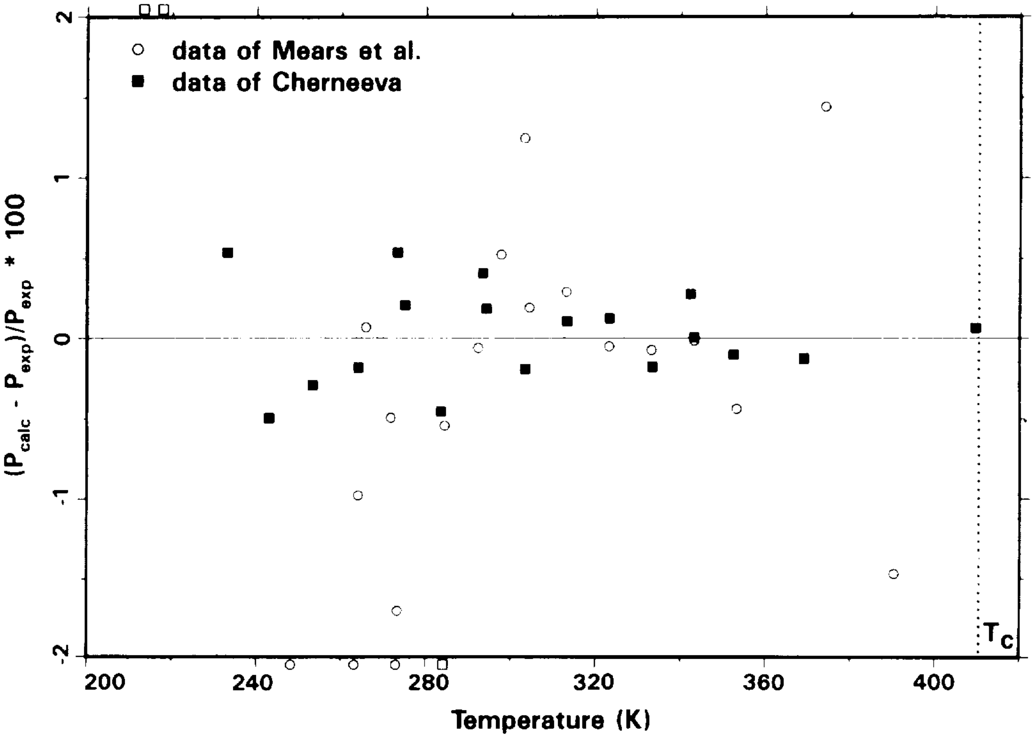


Figure 5. Comparison of correlations with data for R124; a) vapor pressure; b) saturated liquid density.



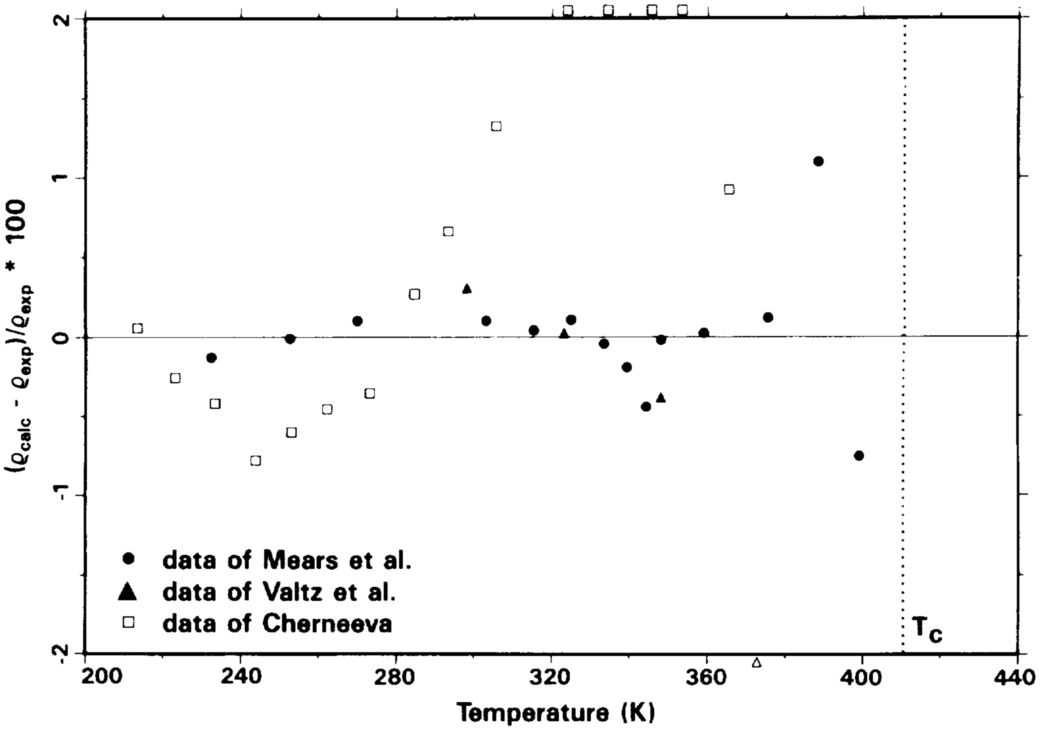


Figure 6. Comparison of correlations with data for R142b; a) vapor pressure; b) saturated liquid density.

Properties of R124

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	26.6	1552.1	
-35.0	34.7	1538.3	
-30.0	44.7	1524.3	
-25.0	56.9	1510.1	
-20.0	71.6	1495.7	
-15.0	89.3	1481.1	
-10.0	110.2	1466.4	
-5.0	134.8	1451.3	
0.0	163.6	1436.1	(259.)
5.0	196.9	1420.5	(321.)
10.0	235.2	1404.7	(394.)
15.0	278.9	1388.5	(480.)
20.0	328.7	1372.1	(581.)
25.0	384.9	1355.2	(699.)
30.0	448.1	1337.9	(836.)
35.0	518.7	1320.2	(994.)
40.0	597.4	1302.0	1175.
45.0	684.5	1283.3	1381.
50.0	780.8	1263.9	1616.
55.0	886.7	1243.9	1882.
60.0	1002.7	1223.1	2181.
65.0	1129.6	1201.4	2517.
70.0	1268.0	1178.6	2893.
75.0	1418.4	1154.7	(3312.)
80.0	1581.6	1129.3	(3777.)
85.0	1758.4	1102.3	(4291.)
90.0	1949.7	1073.1	(4858.)
95.0	2156.3	1041.3	(5481.)
100.0	(2379.5)	1005.8	(6165.)
NBP:-12.0	(101.3)	1472.4	
T_C: 122.5	(3639.8)	560.0	

Properties of R142b

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	24.2	1261.4	
-35.0	31.4	1250.6	
-30.0	40.3	1239.6	
-25.0	51.1	1228.6	
-20.0	64.1	1217.5	
-15.0	79.7	1206.2	
-10.0	98.1	1194.8	
-5.0	119.8	1183.3	
0.0	145.1	1171.6	(29.)
5.0	174.4	1159.7	(389.)
10.0	208.0	1147.7	(457.)
15.0	246.5	1135.4	(534.)
20.0	290.2	1122.8	(621.)
25.0	339.7	1110.0	719.
30.0	395.3	1096.9	827.
35.0	457.5	1083.5	948.
40.0	526.9	1069.7	1081.
45.0	603.8	1055.4	1229.
50.0	689.0	1040.7	1391.
55.0	782.8	1025.5	1568.
60.0	885.8	1009.7	1761.
65.0	998.7	993.2	1972.
70.0	1122.0	975.9	2200.
75.0	1256.4	957.8	2447.
80.0	1402.5	938.7	(2714.)
85.0	1561.1	918.4	(3001.)
90.0	1733.0	896.8	(3310.)
95.0	1919.1	873.6	(3640.)
100.0	(2120.4)	848.4	(3993.)
NBP: -9.2	(101.3)	1193.0	
T_C: 137.1	(4246.4)	435.0	

Table 3. Saturated Liquid Density

Fluid	Temperature	limits		Coefficients to Equation (2)				RMS
	low (K)	high (K)	β	d_1	d_2 (dimensionless)	d_3	d_4	error (%)
R125	229.	T_C	1/3	1.642389	1.6539076	-1.729574	1.2250132	0.03
R22	210.	T_C	1/3	1.887739	0.5985853	-0.071134	0.4032765	0.1
R134a	239.	T_C	0.34	1.723892	1.7176130	-2.269035	1.7074390	0.38
R152a	220.	T_C	0.338	2.000849	-0.0176269	1.374012	-0.5664321	0.21
R124	220.	390.	1/3	1.723120	1.2093710	-1.189464	1.0189435	0.15
R142b	213.	365.	1/3	-0.276715	10.1472750	-13.917142	7.1135587	0.37
R123	240.	T_C	1/3	1.898571	0.2369317	0.654672	-0.0736059	0.22
R141b	263.	432.	1/3	-0.298060	9.6097677	-13.651652	7.3068081	0.09
methyl chlr.	263.	333.	1/3	8.751564	-24.2030418	28.987334	-10.7700329	

source of data (Valtz et al., 1986), although limited, is more consistent with the data of Mears, et al. There is a second, more subtle, means of deciding between conflicting data: the coefficients to Equation (2) are all of the same order of magnitude for the set of similar compounds considered here. When fit to the data of Cherneeva, however, the coefficients to Equation (2) are radically different from any other fluid considered in this report. The fit based on the data of Mears, et al. and Valtz, on the other hand, result in coefficients that are similar to those for the structurally analogous R141b (see Table 3). For these two reasons, the fit adopted here is based on the data of Mears, et al. and Valtz, et al.

For the solubility of R142b in water, Allied (1989) gives three data points over the temperature range 273-304 K; these were used in fitting Equation (4). The single datum (at 299 K) reported by Dupont (1989) is 19% higher than the solubility given by Equation (4) based on the Allied data.

R123

Refrigerant 123 (1,1-dichloro-2,2,2-trifluoroethane) is, along with R134a, one of the two most publicized new refrigerants, and, thus, property data are starting to become available. Critical parameters have been measured by Weber and Levelt-Sengers (1989), and have been reported on the data sheets of at least three chemical manufacturers (Allied, 1989; DuPont, 1989; and Daikin, 1989). The reported critical temperatures range from 456.94-459.45 K. An uncertainty involved with all R123 data is the isomeric purity of the sample. Commercial-grade R123 will likely contain a significant percentage, perhaps as much as 10%, of the isomer R123a (1,2-dichloro-1,2,2-trifluoroethane). For most of the available data there is no information on whether the measurements were conducted on isomerically pure R123 or on the R123/R123a mixture produced by the process of a particular company. The presence of a small amount of R123a will probably not affect the vapor pressure or liquid density significantly, but will likely affect the critical parameters. An isomerically pure sample of R123 was used in the critical point determination of Weber and Levelt-Sengers at NIST (as well as all the other NIST measurements). For this reason, and others, the NIST critical parameters are recommended. A freezing temperature of 166 K is reported by both DuPont and Daikin.

Two sources for the vapor pressure of R123 were used in fitting Equation (1). Weber (1989) has measured 43 values at temperatures above 338.1 K. Allied (1989) provide 16 points extending down to 234K. Although the two data sets are consistent (see Figure 7), only Weber's data were used for the fit above 338 K because of their very high accuracy and precision. Yamashita, et al. (1988) have also measured the vapor pressure of R123 at 38 temperatures from 270 K to the critical temperature but do not present their data. Yamashita, et al. have also carried out a similar set of vapor pressure measurements for R123a. They indicate a normal boiling point of 302.7 K for R123a and 300.7 K for R123; their boiling point for R123 is 0.4 K lower than the value evaluated from Equation (2).

No less than six sets of data, measured at two laboratories using five different methods are available for the saturated liquid density of R123. At NIST, Schmidt (1988) has employed a buoyancy technique, Weber has used a constant volume cell described by Weber and Levelt-Sengers (1989), and Morrison

Table 4. Solubility in Water

Fluid	**Temperature. low**	**limits high**	**Coefficients to Equation (4)**			**Solubility @101. kPa, 25°C**	**Comments**
			h_1	**h_2**	**h_3**		
	(K)	**(K)**	**(H in mass%/kPa, T in K)**			**(mass%)**	
R125	298.	333.	-22.88	4750.	0.0	0.097	
R22	283.	353.	-8.689	205.9	-225.1	0.29	
R134a	298.	353.	-15.35	2633.	0.0	0.15	
R152a	273.	348.	-13.60	2300.	0.0	0.29	
R124	313.	348.	-17.38	3229.	0.0	0.14	(1)
R142b	298.	353.	-15.11	2544.	0.0	0.14	
R123	297.	348.	-14.06	2570.	0.0	0.40	(2,3)
R141b	298.	311.	-24.61	5248.	0.0	0.071	(2,3)
methyl chloroform	273.	323.	-20.29	4655.	0.0	0.15	(3)

Comments

(1) Solubility at 25°C is extrapolation of data.

(2) Other sources give solubilities 41% lower to 129% higher than those listed here (see Discussion section).

(3) Normal boiling point is greater than 25°C; values given at a partial pressure equal to the vapor pressure at 25°C.

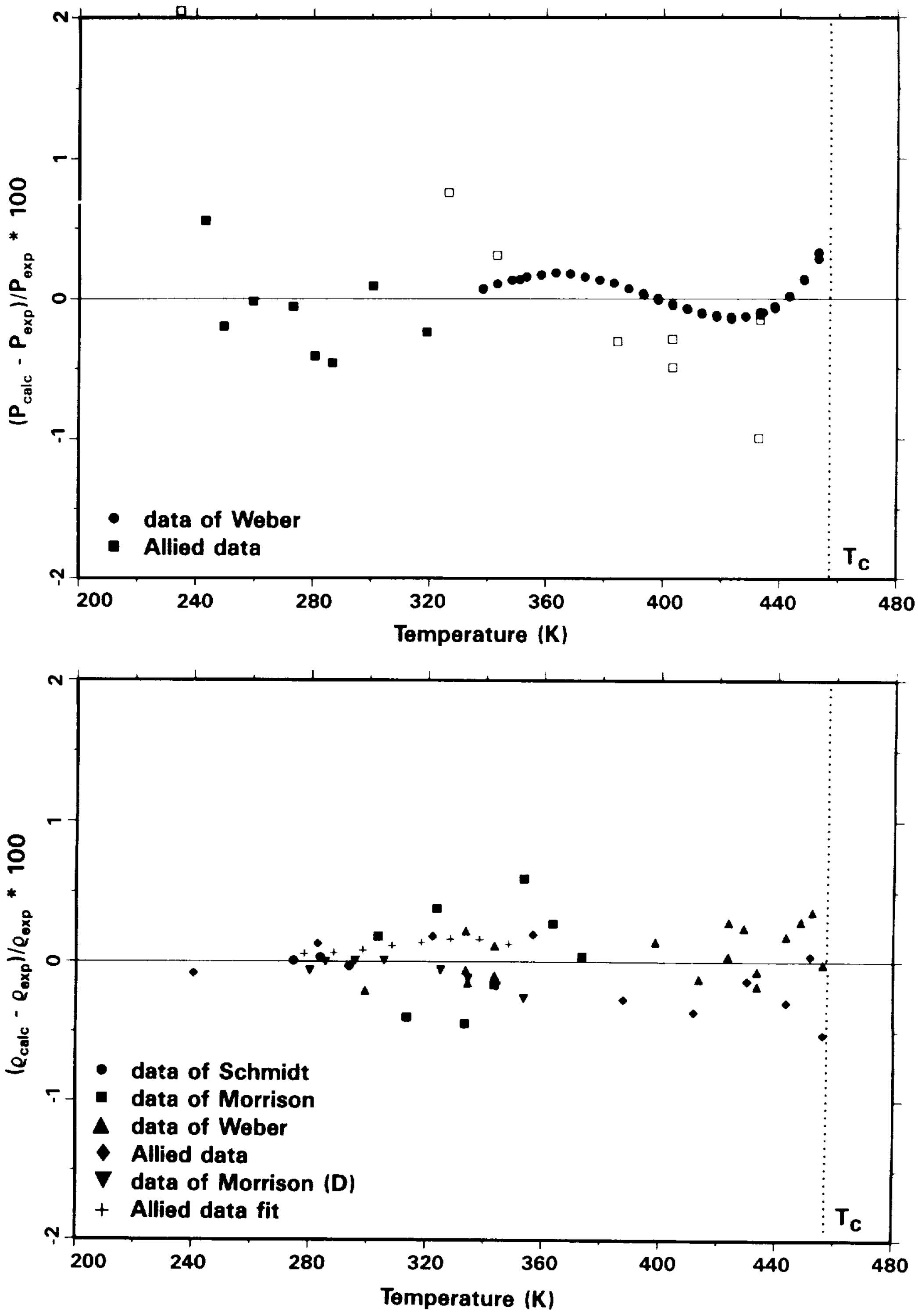


Figure 7. Comparison of correlations with data for R123; a) vapor pressure; b) saturated liquid density.

has used a mercury-displacement variable-volume cell as well as a vibrating-tube densimeter. Allied has employed their glass flotation beads and a vibrating tube densimeter; data for the latter method are available only as a correlation. All of these data were felt to be of comparable accuracy and all were included in the fit of Equation (2). As indicated in Figure 7, the different data sets are in essential agreement with an RMS deviation of 0.22%.

DuPont and Allied report solubility data. The data of DuPont cover the temperature range 297-348 K and are presented in terms of coefficients to a correlation similar to Equation (4); these coefficients are reported in Table 4 after the appropriate conversion of units. The single Allied datum at 295 K gives a solubility 41% lower than the DuPont data.

R141b

Although R141b (1,1-dichloro-1-fluoroethane) is being actively developed by several chemical manufacturers, only scattered unpublished data are available. Reported values for the critical temperature range from 480.9-483.4 K. The selection of the value of 481.5 K given by Solvay (1989) is largely arbitrary--none of the values are documented nor are uncertainties given. The adopted critical density is based on the critical compressibility factor given by Solvay (1989). The critical pressure and estimated critical density reported by Dupont were rejected primarily because they yielded a critical compressibility factor that was felt to be unrealistically high (0.314). A freezing point of 170. K is one parameter that Daikin (1989), DuPont, and Solvay agree on.

The vapor pressure data for R141b leave much to be desired. DuPont graphically presents 21 data points from 298-480 K and also a correlation of these data.The pressures could not be accurately read off their graph, and, thus, the vapor pressure was evaluated from their correlation at the temperatures corresponding to the data points. Another correlation from Allied (1989) for the temperature range 278-338 was handled in a similar fashion. Solvay reports six points from 243-368 K. Large differences are seen (Figure 8) for the residuals of these data fit to Equation (1). (Note that the range of the ordinate in this figure is twice that of the preceding figures.) Despite the inconsistencies in these data, all were included in the fit of Equation (1) because no single set spanned the full temperature range.

For liquid density, two data sets from Allied were used in fitting Equation (2). As seen in Figure 8, the densities measured with the glass bead technique agree very well with the densimeter data (presented in terms of a correlation).

The solubility data for R141b is particularly sparse and conflicting. The two data points of Allied at 298 and 311 K were used to fit Equation (4). The single datum of DuPont at 298 K gives a solubility 129% higher than the Allied datum at the same temperature.

Methyl chloroform

The critical temperature and pressure of methyl chloroform (1,1,1-trichloroethane) were determined by Ambrose, et al. (1973). The critical temperature of 545 K is subject to some uncertainty due to decomposition of the sample at high temperatures as discussed by Ambrose, et al. The critical density has appar-

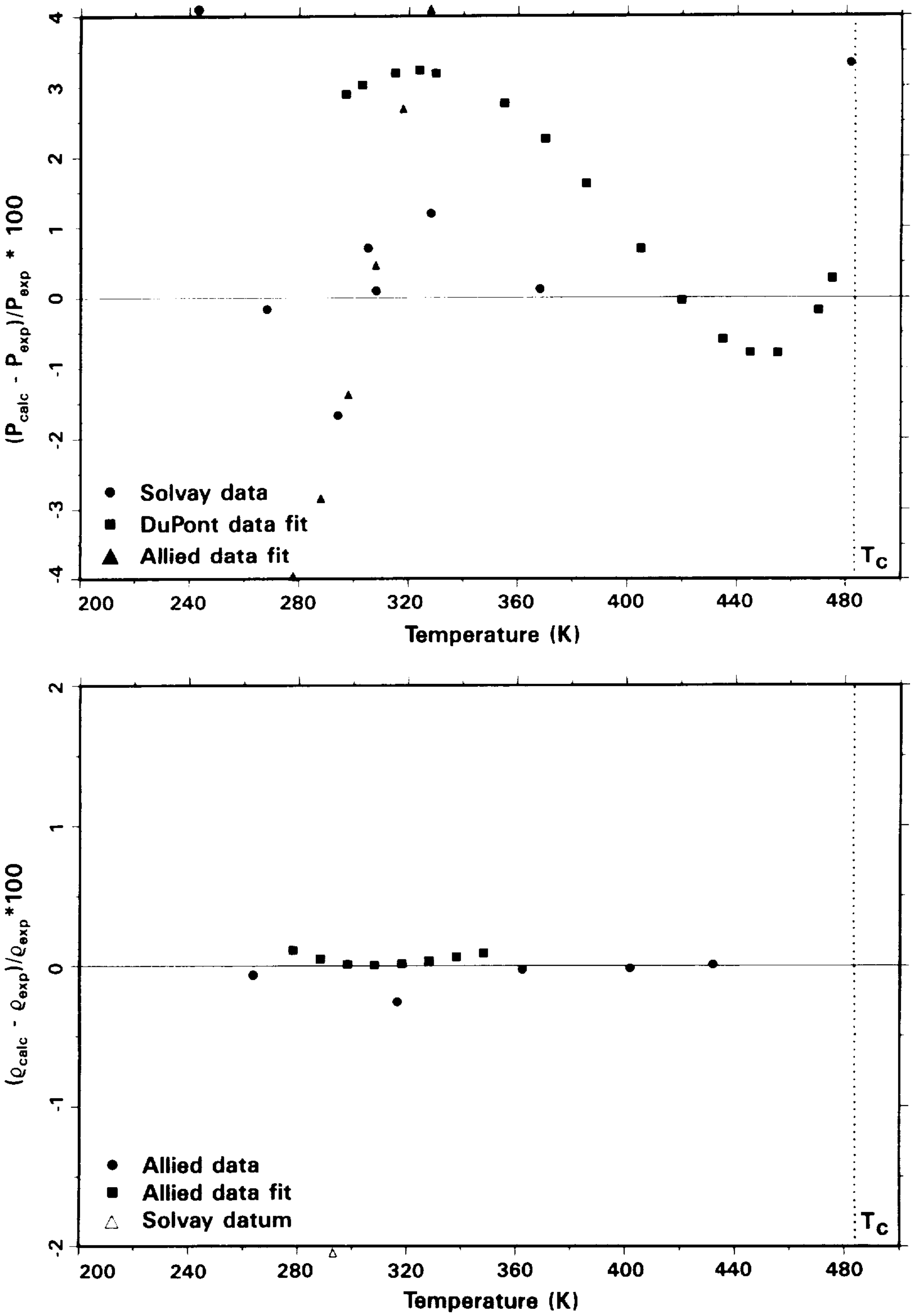


Figure 8. Comparison of correlations with data for R141b; a) vapor pressure; b) saturated liquid density.

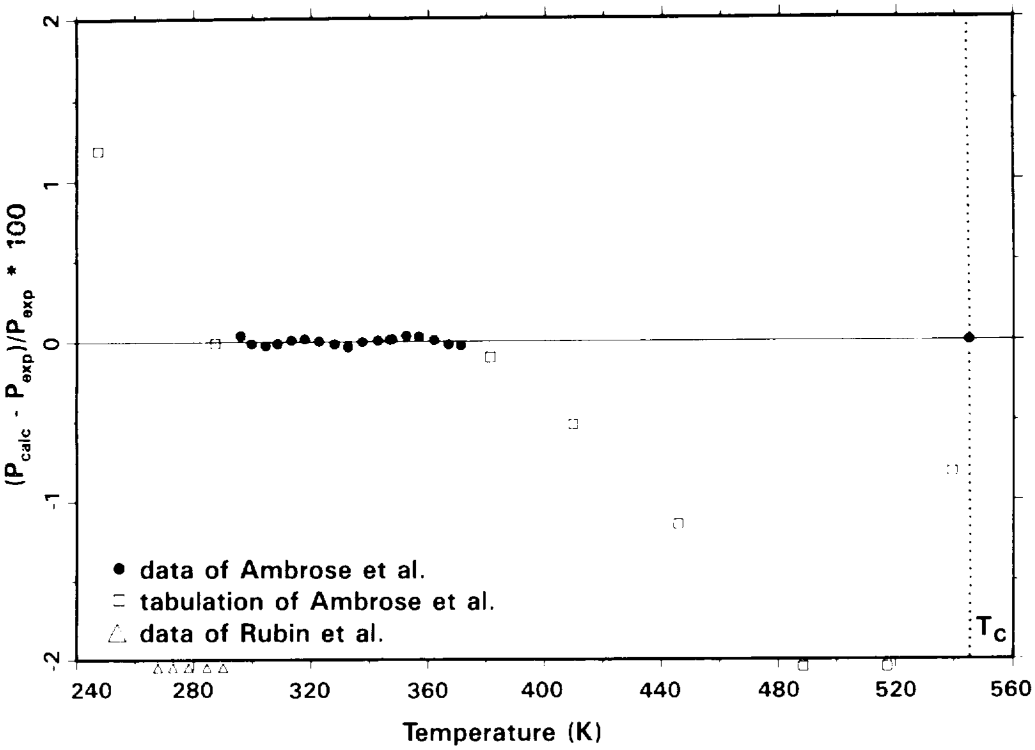


Figure 9. Comparison of vapor pressure correlation with data for methyl chloroform.

ently not been measured and thus had to be estimated. The estimation techniques of Ambrose and the Joback modification of Lydersen's method (both as reported in Reid, et al. 1987)) yield values of 468 kg/m³ and 471 kg/m³, respectively. A value of 470 kg/m³ is used in this work. Different sources for the triple point temperature differ by as much as 3 K (Rubin, et al. 1944); the value of 243.1 K measured by Andon, et al. (1973) is selected because of the high stated accuracy and high purity sample used.

The vapor pressure of methyl chloroform was measured by Ambrose, et al. from 296-371 K. They also represent their data in terms of a Chebyshev polynomial which they state can be accurately used outside the temperature range of the data. Equation (1) fits the measured data very well but not the tabulated values obtained from the Chebyshev polynomial (Figure 9). The data of Rubin, et al. (1974) are not consistent with the data of Ambrose, et al. and were not included in the fit of Equation (1).

Liquid densities tabulated by the Thermodynamics Research Center of Texas A&M University (1986) were used in the fit of Equation (2). Although the RMS deviation between the fit and the tabulated values was 0.003%, the accuracy of the tabulation was not given, and, thus, the accuracy of the correlation presented here cannot be stated.

The correlation for the solubility in water is based on the correlation of solubility presented by Walraevens, et al. (1974). Because they do not present their solubility data, their correlation was used to generated points which were then used to fit Equation 4.

Properties of R123

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(3.7)	(1614.5)	
-35.0	(5.1)	(1603.7)	
-30.0	6.9	1592.7	
-25.0	9.2	1581.6	
-20.0	12.2	1570.4	
-15.0	15.8	1559.1	
-10.0	20.4	1547.7	
-5.0	26.0	1536.1	
0.0	32.7	1524.4	(05.)
5.0	40.9	1512.5	(124.)
10.0	50.6	1500.5	(146.)
15.0	62.1	1488.4	(171.)
20.0	75.6	1476.0	(199.)
25.0	91.4	1463.5	230.
30.0	109.6	1450.9	266.
35.0	130.6	1438.0	305.
40.0	154.7	1424.9	348.
45.0	182.0	1411.7	396.
50.0	212.9	1398.2	449.
55.0	247.8	1384.4	507.
60.0	286.8	1370.5	570.
65.0	330.3	1356.2	639.
70.0	378.7	1341.6	714.
75.0	432.2	1326.8	(795.)
80.0	491.1	1311.6	(882.)
85.0	555.9	1296.0	(977.)
90.0	626.9	1280.1	(1078.)
95.0	704.3	1263.7	(1187.)
100.0	788.7	1246.9	(1303.)
NBP: 27.8	101.3	1456.4	
T_C: 183.8	3691.4	549.9	

Properties of R141b

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(2.9)	(1356.3)	
-35.0	(4.0)	(1346.7)	
-30.0	5.5	(1337.1)	
-25.0	7.5	(1327.5)	
-20.0	9.9	(1317.9)	
-15.0	13.0	(1308.2)	
-10.0	16.9	1298.6	
-5.0	21.6	1288.9	
0.0	27.4	1279.2	(221.)
5.0	34.4	1269.5	(312.)
10.0	42.8	1259.8	(435.)
15.0	52.7	1250.0	(600.)
20.0	64.4	1240.1	(819.)
25.0	78.0	1230.2	1106.
30.0	93.9	1220.3	1478.
35.0	112.1	1210.2	1957.
40.0	132.9	1200.1	(2569.)
45.0	156.6	1189.9	(3343.)
50.0	183.5	1179.7	(4315.)
55.0	213.6	1169.3	(5527.)
60.0	247.4	1158.7	(7026.)
65.0	285.1	1148.1	(8868.)
70.0	326.8	1137.3	(11119.)
75.0	372.9	1126.3	(13850.)
80.0	423.7	1115.2	(17145.)
85.0	479.4	1103.8	(21098.)
90.0	540.2	1092.3	(25814.)
95.0	606.5	1080.4	(31412.)
100.0	678.5	1068.4	(38023.)
NBP: 32.1	101.3	1216.0	
T_C: 208.4	4541.0	464.1	

Properties of methyl chloroform

(Parentheses indicate extrapolation of data)

Temp. (°C)	Vapor Pressure (kPa)	Sat. Liq. Density (kg/m³)	Henry's const. (kPa/Mass%)
-40.0	(.4)	(1435.6)	
-35.0	(.5)	(1427.5)	
-30.0	(.8)	(1419.5)	
-25.0	(1.1)	(1411.4)	
-20.0	(1.5)	(1403.3)	
-15.0	(2.0)	(1395.2)	
-10.0	(2.8)	1387.0	
-5.0	(3.7)	1378.9	
0.0	(4.9)	1370.7	26.
5.0	(6.3)	1362.6	35.
10.0	(8.2)	1354.4	47.
15.0	(1.4)	1346.2	63.
20.0	(13.2)	1338.1	82.
25.0	16.5	1329.9	107.
30.0	20.5	1321.7	139.
35.0	25.2	1313.6	178.
40.0	30.9	1305.4	227.
45.0	37.4	1297.3	287.
50.0	45.1	1289.1	(360.)
55.0	54.0	1281.0	(448.)
60.0	64.2	(1272.9)	(554.)
65.0	75.9	(1264.8)	(681.)
70.0	89.2	(1256.8)	(833.)
75.0	104.2	(1248.8)	(1012.)
80.0	121.2	(1240.8)	(1222.)
85.0	140.3	(1232.9)	(1469.)
90.0	161.5	(1224.9)	(1757.)
95.0	185.2	(1217.1)	(2092.)
100.0	(211.4)	(1209.3)	(2478.)
NBP: 74.1	(101.3)	(1250.3)	
Tc: 271.9	(4300.0)	(470.0)	

Table 5. Comparison of Solubilities Evaluated from Data with Those Estimated by Method of Irmann

Fluid	Solubility (mass%) @ 25°C (partial pres = 101.325 kPa) data	estimated
R125	0.097	0.044
R22	0.29	0.31
R134a	0.15	0.13
R152a	0.29	0.29
R124	0.14	0.13
R142b	0.14	0.15
R123*	0.40	0.38
R141b*	0.071	0.39
methyl chloroform*	0.15	0.13

*Normal boiling point is greater than 25°C; values given for a partial pressure equal to the vapor pressure at 25°C.

4. CONCLUDING REMARKS

This report presents recommended values and correlations of selected physical properties of several alternatives to the fully halogenated chlorofluorocarbons. The quality of the data used in this compilation varies widely, ranging from well-documented, high accuracy measurements from published sources to completely undocumented values listed on anonymous data sheets. That some properties for some fluids are available only from the latter type of source is clearly not the desired state of affairs. While some would reject all such data, the compilation given here is presented in the spirit of laying out the present state of knowledge and making available a set of data in a timely manner, even though its quality is sometimes uncertain. The correlations presented here are certain to change quickly as additional information becomes available. Indeed, one use of this report could be to identify areas where additional work is needed.

III. REACTION RATE CONSTANTS

Evaluated Rate Constants for Selected HCFC's and HFC's with OH and O(^1D)

Robert F. Hampson and **Michael J. Kurylo**
Center for Chemical Technology
National Institute of Standards and Technology
Gaithersburg, MD 20899

and

Stanley P. Sander
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

EXECUTIVE SUMMARY

The chemistry of HCFC's and HFC's in the troposphere is controlled by reactions with OH in which a hydrogen atom is abstracted from the halocarbon to form water and a halo-alkyl radical. The halo-alkyl radical subsequently reacts with molecular oxygen to form a peroxy radical. The reactions of HCFC's and HFC's with $O(^1D)$ atoms are unimportant in the troposphere but may be important in producing active chlorine or OH in the stratosphere.

In this chapter, the rate constants for the reactions of OH and $O(^1D)$ with many HFC's and HCFC's have been evaluated. Recommendations are given for the five HCFC's and three HFC's specified by AFEAS as primary alternatives as well as for all other isomers of C_1 and C_2 HCFC's and HFC's where rate data exist. In addition, recommendations are included for CH_3CCl_3, CH_2Cl_2, and CH_4.

The format used for the presentation of the recommended rate constant data is the same as that used by the NASA Panel for Data Evaluation (see DeMore et al., JPL Publication 87-41, September 15, 1987). The rate constant tabulation is given in Arrhenius form, $k(T) = A \exp(-E/RT)$, and contains the following information:

1. Reaction stoichiometry and products (if known).
2. Arrhenius A factor (in units of cm^3 $molecule^{-1}$ s^{-1}).
3. Temperature dependence ("activation temperature," E/R) and associated uncertainty ($\Delta E/R$).
4. Rate constant at 298 K (in units of cm^3 $molecule^{-1}$ s^{-1}).
5. Uncertainty factor at 298 K.

All of the uncertainties are one standard deviation, 1σ. Hence, 95% confidence limits are given by 2σ. The uncertainty (1σ) at any temperature can be calculated from the expression:

$$f(T) = f(298)\exp\{\Delta E/R(1/T - 1/298)\}$$

For all of the OH reactions, the recommendations were derived from linear least squares Arrhenius fits of the selected data bases for temperatures below 400 K. This temperature restriction was made due to the observed Arrhenius curvature for several of the reactions over more extended temperature ranges. For some reactants, the necessary temperature dependent data do not exist, and the E/R values were estimated by comparison with other similar reactants and the A factor back-calculated using k_{298}. Reasonable values of E/R can be estimated from compounds appearing in a homologous series and by noting that most values of E/R for reactions of OH with halocarbons lie between 1000 and 2000 K. An alternative approach would have involved estimating, or calculating from transition state theory, the A factor and using k_{298} to obtain E/R. These two approaches yield similar results if the data are not extrapolated very far from room temperature and, thus, are nearly equivalent for the calculation of ozone depletion or greenhouse warming potentials. These two estimation procedures can result in significant differences when used for extrapolations over a wide temperature range. In addition, they can yield disparate predictions when there are no direct kinetic data for either the species of interest or for one of similar structure.

Rate constants for the $O(^1D)$ reactions are associated with actual chemical reaction (leading to chemical breakdown of the HCFC or HFC) and do not include contributions due to simple physical deactivation (quenching) of the excited oxygen atom. Temperature data do not exist for most of the $O(^1D)$ reactions and the estimated temperature independencies are taken from comparisons with the few HCFC's and CFC's for which such data do exist. The following two tables summarize the results of this evaluation.

RATE CONSTANTS

Recommended rate constants and uncertainties for reactions of OH with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A^1	$E/R \pm \Delta E/R^2$	$k_{298}{}^1$	f(298)
OH + $CHFCl_2$	HCFC-21	1.2(-12)	1100 ± 150	3.0(-14)	1.1
OH + CHF_2Cl	HCFC-22	1.2(-12)	1650 ± 150	4.7(-15)	1.1
OH + CHF_3	HFC-23	1.5(-12)	2650 ± 500	2.1(-16)	1.5
OH + CH_2Cl_2	30	5.8(-12)	1100 ± 250	1.4(-13)	1.2
OH + CH_2FCl	HCFC-31	3.0(-12)	1250 ± 200	4.5(-14)	1.15
OH + CH_2F_2	HFC-32	2.5(-12)	1650 ± 200	1.0(-14)	1.2
OH + CH_3F	HFC-41	5.4(-12)	1700 ± 300	1.8(-14)	1.2
OH + CH_4	50	2.3(-12)	1700 ± 200	7.7(-15)	1.2
OH + $CHCl_2CF_3$	HCFC-123	6.4(-13)	850 ± 250	3.7(-14)	1.2
OH + $CHFClCF_3$	HCFC-124	6.6(-13)	1250 ± 300	1.0(-14)	1.2
OH + CHF_2CF_3	HFC-125	8.9(-13)	1750 ± 500	2.5(-15)	2.0
OH + CH_2ClCF_2Cl	HCFC-132b	3.6(-12)	1600 ± 400	1.7(-14)	2.0
OH + CH_2ClCF_3	HCFC-133a	5.2(-13)	1100 ± 300	1.3(-14)	1.3
OH + CHF_2CHF_2	HFC-134	8.7(-13)	1500 ± 500	5.7(-15)	2.0
OH + CH_2FCF_3	HFC-134a	1.7(-12)	1750 ± 300	4.8(-15)	1.2
OH + CH_3CCl_3	140	5.0(-12)	1800 ± 300	1.2(-14)	1.3
OH + CH_3CFCl_2	HCFC-141b	4.2(-13)	1200 ± 300	7.5(-15)	1.3
OH + CH_3CF_2Cl	HCFC-142b	9.6(-13)	1650 ± 250	3.8(-15)	1.2
OH + CH_2FCHF_2	HFC-143	2.8(-12)	1500 ± 500	1.8(-14)	2.0
OH + CH_3CF_3	HFC-143a	6.0(-13)	1750 ± 500	1.7(-15)	2.0
OH + CH_2FCH_2F	HFC-152	1.7(-11)	1500 ± 500	1.1(-13)	2.0
OH + CH_3CHF_2	HFC-152a	1.5(-12)	1100 ± 200	3.7(-14)	1.1
OH + CH_3CH_2F	HFC-161	1.3(-11)	1200 ± 300	2.3(-13)	2.0

1 units are cm^3 $molecule^{-1}$ s^{-1}
2 units are K

Recommended rate constants and uncertainties for reactions of $O(^1D)$ with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A^1	$E/R \pm \Delta E/R^2$	$k_{298}{}^1$	f(298)
$O(^1D) + CHFCl_2$	HCFC-21	1.9(-10)	0 ± 100	1.9(-10)	1.3
$O(^1D) + CHF_2Cl$	HCFC-22	1.0(-10)	0 ± 100	1.0(-10)	1.3
$O(^1D) + CHF_3$	HFC-23	1.9(-12)	0 ± 500	1.9(-12)	3.0
$O(^1D) + CH_2F_2$	HFC-32	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D) + CH_3F$	HFC-41	1.0(-10)	0 ± 100	1.0(-10)	2.0
$O(^1D) + CHCl_2CF_3$	HCFC-123	2.3(-10)	0 ± 100	2-3(-10)	2.0
$O(^1D) + CHFClCF_3$	HCFC-124	1.0(-10)	0 ± 100	1.0(-10)	3.0
$O(^1D) + CHF_2CF_3$	HFC-125	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D) + CH_2ClCF_2Cl$	HCFC-132b	1.7(-10)	0 ± 100	1.7(-10)	2.0
$O(^1D) + CH_2ClCF_3$	HCFC-133a	1.6(-10)	0 ± 100	1.6(-10)	2.0
$O(^1D) + CH_2FCF_3$	HFC-134a	5.0(-11)	0 ± 100	5.0(-11)	3.0
$O(^1D) + CH_3CFCl_2$	HCFC-141b	1.5(-10)	0 ± 100	1.5(-10)	3.0
$O(^1D) + CH_3CF_2Cl$	HCFC-142b	1.4(-10)	0 ± 100	1.4(-10)	2.0
$O(^1D) + CH_3CF_3$	HFC-143a	6.0(-11)	0 ± 100	6.0(-11)	2.0
$O(^1D) + CH_3CHF_2$	HFC-152a	1.0(-10)	0 ± 100	1.0(-10)	3.0

1 units are cm^3 $molecule^{-1}$ s^{-1}

2 units are K

N92-15437

EVALUATED RATE CONSTANTS FOR SELECTED HCFC'S AND HFC'S WITH OH AND O(^{1}D)

Robert F. Hampson and Michael J. Kurylo
Center for Chemical Technology
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

Stanley P. Sander
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

INTRODUCTION

The anthropogenic release of chlorofluorocarbons (CFC's) can cause significant perturbations to the odd oxygen budget of the stratosphere through catalytic processes. The partially halogenated CFC's react much more quickly in the troposphere than their fully halogenated counterparts. The substitution of hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's) for fully halogenated species in industrial applications may therefore lessen the problem of catalytic ozone destruction in the stratosphere. In order to evaluate the effects of HCFC releases we must achieve a reasonable understanding of the rates and mechanisms of the reactions of HCFC's and HFC's with other tropospheric constituents. The chemistry of HCFC's and HFC's in the troposphere is controlled by reactions with OH in which a hydrogen atom is abstracted from the halocarbon to form water and a halo-alkyl radical. The halo-alkyl radical subsequently reacts with molecular oxygen to form a peroxy radical. The reactions of HCFC's and HFC's with $O(^1D)$ atoms are unimportant in the troposphere but may be important in producing active chlorine or OH in the stratosphere.

Scope

This paper is a critical evaluation of the available data on the reactions of OH and $O(^1D)$ with selected partially hydrogenated C_1 and C_2 haloalkanes. Of the 6 C_1 and 36 C_2 HFC's and HCFC's that exist, eight compounds have been identified as being of particular interest to the fluorocarbon industry as possible CFC substitutes. These include HCFC-22 (CHF_2Cl), HCFC-152a (CH_3-CHF_2), HFC-134a (CH_2F-CF_3), HFC-125 (CHF_2-CF_3), HCFC-142b (CH_3-CF_2Cl), HCFC-124 ($CHFCl$-CF_3), HCFC-141b (CH_3-$CFCl_2$) and HCFC-123 ($CHCl_2$-CF_3). Accordingly, the reactions of OH and $O(^1D)$ with these compounds were evaluated where data existed and estimated where experimental results were not available. In addition, all other C_1 and C_2 HCFC's and HFC's for which kinetic data existed were included. These are HFC-41 (CH_3F), HFC-32 (CH_2F_2), HFC-23 (CHF_3), HCFC-31 (CH_2FCl), HCFC-21 ($CHFCl_2$), HFC-161 (CH_3-CH_2F), HFC-152 (CH_2F-CH_2F), HFC-143 (CH_2F-CHF_2), HFC-143a (CH_3-CF_3), HFC-134 (CHF_2-CHF_2), HCFC-133a (CH_2Cl-CF_3) and HCFC-132b (CH_2Cl-CF_2Cl) for a total of 20 HFC and HCFC species being reviewed. There are currently temperature dependence OH reaction rate data for all the compounds in the first group. In the second group, there are room temperature OH kinetics data for all species, but temperature dependence data are lacking for HFC-161 and HFC-152. We have also included evaluations for CH_3CCl_3 and CH_2Cl_2 since these compounds play a role in most chlorine-ozone modeling scenarios. An evaluation for CH_4 was included because of its important role in atmospheric HO_x chemistry. The previous kinetics studies of the species of interest, including the temperature ranges and measurement techniques are summarized in Table 1.

Reactions of HFC's and HCFC's with OH

Several recent evaluations of OH reaction rate data for these species have been published including DeMore et al. (1987) (hereafter called NASA (1987)), Atkinson et al. (1989) (hereafter called IUPAC (1989)), Atkinson (1989) and Cohen and Westberg (1988). The emphasis of all these evaluations with the exception of the last one has been on data relevant to atmospheric modelling. Because the Cohen and Westberg review is oriented toward high temperature combustion conditions, the recommendations from their evaluation are not included. No single review encompasses the data for all the reactions considered here. In addition, this review includes data from the recent, unpublished studies of Kurylo (1989) and Ravishankara (1989)

Table 1. Laboratory studies of the reactions of OH with C_1 and C_2 HFC's and HCFC's.

Reference	Fluorocarbon Number	Technique[1]	Temp. Range (K)
Atkinson et al. (1975)	22	FP/RF	297-434
Davis et al. (1976)	30	FP/RF	245-375
Howard and Evenson (1976a)	21,22,23,30,31,32,41	DF/LMR	296
Howard and Evenson (1976b)	123,124,133a,140 142b,152a	DF/LMR	296
Perry et al. (1976)	21,30	FP/RF	298-423
Watson et al. (1977)	21,22,31,140,142b	FP/RF	250-350
Chang and Kaufman (1977)	21,22	DF/RF	250-400
Handwerk and Zellner (1978)	22,31,133a,142b,152a	FP/RA	260-370
Ernst et al. (1978)	23	FP-ST/RA	1000-1500
Clyne and Holt (1979a)	140	DF/RF	293-425
Clyne and Holt (1979b)	21,22,23,32,123,125 133,134,134a,142b,143 143a,152a	DF/RF	293-425
Jeong and Kaufman (1979)	140	DF/RF	250-480
Kurylo et al. (1979)	140	FP/RF	222-363
Nip et al. (1979)	23,32,41,152a,161	FP/RA	297
Watson et al. (1979)	123,124,132b	FP/RF	250-375
Singleton et al. (1980)	161	GC/MS	298
Paraskevopoulos et al. (1981)	21,22,31,142b	FP/RA	297
Jeong and Kaufman (1982a)	21,22,23,30,31,32,41	DF/RF	250-480
Martin & Paraskevopoulos (1983)	125,134a,143,143a,152	FP/RA	298
Jeong et al. (1984)	132b,134a	DF/RF	250-470
Ravishankara (1989)	134a,141b,142b 152a,123	LP/FP/LIF & DF/LMR	235-425
Kurylo (1989)	123,134a,141b,142b 152a	FP/RF	270-400

[1] DF - discharge flow, FP - flash photolysis, GC - gas chromatography, LMR - laser magnetic resonance, LP - laser photolysis, MS - mass spectrometry, RA - resonance absorption, RF - resonance fluorescence, ST - shock tube.

which are not included in the previous evaluations. Ten of the twenty reactions reviewed here were previously evaluated in NASA (1987). Of these ten, the new rate data encompass five of the ten reactions.

The format of this evaluation combines aspects of the NASA and IUPAC review formats. For each reaction, there is a set of data sheets listing the rate constants and measurement temperatures from every paper where data are presented. Also included are the Arrhenius parameters derived in the original study and in subsequent reviews. The recommended Arrhenius parameters from this evaluation are then listed with the uncertainties in k_{298} and E/R. The data sheet includes a note which discusses the studies and temperature ranges which were considered in the review. Finally a plot of ln k vs. 1/T is presented for each reaction showing the data from the original studies and the line derived from the recommended Arrhenius parameters. In all cases, the temperature limits for the recommended rate expression are 220 to 400 K. This temperature restriction was made due to the observed Arrhenius curvature for several of the reactions over more extended temperature ranges. The recommended rate expressions and uncertainties are summarized in Table 2. The data point symbols on the plots are identified in Table 4.

For virtually every reaction evaluated, the experimental data were obtained from studies which monitored the loss of OH in the presence of excess halocarbon. For relatively slow reactions, which proceed under conditions where the rate constant is 10^{-15} cm^3 $molecule^{-1}$ s^{-1} or less, this procedure can lead to an overestimation of the true rate constant due to the presence of trace reactive impurities or to secondary reactions involving the primary radical product. One of the early studies (Clyne and Holt, 1979a,b) may have suffered from such interferences. Because of these discrepancies the Clyne and Holt results were not considered in the evaluation.

For those reactions for which temperature dependence data did not exist or were available only from the Clyne and Holt study, we chose to estimate the value of E/R and back-calculate the A-factor using k_{298}. Reasonable values of E/R can be estimated from compounds appearing in a homologous series, and by noting that most values of E/R for reactions of OH with halocarbons lie between 1000 and 2000 K. An alternative approach would have involved estimating, or calculating from transition state theory, the A factor and using k_{298} to obtain E/R. These two approaches yield similar results if the data are not extrapolated very far from room temperature and, thus, are nearly equivalent for the calculation of ozone depletion or greenhouse warming potentials. These two estimation procedures can result in significant differences when used for extrapolations over a wide temperature range. In particular, they can yield disparate predictions when there are no direct kinetic data for either the species of interest or for one of similar structure. In addition, it should be noted that several OH + fluorocarbon reactions have experimentally derived A factors which are lower than expected for hydrogen abstraction (assumed to be the dominant pathway for these reactions). While this may be due to systematic experimental errors of the type mentioned earlier, it appears to be particularly characteristic of the highly fluorinated compounds.

Reactions of HFC's and HCFC's with $O(^1D)$

Recommended rate constants for the reactions of HFC's and HCFC's with $O(^1D)$ are given in Table 3. Rate constant values for the $O(^1D)$ reactions are associated with actual chemical reaction (leading to chemical breakdown of the HCFC or HFC) and do not include contributions due to simple physical deactivation (quenching) of the excited oxygen atom. Force and Wiesenfeld (1981) determined that chemical reaction played a dominant role in the overall interaction with all halomethanes they studied except for

Table 2. Recommended rate constants and uncertainties for reactions of OH with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A^1	$E/R \pm \Delta E/R^2$	$k_{298}{}^1$	f(298)
OH + $CHFCl_2$	HCFC-21	1.2(-12)	1100 ± 150	3.0(-14)	1.1
OH + CHF_2Cl	HCFC-22	1.2(-12)	1650 ± 150	4.7(-15)	1.1
OH + CHF_3	HFC-23	1.5(-12)	2650 ± 500	2.1(-16)	1.5
OH + CH_2Cl_2	30	5.8(-12)	1100 ± 250	1.4(-13)	1.2
OH + CH_2FCl	HCFC-31	3.0(-12)	1250 ± 200	4.5(-14)	1.15
OH + CH_2F_2	HFC-32	2.5(-12)	1650 ± 200	1.0(-14)	1.2
OH + CH_3F	HFC-41	5.4(-12)	1700 ± 300	1.8(-14)	1.2
OH + CH_4	50	2.3(-12)	1700 ± 200	7.7(-15)	1.2
OH + $CHCl_2CF_3$	HCFC-123	6.4(-13)	850 ± 250	3.7(-14)	1.2
OH + $CHFClCF_3$	HCFC-124	6.6(-13)	1250 ± 300	1.0(-14)	1.2
OH + CHF_2CF_3	HFC-125	8.9(-13)	1750 ± 500	2.5(-15)	2.0
OH + CH_2ClCF_2Cl	HCFC-132b	3.6(-12)	1600 ± 400	1.7(-14)	2.0
OH + CH_2ClCF_3	HCFC-133a	5.2(-13)	1100 ± 300	1.3(-14)	1.3
OH + CHF_2CHF_2	HFC-134	8.7(-13)	1500 ± 500	5.7(-15)	2.0
OH + CH_2FCF_3	HFC-134a	1.7(-12)	1750 ± 300	4.8(-15)	1.2
OH + CH_3CCl_3	140	5.0(-12)	1800 ± 300	1.2(-14)	1.3
OH + CH_3CFCl_2	HCFC-141b	4.2(-13)	1200 ± 300	7.5(-15)	1.3
OH + CH_3CF_2Cl	HCFC-142b	9.6(-13)	1650 ± 250	3.8(-15)	1.2
OH + CH_2FCHF_2	HFC-143	2.8(-12)	1500 ± 500	1.8(-14)	2.0
OH + CH_3CF_3	HFC-143a	6.0(-13)	1750 ± 500	1.7(-15)	2.0
OH + CH_2FCH_2F	HFC-152	1.7(-11)	1500 ± 500	1.1(-13)	2.0
OH + CH_3CHF_2	HFC-152a	1.5(-12)	1100 ± 200	3.7(-14)	1.1
OH + CH_3CH_2F	HFC-161	1.3(-11)	1200 ± 300	2.3(-13)	2.0

1 units are cm^3 $molecule^{-1}$ s^{-1}
2 units are K

Table 3. Recommended rate constants and uncertainties for reactions of $O(^1D)$ with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A[1]	E/R ± ΔE/R[2]	k_{298}[1]	f(298)
$O(^1D) + CHFCl_2$	HCFC-21	1.9(-10)	0 ± 100	1.9(-10)	1.3
$O(^1D) + CHF_2Cl$	HCFC-22	1.0(-10)	0 ± 100	1.0(-10)	1.3
$O(^1D) + CHF_3$	HFC-23	1.9(-12)	0 ± 500	1.9(-12)	3.0
$O(^1D) + CH_2F_2$	HFC-32	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D) + CH_3F$	HFC-41	1.0(-10)	0 ± 100	1.0(-10)	2.0
$O(^1D) + CHCl_2CF_3$	HCFC-123	2.3(-10)	0 ± 100	2-3(-10)	2.0
$O(^1D) + CHFClCF_3$	HCFC-124	1.0(-10)	0 ± 100	1.0(-10)	3.0
$O(^1D) + CHF_2CF_3$	HFC-125	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D) + CH_2ClCF_2Cl$	HCFC-132b	1.7(-10)	0 ± 100	1.7(-10)	2.0
$O(^1D) + CH_2ClCF_3$	HCFC-133a	1.6(-10)	0 ± 100	1.6(-10)	2.0
$O(^1D) + CH_2FCF_3$	HFC-134a	5.0(-11)	0 ± 100	5.0(-11)	3.0
$O(^1D) + CH_3CFCl_2$	HCFC-141b	1.5(-10)	0 ± 100	1.5(-10)	3.0
$O(^1D) + CH_3CF_2Cl$	HCFC-142b	1.4(-10)	0 ± 100	1.4(-10)	2.0
$O(^1D) + CH_3CF_3$	HFC-143a	6.0(-11)	0 ± 100	6.0(-11)	2.0
$O(^1D) + CH_3CHF_2$	HFC-152a	1.0(-10)	0 ± 100	1.0(-10)	3.0

1 units are cm^3 molecule^{-1} s^{-1}
2 units are K

highly fluorinated species. Of the species considered here, only for CF_3H is physical deactivation important. For these species absolute rate constants have been reported in the following studies: Fletcher and Husain (1976) for HCFC-21 and HCFC-22; Davidson et al. (1978) for HCFC-21 and HCFC-22; and Force and Wiesenfeld (1981) for HFC-23 and HFC-41. In the first two studies overall rate constants for collisional deactivation were reported, while in the study by Force and Wiesenfeld both the overall rate constants and those for chemical reaction were determined. Green and Wayne (1976) conducted a competitive study in which the rate constants only for the chemical reactions were determined relative to the reaction with N_2O for HCFC-22, HFC-32, HCFC-123, HFC-125, HCFC-132b, HCFC-133a, HCFC-142b, and HFC-143a. The values given here are based upon a value of 1.2(-10) cm^3 molecule^{-1} s^{-1} for the rate

Table 4. Symbols used in Data Plots for Reactions of OH with HFC's and HCFC's.

Symbol	Reference(s)
■	Howard and Evenson (1976a), Howard and Evenson (1976b)
△	Watson et al. (1977), Watson et al. (1979), Davis et al. (1976)
□	Handwerk and Zellner (1978)
●	Nip et al. (1979), Paraskevopoulos et al. (1981), Martin and Paraskevopoulos (1983)
◇	Clyne and Holt (1979a,b)
▽	Jeong and Kaufman (1979, 1982a), Jeong et al. (1984)
▼	Chang and Kaufman (1977)
◆	Atkinson et al. (1975), Perry et al. (1976)
○	Ravishankara (1989)
▲	Kurylo et al. (1979), Kurylo (1989)

constant of the reference reaction of $O(^1D)$ with N_2O. For HCFC-124, HFC-134a, HCFC-141b, and HFC-152a no data have been reported. For the reactions with these species the values given here have been estimated by analogy with reactions of similar species for which data exist. In these cases an uncertainty factor of three was assigned. Only for HCFC-21 and HCFC-22 do data exist over a range of temperature. The temperature independencies recommended here for all $O(^1D)$ reactions are based upon the temperature independencies observed for reactions with these two species and with several CFC's.

Uncertainties

All of the uncertainties are one standard deviation, 1σ. Hence, 95% confidence limits are given by 2σ. The uncertainty (1σ) at any temperature can be calculated from the expression:

$$f(T) = f(298) \exp\{(\Delta E/R)(1/T - 1/298)\}$$

OH + $CHFCl_2$ (HCFC-21) → H_2O + $CFCl_2$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	26	Howard and Evenson (1976a)
298	27	Perry et al. (1976)
349	48	
422	91	
245	11.2	Watson et al. (1977)
273	20.9	
298	28.8	
375	66.8	
241	12.8	Chang and Kaufman (1977)
250	17.3	
288	27.0	
296	30.4	
380	71.7	
396	75.2	
293	35.4	Clyne and Holt (1979b)
330	65.7	
373	97.7	
413	152	
297	33.9	Paraskevopoulos et al. (1981)
250	18.8	Jeong and Kaufman (1982a)
295	33.7	
315	42.5	
354	58.5	
392	78.6	
433	105	
483	148	

$OH + CHFCl_2$ (HCFC-21) $\rightarrow H_2O + CFCl_2$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
1.75	-	1253	298-422	Perry et al. (1976)
1.87	-	1245	245-375	Watson et al. (1977)
1.16	-	1073	241-396	Chang and Kaufman (1977)
4.79	-	1400	293-413	Clyne and Holt (1979b)
1.19	-	1052	250-483	Jeong et al. (1984)

Reviews and Evaluations

0.86	-	1000	230-300	NASA (1987)
1.1	-	1070	240-350	IUPAC (1989)
1.7(-18)	2.0	479	241-483	Atkinson (1989)

Preferred Values

$k = 1.2\text{x}10^{-12} \exp[-(1100 \pm 150)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

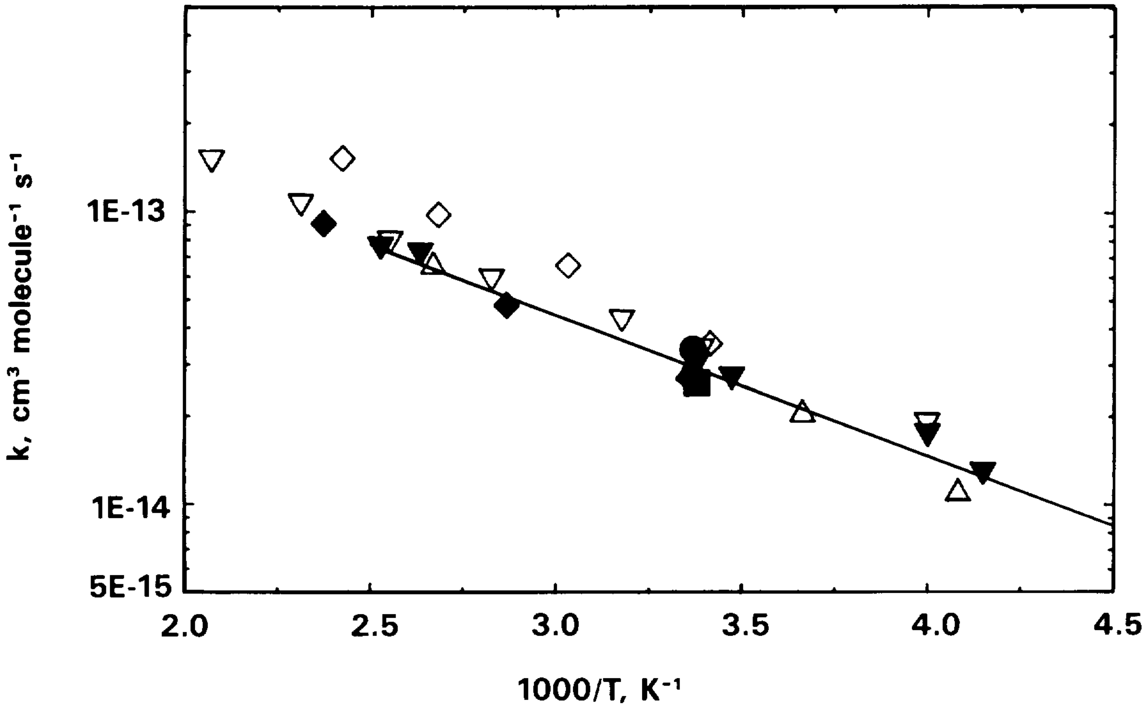
$k_{298} = 3.0\text{x}10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

The data base for this reaction is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b) which have a significantly larger temperature dependence than all the other studies. The rate constants from the latter study are consistently larger than those obtained in all other studies. The expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.

OH + HCFC-21



OH + CHF_2Cl (HCFC-22) → H_2O + CF_2Cl

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
297	4.75	Atkinson et al. (1975)
348	11.5	
434	27.1	
296	3.4	Howard and Evenson (1976a)
250	1.7	Watson et al. (1977)
273	2.77	
298	4.8	
350	10.1	
253	1.77	Chang and Kaufman (1977)
296	4.25	
358	12.0	
427	24.9	
263	2.0	Handwerk and Zellner (1978)
273	2.7	
283	5.1	
293	4.6	
373	17	
294	3.3	Clyne and Holt (1979b)
321	7.7	
343	12.8	
376	19.7	
391	27.7	
426	39.0	
297	4.58	Paraskevopoulos et al. (1981)
293	4.83	Jeong and Kaufman (1982a)
327	7.68	
360	10.8	
391	17.9	
436	27.5	
482	43.9	

$OH + CHF_2Cl$ (HCFC-22) → $H_2O + CF_2Cl$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.21	-	1636	297-434	Atkinson et al. (1975)
0.925	-	1575	250-350	Watson et al. (1977)
2.1	-	1780	263-373	Handwerk and Zellner (1978)
9.5	-	2300	294-426	Clyne and Holt (1979b)
1.27	-	1660	293-482	Jeong et al. (1984)
		Reviews and Evaluations		
0.83	-	1550	230-300	NASA (1987)
1.1	-	1620	250-360	IUPAC (1989)
1.51(-18)	2.0	1000	250-482	Atkinson (1989)

Preferred Values

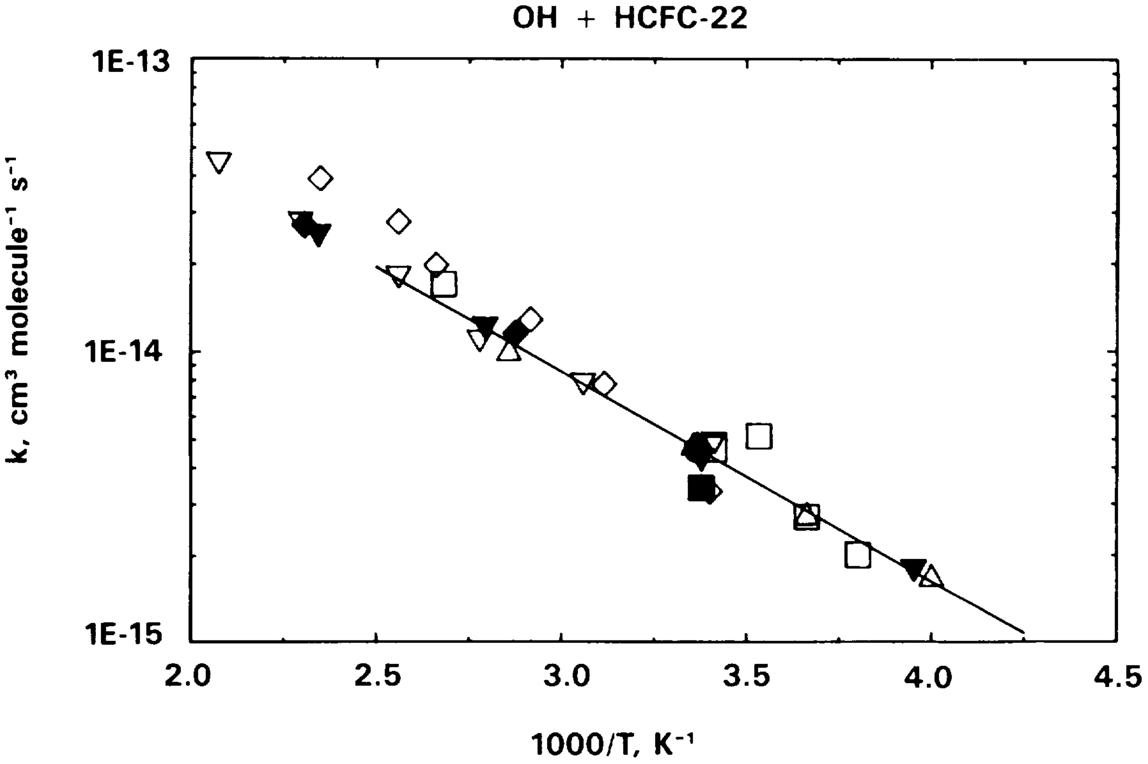
$k = 1.2 \times 10^{-12} \exp[-(1650 \pm 150)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 4.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

The data base for this reaction is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b), which have a significantly larger temperature dependence than all the other studies. The expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.


OH + HCFC-22
k, cm^3 molecule^{-1} s^{-1}
1E-13
1E-14
1E-15
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K^{-1}

$OH + CHF_3$ (HFC-23) → $H_2O + CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	0.2	Howard and Evenson (1976a)
296	1.3	Clyne and Holt (1979b)
430	1.4	
297	0.35	Nip et al. (1979)
387	1.69	Jeong and Kaufman (1982a)
410	2.37	
428	3.31	
447	4.48	
465	5.64	
480	7.19	
1255	550	Ernst et al. (1978)
1320	600	
1345	830	
1395	700	
1400	550	
1445	930	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp K	Reference
2.98	-	2910	387-480	Jeong et al. (1984)

Reviews and Evaluations

1.49(-18)	2.0	1887	387-1445	Atkinson (1989)

$OH + CHF_3$ (HFC-23) $\rightarrow H_2O + CF_3$

Preferred Values

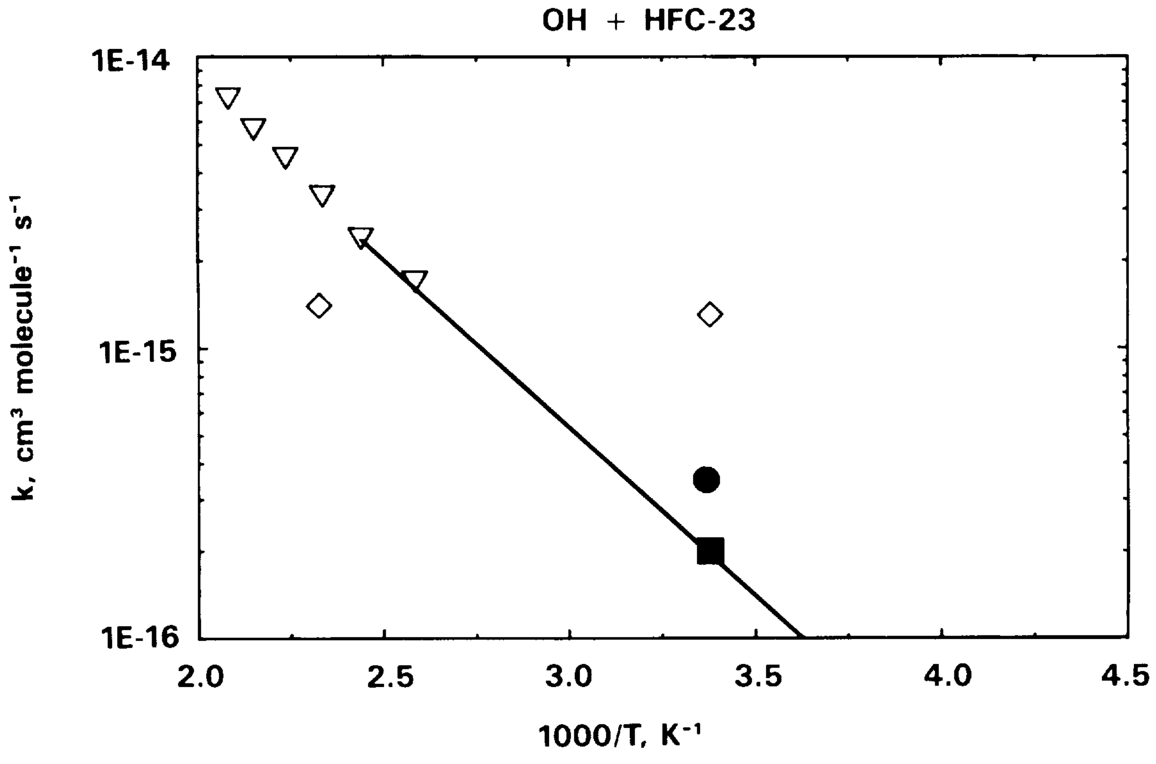
$k = 1.5\times10^{-12} \exp[-(2650\pm500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 2.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.5$

Comments on Preferred Values

The recommendation is based on three data points: the room temperature points of Howard and Evenson (1976a), and the 387 K and 410 K points of Jeong and Kaufman (1982a). The data of Clyne and Holt (1979b) were not considered because of the large disparity with other studies. Because of experimental complications associated with the measurement of rate constants near 10^{-16} cm^3 molecule^{-1} s^{-1}, the k_{298} determinations of Howard and Evenson (1976a) and Nip et al. (1979) should be considered upper limits. The Howard and Evenson value, being the smaller of the two, was therefore used as the basis for the k_{298} recommendation.



$OH + CH_2Cl_2$ (Halocarbon-30) → $H_2O + CHCl_2$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	155	Howard and Evenson (1976a)
298	145	Perry et al. (1976)
245	47.5	Davis et al. (1976)
298	116	
375	223	
251	95.9	Jeong and Kaufman (1982)
292	153	
323	208	
342	276	
384	352	
415	450	
455	609	

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
4.27	-	1094	245-375	Davis et al. (1976)
5.57	-	1042	251-455	Jeong et al. (1984)

Reviews and Evaluations

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
4.7	-	1050	245-455	NASA (1987)
4.4	-	1030	240-300	IUPAC (1989)
8.54(-18)	2.0	500	245-455	Atkinson (1989)

$OH + CH_2Cl_2$ (Halocarbon-30) → $H_2O + CHCl_2$

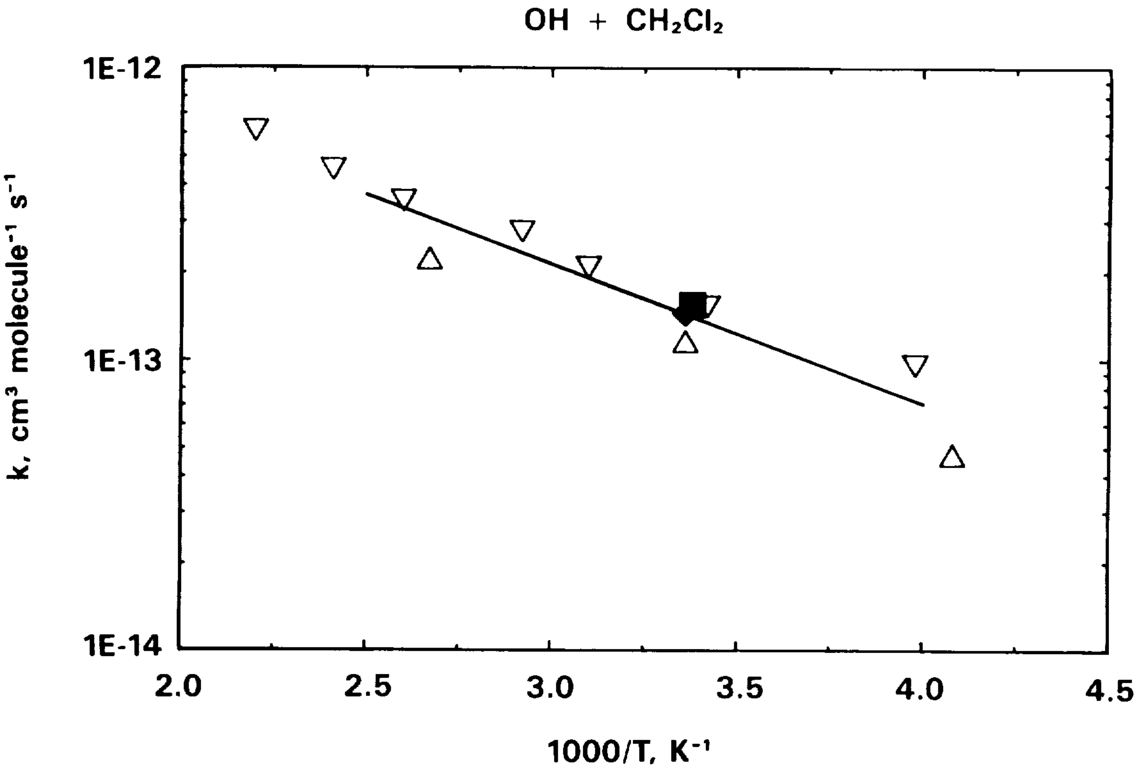
Preferred Values

$k = 5.8\times10^{-12} \exp[-(1100\pm250)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

$k_{298} = 1.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1}
$f_{298} = 1.2$

Comments on Preferred Values

The data of Howard and Evenson (1976a), Perry et al. (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are in reasonable agreement. The temperature dependence data of Davis et al. tend to somewhat smaller values than Jeong and Kaufman but the resulting activation energies are in good agreement. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. The recommended room temperature value was derived from the Arrhenius expression at 298 K.



$OH + CH_2FCl$ (HCFC-31) → $H_2O + CHFCl$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	37	Howard and Evenson (1976a)
245	16.5	Watson et al. (1977)
298	42.1	
375	98	
273	28	Handwerk and Zellner (1978)
293	35	
373	110	
297	44.5	Paraskevopoulos et al. (1981)
250	27.6	Jeong and Kaufman (1982a)
295	49.4	
323	66.0	
348	88.5	
399	140	
438	172	
486	254	

$OH + CH_2FCl$ (HCFC-31) $\rightarrow H_2O + CHFCl$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.84	-	1259	245-375	Watson et al. (1977)
3.1	-	1320	273-373	Handwerk and Zellner (1978)
2.37	-	1137	250-486	Jeong et al. (1984)
Reviews and Evaluations				
2.1	-	1150	230-300	NASA (1987)
2.6	-	1210	245-350	IUPAC (1989)
3.77(-18)	2.0	604	245-486	Atkinson (1989)

Preferred Values

$k = 3.0\text{x}10^{-12} \exp[-(1250 \pm 200)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

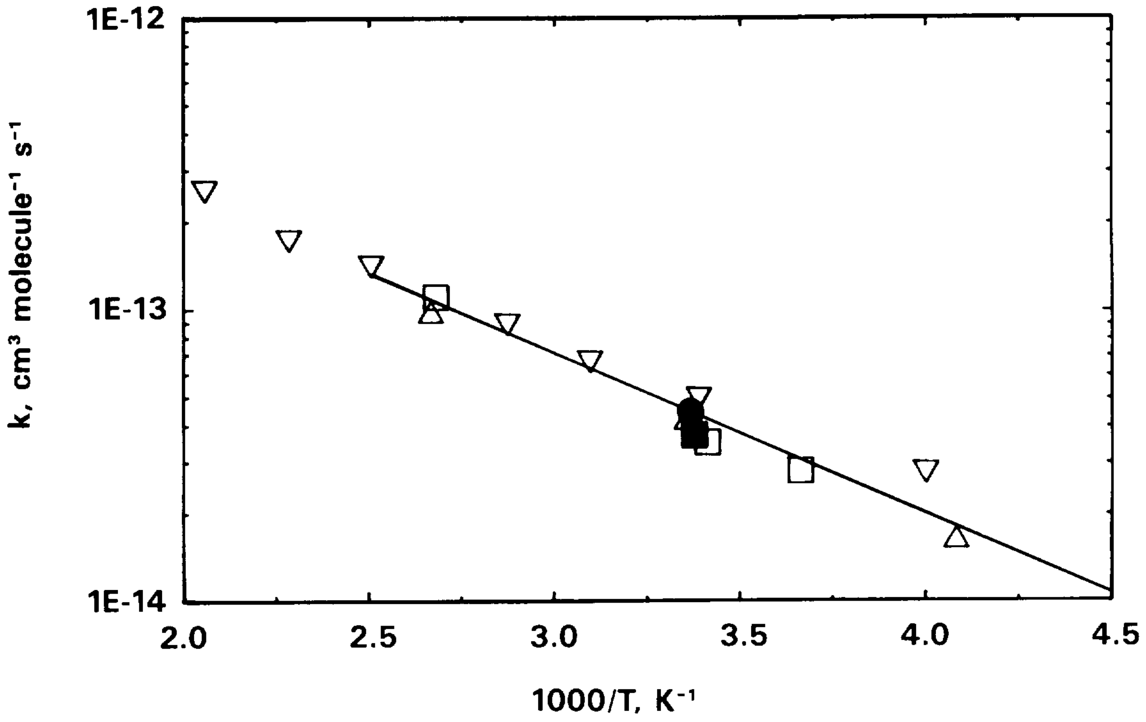
$k_{298} = 4.5\text{x}10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.15$

Comments on Preferred Values

The data for this reaction are in excellent agreement. The recommended Arrhenius expression was derived from the room temperature data of Howard and Evenson (1976a) and Paraskevopoulos et al. (1981), and the temperature dependence data of Watson et al. (1977), Handwerk and Zellner (1978) and Jeong and Kaufman (1982a) below 400 K. The expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.

OH + HCFC-31



$OH + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	7.8	Howard and Evenson (1976a)
293	5.8	Clyne and Holt (1979b)
327	16.1	
368	24.1	
429	60.3	
297	11.7	Nip et al. (1979)
250	4.29	Jeong and Kaufman (1982a)
298	11.2	
336	21.0	
384	43.4	
432	72.7	
464	95.1	
492	141	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
7.41	-	2100	293-429	Clyne and Holt (1979b)
4.37	-	1766	250-492	Jeong et al. (1984)

Reviews and Evaluations

5.06(-18)	2.0	1107	250-492	Atkinson (1989)

$OH + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

Preferred Values

$k = 2.5\times10^{-12}\exp[-(1650\pm200)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

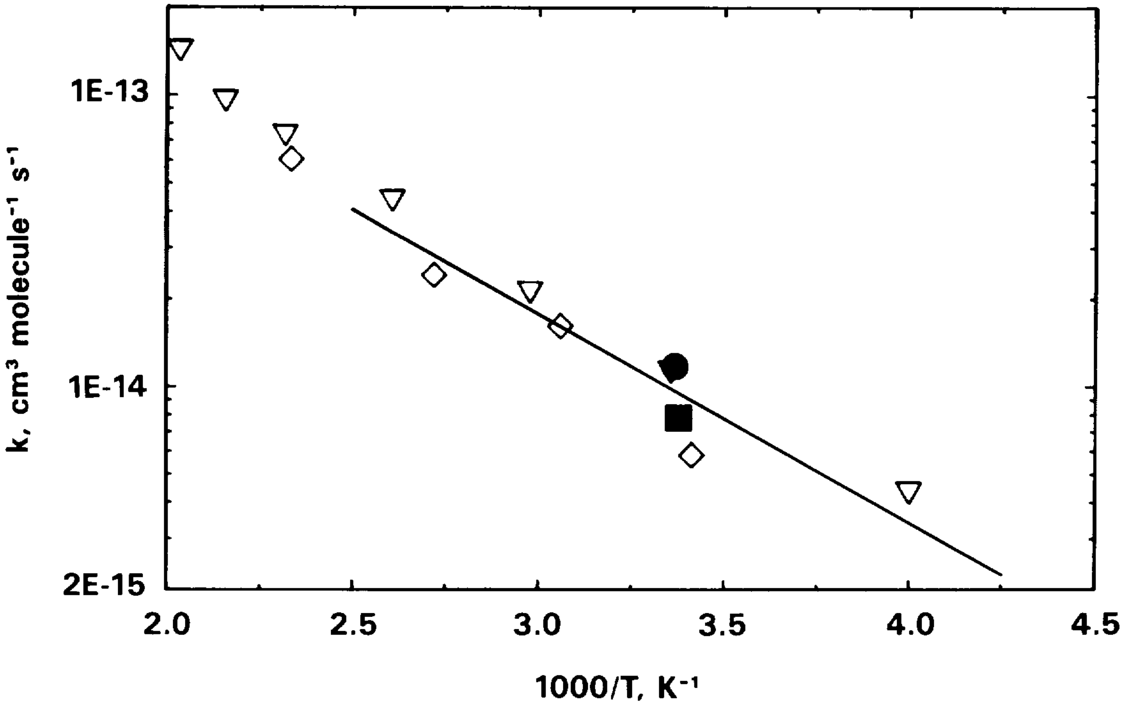
$k_{298} = 1.0\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982a) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982a), Howard and Evenson (1976a) and Nip et al. (1979). Although the data of Clyne and Holt (1979b) are consistent with the data from the other studies, this study is not included in the least squares fit.

OH + HFC-32



$OH + CH_3F$ (HFC-41) → $H_2O + CH_2F$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	16	Howard and Evenson (1976a)
297	21.7	Nip et al. (1979)
292	14	Jeong and Kaufman (1982a)
330	25	
356	38.6	
368	47.6	
385	54.8	
416	85.6	
455	131	
480	171	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
8.11	-	1887	292-480	Jeong et al. (1984)

Reviews and Evaluations

5.51(-18)	2.0	1005	292-480	Atkinson (1989)

Preferred Values

$k = 5.4\times10^{-12} \exp[-(1700 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

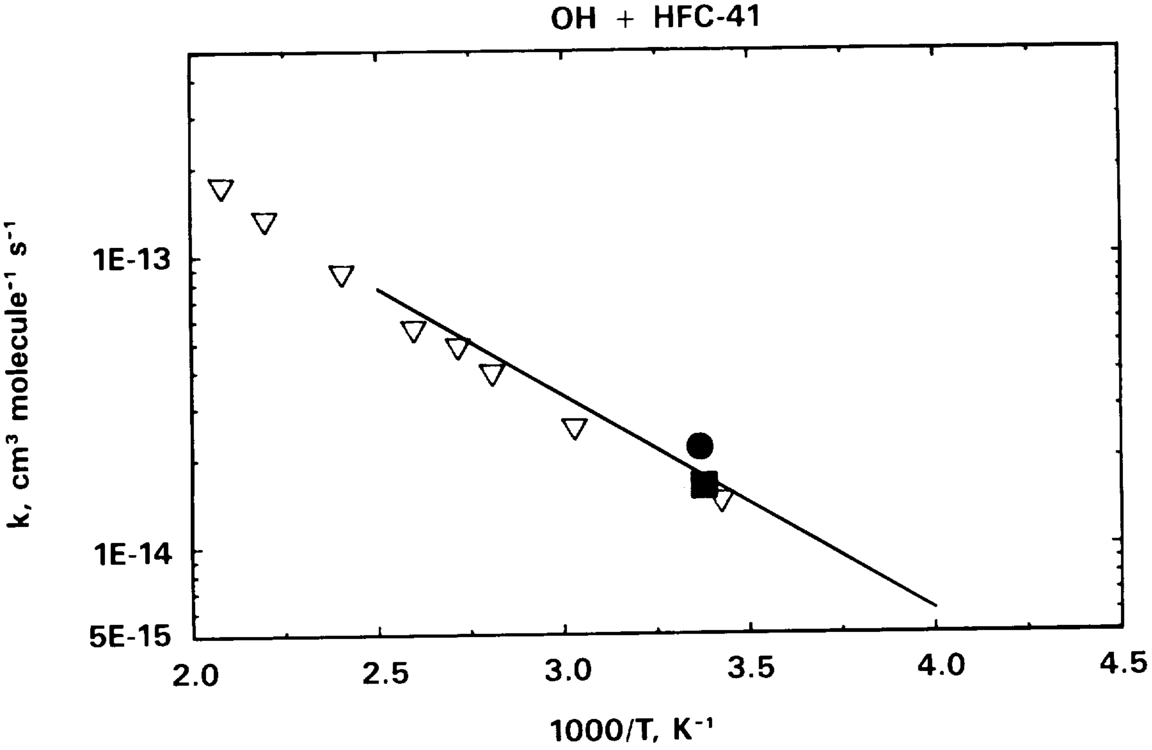
$k_{298} = 1.8\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

$OH + CH_3F$ (HFC-41) → $H_2O + CH_2F$

Comments on Preferred Values

The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982a) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982a), Howard and Evenson (1976a) and Nip et al. (1979).



$OH + CHCl_2CF_3$ (HCFC-123) $\rightarrow H_2O + CCl_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	28.4	Howard and Evenson (1976b)
245	16.2	Watson et al. (1979)
298	36	
375	72	
293	38.6	Clyne and Holt (1979b)
329	58.6	
366	80.1	
429	111	
223	15.9	Ravishankara (1989)
229	18.6	
251	22.0	
298	37.5	
322	47.2	
380	71.6	
468	134	
270	25.0	Kurylo (1989)
298	35.2	
330	47.0	
350	49.9	
375	73.6	
400	88.4	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
1.4	-	1102		Watson et al. (1979)
1.12	-	1000		Clyne and Holt (1979b)

$OH + CHCl_2CF_3$ (HCFC-123) → $H_2O + CCl_2CF_3$

Reviews and Evaluations

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
1.1	-	1050	245-375	NASA (1987)
1.2	-	1060	245-375	IUPAC (1989)
1.2	-	1060	245-375	Atkinson (1989)

Preferred Values

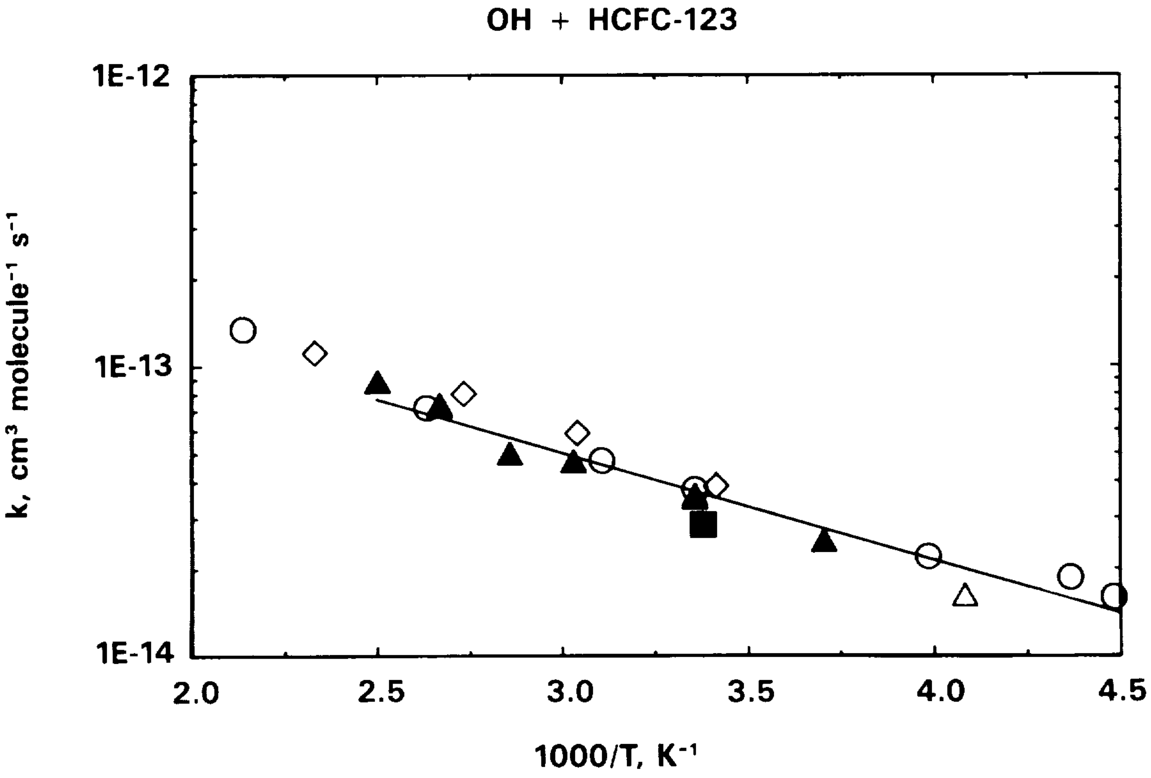
$k = 6.4\times10^{-13} \exp[-(850\pm250)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

$k_{298} = 3.7\times10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data below 400 K of Ravishankara (1989), Kurylo (1989), Watson et al. (1979), and the room temperature data of Howard and Evenson (1976b). The recommended value of k_{298} is derived from the temperature dependence expression. The data of Clyne and Holt (1979b) were not considered.


OH + HCFC-123
1E-12
1E-13
1E-14
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CHFClCF_3$ (HCFC-124) → $H_2O + CFClCF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	12.4	Howard and Evenson (1976b)
250	4.33	Watson et al. (1979)
301	9.4	
375	22.8	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
0.613	-	1244	298-422	Watson et al. (1979)
Reviews and Evaluations				
0.72		1250	250-375	NASA (1987)
0.64		1240	250-375	IUPAC (1989)
0.64		1233	250-375	Atkinson (1989)

Preferred Values

$k = 6.6\times10^{-13} \exp[-(1250\pm300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

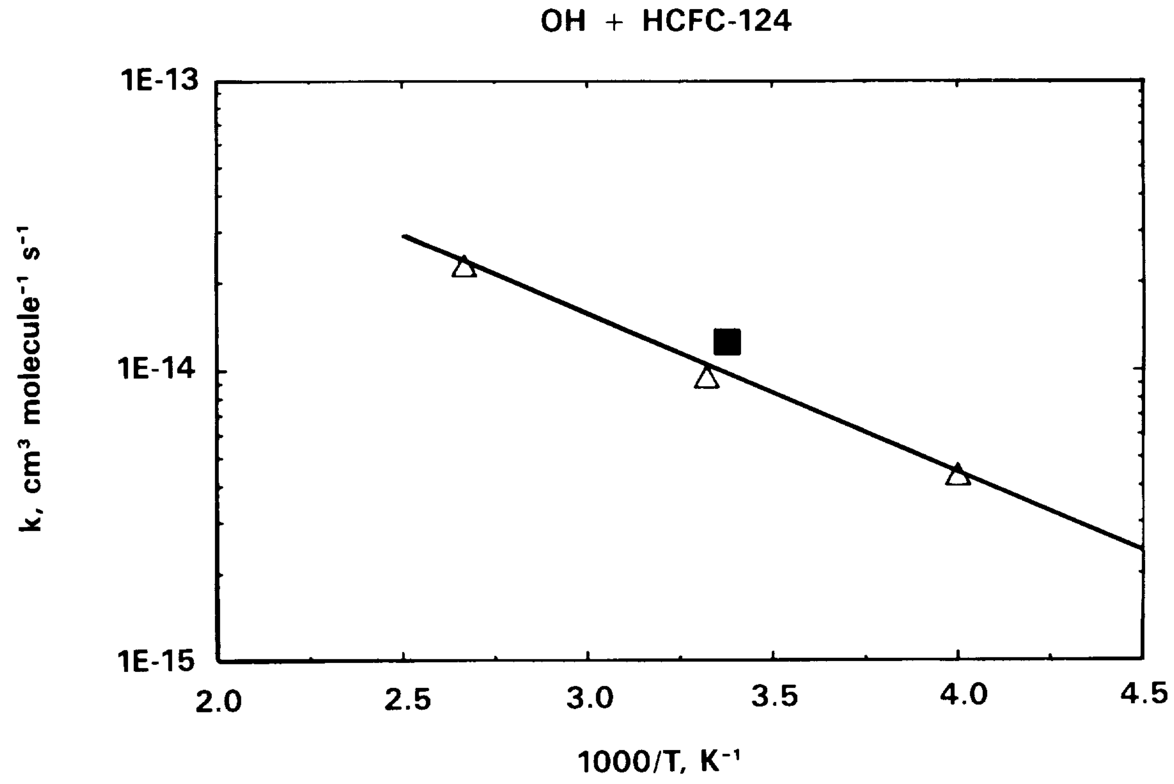
$k_{298} = 1.0\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

$OH + CHFClCF_3$ (HCFC-124) → $H_2O + CFClCF_3$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data of Watson et al. (1979), and the room temperature data of Howard and Evenson (1976b). The recommended value of k_{298} is derived from the temperature dependence expression.



$OH + CHF_2CF_3$ (HFC-125) → $H_2O + CF_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
294	5.0	Clyne and Holt (1979b)
294	4.9	
336	6.2	
378	11.3	
441	15.8	
298	2.5	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
0.17	-	1100	298-441	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 8.9\text{x}10^{-13} \exp[-(1750 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

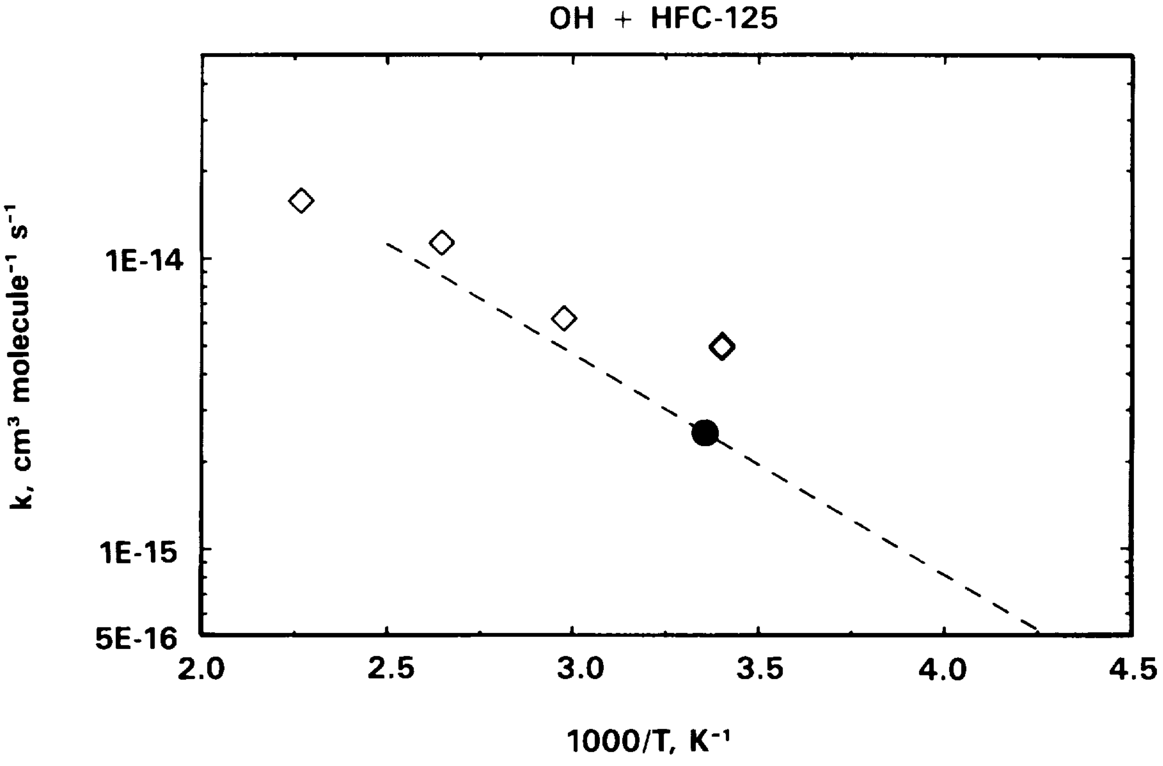
$k_{298} = 2.5\text{x}10^{-15}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

$OH + CHF_2CF_3$ (HFC-125) $\rightarrow H_2O + CF_2CF_3$

Comments on Preferred Values

The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreeement between the Clyne and Holt data and that of other workers for many other halomethanes and haloethanes, the Clyne and Holt data were not used. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by analogy with HFC-134a.



$OH + CH_2ClCF_2Cl$ (HCFC-132b) → $H_2O + CHClCF_2Cl$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
250	6.12	Watson et al. (1979)
298	16.7	
350	37.2	
249	14.2	Jeong et al. (1984)
253	16.0	
267	19.1	
295	27.2	
297	24.2	
333	43.1	
365	59.5	
383	80.6	
418	104	
473	160	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
3.0	-	1578	250-350	Watson et al. (1979)
2.02	-	1263	249-473	Jeong et al. (1984)

Reviews and Evaluations

3.4	-	1600	250-350	NASA (1987)
3.0	-	1580	250-350	IUPAC (1989)
2.8(-18)	2.0	672	250-470	Atkinson (1989)

$OH + CH_2ClCF_2Cl$ (HCFC-132b) → $H_2O + CHClCF_2Cl$

Preferred Values

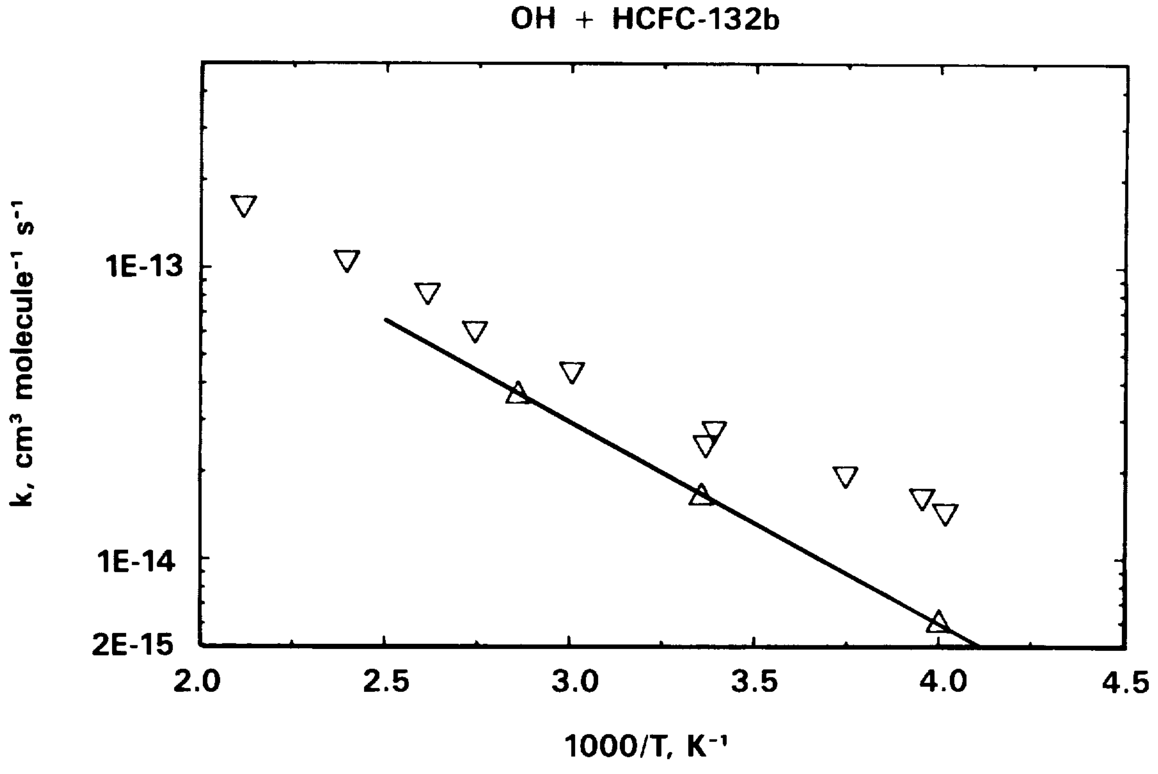
$k = 3.6\text{x}10^{-12} \exp[-(1600 \pm 400)/T]$ cm^3 molecule^{-1} s^{-1} $\quad$ $220 < T < 400$ K

$k_{298} = 1.7\text{x}10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

The recommended temperature dependence was derived from the data of Watson et al. (1979) which were corrected by these authors for the presence of alkene impurities. The data of Jeong et al. (1984), indicating substantially faster rate constants may have been affected by such impurities and hence were not included in deriving the recommendation. The preferred value of k_{298} was derived from the recommended Arrhenius expression. This recommendation is essentially identical to the one in NASA (1987).



$OH + CH_2ClCF_3$ (HCFC-133a) → $H_2O + CHClCF_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	10.5	Howard and Evenson (1976b)
263	11	Handwerk and Zellner (1978)
268	12	
273	12	
283	15	
293	15	
337	28	
373	36	
294	10.3	Clyne and Holt (1979b)
322	38.3	
344	38.6	
358	69.4	
385	65.8	
407	130	
427	154	

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.1	-	1260	263-373	Handwerk and Zellner (1978)
38.9	-	2300	294-427	Clyne and Holt (1979b)

Reviews and Evaluations

8.5(-19)	2.0	458	263-373	Atkinson (1989)

$OH + CH_2ClCF_3$ (HCFC-133a) $\rightarrow H_2O + CHClCF_3$

Preferred Values

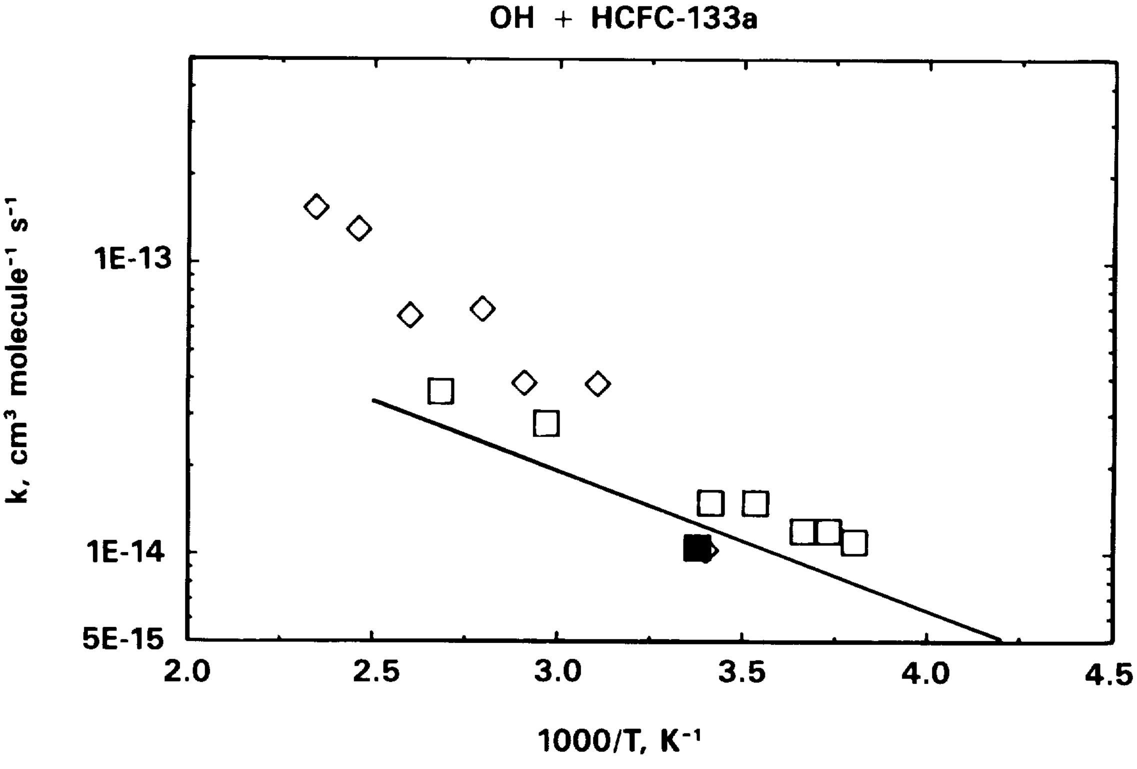
$k = 5.2 \times 10^{-13} \exp[-(1100 \pm 300)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

$k_{298} = 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The temperature dependence of the preferred rate expression was derived from the data of Handwerk and Zellner (1978). The recommended value of k_{298} is the average of the values of Howard and Evenson (1976b) and Handwerk and Zellner (1978) adjusted to 298 K. The data of Clyne and Holt (1979b) were not used in deriving this recommendation..



$OH + CHF_2CHF_2$ (HFC-134) → $H_2O + CF_2CHF_2$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
294	5.3	Clyne and Holt (1979b)
333	18.8	
389	21.2	
434	48.2	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.75	-	1800	294-434	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 8.7\times10^{-13} \exp[-(1500 \pm 500)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

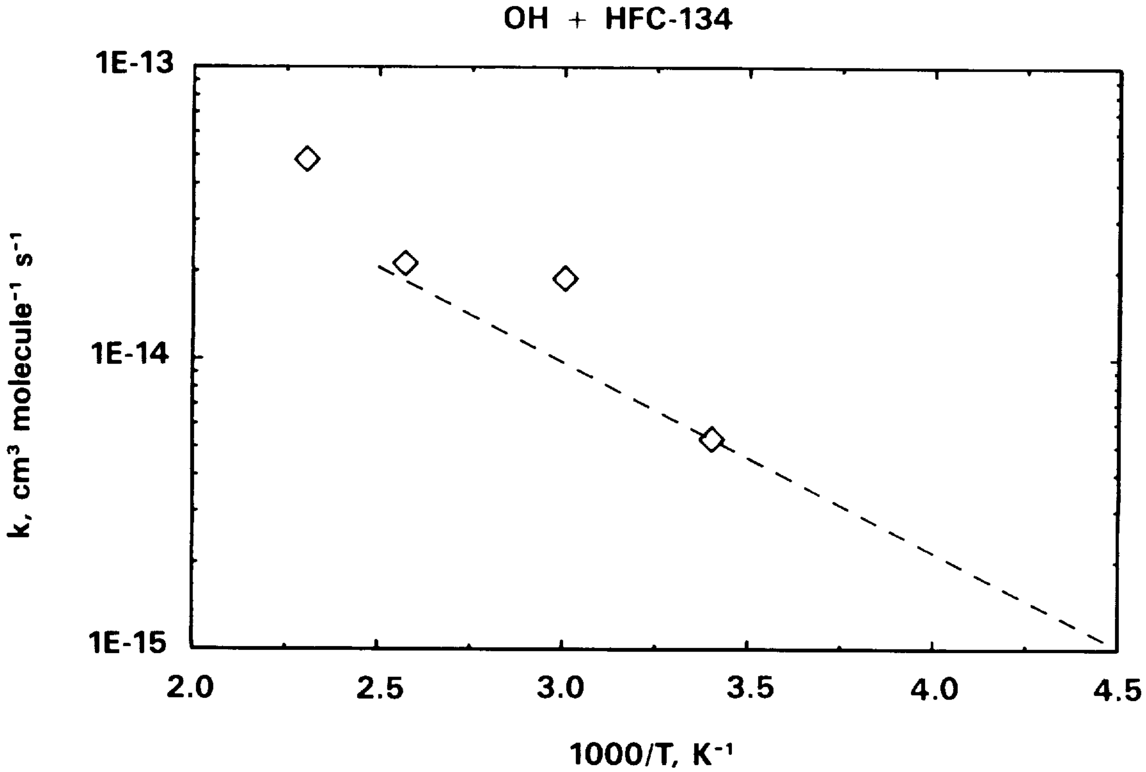
$k_{298} = 5.7\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 2.0$

$OH + CHF_2CHF_2$ (HFC-134) $\rightarrow H_2O + CF_2CHF_2$

Comments on Preferred Values

For the preferred rate expression, the data of Clyne and Holt (1979b) were rejected in favor of an estimated temperature dependence. The recommended value of k_{298} was obtained by adjusting the 294 K value of Clyne and Holt (1979b) to 298 K.



$OH + CH_2FCF_3$ (HFC-134a) → $H_2O + CHFCF_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
294	5.5	Clyne and Holt (1979b)
327	13.2	
344	16.4	
358	19.2	
393	38.3	
424	42.0	
429	36.4	
298	5.2	Martin and Paraskevopoulos (1983)
249	3.9	Jeong et al. (1984)
250	4.4	
268	5.5	
291	7.7	
295	8.2	
298	8.4	
342	15.4	
380	25.4	
430	39.4	
447	45.6	
473	64.4	
298	4.5	Ravishankara (1989)
298	4.3	
294	4.3	
324	7.65	
376	13.9	
425	25.3	
450	32.4	
270	2.63	Kurylo (1989)
298	5.18	
330	8.08	
350	13.1	
375	18.1	
400	27.2	

RATE CONSTANTS

$$OH + CH_2FCF_3 \text{ (HFC-134a)} \rightarrow H_2O + CHFCF_3$$

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.75	-	1800	294-429	Clyne and Holt (1979b)
1.10	-	1424	249-473	Jeong et al. (1984)

Reviews and Evaluations

0.66	-	1300	250-440	NASA (1987)
0.66	-	1300	250-440	IUPAC (1989)
1.27(-18)	2.0	769	250-470	Atkinson (1989)

Preferred Values

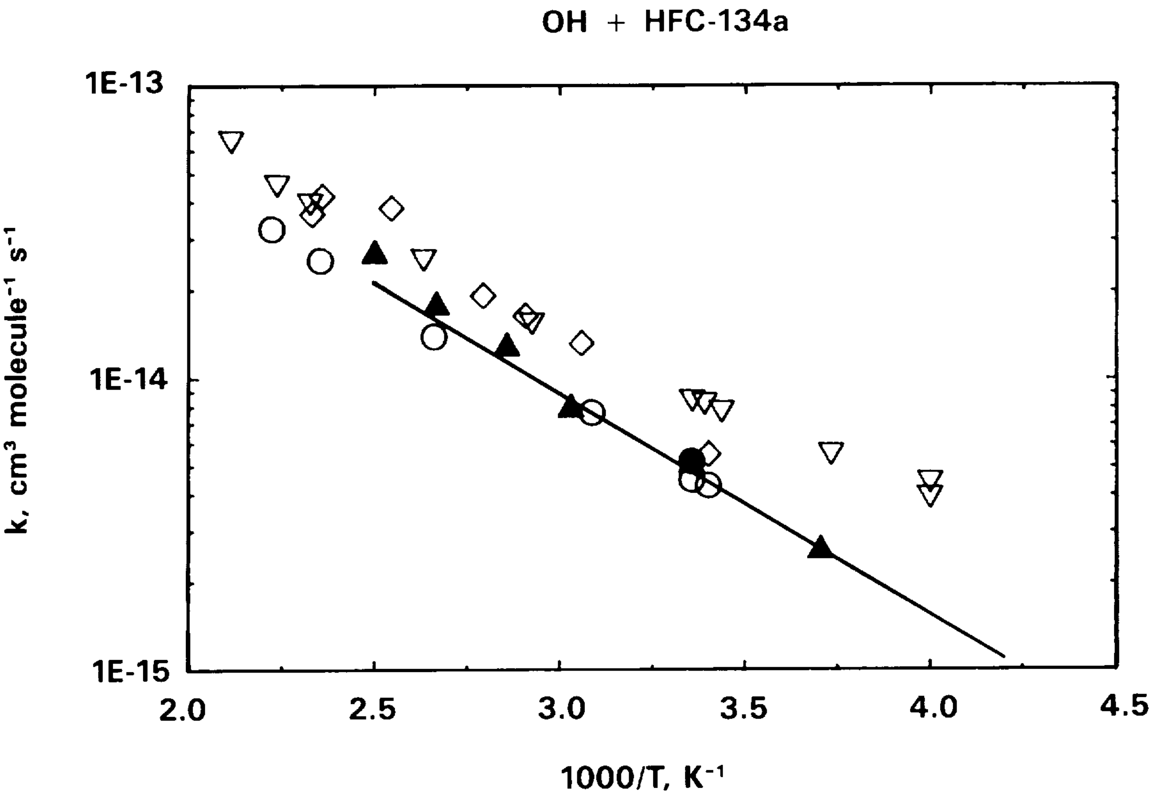
$k = 1.7 \times 10^{-12} \exp[-(1750 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 4.8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The preferred rate expression was derived from the data of Ravishankara (1989), Kurylo (1989) and the room temperature data point of Martin and Paraskevopoulos (1983). The recommended value of k_{298} is obtained from the rate expression. The data of Clyne and Holt (1979b) were not used. With the inclusion of the new data of Ravishankara and Kurylo this recommendation is considerably different from that of NASA (1987), which was based primarily on the data of Jeong (1984). The newer data suggest that the latter study may have overestimated the rate constant due to the presence of reactive impurities which can perturb the relatively slow reaction of OH with HFC-134a. This recommendation therefore results in significantly (factor of 2-4) smaller rate constants at stratospheric temperatures.


OH + HFC-134a
1E-13
1E-14
1E-15
k, cm^3 molecule^{-1} s^{-1}
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K^{-1}

$OH + CH_3CCl_3$ **(Halocarbon-140)** $\rightarrow H_2O + CH_2CCl_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	15	Howard and Evenson (1976b)
260	7.1	Watson et al. (1977)
298	15.9	
375	48.5	
278	8.32	Jeong and Kaufman (1979)
293	10.6	
352	29.3	
400	55.2	
457	102	
222	3.18	Kurylo et al. (1979)
253	4.47	
263	5.40	
296	10.8	
363	38.5	
293	18.1	Clyne and Holt (1979a)
310	27.8	
338	45.9	
371	57.3	
399	72.9	
430	86.3	

$OH + CH_3CCl_3$ (Halocarbon-140) → $H_2O + CH_2CCl_3$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
3.72	-	1627	260-375	Watson et al. (1977)
5.04	-	1797	278-457	Jeong and Kaufman (1979)
5.4	-	1810	253-363	Kurylo et al. (1979)
2.4	-	1394	293-430	Clyne and Holt (1979a)

Reviews and Evaluations

5.0	-	1800	222-457	NASA (1987)
5.1	-	1800	250-460	IUPAC (1989)
5.92(-18)	2.0	1129	253-457	Atkinson (1989)

Preferred Values

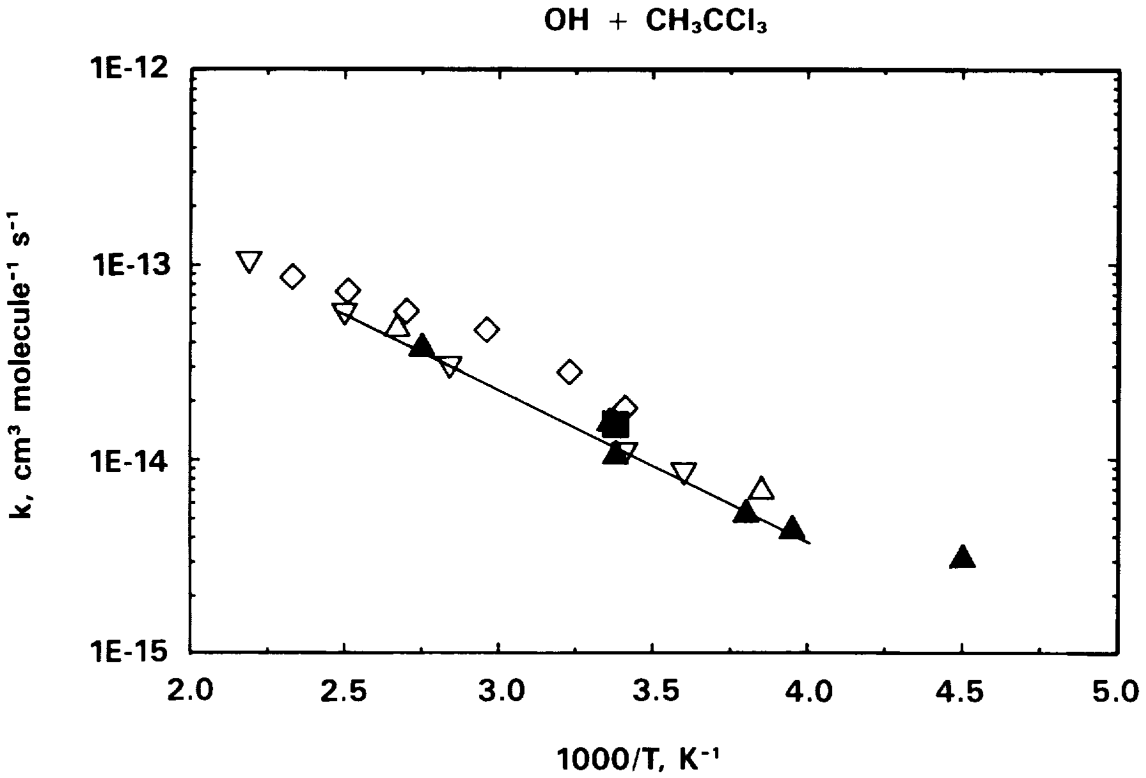
$k = 5.0\times10^{-12} \exp[-(1800 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $250 < T < 400$ K

$k_{298} = 1.2\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The recommendation is the same as that adopted in NASA (1987). The evaluation is based on the data of Jeong and Kaufman (1979) and Kurylo et al. (1979) excluding the value at 222 K.


OH + CH_3CCl_3
1E-12
1E-13
1E-14
1E-15
k, cm^3 $molecule^{-1}$ s^{-1}
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1000/T, K^{-1}

OH + CH_3CFCl_2 (HCFC-141b) → H_2O + CH_2CFCl_2

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
244	4.13 (FP)	Ravishankara (1989)
277	5.77 (FP)	
293	7.2	
301	7.78 (FP)	
326	10.9	
347	13.9	
390	22.8	
434	36.4	
456	48.1	
243	4.20	Kurylo (1989)
273	5.24	
298	7.01	
330	9.62	
350	13.8	
400	19.4	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp.	Reference
		- none -		

Reviews and Evaluations

3.4	-	1800	270-330	NASA (1987) (Estimated; no data)

$OH + CH_3CFCl_2$ (HCFC-141b) $\rightarrow H_2O + CH_2CFCl_2$

Preferred Values

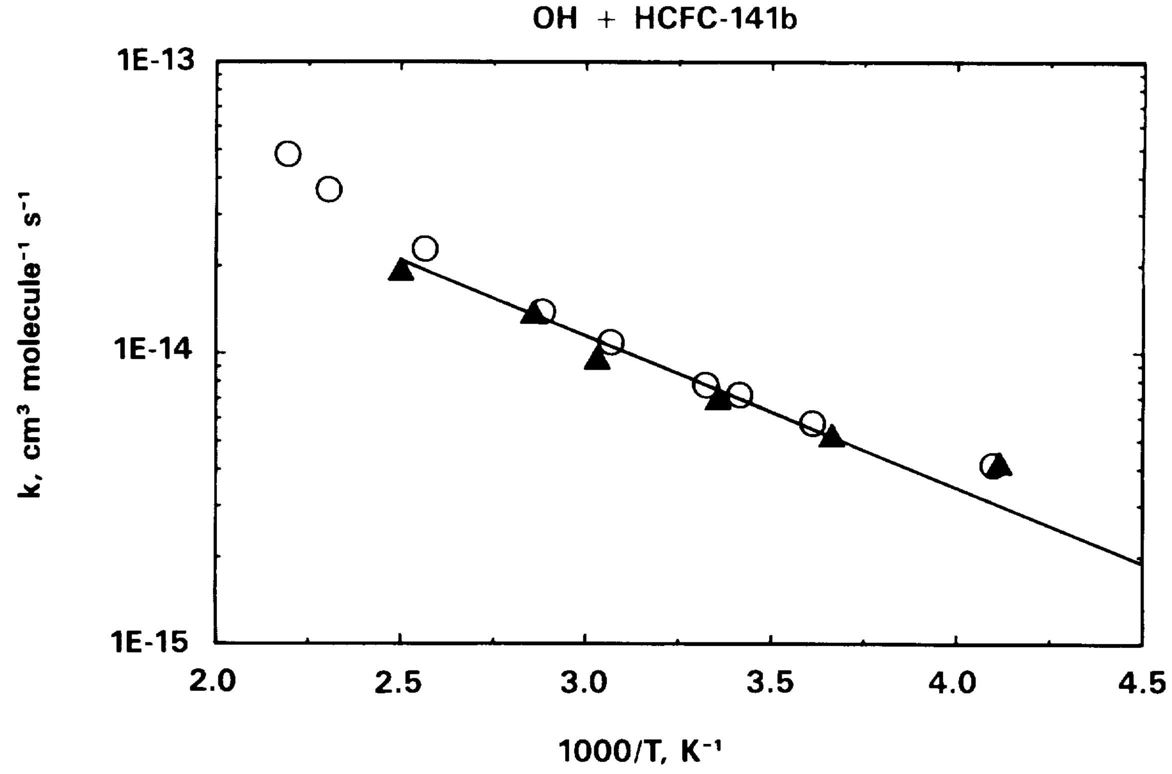
$k = 4.2\times10^{-13} \exp[-(1200 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 7.5\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The preferred rate expression is significantly different from that estimated in NASA (1987) due to the recent availability of kinetics data from Ravishankara (1989) and Kurylo (1989). There is noticeable curvature in the Arrhenius plots from both studies. While the data can be fit to a reasonably straight line over the temperature range 240 - 400 K, a temperature range for the fit of 273 - 400 K was adopted. The reaction rate at the lowest temperature, being so slow, is most likely to be affected by impurities. In addition, inclusion of the lowest temperature points in the fit results in an unusually small A-factor. Rate constants derived from this recommendation are a factor of 1-3 times larger than those from NASA (1987) at low temperatures.



$OH + CH_3CF_2Cl$ (HCFC-142b) $\rightarrow H_2O + CH_2CF_2Cl$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	2.83	Howard and Evenson (1976b)
273	1.92	Watson et al. (1977)
298	3.2	
375	10.9	
293	3.7	Handwerk and Zellner (1978)
373	14	
293	8.4	Clyne and Holt (1979b)
293	6.0	
323	12.0	
363	14.4	
380	30.9	
417	40.6	
297	4.63	Paraskevopoulos et al. (1981)
243	1.22	Ravishankara (1989)
268	2.00	
293	3.48	
352	7.94	
395	14.6	
270	2.14	Kurylo (1989)
298	4.02	
330	6.60	
350	7.97	
375	11.5	
400	17.0	

RATE CONSTANTS

$OH + CH_3CF_2Cl$ (HCFC-142b) $\rightarrow H_2O + CH_2CF_2Cl$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp.	Reference
1.15	-	1748	273-375	Watson et al. (1977)
1.8	-	1790	293-373	Handwerk and Zellner (1978)
3.3	-	1800	293-417	Clyne and Holt (1979b)

Reviews and Evaluations

1.5	-	1800	270-380	NASA (1987)
1.6	-	1820	270-380	IUPAC (1989)
2.0(-18)	2.0	1170	270-380	Atkinson (1989)

Preferred Values

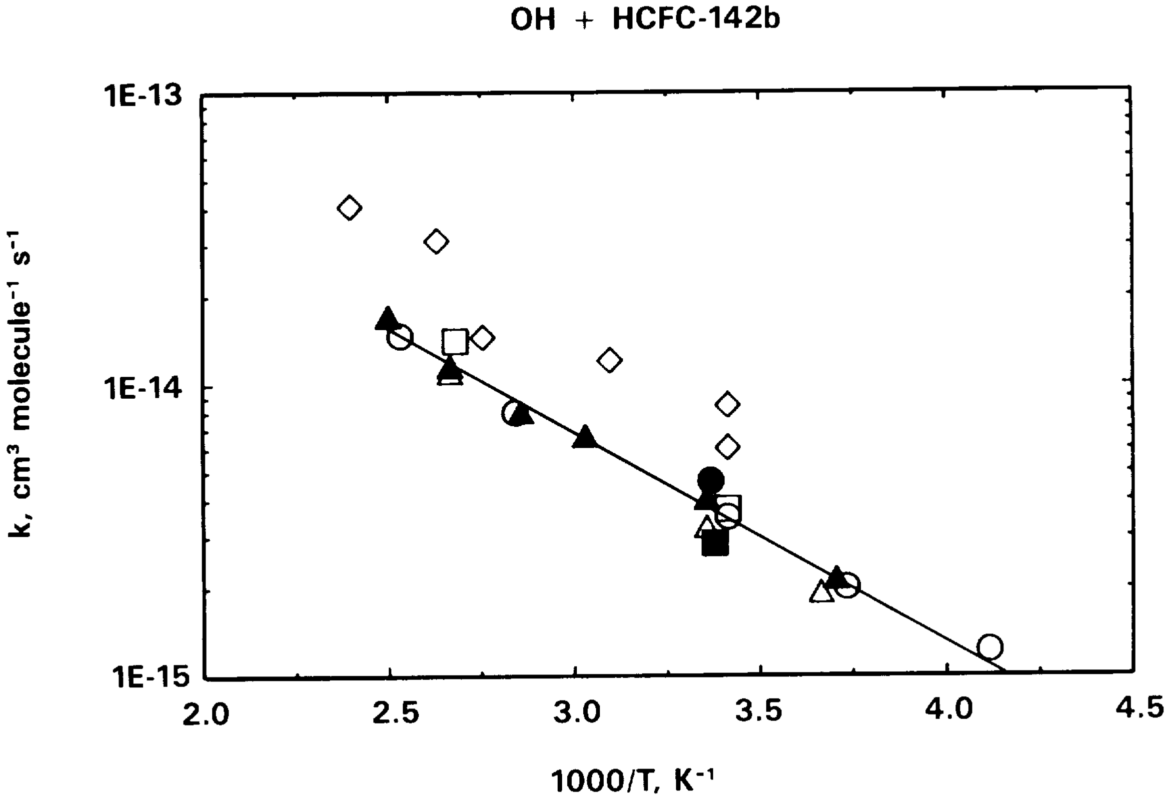
$k = 9.6 \times 10^{-13} \exp[-(1650 \pm 250)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 3.8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The recommended rate expression is derived from a fit to the temperature dependence data of Ravishankara (1989), Kurylo (1989), Watson et al. (1977) and Handwerk and Zellner (1978), and the room temperature data of Howard and Evenson (1976b), and Paraskevopoulos et al. (1981). The value of k_{298} was derived from the rate expression. The preferred rate expression results in rate constants that are up to 25% larger at stratospheric temperatures than those derived from the NASA (1987) recommendation.


OH + HCFC-142b
1E-13
1E-14
1E-15
2.0
2.5
3.0
3.5
4.0
4.5
k, cm^3 molecule^{-1} s^{-1}
1000/T, K^{-1}

$OH + CH_2FCHF_2$ (HFC-143) $\rightarrow H_2O$ + products

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
293	49.8	Clyne and Holt (1979b)
294	46.8	
335	67.4	
383	90.9	
441	189	
298	18.3	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
1.48	-	1000	293-441	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 2.8 \times 10^{-12} \exp[-(1500 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

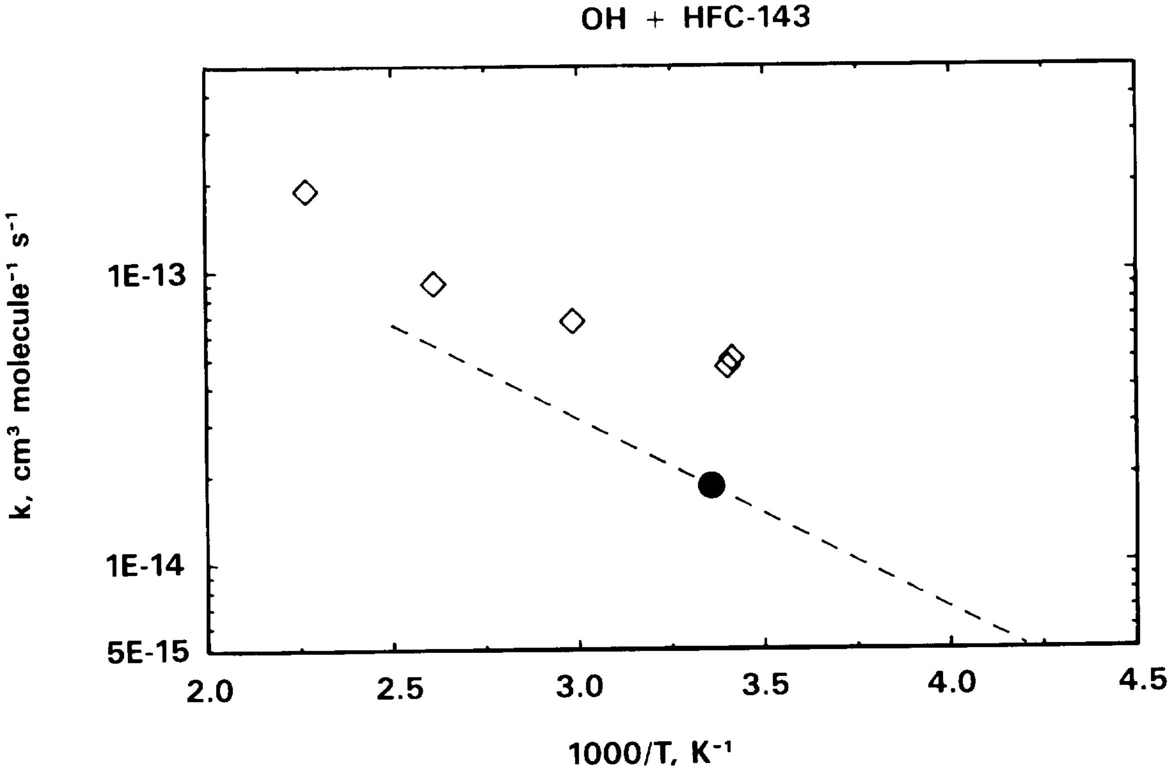
$k_{298} = 1.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

OH + CH_2FCHF_2 (HFC-143) → H_2O + products

Comments on Preferred Values

The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreeement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated.



$OH + CH_3CF_3$ (HFC-143a) $\rightarrow H_2O + CH_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
293	< 1.0	Clyne and Holt (1979b)
333	4.7	
378	12.9	
425	38.4	
298	1.7	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
69	-	3200	293-425	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 6.0 \times 10^{-13} \exp[-(1750 \pm 500)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

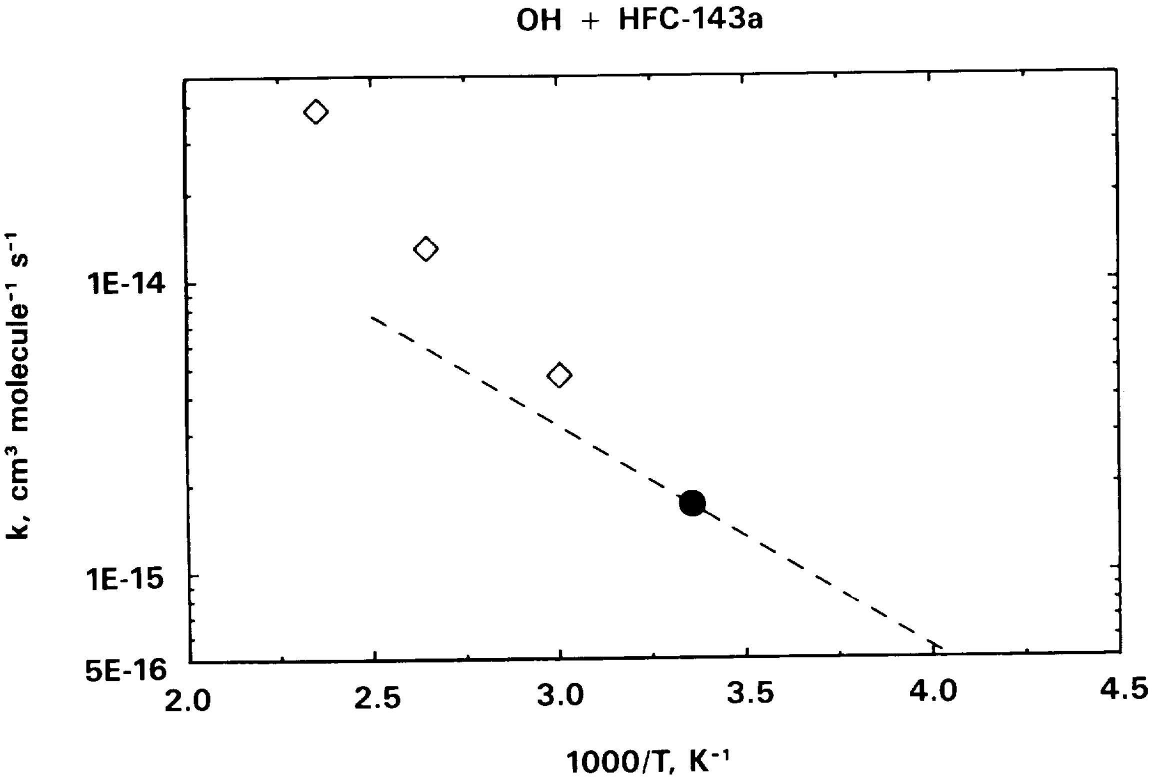
$k_{298} = 1.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 2.0$

$OH + CH_3CF_3$ (HFC-143a) → $H_2O + CH_2CF_3$

Comments on Preferred Values

The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreeement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by comparison with HFC 134a.



$OH + CH_2FCH_2F$ (HFC-152) $\rightarrow H_2O + CH_2FCHF$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
298	112	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference

- none -

Reviews and Evaluations

- none -

Preferred Values

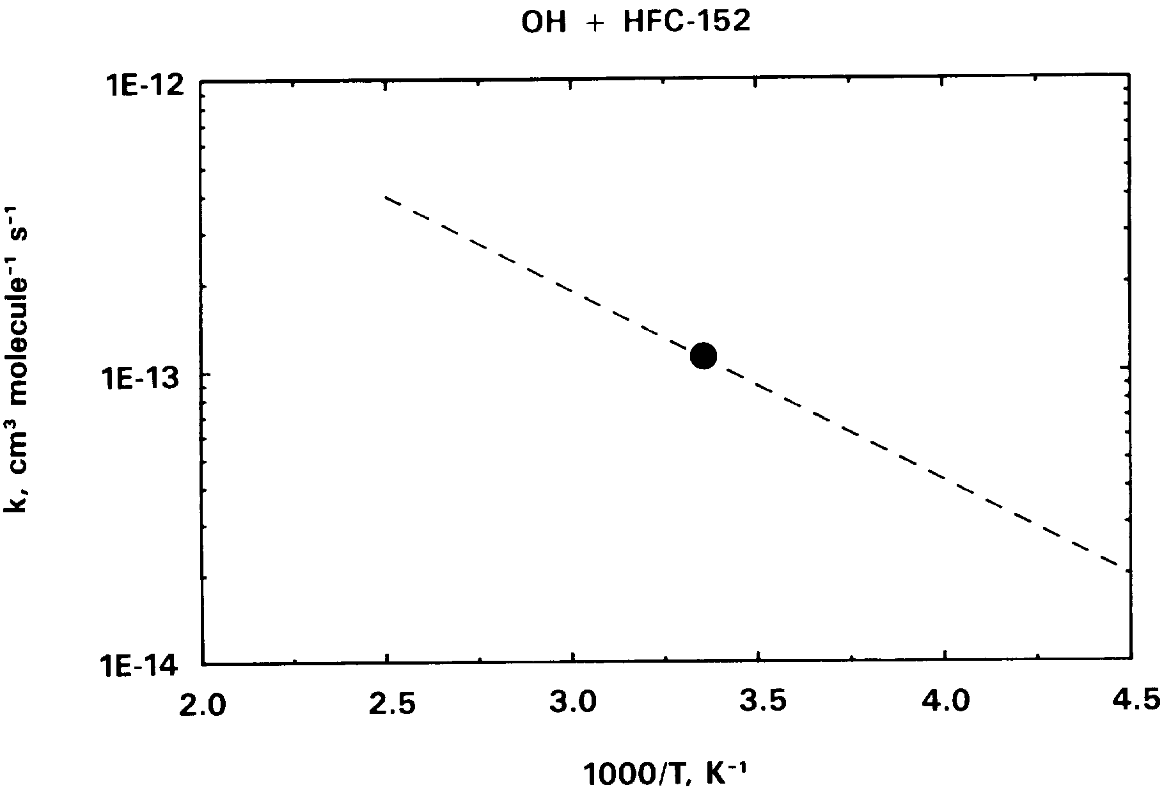
$k = 1.7 \times 10^{-11} \exp[-(1500 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

The preferred rate expression is derived by fitting an estimated temperature dependence to the room temperature data of Martin and Paraskevopoulos (1983).


OH + HFC-152

$OH + CH_3CHF_2$ (HFC-152a) → H_2O + products

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	31	Howard and Evenson (1976b)
293	35	Handwerk and Zellner (1978)
297	37	Nip et al. (1979)
293	46.6	Clyne and Holt (1979b)
323	71.6	
363	101	
417	164	
238	15.3	Ravishankara (1989)
258	20.0	
293	34	
349	64	
388	94.3	
402	113	
409	117	
423	132	
270	29.9	Kurylo (1989)
298	42.2	
330	53.2	
350	68.1	
375	73.0	
400	103	

$OH + CH_3CHF_2$ (HFC-152a) → H_2O + products

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
2.95	-	1200	293-417	Clyne and Holt (1979b)

Reviews and Evaluations

1.9	-	1200	270-330	NASA (1987)

Preferred Values

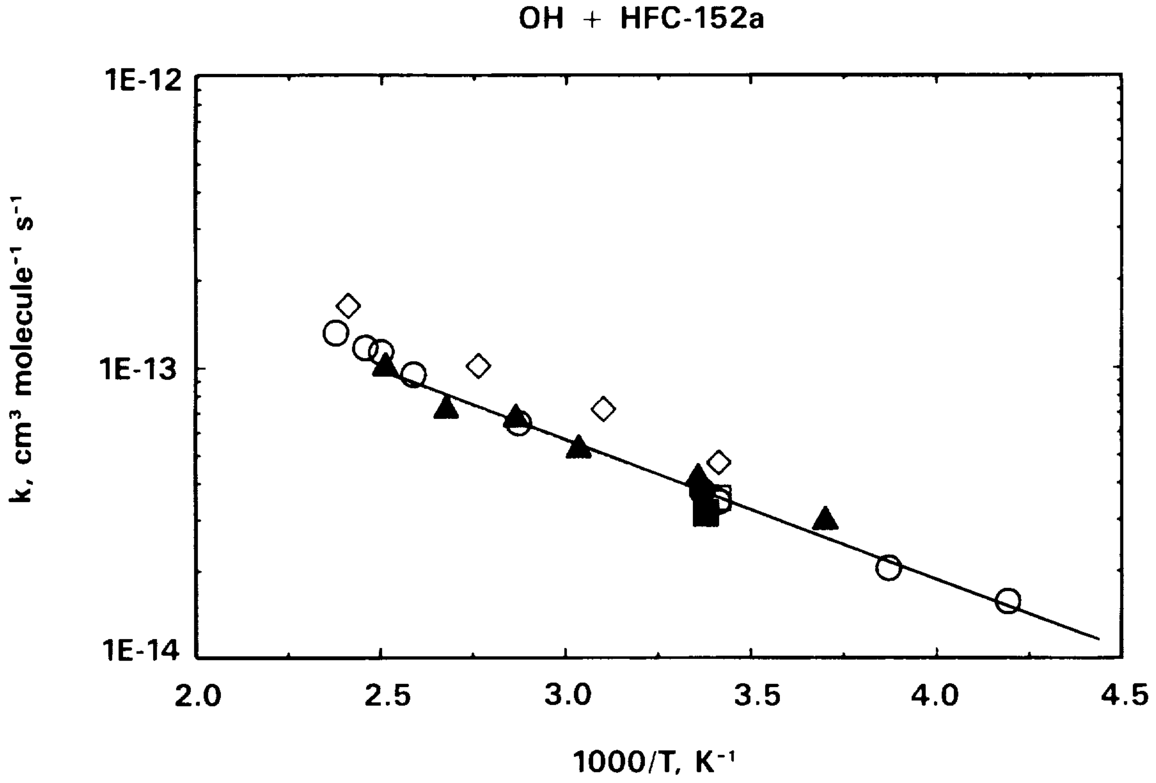
$k = 1.5 \times 10^{-12} \exp[-(1100 \pm 200)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 3.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data of Ravishankara (1989) and Kurylo (1989) and the room temperature data of Howard and Evenson (1976b), Handwerk and Zellner (1978), and Nip et al. (1979). The data of Clyne and Holt (1979b) were not used in this derivation. The value for k_{298} is that calculated from the expression.


OH + HFC-152a
1E-12
1E-13
1E-14
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CH_3CH_2F$ (HFC-161) $\rightarrow H_2O$ + products

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
297	232	Nip et al. (1979)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference

- none -

Reviews and Evaluations

- none -

Preferred Values

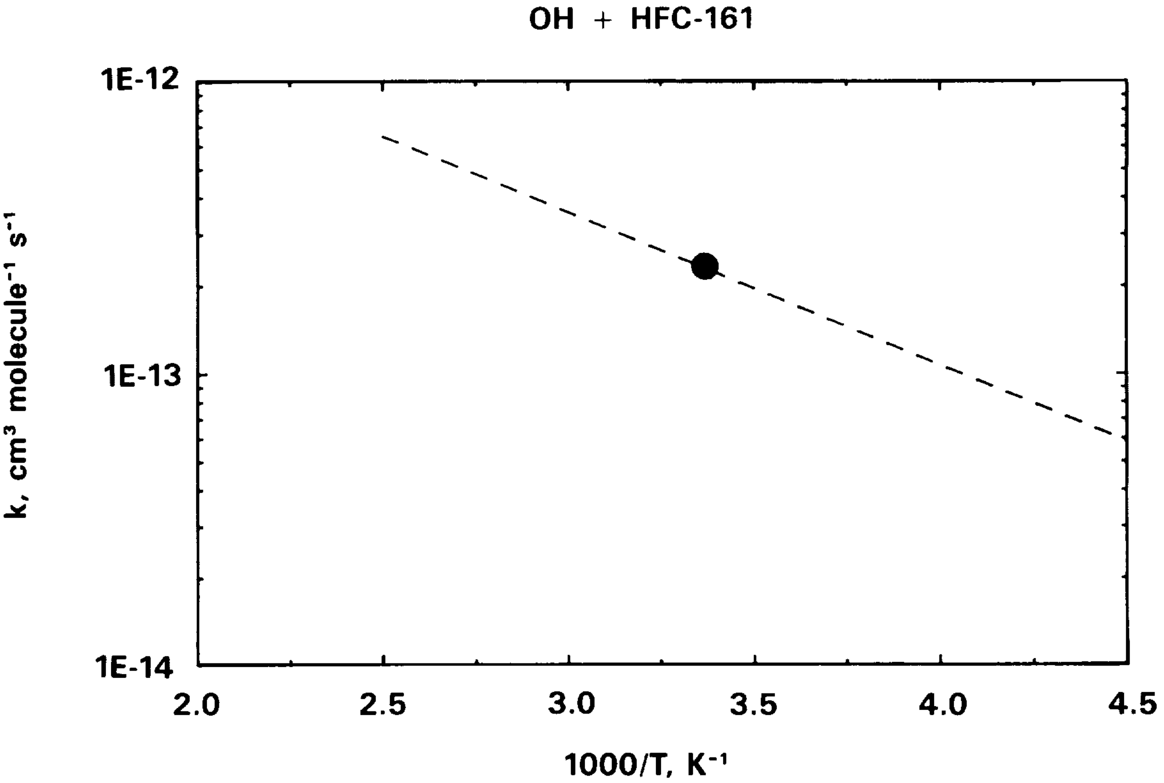
$k = 1.3 \times 10^{-11} \exp[-(1200 \pm 300)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

$k_{298} = 2.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

There are no temperature dependence data for this reaction. The temperature dependence of the recommended expression was derived by analogy with members of the homologous series which includes the $OH + C_2H_6$ and $OH + CH_3CHF_2$ (HFC 152a) reactions. The value of k_{298} was taken from the study of Nip et al. (1979). Singleton et al. (1980) determined that 85 ± 3 % of the abstraction by OH is from the fluorine substituted methyl group.


OH + HFC-161
k, cm^3 molecule^{-1} s^{-1}
1E-12
1E-13
1E-14
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K^{-1}

IV. ABSORPTION CROSS SECTIONS

Review of Ultraviolet Absorption Cross Sections of a Series of Alternative Fluorocarbons

M. J. Molina
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

EXECUTIVE SUMMARY

Solar photolysis is likely to contribute significantly to the stratospheric destruction of those alternative fluorocarbons (HFC's) which have two or more chlorine atoms bonded to the same carbon atom. Two of the eight HFC's considered in this review fall into this category, namely HFC-123 and HFC-141b. For these two species there is good agreement among the various measurements of the ultraviolet cross sections in the wavelength region which is important for atmospheric photodissociation, that is, around 200 nm. There is also good agreement for HFC-124, HFC-22 and HFC 142b; these are the three species which contain one chlorine atom per molecule. The agreement in the measurements is poor for the other species, i.e., those that do not contain chlorine, except in so far as to corroborate that solar photolysis should be negligible relative to destruction by hydroxyl radicals.

REVIEW OF ULTRAVIOLET ABSORPTION CROSS SECTIONS OF A SERIES OF ALTERNATIVE FLUOROCARBONS

Mario J. Molina

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

ULTRAVIOLET SPECTRA

The main atmospheric sink for the alternative fluorocarbons (HFC's) is reaction with hydroxyl radicals. Ultraviolet photolysis can, however, be an important additional destruction process in the stratosphere, and it may affect significantly their ozone depletion potential.

There are very few measurements reported in the literature of UV absorption cross sections for the HFC's that are likely to be of industrial importance. This review is focussed on eight of these compounds, namely HFC-123, 141b, 142b, 22, 124, 134a, 152a and 125. There are three sets of very recent measurements which have not been published yet, but which are included in this review. In general, the agreement around the 200 nm wavelength range—the important atmospheric "window" for solar photodissociation—is good (within 20%) for those species with significant absorptions, namely those containing two chlorine atoms bonded to the same carbon atom (HCFC-123 AND 141b; see Tables 1 and 2). The agreement is equally good for HCFC-124, (Table 3) and it is reasonable for HCFC 142b (Table 4) but it is rather poor for those species not containing chlorine (HFC-134a and 152a). However, it is clear that except for the first

Table 1. Absorption Cross Sections of HCFC-123 ($CHCl_2$-CF_3)

	10^{20} σ (cm^2/molecule) (Ref. #)			
λ (nm)	1	2	3	4
185	—	106.7	115*	96.0
190	56.5	55.8	60.3	52.4*
195	26.7	25.5	28.8*	23.6
200	11.3	10.4	12.2	9.95*
205	4.45	3.94	5.2*	3.88
210	1.73	1.47	0.651	1.53*
215	0.651	0.557	0.268*	0.57
220	0.254	0.198	0.112	0.21*
225	0.099	0.073	0.051*	0.079

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989

Table 2. Absorption Cross Sections of HCFC-141b ($CHCl_2$-CF_3)

	10^{20} σ (cm²/molecule) (Ref. #)			
λ (nm)	1	2	3	4
185	—	142.3	137.5*	109
190	79.5	85.8	86.3	70.5*
195	40.4	41.8	43.2*	38.0
200	17.1	16.8	18.3	17.4*
205	6.38	5.96	7.02*	6.78
210	2.38	2.06	2.35	2.86*
215	0.974	0.692	0.804*	1.24
220	0.482	0.235	0.267	0.51*
225	0.326	0.083	0.094*	—

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989

two species, HCFC-123 and 141b, atmospheric photolysis is a minor process and that reaction with hydroxyl radicals occurs much faster throughout the troposphere and stratosphere.

There are no absorption cross section measurements in the 200 nm wavelength region for HFC-125. However, considering that this is a saturated hydrocarbon with only fluorine, hydrogen and carbon atoms, the absorption in that wavelength region should be negligible. In general, at those wavelengths the absorption increases sharply with the number of chlorine atoms per carbon atom, and it decreases with substitution of fluorine for hydrogen.

The absorption cross sections for the HCFC's have a significant temperature dependency in the atmospherically important wavelength range. Only one group has reported measurements at various temperatures (Orlando et al., 1989). Furthermore, for HFC-123, 141b and 124 the room temperature values measured by this same group around 200 nm are close to the average of the values reported in the other studies. Hence, the recommendation at present is to use the values given by Ravishankara el al. at various temperatures (see Tables 5-7). This provides a more consistent set of data than, for example, the average of

Table 3. Absorption Cross Sections of HCFC-124 ($CHClF-CF_3$)

	10^{20} σ (cm²/molecule) (Ref. #) 1	2	4
λ (nm)			
185	—	1.82	—
190	0.735	0.799	0.77*
195	0.316	0.331	0.32*
200	0.128	0.129	0.125*
205	0.0482	0.0466	0.04
210	0.0182	0.0168	0.02
215	0.0072	0.0062	—
220	0.0032	0.0023	—
225	0.0020	0.00015	—

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
4 Allied-Signal Corp. (Private Communication) 1989

all values, which would then have to be adjusted at each temperature with only one of the data sets contributing to the temperature dependency.

The compound HCFC-142b, namely $CClF_2-CH_3$, appears to absorb UV radiation about as strongly as HCFC 124; both species have a single chlorine atom per molecule, and atmospheric photolysis is unlikely to be of importance. For HCFC-142b there is agreement in the cross section values reported by Orlando et al. (1989), Allied-Signal Corp., Private Communication (1989), (1989), Hubrich and Stuhl (1980), and Gillotay et al. (1989) (see Table 4). The recommendation is, here again, to use the data and the temperature dependency reported by Orlando et al. (Table 8).

For HCFC-22, the recommended cross section values, listed in Table 9, are those obtained by Simon et al. (1988), as a function of temperature. These values are in reasonable agreement with the earlier recommendation in the report of the NASA Panel for Data Evaluation, which was based on room temperature data only. The Allied Co. group reported cross sections for this compound which are also in reasonable agreement with the data of Table 9.

For the HCFC's 123, 141b, 22, 124 and 142b, the error factor in the atmospheric photodissociation rates which arises from uncertainties in the cross section data is estimated as 1.2 (this is the error factor defined in the NASA Panel for Data Evaluation reports). The uncertainty in the cross sections increases rapidly beyond 210 nm, but the available solar intensity in the stratosphere decreases also rapidly. It should be noted that the values given by Orlando et al. beyond 210 nm become significantly larger than the ones

Table 4. Absorption Cross Sections of HCFC-124b ($CHClF_2$-CF_3)

	10^{20} σ (cm^2/molecule) (Ref. #)			
λ (nm)	1	3	4	5
185	—	2.57*	2.47	2.79
190	0.853	1.02	1.07*	1.02
195	0.349	0.403*	0.42	0.405
200	0.132	0.150	0.16*	0.158
205	0.046	0.0527*	0.046	0.0618
210	0.015	0.0172	—	0.0254
215	0.0052	0.0051*	—	0.0108
220	0.0018	—	—	0.0040
225	0.0004	—	—	0.0016

* Estimated by linear interpolation
1 Orlando et al., 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989
5 Hubrich and Stuhl, 1980

measured by Gillotay et al.; this discrepancy remains to be resolved. Also, the ratio of the cross section value at a given temperature to the corresponding value at 295 K is expected to be a smooth function of wavelength and temperature, and this is not the case for the data given in Tables 5 to 8 for wavelengths longer than about 210 nm; this is another indication of the rapidly increasing uncertainties.

As is the case for the fully halogenated hydrocarbons, the quantum yields for photodissociation for the HCFC's are expected to be unity, given the continuous nature of their UV absorption spectra. Furthermore, the primary products at the atmospherically important wavelengths are most likely a chlorine atom plus the residual organic free radical.

As mentioned above, there are no measurements of the UV spectrum of HFC-125, and there is very significant disagreement in the cross section values for the other two fluorocarbons considered in this review which do not contain chlorine (HFC-134a and 152a). Two groups have measured cross sections around 200 nm for these last two species, Molina and Molina (1989) and Allied-Signal Corp. (1989), with values differing by two orders of magnitude. The most likely explanation is that the small absorptions observed around 200 nm are strongly influenced by impurities, which differ from sample to sample. While this is not at all a satisfactory situation from the point of view of the proper spectroscopic characterization of these compounds, it turns out that the atmospheric implications are minor: photolysis can be neglected even assuming the largest reported cross section values.

A very conservative upper limit for the cross section values for HFC-134a and 152a is given by the cross sections corresponding to HCFC-22 (Table 9), for which solar photolysis is unimportant.

Table 5. Recommended Absorption Cross Sections for HCFC-123 ($CHCl_2$-CF_3), taken from Orlando et al., 1989.

	σ (cm²/molecule)	
λ (nm)	295K	223K
190	5.65E-19	5.09E-19
191	4.66E-19	4.33E-19
192	4.08E-19	3.76E-19
193	3.48E-19	3.14E-19
194	3.02E-19	2.71E-19
195	2.54E-19	2.25E-19
196	2.14E-19	1.87E-19
197	1.87E-19	1.58E-19
198	1.53E-19	1.3E-19
199	1.27E-19	1.07E-19
200	1.08E-19	8.87E-20
201	8.9E-20	7.25E-20
202	7.35E-20	5.93E-20
203	6.26E-20	4.99E-20
204	5.14E-20	4.08E-20
205	4.21E-20	3.33E-20
206	3.5E-20	2.71E-20
207	2.86E-20	2.21E-20
208	2.4E-20	1.85E-20
209	1.98E-20	1.51E-20
210	1.62E-20	1.24E-20
211	1.32E-20	1.02E-20
212	1.1E-20	8.47E-21
213	9.04E-21	6.94E-21
214	7.44E-21	5.97E-21
215	6.2E-21	4.92E-21
216	5.14E-21	4.12E-21
217	4.1E-21	3.52E-21
218	3.37E-21	3.01E-21
219	2.86E-21	2.48E-21
220	2.41E-21	2.17E-21

Table 6. Recommended Absorption Cross Sections for HCFC-141b ($CHCl_2$-CF_3), taken from Orlando et al., 1989 .

	σ (cm²/molecule)	
λ (nm)	295K	223K
190	7.95E-19	7.42E-19
191	7.05E-19	6.46E-19
192	6.3E-19	5.71E-19
193	5.4E-19	4.83E-19
194	4.77E-19	4.06E-19
195	4.04E-19	3.47E-19
196	3.43E-19	2.89E-19
197	2.94E-19	2.44E-19
198	2.44E-19	1.97E-19
199	2.02E-19	1.59E-19
200	1.71E-19	1.33E-19
201	1.4E-19	1.06E-19
202	1.15E-19	8.51E-20
203	9.67E-20	7.03E-20
204	7.86E-20	5.61E-20
205	6.38E-20	4.47E-20
206	5.21E-20	3.57E-20
207	4.24E-20	2.84E-20
208	3.56E-20	2.35E-20
209	2.91E-20	1.89E-20
210	2.38E-20	1.52E-20
211	1.95E-20	1.22E-20
212	1.62E-20	1.01E-20
213	1.34E-20	8.14E-21
214	1.16E-20	6.9E-21
215	9.74E-21	5.78E-21
216	8.2E-21	4.82E-21
217	7.11E-21	4E-21
218	6.34E-21	3E-21
219	5.41E-21	2.58E-21
220	4.82E-21	2.21E-21

Table 7. Recommended Absorption Cross Sections for HCFC-124 ($CHClFCF_3$), taken from Orlando, et al., 1989

	σ (cm²/molecule)	
λ (nm)	295K	223K
190	7.35E-21	4.79E-21
191	6.16E-21	4.02E-21
192	5.29E-21	3.52E-21
193	4.41E-21	2.95E-21
194	3.79E-21	2.53E-21
195	3.16E-21	2.09E-21
196	2.61E-21	1.73E-21
197	2.21E-21	1.47E-21
198	1.83E-21	1.21E-21
199	1.51E-21	9.91E-22
200	1.28E-21	8.31E-22
201	1.05E-21	6.77E-22
202	8.6E-22	5.49E-22
203	7.23E-22	4.57E-22
204	5.92E-22	3.71E-22
205	4.82E-22	2.97E-22
206	3.95E-22	2.39E-22
207	3.22E-22	1.93E-22
208	2.62E-22	1.59E-22
209	2.21E-22	1.28E-22
210	1.82E-22	1.03E-22
211	1.48E-22	8.25E-23
212	1.22E-22	6.76E-23
213	1E-22	5.44E-23
214	8.29E-23	4.57E-23
215	7.2E-23	3.8E-23
216	6.05E-23	3.17E-23
217	5.03E-23	2.81E-23
218	4.33E-23	2.42E-23
219	3.77E-23	2.1E-23
220	3.22E-23	1.88E-23

Table 8. Recommended Absorption Cross Sections for HCFC-142b ($CHCl_2F$-CH_3), taken from Orlando et al., 1989

	σ (cm²/molecule)	
λ (nm)	295K	223K
190	8.53E-21	6.38E-21
191	7.16E-21	5.27E-21
192	6.18E-21	4.47E-21
193	5.01E-21	3.61E-21
194	4.29E-21	3.05E-21
195	3.49E-21	2.45E-21
196	2.86E-21	1.98E-21
197	2.39E-21	1.64E-21
198	1.95E-21	1.32E-21
199	1.59E-21	1.06E-21
200	1.32E-21	8.72E-22
201	1.07E-21	6.96E-22
202	8.65E-22	5.53E-22
203	7.18E-22	4.57E-22
204	5.79E-22	3.62E-22
205	4.65E-22	2.87E-22
206	3.71E-22	2.31E-22
207	3.01E-22	1.83E-22
208	2.48E-22	1.51E-22
209	1.97E-22	1.22E-22
210	1.58E-22	9.8E-23
211	1.26E-22	7.94E-23
212	1.01E-22	6.58E-23
213	8.19E-23	5.21E-23
214	6.86E-23	4.46E-23
215	5.41E-23	3.88E-23
216	4.43E-23	3.5E-23
217	3.71E-23	2.93E-23
218	2.98E-23	2.69E-23
219	2.37E-23	2.44E-23
220	2.08E-23	2.17E-23

Table 9. Absorption Cross Section of HCFC-22 ($CHClF_2$), taken from Simon et al., 1988.

	$10^{20}\ \sigma$ (cm^2/molecule)				
λ (nm)	295K	270K	250K	230K	210K
174	5.72	5.72	5.72	5.72	5.72
176	4.04	4.04	4.04	4.04	4.04
178	2.76	2.76	2.76	2.76	2.76
180	1.91	1.91	1.91	1.91	1.91
182	1.28	1.28	1.28	1.28	1.28
184	0.842	0.842	0.842	0.842	0.842
186	0.576	0.576	0.576	0.576	0.576
188	0.372	0.372	0.372	0.372	0.372
190	0.245	0.245	0.245	0.245	0.245
192	0.156	0.156	0.156	0.152	0.148
194	0.103	0.102	0.099	0.096	0.093
196	0.072	0.069	0.067	0.064	0.062
198	0.048	0.045	0.043	0.041	0.039
200	0.032	0.029	0.0278	0.0259	0.0246
202	0.0220	0.0192	0.0184	0.0169	0.0159
204	0.0142	0.0121	0.0114	0.0104	0.0096

V. TROPOSPHERIC OH AND HCFC/HFC LIFETIMES

Combined Summary and Conclusions

Atmospheric Lifetimes for HCFCs Table

The Tropospheric Lifetimes of Halocarbons and their Reactions with OH Radicals: An Assessment Based on the Concentration of ^{14}CO

Richard G. Derwent
Modelling and Assessments Group
Environmental and Medical Sciences Division
Harwell Laboratory
Oxfordshire, United Kingdom
and
Andreas Volz-Thomas
Institut für Chemie der Belasteten Atmosphere, ICH2
Kernforschungsanlage KFA
D5170 Julich, Federal Republic of Germany

Tropospheric Hydroxyl Concentrations and the Lifetimes of Hydrochlorofluorocarbons (HCFCs)

Michael J. Prather
NASA
Goddard Institute for Space Studies
2880 Broadway
New York, NY 10025

COMBINED SUMMARY AND CONCLUSIONS

The atmospheric lifetime of HCFCs is determined predominantly by reaction with tropospheric OH. Stratospheric loss is secondary and may contribute at most 10% of the total budget.

The lifetimes of HCFCs are determined here by three separate approaches:

(1) 2-D chemical transport model with semi-empirical fit to ^{14}CO;
(2) photochemical calculation of 3-D OH fields and integrated loss;
(3) scaling of the inferred CH_3 CCl_3 lifetime by rate coefficients.

Resulting lifetimes from all three independent approaches generally agree within 15%, as shown in the table below. The integrated losses calculated from the global OH fields in the models (1 & 2) are constrained by modelling of the observations and budgets for ^{14}CO and CH_3CDCl_3 (respectively). Method (3) may be expressed simply as

$$\text{lifetime (HCFC)} = 6.3 \text{ yr x } k(CH_3\ CCl_3 \text{ at } 277 \text{ K}) \ / \ k(\text{HCFC at } 277 \text{ K}),$$

where the current estimate of the lifetime for methyl chloroform (6.3 yr) is based on the ALE/GAGE analysis (Prinn et al., 1987). Some of the errors associated with this scaling have been tested with the 3-D OH fields from method (2); method (3) should be reliable for calculating HCFC lifetimes in the range 1 to 30 years.

The calculated local concentrations of OH in these models (1 & 2) are not well tested since there are few observations of OH with which to compare. Based on method (2), the middle tropical troposphere (2-6 km) dominates the atmospheric loss and would be an important region in which to make observations of OH.

Estimated uncertainties in the HCFC lifetimes between 1 and 30 years are ±50% for (1) and ±40% for (2) & (3). Global OH values that give lifetimes outside of these ranges of uncertainty are inconsistent with detailed analyses of the observed distributions for ^{14}CO and CH_3CCl_3. The expected spatial and seasonal variations in the global distribution of HCFCs with lifetimes of 1 to 30 yr have been examined with methods (1) & (2) and found to have insignificant effect on the calculated lifetimes. Larger uncertainties apply to gases with lifetimes shorter than one year; however, for these species our concern is for destruction on a regional scale rather than global accumulation.

Future changes in the oxidative capacity of the troposphere, due to changing atmospheric composition, will affect HCFC lifetimes and introduce additional uncertainties of order ±20%.

Atmospheric Lifetimes for HCFCs

	k (cm^3 $molec^{-1}$ s^{-1})		lifetime (yr) for method*		
HCFC			(1)	(2)	(3)
CH_3CCl_3	5.0×10^{-13}	exp(-1800/T)	5	5.4	6.3
(range)			(3-7)	(4-7)	(5.4-7.5)
CH_3F	5.4×10^{-12}	exp(-1700/T)	3.3	3.8	4.1
CH_2F_2	2.5×10^{-12}	exp(-1650/T)	6.0	6.8	7.3
CHF_3	7.4×10^{-13}	exp(-2350/T)	635.	289.	310.
CH_2FCl	3.0×10^{-12}	exp(-1250/T)	1.26	1.33	1.44
$CHFCl_2$	1.2×10^{-12}	exp(-1100/T)	1.80	1.89	2.10
CHF_2Cl (22)	1.2×10^{-12}	exp(-1650/T)	13.0	14.2	15.3
CH_3CH_2F	1.3×10^{-11}	exp(-1200/T)	0.31	0.25	0.28
CH_2FCH_2F (152a)	1.7×10^{-11}	exp(-1500/T)	0.60	0.58	0.63
CH_3CHF_2	1.5×10^{-12}	exp(-1100/T)	1.46	1.53	1.68
CH_2FCHF_2	2.8×10^{-12}	exp(-1500/T)	3.2	3.5	3.8
CH_3CF_3	2.6×10^{-13}	exp(-1500/T)	40.	38.	41.
CHF_2CHF_2	8.7×10^{-13}	exp(-1500/T)	10.4	11.4	12.3
CH_2FCF_3 (134a)	1.7×10^{-12}	exp(-1750/T)	13.1	14.4	15.5
CHF_2CF_3 (125)	3.8×10^{-13}	exp(-1500/T)	24.9	26.1	28.1
CH_3CFCl_2 (141b)	2.7×10^{-13}	exp(-1050/T)	6.7	6.7	7.8
CH_3CF_2Cl (142b)	9.6×10^{-13}	exp(-1650/T)	16.6	17.8	19.1
CH_2ClCF_2Cl	3.6×10^{-12}	exp(-1600/T)	3.5	4.0	4.2
CH_2ClCF_3	5.2×10^{-13}	exp(-1100/T)	4.1	4.4	4.8
$CHCl_2CF_3$ (123)	6.4×10^{-13}	exp(-850/T)	1.40	1.42	1.59
$CHFClCF_3$ (124)	6.6×10^{-13}	exp(-1250/T)	5.5	6.0	6.6

*Lifetimes from method (1) do not include stratospheric loss; those from method (2) include small additional stratospheric loss. Method (3) is based on scaling the methylchloroform lifetime of 6.3 yrs from Prinn et al. (Science, 238, 945-950, 1988) by the ratio of the rate coefficients at 277 K.

N92-15439

THE TROPOSPHERIC LIFETIMES OF HALOCARBONS AND THEIR REACTIONS WITH OH RADICALS: AN ASSESSMENT BASED ON THE CONCENTRATION OF ^{14}CO

Richard G. Derwent
Modelling and Assessments Group
Environmental and Medical Sciences Division
Harwell Laboratory
Oxfordshire
United Kingdom

Andreas Volz-Thomas
Institut für Chemie der Belasteten Atmosphere, ICH2
PO Box 1913
D5170 Julich
Federal Republic of Germany

EXECUTIVE SUMMARY

Chemical reaction with hydroxyl radicals formed in the troposphere from ozone photolysis in the presence of methane, carbon monoxide and nitrogen oxides provides an important removal mechanism for halocarbons containing C-H and C = C double bonds. The isotopic distribution in atmospheric carbon monoxide has been used to quantify the tropospheric hydroxyl radical distribution. This review reevaluates this methodology in the light of recent chemical kinetic data evaluations and new understanding gained in the life cycles of methane and carbon monoxide. None of these changes has forced a significant revision of the ^{14}CO approach. However, it is now somewhat more clearly apparent how important basic chemical kinetic data are to the accurate establishment of the tropospheric hydroxyl radical distribution.

The two-dimensional (altitude-latitude) time-dependent (seasonal) hydroxyl radical distribution obtained by the ^{14}CO approach has then been used in the Harwell model to estimate halocarbon lifetimes together with their confidence limits. A simple graphical procedure suffices to relate halocarbon lifetime to the pre-exponential factors and activation energy parameters which describe the temperature dependent OH + halocarbon rate coefficients. Lifetimes and their 1-sigma confidence limits are calculated using the Harwell two-dimensional model for a range of alternative fluorocarbons.

1. INTRODUCTION

The role of homogeneous gas phase reaction in the lower atmosphere was first investigated in the 1950's, in attempts to understand the phenomenon of photochemical smog and the chemistry involved in its formation (Leighton, 1961). It was Levy (1971) who first suggested that free-radical chemistry, driven by photochemical dissociation of ozone and nitrogen oxides, might be important in the background troposphere. He proposed that relatively high concentrations of the reactive hydroxyl radicals could be maintained in steady state in the background sunlit troposphere and that this steady state could provide an efficient scavenging mechanism for both natural and man-made trace constituents on a global scale.

Since then attempts have been made to unravel the free-radical chemistry of the troposphere and to quantify its role in the trace gas cycles. The reactions of the hydroxyl radical in the troposphere have been linked to a growing list of trace gases including ozone and NO (Levy 1971; Crutzen 1974), carbon monoxide (Weinstock and Niki 1972), methane (Ehhalt 1974), hydrogen (Seiler and Schmidt 1974) followed somewhat later by the sulphur compounds (Crutzen 1976) and halocarbons (Cox et al 1976). This review concerns the distributions of tropospheric hydroxyl radicals and their role in determining the lifetimes of halocarbons. Figure 1 shows some of the species and some of the atmospheric chemical reactions of importance in the global troposphere.

Interest in tropospheric chemistry has been stimulated by the problem of depletion of stratospheric ozone by chlorofluoromethanes and other chlorine-containing species (HMSO 1976; NAS 1977). The extent to which chlorine compounds injected at the earth's surface reach the stratosphere depends on the efficiency with which they are scavenged in the troposphere. Quantitative determination of the sink strength is required to assess the impact of various chlorine-containing species, both natural and man-made, on stratospheric ozone.

The scavenging processes acting in the troposphere may be divided into physical removal processes, in which species are absorbed irreversibly at the earth's surface or in precipitation elements (cloud and rain droplets, aerosols) and chemical removal processes which involve reactions in the atmosphere. Physical removal is often referred to as wet and dry deposition and may be highly efficient for some trace constituents such as ozone, sulphur dioxide and nitric acid. However for halocarbons it is not generally a particularly efficient process and it may be neglected for most species.

Chemical removal of halocarbons by destruction with tropospheric hydroxyl radicals has been shown to be an important sink for those halocarbons which contain H atoms and C = C double bonds, (Cox et al 1976). This sink process may be represented simply by the equation (1), below:

$$\mathrm{OH} + \mathrm{Halocarbon} \xrightarrow{k} \mathrm{sink} \tag{1}$$

where k is some temperature dependent OH rate coefficient and OH is some form of globally averaged concentration of hydroxyl radicals.

Early two-dimensional model studies (Derwent and Eggleton 1978) have shown that because of the covariance of the temperature dependent value of k, the hydroxyl radical concentration [OH] and the halocar-

PRECEDING PAGE BLANK NOT FILMED

bon concentration itself [Hal], the lifetime due to OH reaction, τ, cannot be adequately represented by the simple box model equation (2), below:

$$\text{lifetime due to OH reaction} = \frac{\overline{[\mathrm{Hal}]}}{\overline{k\,[\mathrm{OH}]\,[\mathrm{Hal}]}} = \frac{1}{\bar{k}\,\overline{[\mathrm{OH}]}} \qquad (2)$$

The more reactive halocarbons are not distributed uniformly throughout the troposphere and the sink strength reflects only the OH distribution close to the source, normally close to the surface in midlatitudes of the northern hemisphere. The more reactive the halocarbon, the larger the discrepancy between the "true" average OH concentration and that derived from the box model approach. The less reactive halocarbons often exhibit a more marked temperature dependence in their rate coefficients for OH radical attack. This concentrates oxidation close to the surface and makes chemical removal in the middle and upper troposphere relatively unimportant. The less reactive the halocarbon therefore the lower the tropospheric mean temperature required to calculate the mean reaction rate coefficient in equation (2).

For halocarbons of low reactivity with respect to hydroxyl radicals, mean lifetimes may extend to several years. Under these conditions, inter-hemispheric exchange will give a much more uniform distribution between the two hemispheres. As the halocarbon lifetime increases, then fraction of the surface injection which can reach the stratosphere will also increase. For a halocarbon with a lifetime of 10 years, up to 20% of the surface injection could be transported into the stratosphere. On this basis, methyl chloride and methyl chloroform have been identified as significant chlorine carriers to the stratosphere from natural and man made sources, respectively.

An accurate, quantitative assessment of the impact of a given halocarbon on stratospheric ozone, therefore requires a thorough understanding of tropospheric OH destruction. Such an understanding requires information on the following aspects:

- the reaction rate coefficient of the halocarbon with OH radicals, and its variations throughout the troposphere driven by temperature and pressure,
- the tropospheric distribution of OH radicals,
- the transport mechanisms of halocarbons within the troposphere,
- the halocarbon source strength and its spatial distribution,
- the nature and behaviour of any longer-lived degradation products,
- the transport mechanisms of halocarbons to the stratosphere.

Since the 1970s understanding of many of the above areas has grown tremendously as a result of the many field and laboratory investigations which have been carried out, carefully interpreted with theoretical modelling studies. Instrumental techniques and computational models are both areas which have seen impressive and powerful gains in performance which have had repercussions on our understanding on atmospheric composition and the influence of man's activities. It is now clearly understood that man has had and continues to have a significant influence on the global concentrations of many trace constituents. The number of species whose tropospheric concentrations have a significant upwards trend is being continually revised. In addition to carbon dioxide, now must be added the chlorofluoromethanes (CCl_3F, CCl_2F_2), carbon tetrachloride, methyl chloroform, methane and ozone, itself. Man's activities will most certainly have had an additional influence of the tropospheric distribution of hydroxyl radicals, however, it is not yet possible to quantify what this influence has been.

The tropospheric distribution of the hydroxyl radical has yet to be unambiguously defined. Despite the pioneering investigations of the KFA Julich group using long path ultraviolet absorption spectroscopy, a reliable climatology of hydroxyl concentrations with adequate three-dimensional and temporal resolution is unlikely to be available in the near future. To advance the assessment process for halocarbons in the absence of an observed tropospheric hydroxyl distribution, recourse has been made to derived or inferred distributions from the following principal sourcs:

- chemical modelling studies, (Crutzen and Fishman 1977),
- studies of halocarbon behaviour, particularly methyl chloroform, (Singh 1977; Neely and Plonka 1978),
- studies of the isotopic distribution in atmospheric carbon monoxide, (Volz, Ehhalt and Derwent 1981).

The results from all three methods agree relatively well with each other and with the available observations from the KFA Julich group, within their respective estimated confidence limits. It is, however, important to review these different methods and to form a judgement as to whether current understanding is adequate for assessment purposes.

This review addresses the isotopic distribution in atmospheric carbon monoxide with a view to quantifying the tropospheric hydroxyl distribution. The aim is to examine its potential role in removing from the atmospheric circulation, the proposed alternative aerosol propellants, foam blowing agents, solvents and refridgerants which are currently under consideration as replacements for those halocarbons containing chlorine which may reach the stratosphere. This review has been commissioned within the framework of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS).

2. THE ISOTOPIC DISTRIBUTION IN ATMOSPHERIC CARBON MONOXIDE

The first attempts to calculate the global mean tropospheric hydroxyl concentration from isotopic distribution in atmospheric carbon monoxide were made by Weinstock 1969 and by Weinstock and Niki (1972). They used the three available ^{14}CO measurements by McKay et al (1963), an estimate of the global source strength for ^{14}CO from the well-known cosmic ray bombardment of atmospheric nitrogen molecules, the $OH + CO$ rate coefficient and derived an estimate for the atmospheric turnover time for ^{12}CO of the order of 1 month. Furthermore, they suggested that OH radicals were responsible for the CO removal and obtained an estimate of their global mean abundance. Seiler (1974) argued that these early measurements of ^{14}CO might be too low and thus have given rise to too short a lifetime and too high a mean tropospheric hydroxyl radical concentration.

Volz, Ehhalt and Derwent (1981) repeated the methodology and obtained a mean tropospheric hydroxyl radical concentration of $(6.5\ ^{+3}_{-2})$ x 10^5 molecule cm^{-3} based on four refinements, viz:

- additional measurements of ^{14}CO in the lower troposphere,
- evaluated chemical kinetic data for the OH + CO reaction,
- improved life cycle data for ^{14}C and ^{12}C in the troposphere,
- a global two-dimensional time-dependent model to investigate the coupled CH_4-H_2-CO-NO_X-O_3 life cycles, replacing the box model approach.

In the intervening years since the publication of these early studies (Weinstock and Niki 1972; Volz, Ehhalt and Derwent 1981), understanding of the oxidizing capacity of the troposphere has developed significantly. The paragraphs which follow have therefore been devoted to a reevaluation of some of the measurements, data and assumptions which were essential in the Volz, Ehhalt and Derwent (1981) study. The general impression gained from this reevaluation is that subsequent research does appear to have neither undermined nor found the ^{14}CO method seriously flawed. It therefore remains a viable method for determining the tropospheric hydroxyl distribution. Nevertheless, some of the input assumptions could now be questioned in detail and these areas are highlighted and their impact on the determination of the tropospheric hydroxyl distribution assessed.

The Methodology Used

The methodology adopted by Volz, Ehhalt and Derwent (1981) was to take a precalculated two-dimensional (altitude, latitude), time-dependent (monthly) field of tropospheric hydroxyl radicals and linearly scale it until it generated surface ^{14}CO and ^{12}CO concentrations which balanced observations. At the point of balance, the methodology simultaneously determined the tropospheric hydroxyl distribution and the biogenic source strength of ^{12}CO, both of which are coupled unknowns.

The estimated tropospheric hydroxyl distribution contains uncertainties which derive directly from the uncertain ^{14}CO measurements, the uncertainties in the ^{14}CO and ^{12}CO life cycles, the uncertainties in the parameters used in the two-dimensional model and the uncertainties inherent all the assumptions made in the model formulation itself. The uncertainty analysis treatment in Volz, Ehhalt and Derwent (1981) considered the contributions from the likely errors in:

- the ^{14}CO production from cosmic rays, (Lingenfelter 1963),
- the ^{12}CO emission from fossil fuel burning, (Seiler 1974; Logan et al 1981),
- the ^{14}CO measurements, (McKay et al 1963; Volz, Ehhalt and Derwent 1981),
- the ^{12}CO latitudinal distribution, (Seiler and Schmidt 1974),
- the transport and chemistry schemes employed in the two-dimensional model, (Derwent and Curtis 1977).

Experimental Techniques

The measurement of the concentration of ^{14}CO is essential to the ^{14}CO approach. The early measurements of McKay et al 1963 relied on the isotopic ratio viz. $^{14}CO/^{12}CO$ in air samples obtained from an air liquefaction plant. McKay et al however failed to determine simultaneously the ^{12}CO concentration and this led to the introduction of uncertainties in using the ^{14}CO approach. A major challenge in the study by Volz, Ehhalt, Derwent and Khedim (1979) was therefore the measurement of the ^{14}CO concentration.

Volz, Ehhalt, Derwent and Khedim (1979) have described their experimental procedures in some detail and only a brief outline is given in the paragraphs below. The procedure consists of two steps,

- the quantitative separation and the collection of the CO from ambient air,
- the determination of its isotopic ratios, $R_{\infty} = [^{14}CO]/[^{12}CO]$.

The ^{14}CO concentration is then given by:

$$[^{14}CO] = R_{\infty} \cdot [^{12}CO]$$

The separation of the CO from ambient air was achieved by quantitative oxidation to CO_2 on a hot platinum catalyst, followed by absorption in CO_2-free aqueous NaOH. Prior to this the atmospheric CO_2 was removed from the air sample by absorption in NaOH. Interferences from any remaining CO_2 were determined by gas chromatography and were found to be less than 5%. The CO concentration in the air was measured by gas chromatography and, in addition, calculated from the amount of CO collected and the volume of air sampled, (100-200 m^3).

The isotopic ratio of the sampled CO was measured in a low-level counting system, similar to those used for ^{14}C dating, with an accuracy of ± 3-5%. The counting system was calibrated against the ^{14}CO standard of the Institut für Umweltphysik, Universitat Heidelberg. The overall accuracy in the determination of the ^{14}CO concentration was largely determined by uncertainties associated with the sampling procedure as discussed by Volz, Ehhalt, Derwent and Khedim (1979), and was generally on the order of ±10% (1σ), including any possible systematic bias.

Measured ^{14}CO Concentrations

So far measurements of the ^{14}CO concentration have been reported only for the northern hemisphere, (Volz, Ehhalt and Derwent 1981). Most of the samples were collected during 1977 and 1978 at a remote, rural site in the Eifel mountains (51^0N 2^0W) in the Federal Republic of Germany. In addition, three samples were collected during a cruise of the RV Knorr over the Mediterranean Sea and the Atlantic (36^0 to 46^0N) in April 1976 and two samples at Miami, Florida (27^0N) in September 1977, (Volz, Ehhalt, Derwent and Khedim 1979).

The ^{14}CO concentration data exhibit a well-defined seasonal cycle with a winter maximum of about 20 molecule cm^{-3} and a summer minimum of 10 molecule cm^{-3}. The annual cycle in ^{14}CO reflects the influence of the chemical sink due to destruction by tropospheric OH radicals.

The ^{14}CO concentration data also show evidence of a latitudinal gradient increasing from the equator to the North Pole. The concentrations at Miami (27°N) in September 1972, 4.2 ± 0.7 molecule cm^{-3} are almost a factor of three smaller than those found at 51°N for the same time of year. Similarly, the concentrations measured over the Atlantic Ocean show an increase from 15 molecule cm^{-3} at 36°N to 19 molecule cm^{-3} at 43°N. This latitudinal distribution in ^{14}CO reflects the influence of the tropospheric OH distribution increasing from the North Pole towards the equator.

Evaluated Rate Coefficient Data

An important aspect of the two-dimensional model used to calculate the tropospheric distribution of hydroxyl radicals, is the chemical kinetic input data adopted. Figure 1 illustrates the main free radical reactions which are believed to be occurring in the sunlit free troposphere. To a degree, the OH distribution estimated by Volz, Ehhalt and Derwent (1981) is sensitive to all the chemical kinetic assumptions. However, some of the chemical kinetic input parameters exert a more significant influence on the OH concentrations than others and it is upon these that we have concentrated upon in the paragraphs below. The Volz, Ehhalt and Derwent (1981) paper drew much of its chemical kinetic input data from the 1979 CODATA review (Baulch et al 1980). This can be directly compared with the 1988 IUPAC evaluation (Atkinson et al 1989).

OH to HO_2 interconversion reactions

The conversion of hydroxyl to hydroperoxyl radicals is driven largely by the reaction of OH radicals with carbon monoxide, methane and hydrogen. There has been an important revision in the OH + CO rate coefficient over the intervening years from $1.4 \times 10^{-13} (1 + p_{atm})$ cm^3 $molecule^{-1}$ s^{-1} to $1.5 \times 10^{-13} (1 + 0.6\ p_{atm})$ cm^3 $molecule^{-1}$ s^{-1}. This reevaluation reduces the rate coefficient by 14% at 1 atmosphere pressure and increases it by about 3% under the conditions in the upper troposphere. There have been revisions to the OH + CH_4 and OH + H_2 rate coefficients. Under the conditions approproate to the lower troposphere, the OH + CH_4 rate coefficient has been increased by about 6%, whereas the OH + H_2 rate coefficient has decreased by about 4%. Overall, these latter reevaluations are not likely to be significant compared with that of the OH + CO reaction.

In the two-dimensional model study, the concentration fields of CO, CH_4 and H_2 were taken from the available measurements and sufficient CO, CH_4 and H_2 were injected into the model at every time step to balance removal by all processes in the surface layer including the reaction with hydroxyl radicals. If a lower OH + CO rate coefficient had been employed then, to maintain the same $OH \rightarrow HO_2$ flux, a 10-15% higher OH concentration would be required.

HO_2 to OH interconversion reactions

The conversion of HO_2 radicals to OH radicals is largely driven by the reactions of HO_2 radicals with ozone and nitric oxide. The rate coefficients of these two reactions under conditions appropriate to lower troposphere have not changed by more than 1-7%. These reevaluations are of negligible importance.

HO_2 recombination to form hydrogen peroxide

The recombination of HO_2 radicals to form hydrogen peroxide dominates free radical termination in the free troposphere at all heights and latitudes where NO_x levels are low. The reaction has generally

Free Radical Production

$$\begin{aligned}
&O_3 = \text{radiation } (280 \text{ nm} < \lambda < 310 \text{ nm}) = O(^1D) + O_2 \\
&O(^1D) + H_2 = OH + OH
\end{aligned}$$

$$\begin{aligned}
&RCHO + \text{radiation } (280 \text{ nm} < \lambda < 360 \text{ nm}) = R + HCO \\
&HCO + O_2 = HO_2 + CO
\end{aligned}$$

HO to HO_2 Interconversion

$$\begin{aligned}
OH + CO &= H + CH_2 \\
OH + CH_4 &= CH_3 + H_2O \\
OH + H_2 &= H + H_2O \\
OH + O_3 &= HO_2 + O_2 \\
OH + RCHO &= RCO + H_2O
\end{aligned}$$

HO_2 to OH Interconversion

$$\begin{aligned}
&HO_2 + NO = OH + NO_2 \\
&NO_2 + \text{radiation } (280 \text{ nm} < \lambda < 430 \text{ nm}) = O + NO \\
&O + O_2 + M = O_3 + M \\
&HO_2 + O_3 = OH\ O_2 + O_2
\end{aligned}$$

Free Radical Loss Processes

$$\begin{aligned}
&HO_2 + HO_2 + M = H_2O_2 + M \\
&OH + NO_2 + M = HNO_3 + M
\end{aligned}$$

Temporary Reservoir Formation

$$\begin{aligned}
RCO(O_2) + NO_2 &= RCO(O_2)NO_2 \\
RCO(O_2)NO_2 &= RCO(O_2) + NO_2 \\
RCO(O_2) + NO &= R + CO_2 + NO_2
\end{aligned}$$

Nighttime Chemistry

$$\begin{aligned}
NO_2 + O_3 &= NO_3 + O_2 \\
NO_3 + NO_2 + M &= N_2O_5 + M \\
N_2O_5 + M &= NO_3 + NO_2 + M
\end{aligned}$$

Heterogeneous Processes

$$\begin{aligned}
HNO_3 + NaCl &= NaNO_3 + HCl \\
N_2O_5 &= \text{aerosol nitrate}
\end{aligned}$$

Figure 1. The main species and atmospheric chemical reactions of importance in the global troposphere.

not been intensively investigated in laboratory chemistry studies and evaluations have had only a few studies to draw upon. It is not surprising to find that this reaction has undergone a dramatic reevaluation between the 1979 CODATA (Baulch et al 1980) and 1988 IUPAC (Atkinson et al 1989) studies. The unusually large negative activation energy reported previously has been replaced by a significantly smaller but nevertheless still negative value. The effect of the reevaluations is to produce a HO_2 + HO_2 rate coefficient which is about a factor of 1.7 lower in the lower troposphere and a factor of 4 lower in the upper troposphere.

Because of the square dependence of the free radical destruction rate on the HO_2 radical concentration, the reevaluation of the HO_2 + HO_2 rate data should lead to OH and HO_2 radical concentrations about a factor of two higher in the upper troposphere and about thirty percent higher in the lower troposphere.

The reevaluations in the chemical kinetic data indeed strengthen the results of Volz, Ehhalt and Derwent, 1981: at the time of their evaluation, the OH concentrations required to balance the budgets of both ^{12}CO and ^{14}CO were a factor of 1.7 greater than those derived from photochemical models. It appears now that inadequacies in the chemical kinetic data, most important the rate coefficients for the OH +

Table 1. The budget for atmospheric carbon monoxide (^{12}CO) as estimated by Volz, Ehhalt and Derwent (1981) and compared with a more recent assessment (Seiler and Conrad 1987)

Source Strength, g yr^{-1}	^{14}CO Methodology	Present View
Terpenes and isoprene	1150×10^{12}[a]	1000×10^{12}
Ocean[b]	100×10^{12}	100×10^{12}
Methane oxidation	880×10^{12}[c]	600×10^{12}
Man made sources[c]	640×10^{12}	640×10^{12}
Biomass burning	-	1000×10^{12}
Sink Strength, g yr^{-1}		
OH oxidation	2450×10^{12}[d]	2000×10^{12}
Surface removal	320×10^{12}[e]	390×10^{12}
Stratospheric removal	-	110×10^{12}
Total Source Strength, g yr^{-1}	2770×10^{12}	3300×10^{12}
Total Atmospheric Mass, g	480×10^{12}	550×10^{12}
Lifetime, yrs	0.17	0.17

Notes:
a. calculated assuming mass balance.
b. Seiler (1974). Logan (1981).
c. Seiler (1974).
d. from Derwent and Curtis (1977).
e. Liebl and Seiler (1976).

CO and HO_2 + HO_2 reactions, indeed resulted in too low OH concentrations in the photochemical models at that time. With the revised rate coefficients, the OH distributions from ^{14}CO and from photochemical models are in much better agreement.

Life Cycle Data

Inherent in the methodology were some basic assumptions concerning the methane, carbon monoxide, hydrogen, nitrogen oxides and ozone life cycles in the two-dimensional model of ^{14}CO and in the two-dimensional model used to estimate the hydroxyl radical concentrations, themselves. At the point where the ^{12}CO and ^{14}CO distributions balanced, the methodology returned the biospheric source strength of ^{12}CO allowing a solution to the ^{12}CO budget.

In Table 1, this budget is examined in some detail and compared with a more recent evaluation by Seiler and Conrad (1987). The overall conclusion is that the broad features of the carbon monoxide budget have remained unchanged. In detail, though, there is a major difference in the significance given to biomass burning. The Volz, Ehhalt and Derwent (1981) study was unable to resolve the difference between biomass burning, on the one hand, and terpene and isoprene oxidation on the other, as both are sources of ^{14}CO and ^{12}CO. Subsequently, field campaigns in the tropical regions of South America have led to a quantification of this source as shown in Table 1.

The inclusion of the biomass burning source would have an impact on the Volz, Ehhalt and Derwent (1981) analysis because of the different latitudinal distributions of the ^{12}CO and ^{14}CO source strengths.

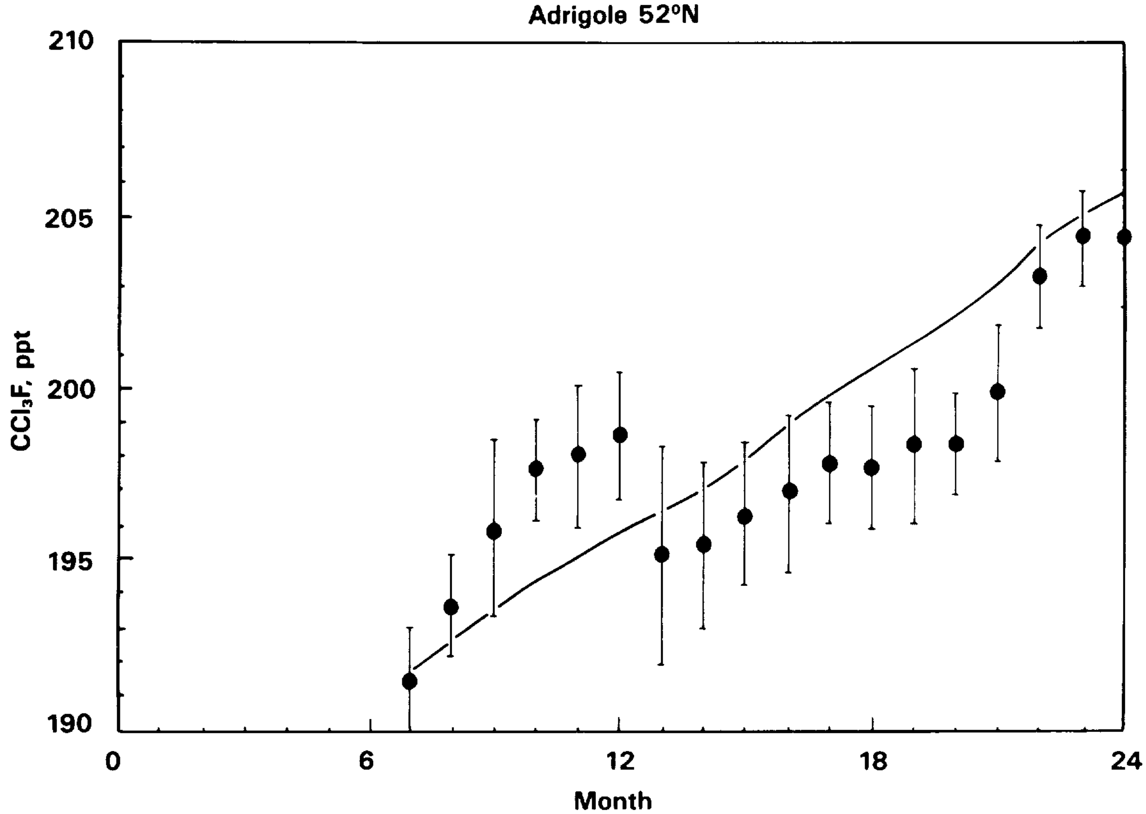


Figure 2. The time series of CCl_3F concentrations at Adrigole 52°N (Cunnold et al. 1986) and the two-dimensional model results.

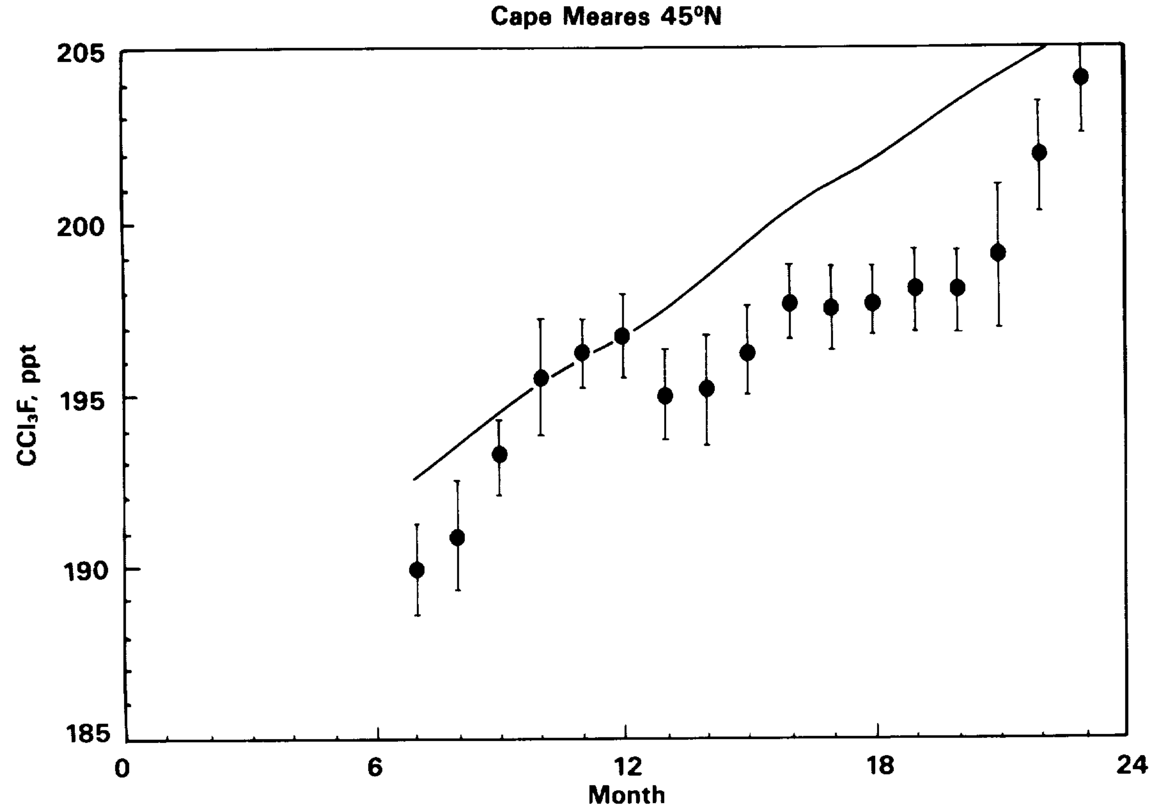


Figure 3. The time series of CCl_3F concentrations at Cape Meares 45°N (Cunnold et al. 1986) and the two-dimensional model results.

The difference is minor because ^{14}CO is rather insensitive to this source and is unlikely to have seriously distorted the 2-D model study.

The revised OH + CO rate coefficient has a direct influence on the evaluation of the tropospheric OH distribution through the ^{14}CO life cycle. An important source of ^{14}CO is located in the upper troposphere where the OH + CO rate coefficient has been reevaluated. A fixed ^{14}CO injection was assumed so that the increase in OH + CO rate coefficient would lead to a decreased ^{14}CO penetration into the free troposphere. The reduced OH + CO rate coefficient at the surface would reduce ^{14}CO fluxes there. Overall the OH + CO rate coefficient reevaluation would induce small changes in the tropospheric OH distribution of the order of ± 7%, downwards. The biospheric source strength of ^{12}CO would accordingly require downwards revision to about 1000 x 10^{12} g yr^{-1}. This latter estimate of the ^{12}CO source strength is identical with the more recent assessment of Seiler and Conrad (1987) quoted in Table 1.

Two-dimensional model transport data

The version of the Harwell two-dimensional model used by Volz, Ehhalt and Derwent (1981) had 7 vertical layers of 2.5 km depth and 18 latitude ranges weighted equally by the sine of latitude. Transfer between the boxes both horizontally and vertically was driven by advection and turbulent mixing. The zonally averaged wind fields were taken from Newell et al (1972) and the eddy diffusion coefficients from Louis (1975).

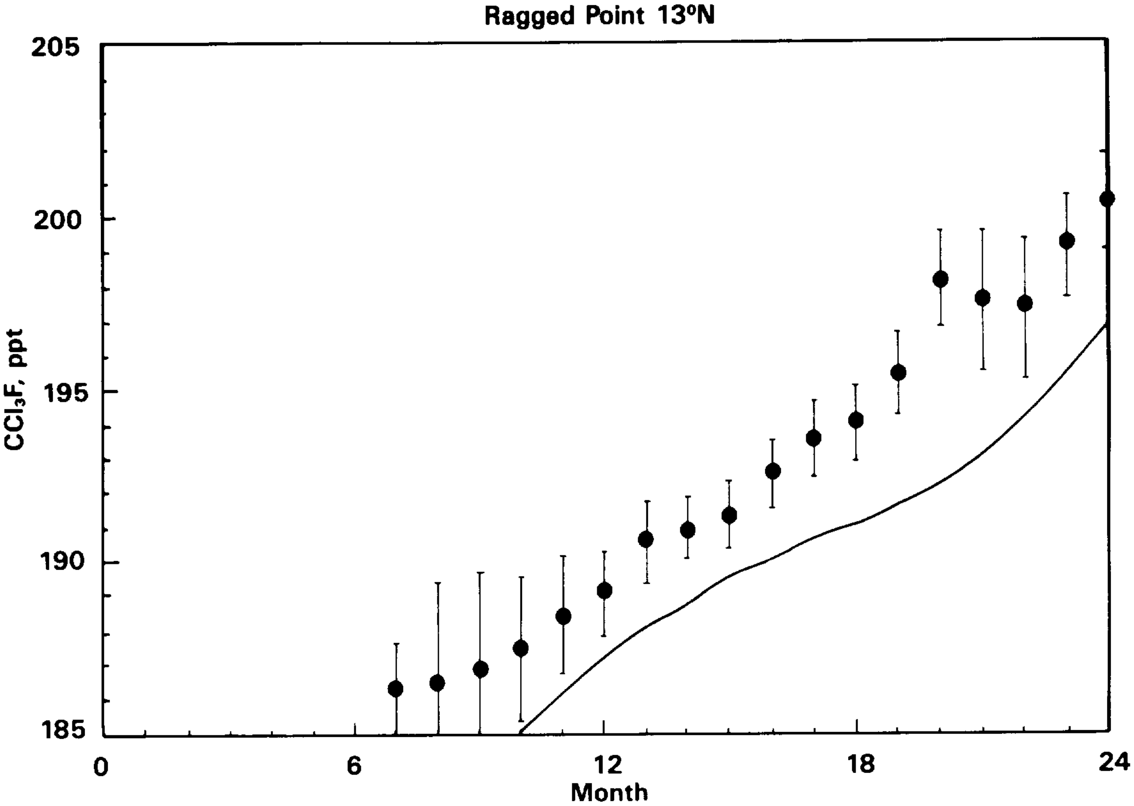


Figure 4. The time series of CCl_3F concentrations at Ragged Point 13°N (Cunnold et al. 1986) and the two-dimensional model results.

The sensitivity of the tropospheric OH distribution derived from the ^{14}CO approach to changes in the transport parameters was investigated by Volz, Ehhalt and Derwent (1981). They concluded that large changes in the transport coefficients of up to a factor of two increase or decrease made little difference to the tropospheric OH distribution required to balance the ^{12}CO and ^{14}CO life cycles. The estimated tropospheric OH distributions changed by less than ± 20%.

In the intervening years since the first studies with the Harwell two-dimensional model, the ALE experiment has made available high quality halocarbon emissions and time series concentration data for a wide latitude range covering both hemispheres (Cunnold et al 1986). These halocarbon measurements provide an excellent database to validate the transport schemes in two-dimensional models.

The CCl_3F emissions for the period 1931-1982 (Chemical Manufacturers Association 1983, 1988) were used in the Harwell two-dimensional model and an upper boundary condition was applied representing stratospheric photolysis, adjusted to give a CCl_3F lifetime in the range 50-75 years.

Figures 2-6 illustrate the model calculated and measured concentrations of CC_3F at Adrigole, Republic of Ireland (52°N 10°W) Cape Meares, Oregon (45°N, 124°W), Ragged Point, Barbados (13°N 59°W), Point Matatula, American Samoa (14°S, 171°W) and Cape Grim, Tasmania (41°S, 145°E) for the eight-

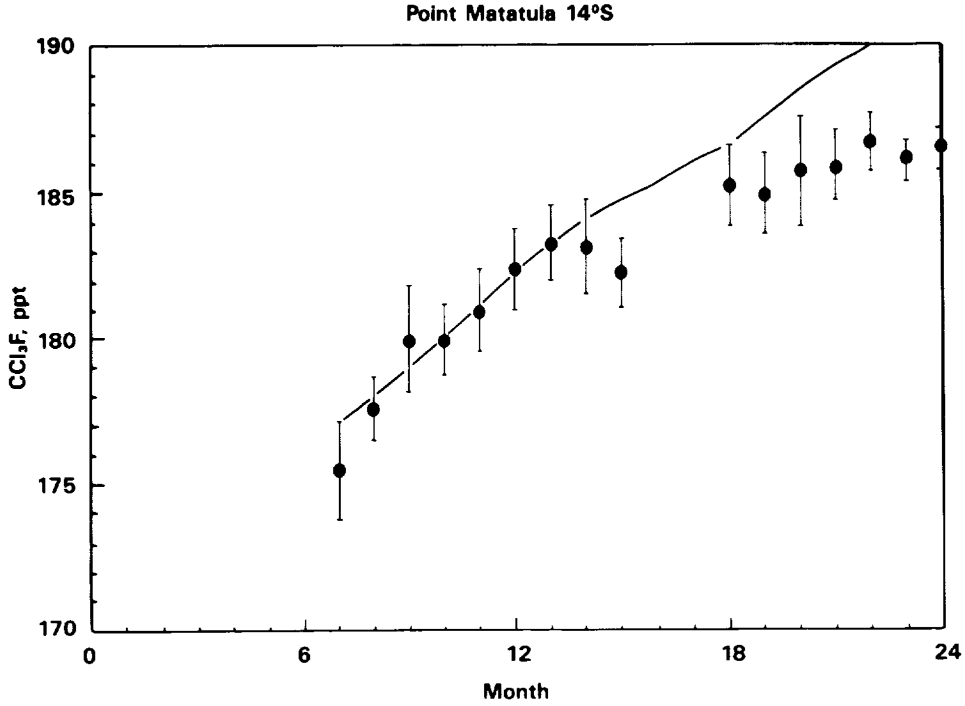


Figure 5. The time series of CCl_3F concentrations at Point Matatula 14°S (Cunnold et al. 1986) and the two-dimensional model results.

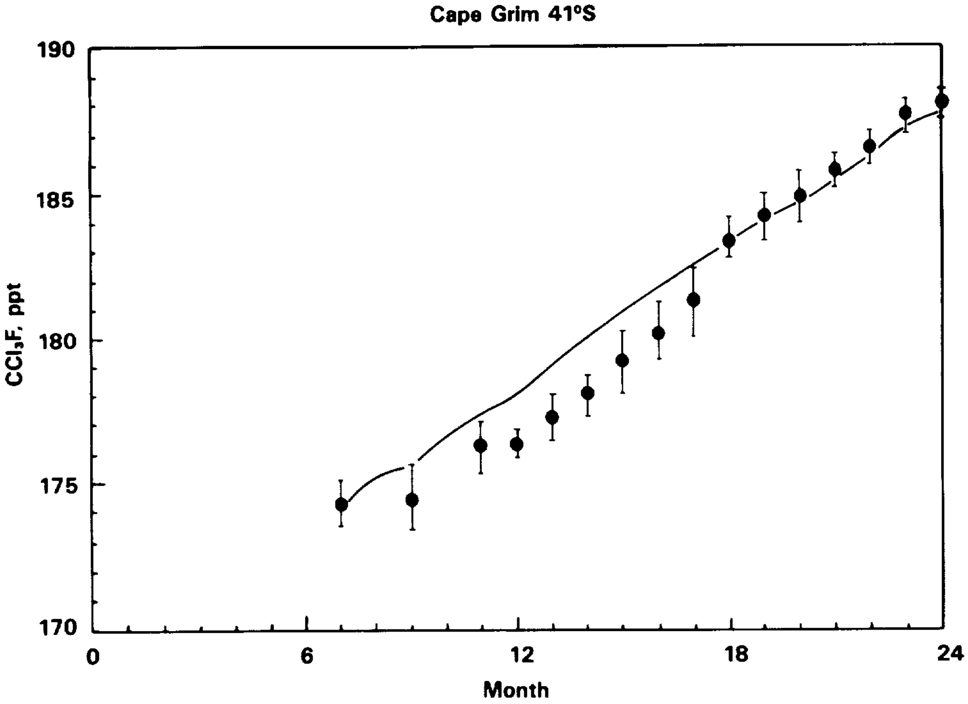


Figure 6. The time series of CCl_3F concentrations at Cape Grim 41°S (Cunnold et al. 1986) and the two-dimensional model results.

een month period from July 1981 to December 1982 (Cunnold et al 1986). Viewed against the ALE measurements, the transport scheme in the Harwell two-dimensional model is clearly performing adequately and without systematic bias.

The conclusion is that the transport scheme adopted in the Volz, Ehhalt and Derwent (1981) study represents adequately the gross features of halocarbon transport and this is an important model validation. Furthermore, the sensitivity of the estimated tropospheric OH distribution to the magnitudes of the transport coefficients is not strong. It is unlikely therefore that inadequacies in present understanding of global transport have seriously influenced the uncertainty in the estimated tropospheric OH distribution using the ^{14}CO method.

3. THE TROPOSPHERIC DISTRIBUTION OF OH RADICALS AND HALOCARBON LIFETIMES

Halocarbon Lifetimes

The behaviour of a halocarbon in a two-dimensional (altitude-latitude) atmosphere injected at the earth's surface, subject to stratospheric destruction and oxidation by hydroxyl radicals can be described by the differential equation:

$$\frac{d}{dt}[\mathrm{Hal}] + \mathrm{div}\,([\mathrm{Hal}]\,.\,U) - \mathrm{div}\,(K.N.\,\mathrm{grad}\,([\mathrm{Hal}]/N)$$

$$= E - k[\mathrm{OH}][\mathrm{Hal}] - SL[\mathrm{Hal}] \tag{3}$$

The time behaviour of the halocarbon concentration [Hal] in molecule cm^{-3} was computed by solving the above continuity equation over a 6 x 18 mesh point grid extending vertically in 2.5 km steps and in 18 steps latitudinally with equal spacing in sine ϕ where ϕ is the latitude angle. The two-dimensional wind field, U, and the eddy diffusion tensor, K, were taken from Newell et al (1972) and Louis (1975), respectively. The detailed procedures used in the finite-differencing scheme have been described elsewhere (Derwent and Curtis 1977). The finite difference form of the above equation was integrated numerically using the Harwell program FACSIMILE (Curtis and Sweetenham 1987). For a 100 year model simulation, 15 minutes computer time were required using an IBM compatible 80386/80387-based microcomputer (Dell System 310).

The terms in the above continuity equation describing the halocarbon behaviour were derived as follows:

- E: a time-independent halocarbon injection was assumed with a spatial distribution which closely followed the population distribution between the hemispheres,
- SL: stratospheric loss coefficient, which was set to give a lifetime due to stratospheric removal, acting on its own, of 50-100 years,
- [OH]: this is the time dependent two-dimensional distribution of tropospheric hydroxyl radicals determined by Volz, Ehhalt and Derwent (1981) and illustrated in figure 7,
- k: this is the temperature dependent rate coefficient for hydroxyl radical attack on the halocarbon of interest.

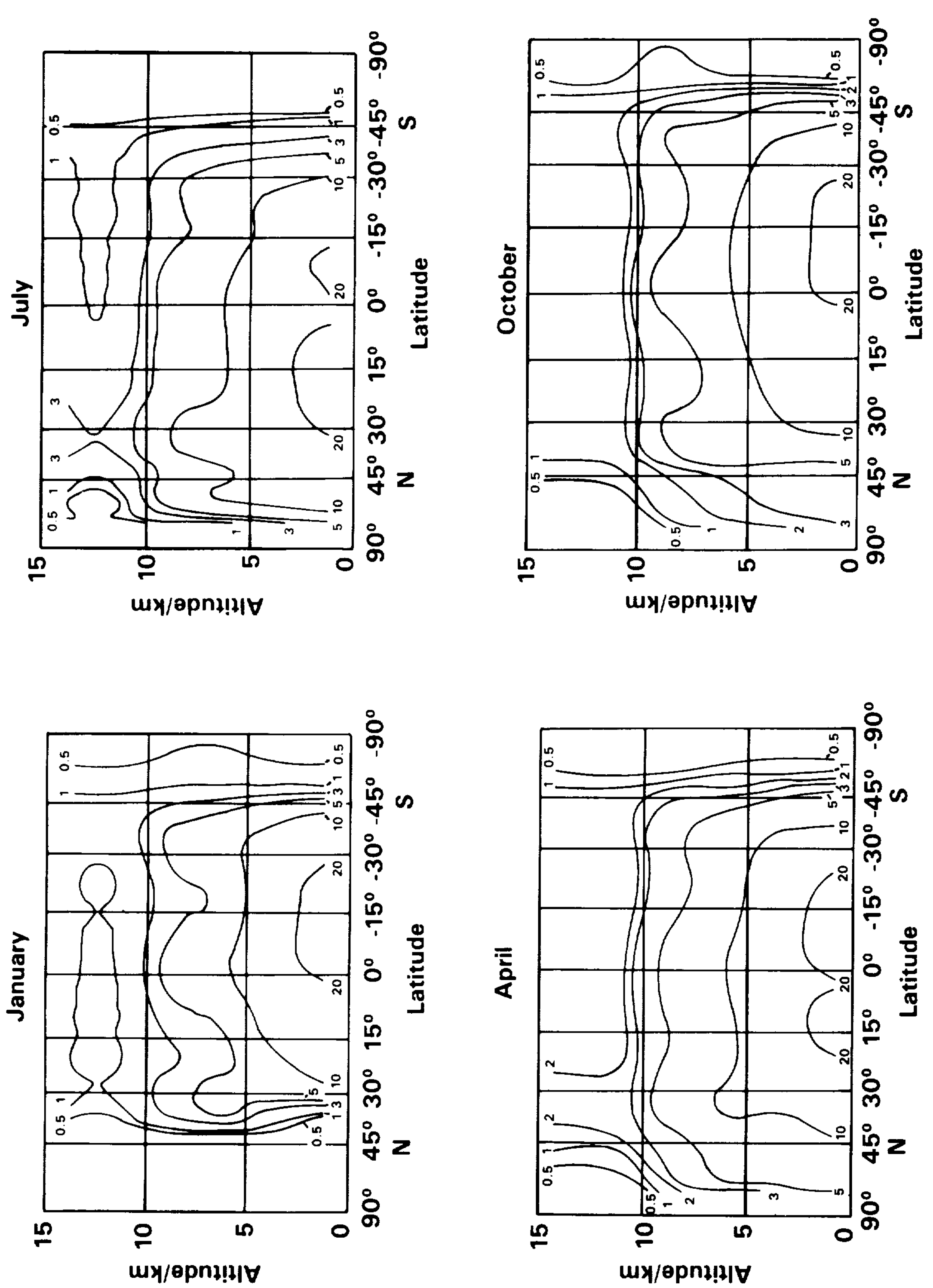


Figure 7. Distribution of hydroxyl radicals ^{14}CO method in 10^5 molecule cm^{-3}

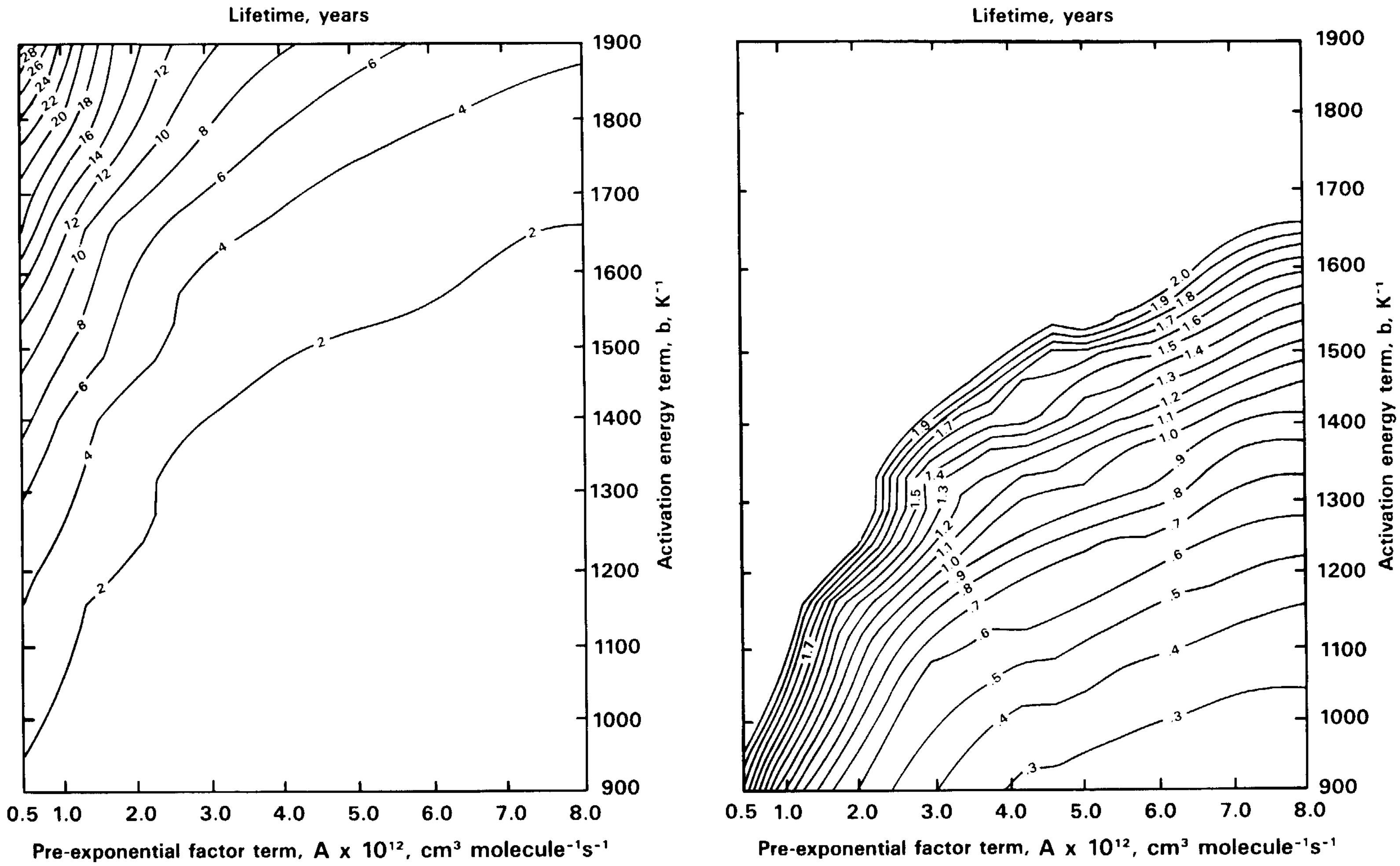


Figure 8. Halocarbon lifetimes in years determined by the ^{14}CO method for halocarbons reacting with OH radicals with a rate coefficient of A exp (-b/T) where T is the temperature in K.

At the end of the 100 year model experiment, the total model halocarbon inventory was divided by the total halocarbon injection rate to determine the halocarbon lifetime. The assumption of fixed tropospheric hydroxyl radical concentrations implies low tropospheric halocarbon loadings so as not to perturb the tropospheric hydroxyl radical concentrations. For reactive halocarbons, this implies that halocarbon concentrations are not more than 1 ppb at the most.

Figure 8 shows the total lifetimes including both tropospheric OH oxidation and stratospheric removal calculated for various assumptions concerning the form of the temperature dependent OH + halocarbon rate coefficient. Clearly, this temperature dependent parameter exerts a dominant influence on halocarbon lifetime, with lifetimes covering 0.2 - 30 years for reasonable ranges in expected values of preexponential factors and activation energies.

However the ^{14}CO method is not uncertainty-free and its accuracy and precision as a means of determining halocarbon lifetime is dependent on a whole range of experimental, life cycle and modelling assumptions which may be called into question. Volz, Ehhalt and Derwent (1981) gave some thought to uncertainty limits on their tropospheric OH distribution which this reevaluation has not changed. They recommended a mean tropospheric OH concentration of $6.5\,^{+3}_{-2}$ molecule cm^{-3}. Assuming that the kinetic parameters defining the OH + halocarbon rate coefficient are described with complete certainty, we can use the 1-sigma confidence limits for the tropospheric OH distribution to determine the confidence limits of the halocarbon lifetime. The Harwell two-dimensional model was therefore rerun with the entire tropospheric OH distribution scaled upwards and downwards to the 1-sigma confidence limits. The resulting upper and lower 1-sigma confidence limits of the halocarbon lifetimes encompassed the range of a factor of two for all the halocarbons examined. Lifetimes were apparently slightly more accurately determined for the longer-lived halocarbons, reflecting the influence of the assumed constant stratospheric removal.

Lifetimes of Alternative Fluorocarbons

For some of the candidate alternative fluorocarbons evaluated chemical kinetic data for the OH + halocarbon degradation reactions are already available, Table 2. The lifetimes of these halocarbons due to stratospheric removal and tropospheric OH radical degradation can therefore be determined using the Harwell two-dimensional model. Table 2 gives the atmospheric lifetimes calculated for a constant injection in midlatitudes of the northern hemisphere from a 100 year model calculation. The tropospheric OH distribution calculated with the ^{14}CO method gives lifetimes for the alternative fluorocarbons in the range 0.3-635 years. For most of the alternative halocarbons, these lifetimes are considerably shorter than the corresponding lifetimes for the fully halogenated halocarbons.

To complete the environmental acceptability work, modelling studies are required following up the behaviour of any chlorine-containing molecular fragments produced by the halocarbon degradation. The behaviour of the fragments could readily be incorporated into the two-dimensional model to determine the magnitude of any stratospheric fluxes of species such as $COCl_2$, COHCl, CF_3COCl, $CFCl_2CHO$, $CFCl_2CO(O_2)NO_2$, CF_2ClCHO, $CF_2ClCO(O_2)NO_2$, COFCl and so on. Competing processes for these chlorine-containing fragments would include tropospheric degradation, dry deposition, photolysis and wet scavenging.

Table 2. OH + halocarbon rate coefficients and atmospheric lifetimes for a range of alternative fluorocarbons

Formulae	OH + halocarbon rate coefficient, cm^3 $molecule^{-1}$ s^{-1}	Lifetime,[c] yrs Stratospheric loss	None
CH_3F	5.4×10^{-12} exp(-1700/T)	3.12	3.33
CH_2F_2	2.5×10^{-12} exp(-1650/T)	5.40	6.0
CHF_3	7.4×10^{-13} exp(-2350/T)	46.35	635.0
CH_2FCl	3.0×10^{-12} exp(-1250/T)	1.23	1.26
$CHFCl_2$	1.2×10^{-12} exp(-1100/T)	1.74	.80
CHF_2Cl	1.2×10^{-12} exp(-1650/T)	10.35	13.0
CH_3CH_2F	1.3×10^{-11} exp(-1200/T)	0.31	0.31
CH_2FCH_2F	1.7×10^{-11} exp(-1500/T)	0.59	0.60
CH_3CHF_2	1.5×10^{-12} exp(-1100/T)	1.42	1.46
CH_2FCHF_2	2.8×10^{-12} exp(-1500/T)	2.98	3.17
CH_3CF_3	2.6×10^{-13} exp(-1500/T)	22.29	40.2
CHF_2CHF_2	8.7×10^{-13} exp(-1500/T)	8.64	10.4
CH_2FCF_3	1.7×10^{-12} exp(-1750/T)	10.40	13.1
CHF_2CF_3	3.8×10^{-13} exp(-1500/T)	17.06	25.9
CH_3CFCl_2	2.7×10^{-13} exp(-1050/T)	5.89	6.68
CH_3CF_2Cl	9.6×10^{-13} exp(-1650/T)	12.49	16.6
CH_2ClCF_2Cl	3.6×10^{-12} exp(-1600/T)	3.28	3.51
CH_2ClCF_3	5.2×10^{-13} exp(-1100/T)	3.80	4.11
$CHCl_2CF_3$	6.4×10^{-13} exp(-850/T)	1.36	1.40
$CHFClCF_3$	6.6×10^{-13} exp(-1250/T)	4.99	5.54

Notes:

a. Chemical kinetic data from Hampson, Kurylo and Sander (1989)
b. T is absolute temperature in K
c. Lifetimes in steady state have been determined in a two-dimensional model assuming a northern hemispheric and constant injection rate, allowing for either 2% yr stratospheric removal or not
d. The 1-sigma confidence limits on the lifetimes encompass a range of a factor of two.

4. CONCLUSIONS

A review of the ^{14}CO method for determining the tropospheric hydroxyl radical distribution has revealed a number of areas where changes have occurred since the original publication of Volz, Ehhalt and Derwent (1981). None of these changes has however forced a revision of the approach. They have served to complete our understanding of areas which were difficult to understand in the early work. The chemical kinetic data is notable in this regard. It is now much easier to understand why the early hydroxyl radical concentrations may have been under-estimated in the photochemical models as compared to the ^{14}CO evaluation.

For the expected OH + halocarbon chemical rate coefficient parameters defined in terms of preexponential factors and activation energies, it is possible to estimate resulting halocarbon lifetimes using a simple graphical procedure. The ^{14}CO approach allows the determination of tropospheric halocarbons lifetimes, halocarbons with reasonable precision, 1-sigma confidence limits spanning about a factor of two.

It is important to remember that OH + halocarbon rate coefficients, hydroxyl distributions and halocarbon concentrations exhibit important covariance terms so that halocarbon lifetimes are not well-determined quantities. The lifetimes determined in this review are valid only for halocarbons injected at the northern hemisphere surface over the latitude range of the major continental land masses and population centres.

To illustrate the ^{14}CO method, the graphically determined lifetimes for methane and methyl chloroform are found to be $7\,^{+3}_{-2}$ and 5 ± 2 years, respectively, which are in close accord with our two-dimensional model studies (Cox and Derwent 1981; Derwent and Eggleton 1978), and current literature evaluations (Ehhalt 1988; Prinn 1988). The current methyl chloroform lifetime overlaps the ALE/GAGE evaluation, $6.3\,^{+1.2}_{-0.9}$ years and confirms both estimates since they are completely independent.

Lifetimes of some candidate alternative fluorocarbons have been tabulated in Table 2 based on detailed studies using the Harwell two-dimensional model. These studies should be readily extended to include the subsequent transport and fate of the secondary degradation products liberated by OH attack on the parent halocarbon.

There is mounting evidence that man's activities are inducing changes in the composition of the global atmosphere (Rowland and Isaksen 1988). Some of the trace gases for which global trends are beginning to become characterised play an important role in global tropospheric chemistry, as described in figure 1. In considering the environmental acceptability of alternative fluorocarbons, an attempt should be made to investigate their tropospheric sinks in future scenarios in which the composition of the global troposphere has been grossly perturbed by man's activities. For example, future subsonic aircraft operations may increase local tropospheric OH concentrations (Derwent 1982) and other perturbations can be put forward that would decrease tropospheric OH concentrations. A scenario approach could help to put upper and lower bounds on the lifetimes of alternative fluorocarbons over the next 50 years.

5. ACKNOWLEDGEMENTS

The two-dimensional modelling work at Harwell employed in this review was sponsored as part of the United Kingdom Department of the Environment Air Pollution Research Programme.

N92-15440

TROPOSPHERIC HYDROXYL CONCENTRATIONS AND THE LIFETIMES OF HYDROCHLOROFLUOROCARBONS (HCFCs)

Michael J. Prather
NASA/GISS
2880 Broadway, New York, NY 10025

ABSTRACT

Three-dimensional fields of modeled tropospheric OH concentrations are used to calculate lifetimes against destruction by OH for many hydrogenated halocarbons, including the CFC alternatives (hydrochlorofluorocarbons or HCFCs). The OH fields are taken from a 3-D chemical transport model (Spivakovsky et al., 1989) that accurately simulates the global measurements of methyl chloroform (derived lifetime of 5.5 yr). The lifetimes of various hydro-halocarbons are shown to be insensitive to possible spatial variations and seasonal cycles. It is possible to scale the HCFC lifetimes to that of methyl chloroform or methane by using a ratio of the rate coefficients for reaction with OH at an appropriate temperature, about 277 K.

1. INTRODUCTION

Synthetically produced halocarbons that contain chlorine and bromine, often called chlorofluorocarbons (CFCs) and halons, pose a direct threat to the stratospheric ozone layer (e.g., NASA/WMO, 1986; Watson et al., 1988) and also contribute substantially to the greenhouse forcing of the climate (Ramanathan, 1975; Lacis et al., 1981). A single characteristic of CFCs and halons that aggravates these environmental problems is their long atmospheric lifetimes; most are destroyed only by ultraviolet sunlight in the stratosphere. As a result of these environmental concerns, there will soon be international restrictions on CFC growth as agreed upon in the Montreal Protocol, and there is now a search for alternative fluorocarbons, environmentally acceptable substitutes (AFEAS Workshop, 16-17 May 1989, Boulder Colorado). One key property of these alternative compounds must be a short atmospheric residence time, implying efficient loss in the troposphere or at the Earth's surface.

Many of the suggested alternative fluorocarbons contain hydrogen (hydrochlorofluorocarbons or HCFCs), and atmospheric loss of these HCFCs is dominated by reaction with tropospheric OH. Their buildup in the atmosphere (units: kg) will be controlled by the ratio of emissions (kg yr^{-1}) to atmospheric destruction (yr^{-1}). The globally averaged, annual mean lifetime (yr) of the HCFCs (against atmospheric loss) is defined as the global atmospheric content (kg) divided by the total annual loss (kg yr^{-1}).

In this report we derive the lifetime of HCFCs and other hydrogenated halocarbons in two ways. The primary method involves modelling the OH distribution from first principles, specifying or predicting the HCFC distribution, and then integrating the HCFC loss over the globe (e.g., Logan et al., 1981). The tropospheric OH fields are calculated from a global 3-D climatology of sunlight, temperature, O_3, H_2O, NO_x, CO, CH_4 and other hydrocarbons (see Spivakovsky et al., 1989). Uncertainties in the calculated OH concentrations occur not only with the kinetic model, but also with the global climatologies of the other trace gases and cloud-cover needed as input to the photochemical model.

The OH fields used here were developed and applied to study methyl chloroform in a 3-D Chemical Transport Model (CTM). With the CTM, we specified sources, global transport and chemical losses of CH_3CCl_3 in order to simulate the latitudinal and seasonal patterns, and the global trends (see Spivakovsky et al., 1989). Similar CTM modelling of all the HCFCs is impractical and would require also a history and geographical location of emissions. Instead, the four-dimensional OH field (latitude x longitude x altitude x time) is applied here to test various hypotheses on the sensitivity of HCFC lifetimes to their tropospheric distribution; it is used also to test the accuracy of scaling the HCFC lifetimes to an assumed methyl chloroform lifetime.

The second method for deriving HCFC lifetimes selects a reference species with a global budget and atmospheric lifetime (against OH destruction) that is thought to be well understood (see Makide and Rowland, 1981). The lifetime of methyl chloroform, CH_3CCl_3, derived from the ALE/GAGE analysis is often used (Prinn et al., 1987) and is then scaled by the ratio of the rate coefficients for reaction with OH (Hampson, Kurylo and Sander, AFEAS, 1989), $k(OH + CH_3CCl_3)/k(OH + HCFC)$, to calculate the HCFC lifetime. Possible errors in this approach are associated with the assumed lifetime for CH_3CCl_3, and with the use of a single scaling factor that does not reflect the different spatial distribution of the HCFCs. This scaling approximation is tested here for plausible global patterns in the HCFC concentration and for different temperature dependence of the rate coefficients.

The tropospheric chemistry model for OH is described in Section 2. We calculate the global losses for methane and methyl chloroform in Section 3, and then compare the results for methyl chloroform with other published values. The integrated losses for a range of possible distributions of an HCFC are given in Section 4. HCFC lifetimes and uncertainties are discussed in Section 5.

2. THE CHEMICAL MODEL

The lifetimes calculated here for the HCFCs, as well as for CH_3CCl_3, CH_3Cl, CH_3Br and CH_4, use global distributions of OH from the photochemical model developed for the 3-D Chemical Transport Model (CTM developed at GISS & Harvard). The model for tropospheric OH is based on a 1-D photochemical model (an updated version of Logan et al., 1981; DeMore et al., 1987) that has been used to parameterize OH concentrations as a function of sunlight and other background gases (see Spivakovsky et al., 1989). This parameterized chemistry has been used to calculate a three-dimensional set of mean OH concentrations for the CTM grid over one year: the diurnally averaged OH concentrations are stored at 5-day intervals with a spatial resolution of 8 degrees latitude by 10 degrees longitude over 9 vertical layers (see Prather et al., 1987 for CTM documentation) for a total of more than 1/2 million values, even at this coarse resolution. The 5-day average temperatures at each grid point are also stored.

The local independent variables needed to derive OH concentrations are taken from the parent General Circulation Model (5-day averages of pressure, temperature, water vapor and cloud cover; see Hansen et al., 1983) and from observed climatologies (CO, O_3, CH_4, NO_x, H_2O above 500 mbar and stratospheric ozone column). The observational database for most of these species is insufficient to define the necessary 4-D fields, and we have assumed zonally uniform distributions with smooth variations over latitude, altitude and season for most species. One exception is that from the available data we are able to differentiate between the continental and the maritime troposphere up to 3 km altitude. See Spivakovsky et al. (1989) for details of the assumed trace-gas climatology and the chemical parameterization.

The annual averages of the zonal mean OH concentrations are shown in Table 1a; Table 1b gives the corresponding annual average temperatures. Hydroxyl concentrations are highest in the middle troposphere over the tropics. The OH density peaks at 700-800 mbar because cloud cover and Rayleigh scattering reduce solar ultraviolet light below 800 mbar.

The global loss of a gas that reacts with OH is the integral over a wide range of conditions in temperature, density and trace gas abundance. The integrand is extremely non-linear, and thus, the average loss

Table 1a. Annual Average OH concentration (10^4 cm^{-3})

LATITUDE

P(mbar)	90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100									20	26	43	40	35	30	26	19								
150									43	51	68	59	54	49	44	34								
200	33	32	30	25	25	24	30	38	52	57	65	58	52	48	43	36	30	21	17	18	17	20	22	20
300	31	27	24	21	23	26	33	43	62	76	80	77	72	65	59	50	39	28	21	20	21	28	32	33
500	41	36	32	30	36	45	63	81	119	131	135	147	141	124	118	108	80	61	45	40	34	41	46	44
700	51	44	41	42	43	51	68	89	139	154	159	180	182	171	159	139	111	88	64	58	56	53	56	32
800		42	40	44	36	48	65	89	144	157	152	168	168	159	155	140	130	108	79	67	77	52	56	32
900			31	32	14	21	35	65	114	124	123	130	134	135	126	110	116	90	62	53	59	23	26	20
1000				20	11	16	28	52	92	105	103	112	112	112	107	88	86	63	43	40	46	17	21	10

Table 1b. Annual Average Temperature (°K)

LATITUDE

P(mbar)	90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100									207	204	203	202	202	202	203	206								
150									215	215	215	215	215	216	216	215								
200	206	209	209	211	212	213	214	217	222	225	225	225	226	226	225	223	220	217	215	214	214	214	214	215
300	216	217	216	219	221	224	228	233	239	244	246	246	247	246	245	241	236	231	227	225	223	222	222	217
500	232	236	237	240	244	247	252	257	263	268	270	270	270	270	269	266	260	255	250	248	245	244	242	225
700	247	248	248	254	259	263	267	272	277	282	283	283	283	284	283	280	275	270	265	262	259	258	256	235
800		255	256	258	264	268	273	278	283	287	288	289	289	289	289	286	280	275	270	267	264	262	261	239
900			264	262	268	273	278	283	288	291	293	293	294	294	294	291	285	279	275	270	267	265	263	244
1000				267	271	276	282	287	291	295	297	297	297	298	297	293	289	283	277	272	268	268	267	246

Quantities are the annual zonal average of the 4-D fields described in the text.

No values for OH or T are reported for the extra-tropical stratosphere (above 200 mbar).

At higher pressures over Antarctica the number of points are insufficient to report a zonal average.

Table 2. Global Average OH concentrations

integrating kernel	OH (10^4 cm^{-3})	effective T (K)
dm	80	
exp(-1000/T) dm	96	259
exp(-1700/T) dm	105	262
exp(-1800/T) dm	106	263
exp(-2300/T) dm	111	265
(1 + 0.6/P) dm	91	
dz	65	

Integrals over mass (dm, from the surface to 100 mbar) are weighted by different factors: exponential in temperature (e.g., -1700/T for CH_4), and linear in pressure (i.e., 1 + 0.6/P for CO). Integrals over volume (dz) preferentially weight the lower atmospheric densities in the upper troposphere. Use of the average OH with the effective temperature in the exponential gives the correct global integral.

is not equal simply to the product of averages (Makide and Rowland, 1981). It is misleading to report a single "global average OH concentration" without qualifying it as to the averaging kernel. The global OH concentrations averaged over the atmosphere (100-1000 mbar with no stratospheric contribution) are reported here in Table 2 for a variety of integrating kernels. The average OH is largest, $111\text{x}10^4$ cm^{-3}, when weighted appropriately (by mass) for loss of an HCFC with a large exponential factor of -2300/T. A larger temperature dependence result in greater average OH because the OH densities are maximal at high temperatures in the tropics (see Table 1). The spatially averaged OH density is smallest, $65\text{x}10^4$ cm^{-3}, because of the large volumes of air in the upper troposphere with low OH concentrations. The effective temperatures given in Table 2 are those needed to get the correct globally averaged integral, and should not be confused with the optimal scaling temperature in Section 4. (The scaling temperature must also account for the change in mean OH as the temperature dependence varies.)

3. GLOBAL LOSS OF CH_3CCl_3 AND CH_4

The globally integrated losses for methane and for methyl chloroform are calculated by integrating the loss frequency (OH and temperature fields described above) using realistic, but fixed tropospheric distributions for CH_4 and CH_3CCl_3. Tropospheric reactions with OH dominate the loss of both species, but stratospheric losses cannot be ignored and are used in place of OH densities in layer 9 (0-70 mbar) globally and in layer 8 (70-150 mbar) outside the tropics. The stratospheric losses are calculated from a 1-D vertical diffusion model for stratospheric chemistry evaluated at the appropriate latitude and season.

The assumed conditions and resulting atmospheric losses of CH_4 and CH_3CCl_3 are summarized in Table 3. The lifetime of methane is 8.7 yr with about 6% of the loss occurring in the stratosphere and more

Table 3. Global budgets for CH_4 and CH_3CCl_3

	CH_4	CH_3CCl_3
Rate coefficient		
k(X + OH)	$2.3\text{x}10^{-12}e^{-1700/T}$	$5.0\text{x}10^{-12}e^{-1800/T}$
Concentration		
NH (<28°/>28°)	1700/1700 ppb	140/150 ppt
SH	1600 ppb	110 ppt
Atmospheric content	4580 x 1012g	2930 x 109g
Atmospheric losses		
total	524 x 10^{12}g	534 x 10^9g
tropics (2-6 km)	270 x 10^{12}g	260 x 10^9g
stratosphere	29 x 10^{12}g	53 x 10^9g
Lifetime	8.7 yr	5.5 yr

Budgets based on integration of 4-D tropospheric OH fields with zonally fixed, non-seasonal distributions as noted. Stratospheric profiles and losses are included.

than half in the tropical middle troposphere. The lifetime of methyl chloroform is 5.5 yr. Stratospheric loss for methyl chloroform is about three times more rapid than for methane because photolysis of CH_3CCl_3 becomes important in the stratosphere. Again the tropical middle troposphere accounts for about half of the global loss.

Methyl chloroform is usually chosen as a reference species for tropospheric loss, with a "known" atmospheric lifetime based on the ALE/GAGE analysis of Prinn et al. (1987). We compare the lifetimes in Table 3 for CH_3CCl_3 with those from the ALE/GAGE analysis and the recent 3-D CTM simulations (Spivakovsky et al, 1989). The ALE/GAGE analysis uses observations of CH_3CCl_3 at 5 surface sites, industry data for atmospheric emissions, and a 9-box atmospheric model, to derive an annual average global lifetime of 6.3 yr with a reported 1-sigma range of 5.4-7.5 yr. Errors in the lifetime due to uncertainties in the atmospheric emissions used in the ALE/GAGE study have been reduced by recent analyses of CH_3CCl_3 sources from industry surveys (Midgley, 1989) and from observations (Prather, 1988).

When the same OH and temperature fields are used in the complete CTM simulation of CH_3CCl_3 (Spivakovsky et al., 1989) the integrated loss correctly includes all correlations of OH and temperature with CH_3CCl_3 concentrations. The 3-D CTM simulation showed that the standard OH field (with a resulting lifetime of 5.5 yr) and the OH field scaled by a factor of 0.75 (with a lifetime of 7.1 yr) bracket the observations. This range, however, does not include uncertainties in the observations (i.e., absolute calibration) or in the sources. The observed seasonal cycle of CH_3CCl_3 in the southern hemisphere is not a direct measure of the absolute OH concentrations; however, its accurate simulation in the CTM provides some confirmation of the integrated seasonal variation of the modeled OH fields in the southern hemisphere. Such comparisons emphasize the mid-latitude photochemistry which has the largest seasonal variations, and they are independent of absolute calibration and sources because they depend on the relative (%) changes in CH_3CCl_3.

It is difficult to find other globally distributed trace gases with well defined sources and trends that can be used to test global OH concentrations. For example, Derwent and Volz-Thomas (AFEAS, May, 1989; Volz et al., 1981) have used carbon monoxide, both ^{14}CO and ^{12}CO, to test and recalibrate the OH fields in their 2-D model. Another possibility, HCFC-22 (CHF_2Cl) has limited data on hemispheric abundances, trends and sources. Data for HCFC-22 are sparse and barely able to define the hemispheric ratio and instantaneous trend (N/S = 89/77 ppt, +6.5 ppt/yr in 1985, see NASA/WMO, 1986). Furthermore, significant uncertainties exist currently for the absolute calibration and atmospheric emissions of most HCFCs. HCFC-22 is used as an intermediate chemical in the production of other compounds, and thus its release is only a fraction of production. Recent estimates of HCFC-22 emission (130 Gg/yr in 1985, M. McFarland, personal communication) are twice as large as previous values, and are now barely able to reconcile the current atmospheric budget from the limited observations noted above.

It is not possible at present to put a formal "one-sigma" accuracy on the OH fields used here, either from first principles, or from constraints using the methyl chloroform budget. The uncertainty factor for the OH fields is chosen to be 1.3 and is applied to the lifetimes for HCFCs in Section 5.

4. SENSITIVITY OF HCFC LIFETIME TO GLOBAL DISTRIBUTION

We use the 4-D fields of OH and temperature to understand how to predict the lifetime of one species relative to another. Specifically, how can the lifetime of one species be scaled to another with a different spatial-temporal distribution and loss rate? Idealized tropospheric distributions are used to examine the sensitivity of HCFC lifetime to (a) the temperature dependence of their reaction rates with OH, (b) large interhemispheric gradients, (c) enhanced concentrations in the boundary layer near sources, and (d) seasonal cycles in concentration.

a. Sensitivity to rate coefficient: $k = A \times \exp(-B/T)$

Two species, X and Y, with the same global distribution and with rate coefficients for reaction with OH that differ only by a constant factor, $k(OH+X)/k(OH+Y)$ = constant, will have lifetimes that scale inversely by the same factor. In most cases, however, the rate coefficients have different temperature dependence, B, or pressure dependence (as in the case of CO). We investigate the dependence of HCFC lifetime on values of B ranging from 0 to 2300 K, by integrating the loss for an atmospheric tracer that is uniformly distributed throughout the troposphere and stratosphere. The A coefficient was selected to match the CH_4 rate, $k = 2.3E\text{-}12 \times \exp(-B/T)$ $cm^3\ s^{-1}$, and stratospheric losses were not included.

The integrated global loss rates are given in Table 4a; lifetimes range from 81 yr (B = 2300 K) to 0.02 yr (B = 0 K). In Figure 1 we show the error associated with predicting the lifetime by scaling to a reference lifetime (9.42 yr at B = 1700 K) using an appropriate temperature in the ratio of reaction rates. This scaling temperature is not necessarily the mean temperature of the OH losses, but includes also the shift in the reaction-weighted mean OH as a function of reaction rate (see Section 2 and Table 2). The optimal temperature for scaling the lifetimes is 277 K, and the resulting errors are less than 2% over the range 800 K < B < 2300 K. Use of a temperature 10 K warmer or colder yields errors in the lifetime of order 10% when scaling the reference case (B = 1700 K) to greater (2300 K) or smaller (1000 K) activation energies.

b. Sensitivity to interhemispheric gradient

HCFCs released predominantly from industrialized countries in the northern mid-latitudes will establish a global distribution similar to that for CFCs (see Prather et al., 1987). The north-to-south latitudinal gradient will have an interhemispheric absolute difference about equal to one year's emissions, and higher concentrations will build up over the presumed continental sources at mid-latitudes. The sensitivity of HCFC lifetimes to their interhemispheric gradient will depend on hemispheric asymmetries in the OH fields (and temperatures in so far as they affect the rate coefficients). The base case described above assumes a uniformly distributed tracer with OH reaction rates appropriate for CH_4, and the perturbed case includes doubling the abundance in either hemisphere uniformly. Results are shown in Table 4b. For a factor of 2 asymmetry in the HCFC distribution, the lifetime changes by only 1.5%. Thus the effective OH loss is about 9% greater in the northern hemisphere. Spivakovsky et al. (1989) note that the higher concentrations of CO in the northern hemisphere (reducing OH) are more than offset by the higher levels of O_3 and NO_x.

Table 4. Lifetime for species x against tropospheric OH

a. Sensitivity to rate coefficient k(OH + X) = A/exp(-B/T)

A (cm^3 s^{-1})	B (K)	lifetime (yr)
2.3E-12	2300	81.2
2.3E-12	2000	27.7
2.3E-12	1700	9.42
2.3E-12	1500	4.58
2.3E-12	1100	1.08
2.3E-12	500	.120
2.3E-12	0	.019

b. Sensitivity to interhemispheric ratio

NH:SH	lifetime (yr)
2:1	9.28
1:1	9.42
1:2	9.57

c. Sensitivity to boundary layer enhancements

enhancement	lifetime (yr)
none	9.42
+ 10% (global)	9.33
+ 10% (global, land)	9.35
+ 10% (>30°N)	9.42
+ 10% (>30°N, land)	9.41
+ 100% (>30°N)	9.37
+ 100% (>30°N, land)	9.33

d. Sensitivity to seasonal cycle

amplitude	lifetime (yr)
none	9.42
±1%	9.43
±10%	9.52
±50%	9.97

Except where noted X has a uniform mixing ratio throughout the troposphere and stratosphere, but no loss in the stratosphere. Default values are k(OH + X) = 2.3×10^{-12} exp(-1700/T), boundary layer defined as 984-850 mbar, and no seasonal cycle.

The assumed seasonal cycle is: positive in winter, (DJF >30°N) & (JJA <30°S), negative in summer, (JJA >30°N) & (DJF <30°S).

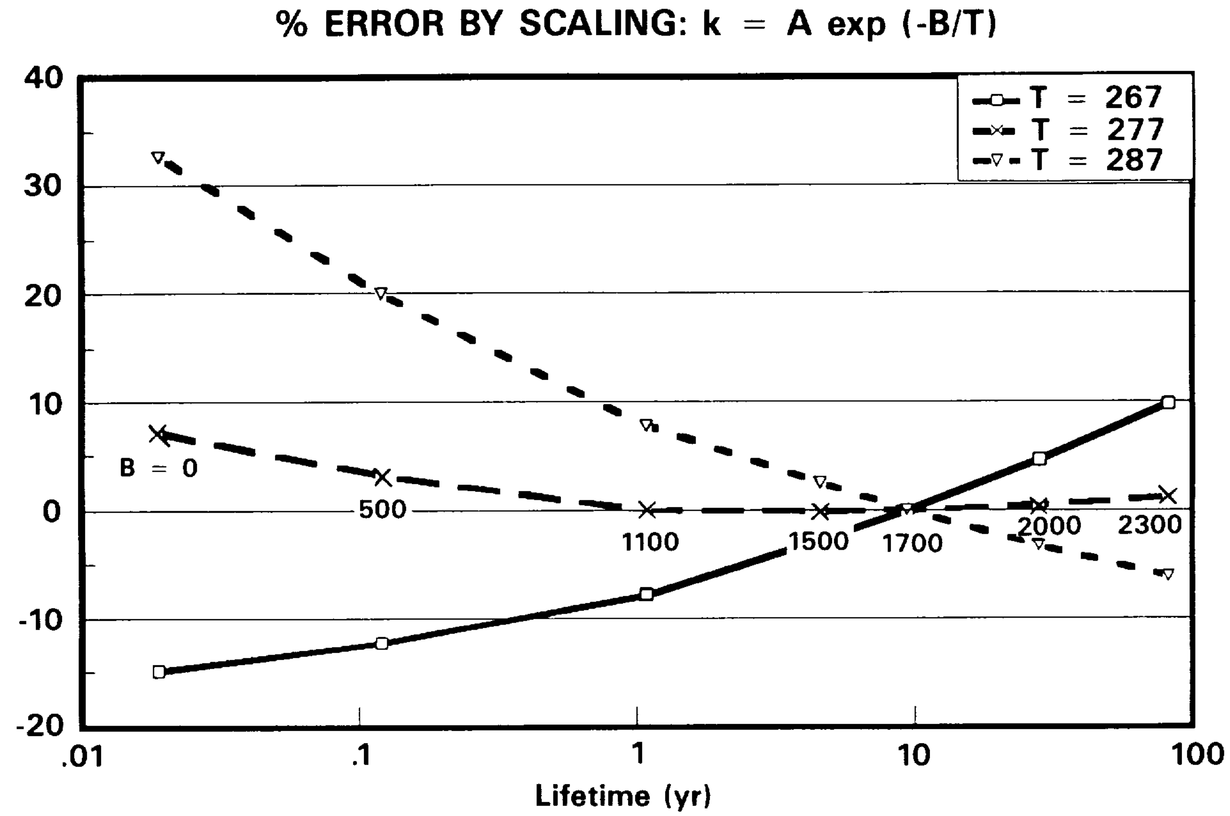


Figure 1. Error (%) in predicting HCFC lifetimes by scaling the rate coefficient for reaction with OH. The lifetime against OH destruction is calculated by integrating the 4-D fields of OH and T with a rate coefficient k = 2.3E-12 exp (-B/T) and a uniformly distributed tracer. The reference case is chosen to be B = 1700 K with a lifetime of 9.42 yr. A range of values for B from 0 K to 2300 K is considered (see Table 4a, noted on graph). Three different effective temperatures (267 K, 277 K and 287 K) have been chosen to predict a lifetimes by scaling the "known" result for B = 1700 K. Minimum error occurs for T = 277 K.

c. Sensitivity to enhancement in the boundary layer

Enhanced abundances of $CFCl_3$ and CF_2Cl_2 are both observed and predicted in the lower troposphere over much of the northern mid-latitudes, especially near continental sources. A similar buildup of HCFCs would be expected. We examine the sensitivity of HCFC lifetimes to boundary layer enhancements in the lowest 1.5 km for several assumptions: northward of 30°N, globally, over land, or over land and ocean. The reference case is that with methane kinetic rates as above. The net effect of boundary layer enhancements, as shown in Table 4c, is negligible ($<1\%$) if they are less than 100% and are restricted to the northern mid-latitudes as expected. If there were a globally uniform source, and hence accumulation in the boundary layer over the tropics also, then a +10% enhancement in the lowest 1.5 km would increase losses and reduce the lifetime by at most 1%.

d. Sensitivity to seasonal cycles

Seasonal variations in the concentrations of a gas should be included when calculating the OH losses. In most cases the seasonal cycle is driven by the corresponding variations in OH, and, thus, the lowest concentrations of the trace gas occur slightly after the greatest OH levels (i.e., late summer). This anticorrelation of OH and trace gas increases the lifetime of the gas relative to that calculated with a fixed concentration. As shown in Table 4d, this effect is negligible ($<0.2\%$) for a gas like CH_4 with a lifetime of about 9 yr and an observed seasonal amplitude of ±1.5%. Since large seasonal variations occur only in short-lived species, we would not expect the seasonal amplitude for an HCFC to exceed ±10% (corresponding to a 1% increase in lifetime) unless the lifetime were very short, less than 1.5 yr. The seasonal effect is so small because the majority of OH loss occurs in the tropics, as noted above, where OH concentrations do not vary significantly with season.

In summary, a short-lived HCFC with a lifetime of about 0.5 yr might be expected to have a seasonal amplitude of ±25% (lifetime correction: +2.5%), a north:south interhemispheric ratio of 2:1 (lifetime correction: -1.5%), and a boundary layer enhancement north of 30°N over land of 100% (lifetime correction: -1%). The sum of these corrections tend to cancel, or be very small, and thus the lifetime predicted from a uniform distribution should be a reasonably accurate, ±10%, evaluation of the true lifetime.

5. SUMMARY OF HCFC LIFETIMES

The lifetimes of HCFCs and other hydrohalocarbons are reported in Table 5. These lifetimes are calculated directly from the tropospheric OH fields using the recommended rate coefficients (Hampson, Kurylo and Sander, AFEAS, 1989) and a fixed, uniform distribution of trace gas (labelled TROP-OH). They have been augmented (labelled TOTAL) with much smaller stratospheric losses that include estimated destruction by OH and photolysis. Stratospheric OH loss is scaled by rate coefficients at a temperature of 250 K to an assumed methane (stratosphere only) loss rate of 1/160 yr^{-1}; stratospheric photolysis is assumed only for species with a $-CCl_3$ group (1/60 yr^{-1}) or a $-CCl_2$ group (1/120 yr^{-1}) and is based on the lifetimes of $CFCl_3$ and CF_2Cl_2. An additional column of lifetimes in Table 5 (labelled SCALED) has been calculated by ratioing the rate coefficients (scaling temperature of 227 K) and multiplying by the methyl chloroform lifetime of 6.3 yr. As expected from the analyses in this report the two approaches agree very well.

An attempt has been made to estimate uncertainty factors for HCFC lifetimes in the same manner as in the kinetics reviews. We identify the uncertainty in the reaction rate of 277 K and then multiply by the estimated uncertainty factor for the OH fields (1.3). The uncertainty associated with a non-uniform distribution is significant only for HCFCs with lifetimes less than 1 yr, and has been increased. The final uncertainty quoted in Table 5 is representative of the likely range, but cannot be treated as a formal statistical error.

Although the ALE/GAGE analysis of the total atmospheric residence time for CH_3CCl_3 agrees with the chemical model's lifetime for destruction by OH, the combined uncertainties in the two lifetimes cannot rule out another sink, such as hydrolysis (Wine and Chameides, AFEAS, 1989), with a lifetime as short as 25 yr.

There is a clear need for other trace species that can be used to test the tropospheric abundance of OH. Such species must have accurate histories of emissions and good, absolutely calibrated measurements. In situ atmospheric tests of the kinetic model for OH should possibly focus on the tropical middle troposphere where most of the destruction of HCFCs will occur.

Table 5. Atmospheric Lifetimes for the HCFCs & other Halocarbons

			LIFETIME (yr)			uncertainty	
species	A	B	TROP-OH	TOTAL	SCALED	f	(CFC)
CH_3F	5.4E-12	1700	4.0	3.8	4.1	1.8	
CH_2F_2	2.5E-12	1650	7.2	6.8	7.3	1.7	
CHF_3	7.4E-13	2350	302.	289.	310.	2.3	
CH_2FCl	3.0E-12	1250	1.42	1.33	1.44	1.8	
$CHFCl_2$*	1.2E-12	1100	2.10	1.89	2.10	1.6	
CHF_2Cl	1.2E-12	1650	15.1	14.2	15.3	1.6	(22)
CH_3CH_2F	1.3E-11	1200	0.27	0.25	0.28	5.	
CH_2FCH_2F	1.7E-11	1500	0.62	0.58	0.63	5.	
CH_3CHF_2	1.5E-12	1100	1.65	1.53	1.68	1.8	(152a)
CH_2FCHF_2	2.8E-12	1500	3.76	3.54	3.81	3.	
CH_3CF_3	2.6E-13	1500	40.5	38.1	41.	3.	
CHF_2CHF_2	8.7E-13	1500	12.1	11.4	12.3	3.	
CH_2FCF_3	1.7E-12	1750	15.3	14.4	15.5	1.8	(134a)
CHF_2CF_3	3.8E-13	1500	27.7	26.1	28.1	3.	(125)
CH_3CFCl_2*	2.7E-13	1050	7.6	6.7	7.8	1.7	(141b)
CH_3CF_2Cl	9.6E-13	1650	18.8	17.8	19.1	1.7	(142b)
CH_2ClCF_2Cl	3.6E-12	1600	4.2	4.0	4.2	3.	
CH_2ClCF_3	5.2E-13	1100	4.7	4.4	4.8	1.8	
$CHCl_2CF_3$*	6.4E-13	850	1.55	1.42	1.59	2.0	(123)
$CHFClCF_3$	6.6E-13	1250	6.5	6.0	6.6	1.8	(124)
CH_4	2.3E-12	1700	9.4	8.9	9.6		
CH_3Cl	1.7E-12	1100	1.45	1.35	1.48		
CH_3Br	6.0E-13	820	1.48	1.37	1.53		
CH_3CCl_3**	5.0E-12	1800	6.2	5.4	6.3		

Rate coefficients are in units of $cm^3\ s^{-1}$, $k = A \exp(-B/T)$.

TROP-OH lifetimes include only the integrated loss with respect to OH in the troposphere. TOTAL lifetimes include the small additional losses estimated to occur in the stratosphere as described below. SCALED lifetimes are keyed to the CH_3CCl_3 lifetime of 6.3 yr (Prinn et al., 1987) and the ratio of the rate constants at 277 K.

Species marked (*) with 2 Cl's on one C are assumed to have a lifetime of 120 yr with respect to stratospheric photolysis; methyl chloroform (**) is assumed to have a stratospheric lifetime of 60 yr due to photolysis. Stratospheric loss due to reaction with OH is scaled to the CH_4 stratospheric lifetime (160 yr) and rate coefficient at 250 K.

The lifetime uncertainty factor (f) is assumed here to be the product of the kinetic factor (at 277 K), the uncertainty in the OH fields (1.3), and an additional uncertainty factor for HCFCs with short lifetimes.

VI. DEGRADATION MECHANISMS

Combined Summary and Conclusions

Fluorine-Containing Products in Atmospheric Degradation Table

Tropospheric Reactions of the Haloalkyl Radicals Formed from Hydroxyl Radical Reaction with a Series of Alternative Fluorocarbons

Roger Atkinson
Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

Degradation Mechanisms of Selected Hydrochlorofluorocarbons in the Atmosphere: An Assessment of Current Knowledge

Richard A. Cox
Engineering Science Division
Harwell Laboratory
DIDCOT, Oxfordshire, United Kingdom
and
Robert Lesclaux
Laboratoire de Photophysique et Photochimie Moleculaire
Universite de Bordeaux 1
33405 TALENCE Cedex, France

An Assessment of Potential Degradation Products in the Gas-Phase Reactions of Alternative Fluorocarbons in the Troposphere

Hiromi Niki
Centre for Atmospheric Chemistry
Department of Chemistry
York University
Ontario, Canada M3J 1P3

Atmospheric Degradation Mechanisms of Hydrogen Containing Chlorofluorocarbons (HCFC) and Fluorocarbons (HFC)

Reinhard Zellner
Institut für Physikalische Chemie und Elektrochemie
Universitat Hannover
Callinstrasse 3 A, 3000 Hannover,
Federal Republic of Germany

COMBINED SUMMARY AND CONCLUSIONS

Tropospheric reaction with the OH radical is the major and rate determining loss process for the HFCs and HCFCs in the atmosphere.

There are virtually no experimental data available concerning the subsequent reactions occurring in the atmospheric degradation of these molecules. By consideration of data for degradation of alkanes and chloroalkanes it is possible to postulate the reaction mechanisms and products formed in the troposphere from HCFC and HFCs. However, the results are subject to large qualitative and quantitative uncertainty, and may even be incorrect.

The current level of support for laboratory work is inadequate to enable significant improvement in the state of knowledge in this area in the near future.

Using the above mentioned analysis, a large variety of chlorine and fluorine containing intermediate products such as hydroperoxides, peroxynitrates, carbonyl halides, aldehydes and acids can be expected from the degradation of the 8 proposed CFC substitutes. These are listed in the accompanying Table.

Based on the available knowledge of gas phase chemistry only four of these products appear to be potentially significant carriers of chlorine to the stratosphere. These are $CClFO$, CF_3CClO, $CClF_2CO_3NO_2$ and $CCl_2FCO_3NO_2$. However physical renewal processes may reduce this potential. In addition, the possibility of pathways and products not predicted by the arguments-by-analogy are a cause for concern.

A large part of the uncertainty of the mechanistic details of the HCFC oxidation arises from all insufficient knowledge of the thermal stability and reactivity of halogenated alkoxyradicals. In particular, the mechanism of oxidation of the CF_3O radical, which is assumed to produce CF_2O, is not known for atmospheric conditions and needs further study.

Particular attention should be paid to obtaining data on the photochemistry, gas phase reactivity and solubility of the carbonyl, acetyl and formyl halides, in order to assess their removal rates and mechanisms.

Based on current knowledge, the products identified are unlikely to cause significant changes to the effective greenhouse warming potential of the 8 proposed CFC substitutes. This conclusion would be modified if long-lived products such as CF_3H were formed by unidentified pathways.

Laboratory tests and atmospheric measurements are urgently needed to test the validity of the proposed degradation mechanisms for HCFCs and HCFs.

Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC 141B	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
		CCl_2FCH_2O	CCl_2FCHO			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		$CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC 142b	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
		$CClF_2CH_2O$	$CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		$CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC 22	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
HCFC 124	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF 134a	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
		CF_3CHFO	$CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		CFO			$CF(O)OOH$	$CF(O)OONO_2$
HFC 52a	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	CHF_2CHO			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	$CHFO$			
		$CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		CFO		$CF(O)OOH$		$CF(O)OONO_2$
HCF 125	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

TROPOSPHERIC REACTIONS OF THE HALOALKYL RADICALS FORMED FROM HYDROXYL RADICAL REACTION WITH A SERIES OF ALTERNATIVE FLUOROCARBONS

Roger Atkinson

Statewide Air Pollution Research Center
University of California
Riverside, California 92521

1. INTRODUCTION

The majority of the chlorofluorocarbons (CFCs) currently in use, such as CFC-11 ($CFCl_3$), 12 (CF_2Cl_2) and 113 ($CF_2ClCFCl_2$), are chemically non-reactive in the troposphere, and transport to the stratosphere, with subsequent photolysis there, then becomes the only significant removal process from the troposphere (see, for example, Molina and Rowland, 1974; WMO, 1986; Hammitt et al., 1987). As replacements for these CFCs, compounds are now being sought which will be removed to a large extent in the troposphere, thus avoiding or minimizing the input of chlorine and other halogens into the stratosphere.

In the present assessment, the hydrogen-containing halocarbons being considered as alternates to the presently used chlorofluorocarbons are the hydrochlorofluorocarbons (HCFCs) 123 (CF_3CHCl_2), 141b ($CFCl_2CH_3$), 142b (CF_2ClCH_3), 22 (CHF_2Cl) and 124 (CF_3CHFCl) and the hydrofluorocarbons (HFCs) 134a (CF_3CH_2F), 152a (CHF_2CH_3) and 125 (CF_3CHF_2). All of these HCFCs and HFCs will react with the hydroxyl (OH) radical in the troposphere, giving rise to haloalkyl ($R^{\cdot}$) radicals which then undergo a complex series of reactions in the troposphere. These reactions of the haloalkyl radicals formed from the initial OH radical reactions with the HCFCs and HFCs under tropospheric conditions are the focus of the present article. The haloalkyl ($R^{\cdot}$) radicals formed from the OH radical reactions with the HCFCs and HFCs listed above are as follows:

HCFC or HFC	Haloalkyl Radical, R
CF_3CHCl_2	$CF_3\dot{C}Cl_2$
$CFCl_2CH_3$	$CFCl_2\dot{C}H_2$
CF_2ClCH_3	$CF_2Cl\dot{C}H_2$
CHF_2Cl	$\dot{C}F_2Cl$
CF_3CHFCl	$CF_3\dot{C}FCl$
CF_3CH_2F	$CF_3\dot{C}HF$
CHF_2CH_3	$CHF_2\dot{C}H_2$ and $CH_3\dot{C}F_2$
CF_3CHF_2	$CF_3\dot{C}F_2$

Of these radicals, only for the $\dot{C}F_2Cl$ radical formed from CHF_2Cl (HCFC-22) are experimental data available concerning certain of the reactions which are expected to take place under tropospheric conditions. It is therefore necessary to postulate the reactions of these haloalkyl radicals based upon the current state of knowledge of the tropospheric reactions of analogous alkyl and haloalkyl radicals and of the corresponding alkyl peroxy ($RO_2^{\cdot}$) and alkoxy ($RO^{\cdot}$) radicals formed from, or subsequent to, these alkyl and haloalkyl radical reactions. At the present time, experimental and theoretical data are available for certain of the tropospheric reactions of several C_1-C_5 alkyl and C_1 haloalkyl radicals which are expected to be common to the haloalkyl radicals dealt with in this article. These reactions, together with the kinetic data available, are dealt with in Appendix A (Section 4). Since several of these reactions of $R^{\cdot}$, $RO_2^{\cdot}$ and $RO^{\cdot}$ radicals have recently been reviewed and evaluated by the National Aeronautics and Space Administration and the International Union of Pure and Applied Chemistry data evaluation panels (NASA, 1987; IUPAC, 1989), in most cases the recommendations from these data evaluations are cited rather than the original literature. Furthermore, since the IUPAC panel (IUPAC, 1989) considered a wider range of relevant reactions than did the NASA (1987) panel, and the differences (if any) between the recommended kinetic expressions from these data evaluations are relatively minor ($<50\%$ for the temperature and pressure conditions encountered in the troposphere), the recommendations of the IUPAC (1989) evaluation are used in this article. The reactions of the individual haloalkyl radicals formed from the HCFCs and HCFs are dealt with in Section 2, using the data base for analogous alkyl and haloalkyl radicals (Section 4; Appendix A) to provide estimates of the reaction pathways and the rate constants for these reactions.

In this article, all rate constants are given in cm molecule s units, and pressures are given in Torr (1 Torr = 133.3 Pa). For reactions which are in the fall-off region between first- and second-order kinetics or between second- and third-order kinetics, the Troe fall-off expression (Troe, 1979) is used,

$$k = \left(\frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}} \right) F^{\left\{1 + [\log(k_0[M]/k_\infty)]^2\right\}^{-1}}$$

where k_0 is the limiting low-pressure rate constant, k_∞ is the limiting high-pressure rate constant, [M] is the concentration of diluent gas (air, N_2 or O_2 in this article, unless otherwise specified) and F is the broadening factor. The rate constants k_0 and k_∞ are generally assumed to have T^n temperature dependences, while the temperature dependence of F is given by $F = e^{-T/T^*}$, where T^* is a constant (Troe, 1979; Baulch et al., 1982).

2. TROPOSPHERIC DEGRADATIONS OF SELECTED HALOGENATED ALKYL RADICALS

In this section, the tropospheric reaction schemes subsequent to OH radical reaction with the alternative HCFCs and HFCs being considered are formulated. While the quantitative assessment of the concentrations of the intermediate species and of chemically reactive and non-reactive products requires the use of atmospheric computer models which include time- and altitude-dependent radiation fluxes and OH, HO_2, $CH_3\dot{O}_2$ and other $R\dot{O}_2$ radicals, NO, NO_2, O_3, H_2O, O_2, and N_2 concentrations, approximate concentrations of these species are used in this section to permit the qualitative assessment of intermediate and product lifetimes. Based upon the tropospheric concentrations given in WMO (1986) for NO, NO_x, CH_4 and CO, the tropospheric O_3 concentrations given by Logan (1985), an average daytime OH radical concentration of 1.5×10^6 molecule cm^{-3} [equivalent to a diurnally-averaged concentration of 7.5×10^5 molecule cm^{-3}] (Prinn et al., 1987) and an approximate consideration of tropospheric CH_4 and CO chemistry, the HO_2 and $CH_3\dot{O}_2$ concentrations were calculated. The concentration of the relevant species are given in Table 1 for the lower and upper levels of the troposphere. The ground level solar flux data given by Hendry and Kenley (1979) were used to approximately estimate lifetimes with respect to photolysis.

The reaction schemes presented are based upon the discussion and review of the literature data for analogous reactions given in Section 4 below. In general, no detailed discussion is given in this section, unless required to assess the relative importance of possible reaction pathways or to point out that the present data base does not permit a judgment to be made. The discussion dealing with the $CF_3\dot{C}Cl_2$ radical in Section 2.1 below applies to many of the haloalkyl radical reaction schemes, and is not repeated in detail in the sections following.

Table 1. Daytime species concentrations used in the assessment of reaction routes and species lifetimes

Species	Concentration (molecule cm^{-3})	
	Lower Troposphere	**Upper Troposphere**
M (N_2 + O_2)	2.5 x 10^{19}	4.5 x 10^{18}
O_2	5 x 10^{18}	9 x 10^{17}
O_3	7 x 10^{11}	4 x 10^{11}
NO	2.5 x 10^{8}	2.5 x 10^{8}
NO_2	2.5 x 10^{8}	2.5 x 10^{8}
OH	1.5 x 10^{6}	1.5 x 10^{6}
HO_2	10^{9}	10^{8}
$CH_3O_2^{\cdot}$	2.5 x 10^{8}	6 x 10^{6}

2.1. The $CF_3\dot{C}Cl_2$ Radical formed from HCFC-123 (CF_3CHCl_2)

A. $CF_3\dot{C}Cl_2$. The $CF_3\dot{C}Cl_2$ radical will react solely with O_2 to form the peroxy radical $CF_3CCl_2O_2^{\cdot}$,

$$CF_3\dot{C}Cl_2 + O_2 \xrightarrow{M} CF_3CCl_2\dot{O}_2$$

with a rate constant k $\geq$5 x 10^{-13} cm^3 molecule^{-1} s^{-1}. This results in a tropospheric lifetime of the $CF_3\dot{C}Cl_2$ radical of <2 x 10^{-6} s.

B. $CF_3CCl_2O_2^{\cdot}$. The expected reactions of this peroxy radical are,

$$CF_3CCl_2O_2^{\cdot} + NO \rightarrow CF_3CCl_2O^{\cdot} + NO_2 \tag{a}$$

$$CF_3CCl_2O_2^{\cdot} + NO_2 \xrightarrow{M} CF_3CCl_2OONO_2 \tag{b}$$

$$CF_3CCl_2O_2^{\cdot} + HO_2 \rightarrow CF_3CCl_2OOH + O_2 \tag{c}$$

$$CF_3CCl_2O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow CF_3CCl_2O^{\cdot} + CH_3O^{\cdot} + O_2 \tag{d1}$$

$$CF_3CCl_2O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow CF_3CCl_2OH + HCHO + O_2 \tag{d2}$$

with rate constants (cm^3 molecule^{-1} s^{-1} units) of k_a ~1.5 x 10^{-11} $(T/300)^{-1.2}$, k_b ~1.0 x 10^{-11}, k_c = 3.4 x 10^{-13} $e^{800/T}$, and k_{d1} + k_{d2} ~2 x 10^{-13}. Based on the approximate concentrations of NO, NO_2, HO_2

and $CH_3O_2^{\cdot}$ given in Table 1, the decay rates (s^{-1}) of the $CF_3CCl_2O_2^{\cdot}$ radical with respect to reactions (a) through (d) for the lower and upper troposphere, respectively, are: reaction (a), 3.8×10^{-3} and 5.4×10^{-3}; reaction (b), 2.5×10^{-3} and 2.5×10^{-3}; reaction (c), 5×10^{-3} and 1.3×10^{-3}; and reaction (d), 5×10^{-5} and 1.2×10^{-7}.

These calculated reaction rates for the $CF_3CCl_2O_2^{\cdot}$ radical suggest that reaction with $RO_2^{\cdot}$ radicals will be of negligible importance, but that the reactions with NO, NO_2 and the HO_2 radical will be of approximately comparable importance and must be considered. The lifetime of the $CF_3CCl_2O_2^{\cdot}$ radical is expected to be $\sim 10^2$ s. The products of reactions (a), (b) and (c) are the $CF_3CCl_2O^{\cdot}$ radical, the peroxynitrate $CF_3CCl_2OONO_2$ and the hydroperoxide CF_3CCl_2OOH, respectively. Formation of the nitrate, $CF_3CCl_2ONO_2$, from the NO reaction (a) is expected to account for <2% of the $CF_3CCl_2O^{\cdot}$ radical yield.

C. $CF_3CCl_2OONO_2^{\cdot}$ Under tropospheric conditions, this haloalkyl peroxynitrate will undergo thermal decomposition and photolysis. The thermal decomposition reaction

$$CF_3CCl_2OONO_2 \xrightarrow{M} CF_3CCl_2O_2^{\cdot} + NO_2$$

is expected to have a rate constant of $\sim 1 \times 10^{15}\, e^{-11000/T}\ s^{-1}$ at the high-pressure limit, leading to calculated loss rates of $0.1\ s^{-1}$ at 298 K and $2 \times 10^{-7}\ s^{-1}$ at 220 K (the rate constants are expected to be close to the high pressure limit). As noted in Section 4.4, the effective lifetime of the peroxynitrate may be longer than calculated from the thermal decomposition rate constant due to reformation from the reverse reaction.

Photolysis of $CF_3CCl_2OONO_2$ can occur by two channels

$$CF_3CCl_2OONO_2 + h\nu \rightarrow CF_3CCl_2O_2^{\cdot} + NO_2$$

$$CF_3CCl_2OONO_2 + h\nu \rightarrow CF_3CCl_2O^{\cdot} + NO_3$$

and the relative importance of these photolysis pathways is not known for any $ROONO_2$ species (IUPAC, 1989). It is expected that the photodissociation quantum yield is unity. Assuming that the absorption cross-section is similar to those of $HOONO_2$, CH_3OONO_2, $CFCl_2OONO_2$ and CCl_3OONO_2 (Morel et al., 1980; NASA, 1987; IUPAC, 1989), the lifetime in the lower troposphere with respect to photodissociation is calculated to be ~5 days.

Hence, in the lower troposphere the dominant loss process of $CF_3CCl_2OONO_2$ will be thermal decomposition, with a lifetime of ~10 s. Thermal decomposition becomes slower with increasing altitude (decreasing temperature), and becomes sufficiently slow in the upper troposphere that photolysis is expected to dominate there, with a lifetime of ~5 days. The products of these reactions are the $CF_3CCl_2O_2^{\cdot}$ radical and, possibly, the $CF_3CCl_2O^{\cdot}$ radical (from photolysis). The reactions of the peroxy radical have been dealt with above, and the haloalkoxy radical reactions are dealt with below.

D. CF_3CCl_2OOH. As for methyl hydroperoxide (CH_3OOH), the gas-phase tropospheric reactions of CF_3CCl_2OOH are expected to be photolysis and reaction with the OH radical. Photolysis is expected to proceed by

$$CF_3CCl_2OOH + h\nu \rightarrow CF_3CCl_2O^{\cdot} + OH$$

Assuming an absorption cross-section similar to that for CH_3OOH and a photodissociation quantum yield of unity (Baulch et al., 1982; NASA, 1987), then the lifetime of CF_3CCl_2OOH with respect to photolysis is calculated to be ∼6 days in the lower troposphere.

Reaction of CF_3CCl_2OOH with the OH radical will lead to formation of the $CF_3CCl_2O_2^{\cdot}$ radical

$$OH + CF_3CCl_2OOH \rightarrow H_2O + CF_3CCl_2O_2^{\cdot}$$

The rate constant for this process can be estimated from the data for the corresponding OH radical reactions with $(CH_3)_3COOH$ (Anastasi et al., 1978) and CH_3OOH (Vaghjiani and Ravishankara, 1989) [noting that the OH radical reaction with CH_3OOH also proceeds to a significant extent by H atom abstraction from the $-CH_3$ group (Vaghjiani and Ravishankara, 1989; Atkinson, 1989b)]. At 298 K both reactions to yield $H_2O + RO_2^{\cdot}$ have rate constants of $(3\text{-}4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1989b). With the temperature dependence determined by Vaghjiani and Ravishankara (1989) for this reaction channel, this yields

$$k(OH + ROOH \rightarrow H_2O + RO_2^{\cdot}) = 1.7 \times 10^{-12} e^{220/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The calculated OH radical reaction rates during daylight hours of $(5\text{-}7) \times 10^{-6}$ s^{-1} throughout the troposphere are a factor of ∼2 higher than the expected photolysis rate. Clearly, both OH radical reaction and photolysis must be considered as gas-phase removal processes, with a lifetime of CF_3CCl_2OOH with respect to these processes of ∼2 to 3 days. These reactions again lead to the formation of the peroxy and haloalkoxy radicals.

In addition to these gas-phase tropospheric removal processes, physical removal processes may occur, leading to the incorporation of CF_3CCl_2OOH in cloud, rain and fog water.

E. $\underline{CF_3CCl_2O^{\cdot}}$. Based upon the discussion in Section 4.3, the reactions of the $CF_3CCl_2O^{\cdot}$ radical which need to be considered are

$$CF_2CCl_2O^{\cdot} \rightarrow CF_3C(O)Cl + Cl \qquad (a)$$

$$CF_3CCl_2O^{\cdot} \rightarrow \dot{C}F_3 + COCl_2 \qquad (b)$$

The value of $\Delta H_f(CF_3C(O)Cl)$, and of most of the other halogenated acetyl halides of interest in this article, must be estimated. The bond additivity method of Benson (1976), in which $\Delta H_f(CXYZC(O)B)$ is obtained from the contributions of C-X, C-Y, C-Z, >CO-C and >CO-B bonds, is one method. The partial bond contributions are given on page 25 of Benson (1976), with the exception that the literature heats of formation of HC(O)Cl (Dewar and Rzepa, 1983) and $CH_3C(O)Cl$ (Wagman et al., 1982) require that the >CO-Cl bond contribution be -34 kcal mol^{-1} instead of -27.0 kcal mol^{-1} as cited. A modification to the group additivity method of Benson (1976) is also used here, in which the contributions from $\Delta H_f[C\text{-}(X)(Y)(Z)(C)]$ and $\Delta H_f[C\text{-}(=O)(B)]$ are summed. Heats of formation of the C(O)H, C(O)Cl and C(O)F groups can be calculated from the literature data for CH_3CHO (IUPAC, 1989), $CH_3C(O)Cl$ (Wagman et al., 1982) and $CH_3C(O)F$ (Wagman et al., 1982) as -29.5, -48.1 and -94.8 kcal mol^{-1}, respectively.

The sum of the heats of formation of the products of pathways (a) and (b) are then: $CF_3C(O)Cl$ + Cl, -177 kcal mol^{-1} [$\Delta H_f(CF_3C(O)Cl)$ = -206 kcal mol^{-1} by both the above methods]; and $\dot{C}F_3 + COCl_2$, -166.5 kcal mol^{-1}. Cl atom elimination [channel (a)] is then expected to dominate, with the concurrent formation of $CF_3C(O)Cl$. This conclusion is in agreement with the discussion given in Section 4.3.B, based upon the experimental data of Sanhueza and Heicklen (1975) and Sanhueza et al. (1976) for analogous halogenated alkoxy radicals.

F. Cl. The chlorine atom will react with organic compounds in the troposphere. The reaction with methane,

$$Cl + CH_2 \rightarrow HCl + \dot{C}H_3$$

which has a rate constant (IUPAC, 1989) of $k = 9.6 \times 10^{-12} e^{-1350/T}$ cm^3 molecule^{-1} s^{-1} (1.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K), will dominate under "clean" tropospheric conditions. Reactions with other organic compounds, mainly the higher alkanes such as ethane, propane and the butanes, will be more important in more polluted areas and will dominate over the reaction with CH_4 in polluted urban areas.

$$Cl + RH \rightarrow HCl + \dot{R}$$

For the alkanes, the room temperature rate constants for these Cl atom reactions are $\sim 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, within a factor of approximately 2 (Lewis et al., 1980; Atkinson and Aschmann, 1985; Wallington et al., 1988a). Reactions of the Cl atom with alkenes and/or aromatic hydrocarbons will be of generally less importance because of the lower ambient concentrations of these organics. In particular, benzene exhibits only a low reactivity towards the Cl atom (Atkinson and Aschmann, 1985; Wallington et al., 1988b), and the reactions of the Cl atom with the aromatic hydrocarbons probably proceed by H atom abstraction from the substituent alkyl groups (Wallington et al., 1988b), again leading to HCl formation. The net result of the reactions of the Cl atom with organic compounds will be the dominant formation of HCl and an alkyl-type radical. These alkyl or related radicals will then undergo reaction sequences similar to those discussed in Section 4, resulting in the chlorine atom-initiated photooxidations of these organic compounds.

G. $CF_3C(O)Cl$. This compound, trifluoroacetyl chloride, is not expected to react with the OH radical to any significant extent (Atkinson, 1987), with an expected room temperature rate constant $< 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Photolysis and/or incorporation into cloud, fog and rain water are then expected to be the major tropospheric removal processes for this compound.

H. HCl. Under tropospheric conditions, HCl does not photolyze (NASA, 1987), and the removal processes are then reaction with the OH radical and wet deposition (or rain-out). The OH radical reaction

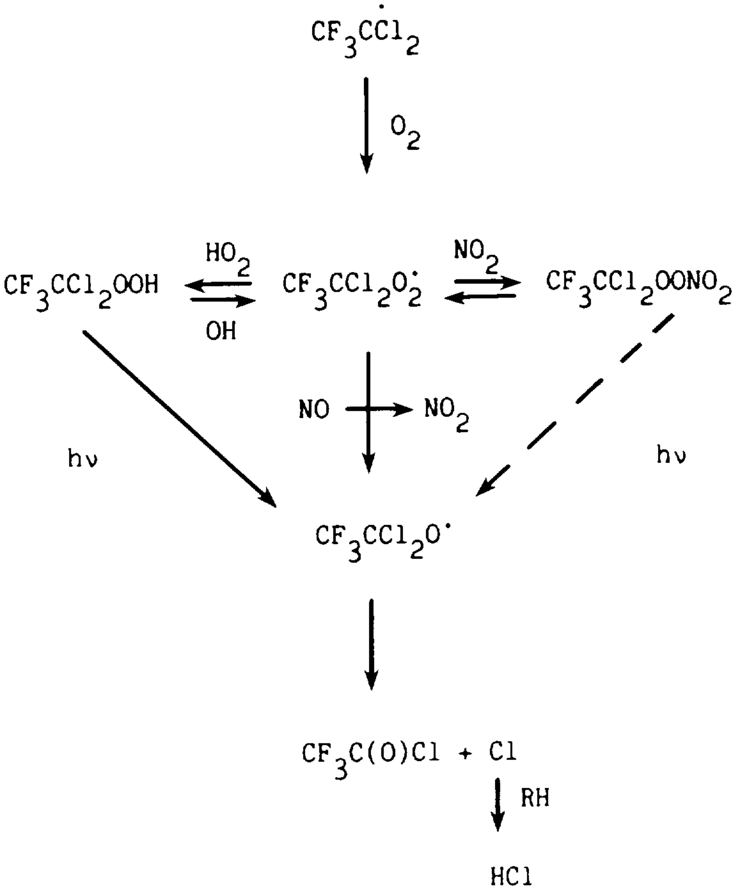
$$OH + HCl \rightarrow H_2O + Cl$$

has a rate constant (IUPAC, 1989) of $k = 2.4 \times 10^{-12} e^{-330/T}$ cm^3 molecule^{-1} s^{-1} (8.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K). This leads to a lifetime of HCl with respect to reaction with the OH radical of $\sim$20 days in the lower troposphere, and longer at higher, and colder, altitudes. Rain out of HCl is then expected to dominate as a loss process.

I. $COCl_2$. Although $COCl_2$ is not expected to be the dominant reaction product of the tropospheric degradation of HCFC-123, its tropospheric reactions need to be considered. Reaction with the OH radical is calculated to be of no importance as a tropospheric loss process (Atkinson, 1987). At wavelengths >220 nm, $COCl_2$ has an absorption maximum at 232 nm, with the absorption cross-section decreasing with increasing wavelength out to 280 nm (Baulch et al., 1982). From the cross-sections given by Baulch et al. (1982) and assuming a quantum yield of unity for photodissociation to CO + 2Cl (Baulch et al., 1982), photolysis in the troposphere will be slow, with a lifetime with respect to this process of >50 days. Physical removal leading to incorporation into rain, cloud and fog water may then be a major tropospheric loss process for this compound.

J. $\dot{C}F_3$. The tropospheric reactions of this radical are dealt with in Section 2.9 below.

The tropospheric degradation scheme for the $CF_3\dot{C}Cl_2$ radical is then as follows



2.2. The $CFCl_2\dot{C}H_2$ Radical formed from HCFC-141b ($CFCl_2CH_3$).

A. $CFCl_2\dot{C}H_2$. The $CFCl_2\dot{C}H_2$ radical will react solely with O_2,

$$CFCl_2\dot{C}H_2 + O_2 \xrightarrow{M} CFCl_2CH_2\dot{O}_2$$

with a rate constant of $k \geq 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The tropospheric lifetime of the $CFCl_2\dot{C}H_2$ radical will thus be $< 2 \times 10^{-6}$ s.

B. $CFCl_2CH_2\dot{O}_2$. As discussed in Section 2.1, the $CFCl_2CH_2\dot{O}_2$ radical will react with NO, NO_2 and the HO_2 radical,

$$CFCl_2CH_2\dot{O}_2 + NO \rightarrow CFCl_2CH_2O^{\cdot} + NO_2$$

$$CFCl_2CH_2\dot{O}_2 + NO_2 \xrightarrow{M} CFCl_2CH_2OONO_2$$

$$CFCl_2CH_2\dot{O}_2 + HO_2 \rightarrow CFCl_2CH_2OOH + O_2$$

with the HO_2 radical reaction possibly also leading to other products [see Jenkin et al. (1988) and Section 4.2.C]. The rate constants for these NO, NO_2 and HO_2 reactions are (in cm^3 molecule^{-1} s^{-1} units): $\sim 1.5 \times 10^{-11} (T/300)^{-1.2}$, $\sim 1.0 \times 10^{-11}$, and $3.4 \times 10^{-13} e^{800/T}$, respectively. With the concentrations of the reactive species given in Table 1, the lifetime of the $CFCl_2CH_2\dot{O}_2$ radical is $\sim 10^2$ s. Formation of the nitrate, $CFCl_2CH_2ONO_2$, from the NO reaction is assumed to be unimportant ($< 2\%$ of the total reaction products).

C. $CFCl_2CH_2OONO_2$. The reactions to be considered are thermal decomposition

$$CFCl_2CH_2OONO_2 \xrightarrow{M} CFCl_2CH_2\dot{O}_2 + NO_2$$

with a rate constant at the high-pressure limit of $\sim 1 \times 10^{15} e^{-11000/T}$ s^{-1}, and photolysis

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2\dot{O}_2 + NO_2$$

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2O^{\cdot} + NO_3$$

which is calculated to have a rate of $\sim 2 \times 10^{-6}$ s^{-1}. As discussed in Section 2.1.C above, in the lower troposphere thermal decomposition will dominate, with photolysis becoming the dominant loss process in the upper troposphere.

D. $CFCl_2CH_2OOH$. The gas-phase removal reactions of this hydroperoxide are photolysis

$$CFCl_2CH_2OOH + h\nu \rightarrow CFCl_2CH_2O^{\cdot} + OH$$

which is calculated to have a rate of $\sim 2 \times 10^{-6}$ s^{-1} in the lower troposphere, and reaction with the OH radical.

$$OH + CFCl_2CH_2OOH \rightarrow H_2O + CFCl_2CH_2\dot{O}_2$$

The rate constant for this reaction pathway is expected to be $k \sim 1.7 \times 10^{-12} e^{220/T}$ cm^3 molecule^{-1} s^{-1}. Abstraction of an H atom from the $-CH_2-$ group to form the $CFCl_2\dot{C}HOOH$ radical is calculated to be a minor reaction pathway, accounting for $\sim$(5-15)% of the overall reaction (Atkinson, 1987), which, however, cannot be neglected. Formation of the $CFCl_2\dot{C}HOOH$ radical is expected to be followed by rapid decomposition to yield an OH radical and $CFCl_2CHO$

$$CFCl_2\dot{C}HOOH \rightarrow CFCl_2CHO + OH$$

Reaction with the OH radical and photolysis of $CFCl_2CH_2OOH$ are calculated to occur at comparable rates in the troposphere, with a lifetime of $CFCl_2CH_2OOH$ of ∿2 to 3 days. Physical removal processes leading to incorporation of $CFCl_2CH_2OOH$ into rain, cloud and fog water may also be important.

E. $\underline{CFCl_2CH_2\dot{O}}$. Based on the discussion in Section 4.3, the reactions of this radical which need to be considered are

$$CFCl_2CH_2\dot{O} + O_2 \rightarrow CFCl_2CHO + HO_2 \quad (a)$$

$$CFCl_2CH_2\dot{O} \rightarrow \dot{C}FCl_2 + HCHO \quad (b)$$

with H atom elimination being totally negligible. The sum of the heats of formation of the products of reactions (a) and (b) are -92.1 kcal mol^{-1} and -48.9 kcal mol^{-1}, respectively. On the basis of the difference in these heats of formation of 43 kcal mol^{-1}, it is expected that pathway (a) will dominate at room temperature, and more so at the lower temperatures of the upper troposphere (taking into account the lower O_2 concentrations). Again, this expectation is in agreement with the conclusions of Sanhueza et al. (1976). The decomposition to HCHO and the $\dot{C}FCl_2$ radical cannot be ruled out at the present time, however. The reactions of the $\dot{C}FCl_2$ radical will be totally analogous to those of the $\dot{C}F_2Cl$ radical discussed in Section 2.4 below, except that the $CFCl_2\dot{O}$ radical will eliminate a Cl atom to yield COFCl (instead of the COF_2 formed from the $CF_2Cl\dot{O}$ radical).

Assuming that the rate constant for the reaction (a) is identical to that for the ethoxy radical of $k_a = 3.7 \times 10^{-14} e^{-460/T}$ cm^3 $molecule^{-1}$ s^{-1}, the lifetime of the $CFCl_2CH_2\dot{O}$ radical will be ∿2×10^{-4} to 2×10^{-5} s in the troposphere.

F. $\underline{CFCl_2CHO}$. The possible tropospheric reactions of dichlorofluoroacetaldehyde are reaction with OH and NO_3 radicals and O_3, and photolysis. By analogy with CH_3CHO, for which the O_3 reaction rate constant at room temperature is $< 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Carter, 1984), reaction with O_3 is expected to be of totally negligible importance as a loss process. Reaction with the NO_3 radical is expected to be no faster than the corresponding reaction with CH_3CHO [$k = 1.4 \times 10^{-12} e^{-1860/T}$ cm^3 $molecule^{-1}$ s^{-1}, $= 2.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, 1989)], and in the clean troposphere this NO_3 radical reaction will be of no importance (Winer et al., 1984), although it should be noted that this reaction yields the same $CFCl_2\dot{C}O$ radical as does the OH radical reaction.

Thus, photolysis and OH radical reaction remain to be considered. The OH radical reaction will proceed by

$$OH + CFCl_2CHO \rightarrow H_2O + CFCl_2\dot{C}O$$

Assuming that the substituent group factor for the $-CFCl_2$ group is similar to those for the $-CCl_3$, $-CF_3$ and $-CF_2Cl$ groups (Atkinson, 1987), the estimation technique of Atkinson (1987) allows an approximate room temperature rate constant of ∿$(0.5\text{-}2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} to be calculated. A rate constant of this magnitude leads to a lifetime of $CFCl_2CHO$ with respect to OH radical reaction of ∼15 days (to within ± a factor of ∼2).

The photolysis rate is not known, but is expected to be less than that of CH_3CHO, which leads to a lifetime with respect to photolysis of $\geq$5-10 days. In the absence of data for the absorption cross-sections, photodissociation quantum yields and photodissociation products of $CFCl_2CHO$, it is assumed that the OH radical reaction, while relatively slow, is the dominant tropospheric loss process, leading to the formation of the $CFCl_2\dot{C}O$ radical.

G. $CFCl_2\dot{C}O$. This acyl radical will rapidly add O_2, with a rate constant of $\sim 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1989a).

$$CFCl_2\dot{C}O + O_2 \xrightarrow{M} CFCl_2C(O)\dot{O}_2$$

This will be the sole reaction of the $CFCl_2\dot{C}O$ radical, which will have a lifetime of $< 10^{-6}$ s^{-1} in the troposphere.

H. $CFCl_2C(O)\dot{O}_2$. Analogous to the alkyl and haloalkyl peroxy ($R\dot{O}_2$) radicals and the acetyl peroxy ($CH_3C(O)\dot{O}_2$) radical, this acyl peroxy radical will react with NO and NO_2.

$$CFCl_2C(O)\dot{O}_2 + NO \rightarrow CFCl_2C\dot{O}_2 + NO_2$$

$$\dot{C}FCl_2 + CO_2$$

$$CFCl_2C(O)\dot{O}_2 + NO_2 \xrightarrow{M} CFCl_2C(O)OONO_2$$

Assuming identical rate constants for these NO and NO_2 reactions to those for the analogous reactions with the acetyl peroxy radical, rate constants of $5.1 \times 10^{-12} e^{200/T}$ cm^3 molecule^{-1} s^{-1} for the NO reaction and 8×10^{-12} cm^3 molecule^{-1} s^{-1} for the NO_2 reaction (at the high pressure limit, which should be a good approximation) are obtained (Atkinson, 1989a). The reaction with NO leads to the formation of the $\dot{C}FCl_2$ radical, while the NO_2 reaction forms an analog to peroxyacetyl nitrate (PAN).

In addition, reaction with the HO_2 radical and, at least in the lower troposphere, with $CH_3\dot{O}_2$ radicals cannot be ruled out as being of importance. The reaction of the $CH_3C(O)\dot{O}_2$ radical with HO_2 has been reported to lead to the formation of $CH_3C(O)OOH + O_2$ and $CH_3COOH + O_3$ in an approximately 3:1 ratio at room temperature (Niki et al., 1985) [see also Moortgat et al., 1987]. The reaction of the $CH_3C(O)\dot{O}_2$ radical with the $CH_3\dot{O}_2$ radical is rapid, with a rate constant of 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K, forming $CH_3O^{\cdot} + CH_3C\dot{O}_2 + O_2$ and $CH_3COOH + HCHO + O_2$ in equal yield at room temperature (IUPAC, 1989; Moortgat et al., 1989).

The analogous products would then be $CFCl_2C\dot{O}_2$, which should rapidly decompose to $\dot{C}FCl_2 + CO_2$, $CFCl_2COOH$ and $CFCl_2C(O)OOH$. The reactions of the $\dot{C}FCl_2$ radical are dealt with below in Section 2.4. By analogy with CH_3COOH, the acid $CFCl_2COOH$ is expected to react only slowly with the OH radical (Atkinson, 1989b), with a lifetime with respect to OH radical reaction of ~25 days, and the major tropospheric loss process for $CFCl_2COOH$ and $CFCl_2C(O)OOH$ will be by wet deposition and rain-out.

I. $CFCl_2C(O)OONO_2$. This halogenated peroxy acylnitrate is expected to react in an analogous manner to PAN, with thermal decomposition and photolysis being the likely tropospheric homogeneous gas-phase loss processes (reaction with the OH radical being of no importance). The rate constant for the thermal decomposition

$$CFCl_2C(O)OONO_2 \xrightarrow{M} CFCl_2C(O)\dot{O_2} + NO_2$$

is expected to be similar to that for PAN, with $k = 2.2 \times 10^{16} e^{-13435/T} s^{-1}$ at the high-pressure limit (IUPAC, 1989). While the thermal decomposition rate constant for PAN is in the fall-off region at atmospheric pressure and below at room temperature, the thermal decomposition rate constant for $CFCl_2C(O)OONO_2$ should be close to the high pressure limit throughout the troposphere. The lifetime of $CFCl_2C(O)OONO_2$ with respect to thermal decomposition will then increase with altitude, from ~1 hr at ground level (298 K) to ~45 yr in the upper troposphere (220 K).

PAN has a weak absorption which extends out to 300 nm, with a cross-section at 300 nm of 1×10^{-21} cm^2 (IUPAC, 1989). Photolysis of $CFCl_2C(O)OONO_2$, presumably to the same products as arise from its thermal decomposition, will then be slow, but may compete with or dominate over thermal decomposition in the upper troposphere. It appears that in the upper troposphere $CFCl_2C(O)OONO_2$ will act as a long-lived intermediate species in the degradation of HCFC-141b.

A portion of the tropospheric degradation scheme for HCFC-141b is shown below

2.3. The $CF_2Cl\dot{C}H_2$ Radical formed from HCFC-142b (CF_2ClCH_3).

The reactions undergone by the $CF_2Cl\dot{C}H_2$ radical in the troposphere are expected to be totally analogous to the reactions of the $CFCl_2\dot{C}H_2$ radical discussed above in Section 2.2. However, the possible reactions of the $CF_2ClCH_2O^{\cdot}$ radical which is formed during the overall reaction scheme need to be evaluated, as follows.

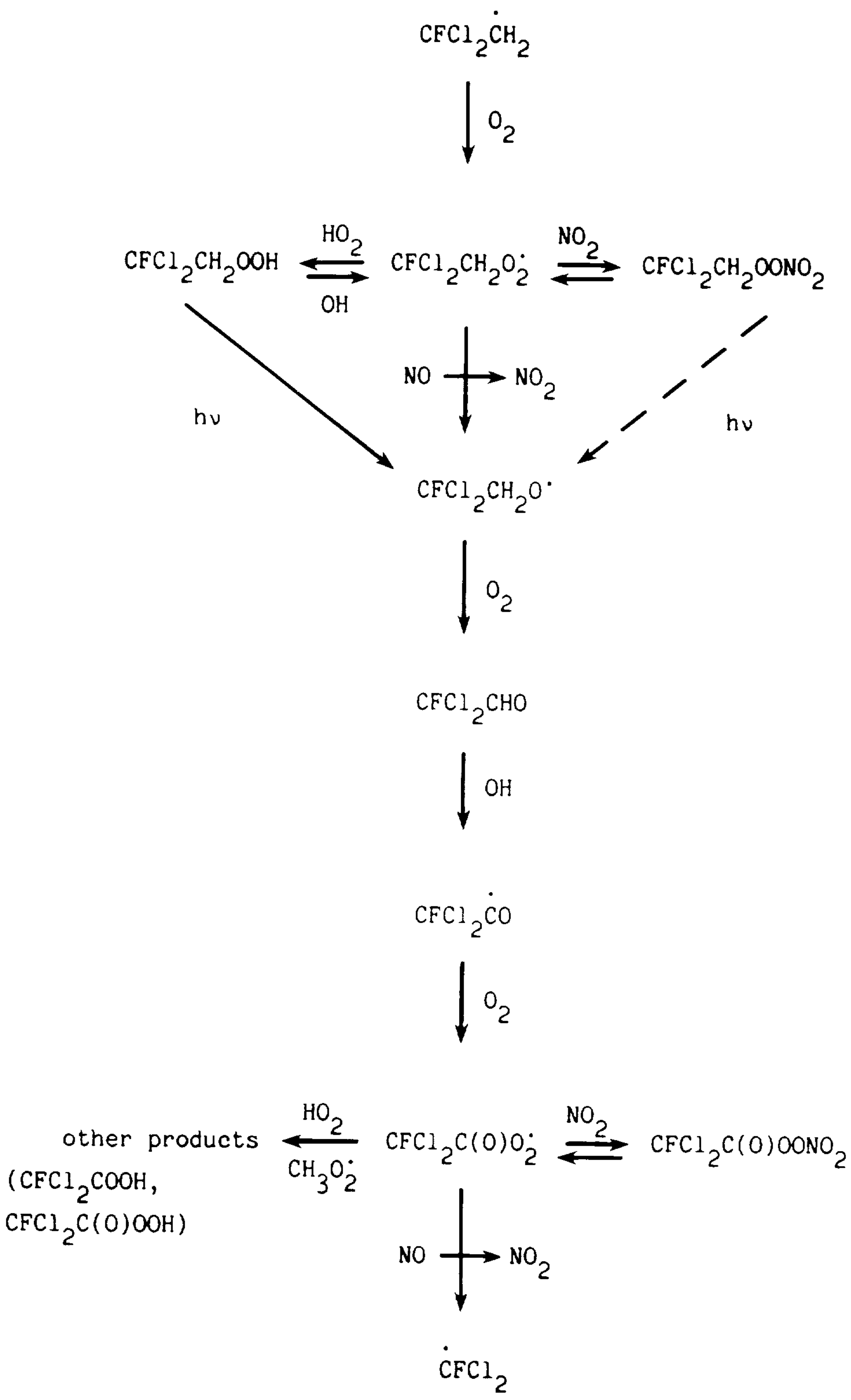
A. $CF_2ClCH_2O^{\cdot}$. The likely reaction pathways are (see Section 2.2.E above)

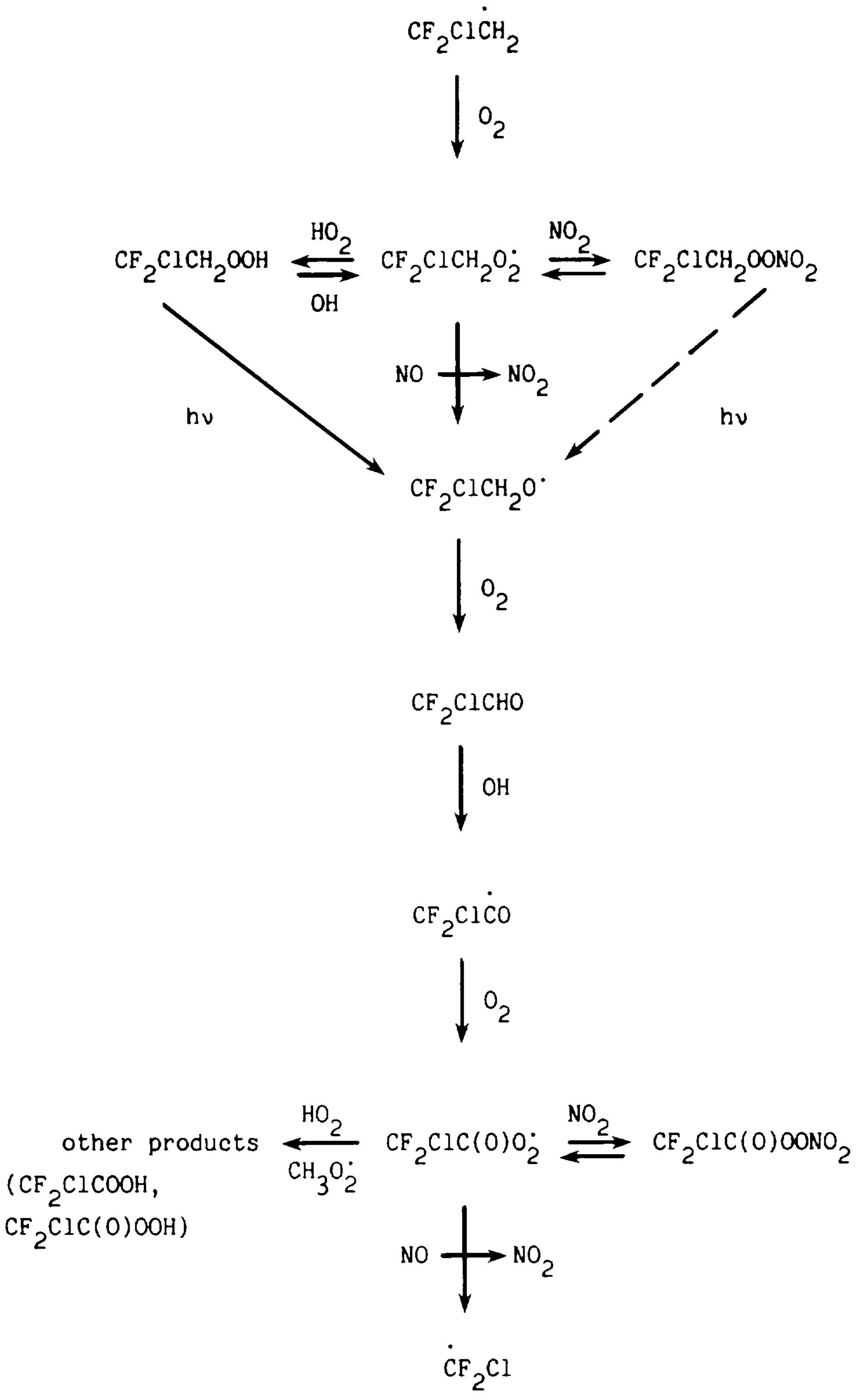
$$CF_2ClCH_2O^{\cdot} + O_2 \rightarrow CF_2ClCHO + HO_2 \quad (a)$$

$$CF_2ClCH_2O^{\cdot} \rightarrow \dot{C}F_2Cl + HCHO \quad (b)$$

The calculated sum of the heats of formation of the products of reactions (a) and (b) are then -135 kcal mol^{-1} for pathway (a) (uncertain to at least ±3 kcal mol^{-1}) and -90.3 kcal mol^{-1} for pathway (b). This again suggests, as for the case for the $CFCl_2CH_2O^{\cdot}$ radical in Section 2.2.E., that pathway (a) will dominate, leading to the formation of CF_2ClCHO.

A portion of the tropospheric degradation scheme of the $CF_2Cl\dot{C}H_2$ radical, leading to the formation of the $\dot{C}F_2Cl$ radical, is shown below.


CFCl2ĊH2
O2
CFCl2CH2OOH
HO2
OH
CFCl2CH2O2·
NO2
CFCl2CH2OONO2
hν
NO
NO2
hν
CFCl2CH2O·
O2
CFCl2CHO
OH
CFCl2ĊO
O2
other products
(CFCl2COOH,
CFCl2C(O)OOH)
HO2
CH3O2·
CFCl2C(O)O2·
NO2
CFCl2C(O)OONO2
NO
NO2
ĊFCl2


CF2ClCH2
O2
CF2ClCH2OOH
HO2
OH
CF2ClCH2O2
NO2
CF2ClCH2OONO2
hν
NO
NO2
hν
CF2ClCH2O
O2
CF2ClCHO
OH
CF2ClCO
O2
other products
(CF2ClCOOH,
CF2ClC(O)OOH)
HO2
CH3O2
CF2ClC(O)O2
NO2
CF2ClC(O)OONO2
NO
NO2
CF2Cl

As noted above, the tropospheric reactions of the $CFCl_2\dot{C}H_2$ and $CF_2Cl\dot{C}H_2$ radicals formed from HCFC-141b and HCFC-142b, respectively, are expected to be totally analogous, except that the $\dot{C}FCl_2$ radical is formed subsequent to the reactions of the $CFCl_2\dot{C}H_2$ radical, while the $\dot{C}F_2Cl$ radical is the subsequent product from the $CF_2Cl\dot{C}H_2$ radical.

2.4. The $\dot{C}F_2Cl$ Radical formed from HCFC-22 (CHF_2Cl)

In addition to being the primary product of the OH radical reaction with CHF_2Cl, the $\dot{C}F_2Cl$ radical is also expected to be formed from the reactions subsequent to the OH radical reaction with HCFC-142b. The analogous radical $\dot{C}FCl_2$ is expected to be formed subsequent to the OH radical reaction with HCFC-141b, and the reaction sequence discussed in this section for the $\dot{C}F_2Cl$ radical is also applicable for the $\dot{C}FCl_2$ radical, with the differences being noted at the appropriate points.

A. $\dot{C}F_2Cl$. No experimental data are available for this particular radical. Experimental data are available for the analogous $\dot{C}FCl_2$ radical reaction (Caralp and Lesclaux, 1983), and the IUPAC (1989) recommended values of k_0, k_∞ and F for the reaction of the $\dot{C}FCl_2$ radical with O_2 are given in Table 2 (see Section 4). Both the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals rapidly add O_2 to form the $CF_2ClO_2^{\cdot}$ and $CFCl_2O_2^{\cdot}$ peroxy radicals, respectively,

$$\dot{C}F_2Cl + O_2 \xrightarrow{M} CF_2ClO_2^{\cdot}$$

$$\dot{C}FCl_2 + O_2 \rightarrow CFCl_2O_2^{\cdot}$$

with rate constants of $\geq 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} under the temperature and pressure conditions in the troposphere. The lifetimes of the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals will then be $<2 \times 10^{-6}$ s in the troposphere.

B. $CF_2ClO_2^{\cdot}$. This peroxy radical can, as described above in Section 2.1, react with NO, NO_2 and the HO_2 radical under tropospheric conditions.

$$CF_2ClO_2^{\cdot} + NO \rightarrow CF_2ClO^{\cdot} + NO_2 \qquad \text{(a)}$$

$$CF_2ClO_2^{\cdot} + NO_2 \xrightarrow{M} CF_2ClOONO_2 \qquad \text{(b)}$$

$$CF_2ClO_2^{\cdot} + HO_2 \rightarrow CF_2ClOOH + O_2 \qquad \text{(c)}$$

The reactions of the $CFCl_2O_2^{\cdot}$ radical are totally analogous. Experimental rate constant data are available for the reactions of the $CF_2ClO_2^{\cdot}$ radical with NO (Dognon et al., 1985), and for the reactions of the $CFCl_2O_2^{\cdot}$ radical with NO (Lesclaux and Caralp, 1984; Dognon et al., 1985) and NO_2 (Lesclaux and Caralp, 1984; Lesclaux et al., 1986; Caralp et al., 1988). The IUPAC (1989) recommendations for these NO and NO_2 reactions (based upon these data) are given in Tables 3 and 4, respectively (see Section 4). As discussed in Section 4.2, the rate constants for the reactions (a), (b) and (c) are (in cm^3 molecule^{-1} s^{-1} units), $k_a = 1.5 \times 10^{-11} (T/300)^{-1.4}$, $k_b \sim 9 \times 10^{-12}$ under tropospheric conditions, and $k_c \sim 3.4 \times 10^{-13} e^{800/T}$. As discussed in Section 2.1 above, all three of these reactions are expected to occur under tropospheric conditions, leading to the formation of the $CF_2ClO^{\cdot}$ radical, $CF_2ClOONO_2$ and CF_2ClOOH.

Formation of the nitrate, CF_2ClONO_2, from the reaction of the $CF_2ClO_2^{\cdot}$ radical with NO is expected to be of negligible importance. Analogous products will be formed from the $CFCl_2O_2^{\cdot}$ radical reactions.

C. $\underline{CF_2ClOONO_2}$. As in Sections 2.1 and 2.2 above, this peroxynitrate can undergo thermal decomposition or photolyze. The thermal decomposition

$$CF_2ClOONO_2 \xrightarrow{M} CF_2ClO_2^{\cdot} + NO_2$$

rate data have been evaluated by IUPAC (1989), and the recommended rate expressions for this reaction and the analogous thermal decomposition of $CFCl_2OONO_2$ are given in Table 10 (Section 4). The lifetimes of these two peroxynitrates with respect to thermal decomposition increase from $\sim$15 s in the lower troposphere to $\sim$(2-3) x 10^7 s ($\sim$290 days) in the upper troposphere.

No absorption cross-section data are available for $CF_2ClOONO_2$. However, data are available for $CFCl_2OONO_2$ (Morel et al., 1980) for wavelengths out to 280 nm. Extrapolation of these cross-sections to longer wavelengths leads to the expectation (Section 4.4.B) that photolysis

$$CF_2ClOONO_2 + h\nu \rightarrow CF_2ClO_2^{\cdot} + NO_2$$

$$CF_2ClOONO_2 + h\nu \rightarrow CF_2ClO^{\cdot} + NO_3$$

will dominate in the upper troposphere, with a lifetime with respect to this process of $\sim$5 days. The photolysis products are not known, but are expected to be mainly the peroxy radical plus NO_2.

D. $\underline{CF_2ClOOH}$. The homogeneous gas-phase tropospheric loss processes for CF_2ClOOH and $CFCl_2OOH$ are photolysis and reaction with the OH radical. As discussed in Section 2.1 above, photolysis

$$CF_2ClOOH + h\nu \rightarrow CF_2ClO^{\cdot} + OH$$

is expected to have a lifetime of $\sim$6 days in the lower troposphere. The OH radical reaction can only proceed to regenerate the peroxy radical

$$OH + CF_2ClOOH \rightarrow H_2O + CF_2ClO_2^{\cdot}$$

and the rate constant for this reaction is estimated to be $k = 1.7 \times 10^{-12} e^{220/T}$ cm^3 molecule^{-1} s^{-1}. Reaction with the OH radical and photolysis are expected to occur at comparable rates in the troposphere, leading to a lifetime of CF_2ClOOH with respect to these reactions of 2 to 3 days. Incorporation into aqueous systems may also be important. The reactions of $CFCl_2OOH$ are expected to be totally analogous.

E. $\underline{CF_2ClO^{\cdot}}$. As discussed in Section 4.3.B., the $CF_2ClO^{\cdot}$ radical will undergo decomposition to yield COF_2 and a Cl atom (Table 8).

$$CF_2ClO^{\cdot} \rightarrow COF_2 + Cl$$

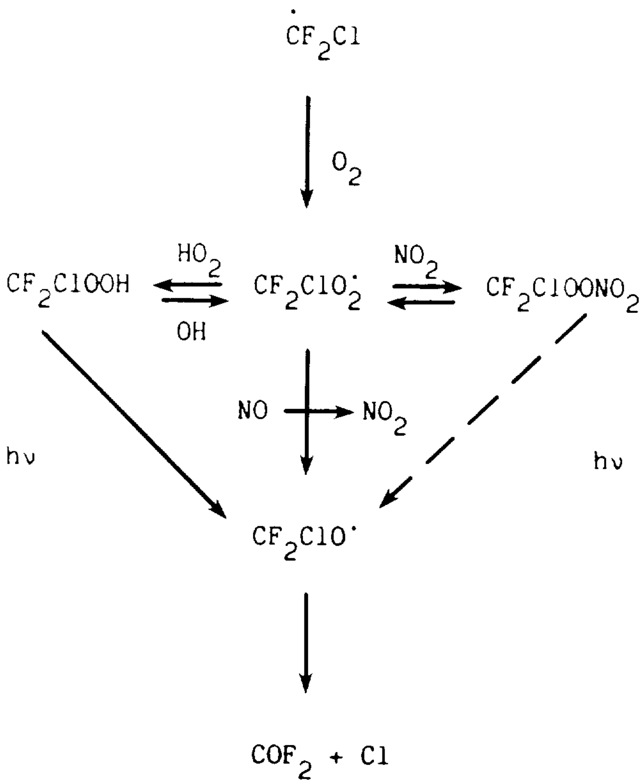
The $CFCl_2O^{\cdot}$ radical decomposes in an analogous manner

$$CFCl_2O^{\cdot} \rightarrow COFCl + Cl$$

The lifetimes of these halomethoxy radicals are calculated (Table 8) to be <0.1 s throughout the troposphere, and reactions with NO and NO_2 will be unimportant.

F. COF_2 and COFCl. Neither of these compounds are expected to react with the OH radical at tropospherically significant rate constants (Atkinson, 1987). Furthermore, photolysis of these species in the troposphere will be of essentially no importance (NASA, 1987). Physical removal processes leading to incorporation into rain, cloud or fog water, with subsequent hydrolysis to form HF and (for COFCl) HCl, are then expected to be the major tropospheric loss processes for these carbonyl halides.

The reaction scheme for the $\dot{C}F_2Cl$ radical is shown below



The reaction scheme for the $\dot{C}FCl_2$ radical is totally analogous, except that the final products are COFCl and a Cl atom.

2.5. The $CF_3\dot{C}FCl$ Radical formed from HCFC-124 (CF_3CHFCl)

The tropospheric reactions of this radical will be totally analogous to those of the $CF_3\dot{C}Cl_2$ radical formed from HCFC-123, discussed in Section 2.1. The reactions of the $CF_3CFClO^{\cdot}$ radical which is formed during the degradation need to be evaluated.

A. $CF_3CFClO^{\cdot}$. The likely reactions of this radical are

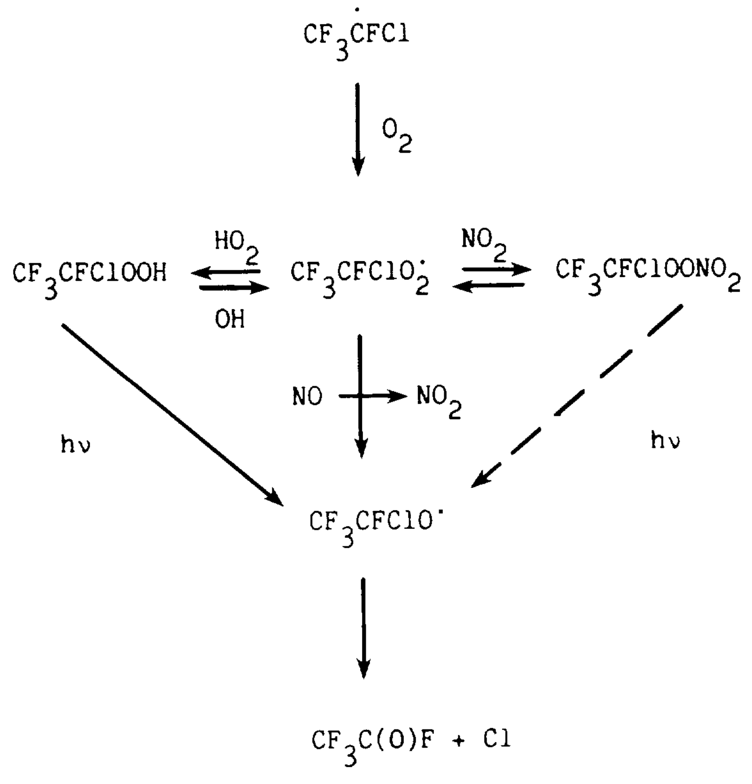
$$CF_3CFClO^{\cdot} \rightarrow CF_3C(O)F + Cl \tag{a}$$

$$CF_3CFClO^{\cdot} \rightarrow \dot{C}F_3 + COFCl \tag{b}$$

The heats of formation of the products of reaction pathways (a) and (b) are: $CF_3C(O)F + Cl$ from pathway (a), -222.1 kcal mol^{-1} ($\Delta H_f(CF_3C(O)F)$ = -251.1 kcal mol^{-1} with an uncertainty of at least 2 kcal mol^{-1}); and $\dot{C}F_3 + COFCl$ from reaction pathway (b), -216.0 kcal mol-1. As expected (Section 4.3.B), the Cl atom elimination pathway (a) is preferred, leading to $CF_3C(O)F$ and a Cl atom.

B. $CF_3C(O)F$. Trifluoroacetyl fluoride is not expected to react with the OH radical with any tropospherically significant rate constant (Atkinson, 1987) since there are no H atoms to abstract. While no data exist concerning photolysis of $CF_3C(O)F$ to $\dot{C}F3$ + FCO or to CF_4 + CO, photodissociation to $\dot{C}F_3$ + FCO is expected to be negligible in the troposphere since the threshold wavelength for this process is calculated to be 296 nm (96.5 kcal mol^{-1}). This then leaves physical processes as the main removal route, with wet deposition/incorporation into cloud, fog and rain water with subsequent hydrolysis (to CF_3COOH + HF) being expected to dominate.

The expected reaction scheme for the $CF_3\dot{C}FCl$ radical is shown below



2.6. The $CF_3\dot{C}HF$ Radical formed from HFC-134a (CF_3CH_2F).

The tropospheric reactions of the $CF_3\dot{C}HF$ radical are expected to be generally similar to those of the

$CF_2Cl\dot{C}H_2$ and $CFCl_2\dot{C}H_2$ radicals discussed above in Sections 2.2 and 2.3.

A. $\underline{CF_3\dot{C}HF}$. Reaction with O_2 to form the peroxy radical will be the sole reaction of this radical in the troposphere.

$$CF_3\dot{C}HF + O_2 \xrightarrow{M} CF_3CHFO_2^{\cdot}$$

The rate constant is expected to be $> 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at the temperatures and pressures encountered in the troposphere, leading to a lifetime of the $CF_3\dot{C}HF$ radical of $< 2 \times 10^{-6}$ s.

B. $\underline{CF_3CHFO_2^{\cdot}}$. The tropospherically important reactions of the $CF_3CHFO_2^{\cdot}$ radical are expected to be with NO, NO_2 and the HO_2 radical

$$CF_3CHFO_2^{\cdot} + NO \rightarrow CF_3CHFO^{\cdot} + NO_2 \qquad \text{(a)}$$

$$CF_3CHFO_2^{\cdot} + NO_2 \xrightarrow{M} CF_3CHFOONO_2 \qquad \text{(b)}$$

$$CF_3CHFO_2^{\cdot} + HO_2 \rightarrow CF_3CHFOOH + O_2 \qquad \text{(c)}$$

The rate constants for these reactions are estimated (in cm^3 molecule^{-1} s^{-1} units) to be $k_a \sim 1.5 \times 10^{-11}$ $(T/300)^{-1.2}$, $k_b \sim 1.0 \times 10^{-11}$, and $k_c \sim 3.4 \times 10^{-13}\, e^{800/T}$, respectively. With the tropospheric concentrations of NO, NO_2 and the HO_2 radical as given in Table 1, all three of these reactions are of comparable importance, and the reactions of the products formed must be considered further. The lifetime of the $CF_3CHFO_2^{\cdot}$ radical is calculated to be $\sim 10^2$ s.

C. $\underline{CF_3CHFOONO_2}$. This species is expected to undergo thermal decomposition and photolysis. Thermal decomposition

$$CF_3CHFOONO_2 \xrightarrow{M} CF_3CHFO_2^{\cdot} + NO_2$$

is expected to have a rate constant at the high-pressure limit of $\sim 1 \times 10^{15}\, e^{-11000/T}$ s^{-1}, leading to lifetimes of this peroxynitrate, with respect to thermal decomposition, of ~ 10 s in the lower troposphere (298 K) and $\sim 10^7$ s in the upper troposphere (220 K). The peroxy radical $CF_3CHFO_2^{\cdot}$ is reformed. Photolysis

$$CF_3CHFOONO_2 + h\nu \rightarrow CF_3CHFO_2^{\cdot} + NO_2$$

$$CF_3CHFOONO_2 + h\nu \rightarrow CF_3CHFO^{\cdot} + NO_3$$

is expected to be slow, with a lifetime of the peroxynitrate due to photolysis of ~ 5 days. Which of the two photolysis pathways occurs is not known. Thus, in the lower and middle troposphere thermal decomposition should dominate, while in the upper troposphere photolysis is expected to be the dominant removal process of $CF_3CHFOONO_2$.

D. $\underline{CF_3CHFOOH}$. As for the hydroperoxides considered in the sections above, photolysis and reaction with the OH radical are expected to be the only significant homogeneous gas-phase removal processes. Photolysis

$$CF_3CHFOOH + h\nu \rightarrow CF_3CHFO^{\cdot} + OH$$

forms the haloalkoxy radical $CF_3CHFO^{\cdot}$. Based upon the absorption cross-section for CH_3OOH (NASA, 1987), the lifetime of $CF_3CHFOOH$ with respect to photolysis is estimated to be ~6 days in the lower troposphere.

The OH radical reaction will proceed mainly by

$$OH + CF_3CHFOOH \rightarrow H_2O + CF_3CHFO_2^{\cdot}$$

with an estimated rate constant of $\sim 1.7 \times 10^{-12} e^{220/T}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction to form the $CF_3\dot{C}FOOH$ radical

$$OH + CF_3CHFOOH \rightarrow H_2O + CF_3\dot{C}FOOH$$

is expected to of minor importance [<5% of the overall reaction (Atkinson, 1987)].

Photolysis and OH radical reaction are expected to be of comparable importance as tropospheric loss processes for $CF_3CHFOOH$, with a lifetime due to these processes of 2-3 days. Physical removal of $CF_3CHFOOH$ from the gas phase into rain, cloud and fog water and aerosols may also be important.

E. $\underline{CF_3CHFO^{\cdot}}$. The possible reactions of this haloalkoxy radical are

$$CF_3CHFO^{\cdot} + O_2 \rightarrow CF_3C(O)F + HO_2 \quad \text{(a)}$$

$$CF_3CHFO^{\cdot} \rightarrow CF_3C(O)F + H \quad \text{(b)}$$

$$CF_3CHFO^{\cdot} \rightarrow \dot{C}F_3 + HC(O)F \quad \text{(c)}$$

$$CF_3CHFO^{\cdot} \rightarrow CF_3CHO + F \quad \text{(d)}$$

The sum of the heats of formation of the products from these reactions are (with $\Delta H_f(CF_3C(O)F) = -251.1$ kcal mol^{-1} being calculated, with an uncertainty of at least ± 2 kcal mol^{-1}): $CF_3C(O)F + HO_2$ from reaction (a), -247.6 kcal mol^{-1}; $CF_3C(O)F + H$ from reaction (b), -199.0 kcal mol^{-1}; $\dot{C}F_3 + HC(O)F$ from reaction (c), -205.3 kcal mol^{-1} (with $\Delta H_f(HC(O)F) = -90.9$ kcal mol^{-1} calculated from bond additivity (Benson, 1976) being in good agreement with the value of -91.8 kcal mol^{-1} obtained by Goldstein et al. (1983) from MINDO calculations); and $CF_3CHO + F$ from reaction (d), -168.0 kcal mol^{-1}. Clearly, H atom [reaction (b)] and F atom [reaction (d)] elimination will be of negligible importance, as expected from the discussion in Section 4.3.B. This leaves reaction with O_2 and C-C bond cleavage as the likely reaction routes of the $CF_3CHF\dot{O}$ radical. The difference in the sums of the heats of formation of the products of these two reactions, $\Delta(\Delta H_f)$, of 42.3 kcal mol^{-1}, with at least ± 2-3 kcal mol^{-1} uncertainty, indicates that both reactions may be of comparable importance at room temperature (with the reaction with O_2 presumably having a smaller temperature dependence than that for the C-C bond cleavage and hence becoming more important in the upper, colder, troposphere).

Thus, the formation of both $CF_3C(O)F$ and of $\dot{C}F_3$ + HC(O)F must be considered.

F. $CF_3C(O)F$. As discussed in Section 2.5 above, the reaction of OH radical with $CF_3C(O)F$ will be unimportant as a tropospheric loss process, and photolysis is also expected to be slow or negligible. The removal of $CF_3C(O)F$ by chemical pathways is thus expected to be slow, and physical removal by wet deposition and incorporation into cloud, rain and fog water will be the dominant tropospheric removal process, with the expectation of subsequent hydrolysis in aqueous media to HF + CF_3COOH.

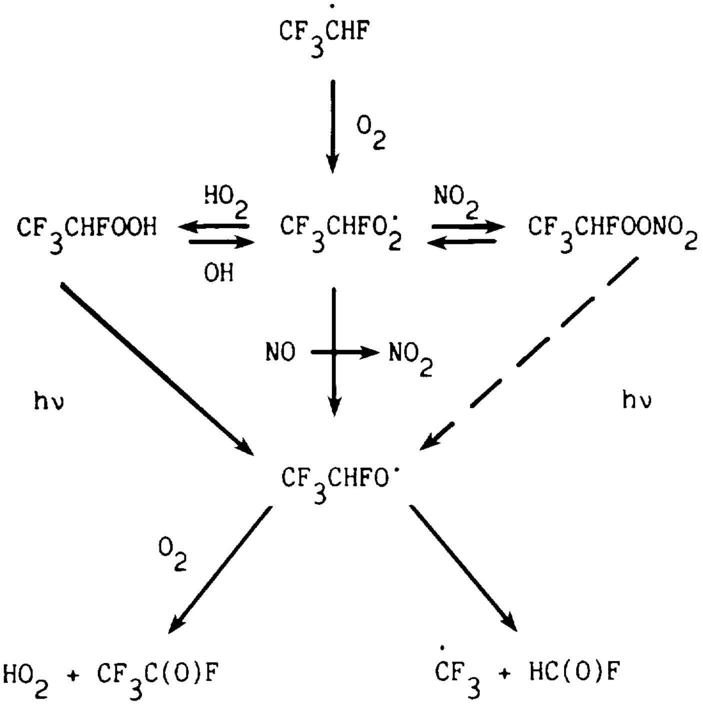
G. HC(O)F. The expected tropospheric removal routes for formyl fluoride are photolysis, reaction with the OH radical and wet deposition. Reaction with the OH radical

$$OH + HC(O)F \rightarrow H_2O + FCO$$

is calculated (Atkinson, 1987) to have a rate constant at room temperature of $\sim 1.6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and the magnitude of this rate constant is reasonably consistent (being high, in fact) with the C-H bond strength of ~102 kcal mol^{-1} in HC(O)F. An OH radical reaction rate constant of this magnitude leads to a lifetime of HC(O)F with respect to OH radical reaction of ~10 days. Photolysis is also expected to be slow in the troposphere (due to the high C-H bond dissociation energy), although no experimental data are available. This leaves wet deposition with subsequent hydrolysis to HF as the most likely tropospheric removal process.

H. $\dot{C}F_3$. The reactions of this radical are dealt with in Section 2.9 below.

The expected reaction scheme in the troposphere for the $CF_3\dot{C}HF$ radical is shown below



2.7. The $CHF_2\dot{C}H_2$ Radical formed from HFC-152a (CHF_2CH_3).

The expected reactions of the $CHF_2\dot{C}H_2$ radical are essentially identical to those of the $CF_2Cl\dot{C}H2$ and $CFCl_2\dot{C}H_2$ radicals discussed above in Sections 2.2. and 2.3. The fate of the resulting haloalkoxy radical $CHF_2CH_2O^{\cdot}$ needs to be considered, as follows.

A. $CHF_2CH_2O^{\cdot}$. The reactions of this radical which need to be considered are,

$$CHF_2CH_2O^{\cdot} + O_2 \rightarrow CHF_2CHO + HO_2 \tag{a}$$

$$CHF_2CH_2O^{\cdot} \rightarrow \dot{C}HF_2 + HCHO \tag{b}$$

with H atom elimination to yield CHF_2CHO + H being of no importance. The sum of the heats of formation of the products from reactions (a) and (b) are: $CHF_2CHO + HO_2$ from reaction (a), -134.1 kcal mol^{-1} [using the bond additivity method of Benson (1976) to calculate $\Delta H_f(CHF_2CHO)$]; and $\dot{C}HF_2$ + HCHO from reaction (b), -84.2 kcal mol^{-1} [$\Delta H_f(\dot{C}HF_2)$ being obtained from McMillen and Golden (1982) and Pickard and Rodgers (1983)]. The difference in the these heats of formation of the products of 50 kcal mol^{-1} indicates that reaction (a) to form $CHF_2CHO + HO_2$ will be the totally dominant reaction pathway for the $CHF_2CH_2\dot{O}$ radical throughout the troposphere, as expected from the discussion in Section 4.3.

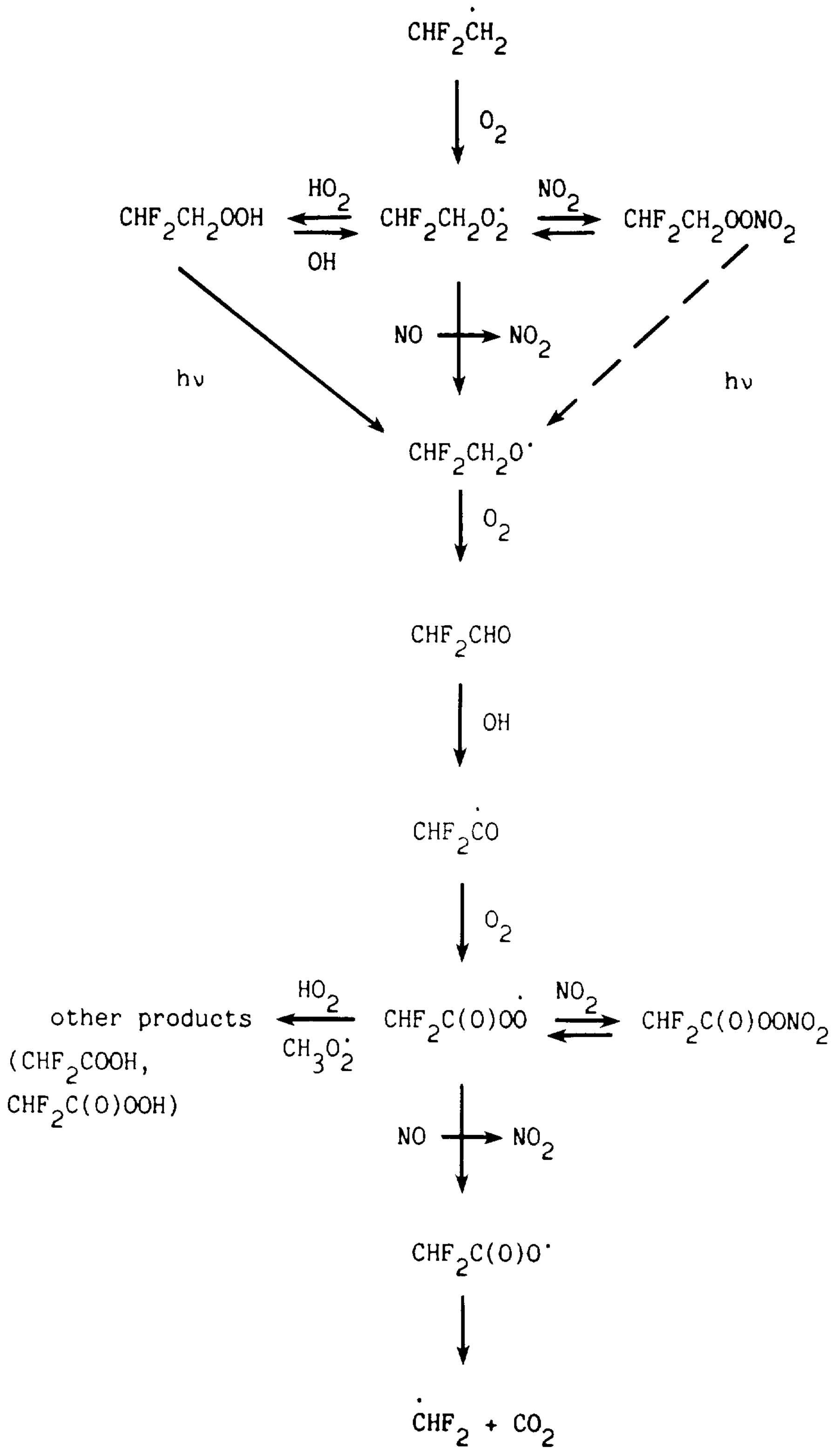
B. CHF_2CHO. Difluoroacetaldehyde will react in a similar manner to CF_2ClCHO and $CFCl_2CHO$ discussed above in Sections 2.2 and 2.3. The OH radical reaction

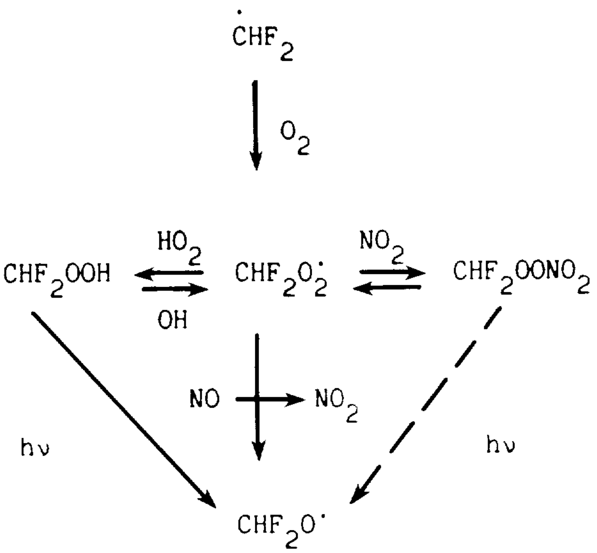
$$OH + CHF_2CHO \rightarrow H_2O + CHF_2\dot{C}O$$

will proceed as shown, with an estimated rate constant of $\sim 1.6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature (Atkinson, 1987). The reaction pathway involving H atom abstraction from the $-CHF_2$ group to form the $\dot{C}F_2CHO$ radical has an estimated room temperature rate constant of $\sim 1.4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1987), and is hence of negligible importance. It should be noted that no data are available concerning the photolysis of CHF_2CHO under tropospheric conditions.

The subsequent reactions of the $CHF_2\dot{C}O$ radical will be as discussed in Section 2.2 above [H atom abstraction by the OH radical from the $-CHF_2$ group will be of no importance during the subsequent reactions of this $CHF_2\dot{C}O$ radical]. The reaction scheme for the $CHF_2\dot{C}H_2$ radical is thus as shown below.

The $CHF_2C(O)O^{\cdot}$ radical formed in the final stages of this reaction sequence is expected to rapidly unimolecularly decompose to CO_2 plus the $\dot{C}HF_2$ radical. Under tropospheric conditions, this $\dot{C}HF_2$ radical will undergo the sequence of reactions generally similar to those discussed above in Section 2.4 for the $\dot{C}F_2Cl$ radical, to yield the $CHF_2O^{\cdot}$ radical. The reactions of this radical are as follows.


$CHF_2\dot{C}H_2$
O_2
CHF_2CH_2OOH
HO_2
OH
$CHF_2CH_2O_2^{\cdot}$
NO_2
$CHF_2CH_2OONO_2$
NO
NO_2
hν
hν
$CHF_2CH_2O^{\cdot}$
O_2
CHF_2CHO
OH
$CHF_2\dot{C}O$
O_2
other products
(CHF_2COOH,
$CHF_2C(O)OOH$)
HO_2
$CH_3O_2^{\cdot}$
$CHF_2C(O)O\dot{O}$
NO_2
$CHF_2C(O)OONO_2$
NO
NO_2
$CHF_2C(O)O^{\cdot}$
$\dot{C}HF_2 + CO_2$



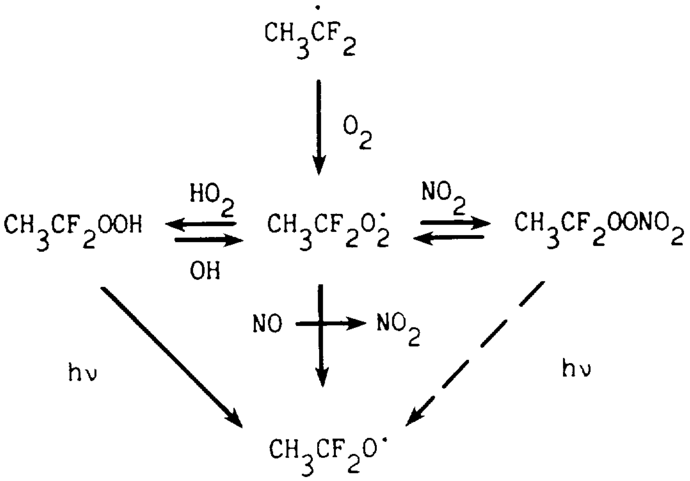
C. $\underline{CHF_2O^{\cdot}}$. Reaction with O_2 will be the only important reaction pathway

$$CHF_2O^{\cdot} + O_2 \rightarrow COF_2 + HO_2$$

under tropospheric conditions (Table 8). The tropospheric loss processes for COF_2 have been dealt with in Section 2.4 above.

2.8. The $CH_3\dot{C}F_2$ Radical formed from HFC-152a (CHF_2CH_3).

The reactions of the $CH_3\dot{C}F_2$ radical in the troposphere will be generally similar to those of the $CF_3\dot{C}Cl_2$ and $CF_3\dot{C}FCl$ radicals dealt with in Sections 2.1 and 2.5 above. The reactions of the $CH_3\dot{C}F_2$ radical leading to the formation of the $CH_3CF_2O^{\cdot}$ radical are then as shown below



The reactions of $CH_3CF_2OONO_2$ and CH_3CF_2OOH with the OH radical by H atom abstraction from the $-CH_3$ group are calculated to be of negligible importance, with a room temperature rate constant for this

H atom abstraction process of $< 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} being expected (Atkinson, 1987). The subsequent reactions of the haloalkoxy radical $CH_3CF_2O^{\cdot}$ need to be considered, as discussed below.

A. $CH_3CF_2O^{\cdot}$. The reactions of this radical which can occur are

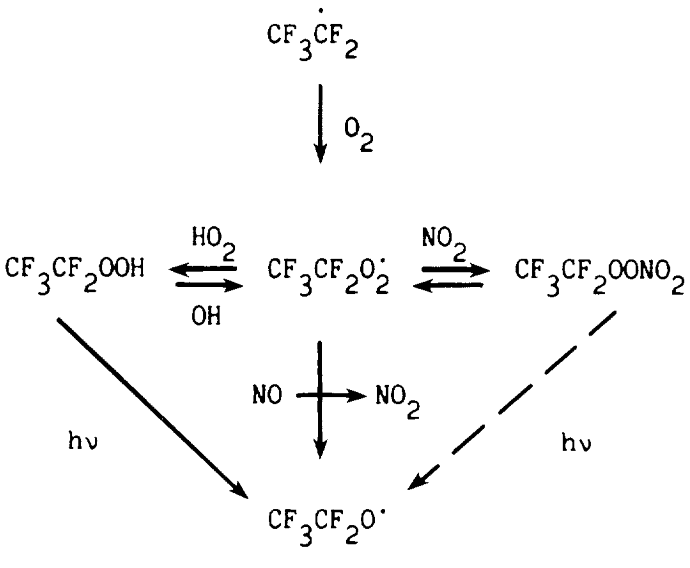
$$CH_3CF_2O^{\cdot} \rightarrow \dot{C}H_3 + COF_2 \tag{a}$$

$$CH_3CF_2O^{\cdot} \rightarrow CH_3C(O)F + F \tag{b}$$

Reaction pathway (a) is calculated to be 32 kcal mol^{-1} more exothermic than pathway (b), and hence the unimolecular decomposition of the $CH_3CF_2\dot{O}$ radical to $\dot{C}H_3$ + COF_2 will totally dominate as a loss process. This conclusion is then in agreement with the discussion in Section 4.3.B below. The tropospheric loss processes of COF_2 have been dealt with in Section 2.4 above. The methyl radical will react as discussed in Section 4 below and by Ravishankara (1988), to yield compounds such as CH_3OOH, CH_3OONO_2 and HCHO, which react further to ultimately form CO, CO_2 and H_2O.

2.9. The $CF_3\dot{C}F_2$ Radical formed from HFC-125 (CF_3CHF_2).

The tropospheric reactions of this radical are analogous to those of the $CF_3\dot{C}Cl_2$, $CF_3\dot{C}FCl$ and $CH_3\dot{C}F_2$ radicals dealt with in Sections 2.1, 2.5 and 2.8, respectively. The reaction sequence leading to the formation of the $CF_3CF_2O^{\cdot}$ haloalkoxy radical will be as shown below.



A. $CF_3CF_2\dot{O}$. The reactions of the $CF_3CF_2O^{\cdot}$ radical are expected to be (reaction with NO and NO_2 are expected to be too slow at the NO and NO_2 concentrations encountered in the troposphere):

$$CF_3CF_2O^{\cdot} \rightarrow \dot{C}F_3 + COF_2 \tag{a}$$

$$CF_3CF_2O^{\cdot} \rightarrow CF_3C(O)F + F \tag{b}$$

Reaction pathway (a) is calculated to be 33.5 kcal mol^{-1} more exothermic than pathway (b), and hence unimolecular decomposition of the $CF_3CF_2O^{\cdot}$ radical to yield $\dot{C}F_3$ + COF_2 will be totally dominant. This conclusion is in agreement with the general discussion in Section 4.3.B below.

The tropospheric fate of COF_2 has been dealt with above in Section 2.4.

B. $\dot{C}F_3$. As discussed in Section 4, reaction with O_2 will be the sole tropospheric reaction of the $\dot{C}F_3$ radical

$$\dot{C}F_3 + O_2 \xrightarrow{M} CF_3O_2^{\cdot}$$

and the rate constant data for this reaction are given in Table 2. The reactions of the $CF_3O_2^{\cdot}$ radical with NO, NO_2 and the HO_2 radical, and the reactions of the CF_3OONO_2 and CF_3OOH species formed, are expected to be totally analogous to those of the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals dealt with in Section 2.4 above. The rate constants for the reactions of the $CF_3O_2^{\cdot}$ radicals with NO and NO_2 are given in Tables 3 and 4 (Section 4), respectively, and the rate data for the thermal decomposition of CF_3OONO_2 are expected to be similar to those for $CF_2ClOONO_2$, $CFCl_2OONO_2$ and CCl_3OONO_2 given in Table 10 (Caralp et al., 1988).

C. Reaction of $CF_3O_2^{\cdot}$ with NO. The rate constant data for this reaction are given in Table 3. Dognon et al. (1985) observed a formation yield of NO_2 from this reaction of 1.5 ± 0.5, strongly suggesting that the reaction proceeds by

$$CF_3O_2^{\cdot} + NO \rightarrow CF_3O^{\cdot} + NO_2$$

as for the other halomethyl peroxy radicals. This reaction is exothermic by 9 kcal mol^{-1} (Batt and Walsh, 1983; IUPAC, 1989).

However, from a low temperature matrix study of the reaction of the $\dot{C}F_3$ radical with O_2 in the presence of NO, Clemitshaw and Sodeau (1987) obtained product data showing that under their experimental conditions, the reaction of $CF_3O_2^{\cdot}$ radicals with NO proceeded, presumably through the expected intermediate CF_3OONO, to yield COF_2 and FNO_2

$$CF_3O_2^{\cdot} + NO \rightarrow COF_2 + FNO_2$$

which is exothermic by 38 kcal mol^{-1} (Batt and Walsh, 1983; IUPAC, 1989).

If, as expected, $CF_3O^{\cdot}$ is formed from the reaction of the $CF_3O_2^{\cdot}$ radical with NO, as well as from the photolysis of CF_3OOH, the subsequent reactions of this radical under tropospheric conditions are not understood. F atom elimination to yield COF_2 + F is endothermic by 24 kcal mol^{-1} and is hence extremely slow (Table 8). The expected reactions of the $CF_3O^{\cdot}$ radical would then be with NO

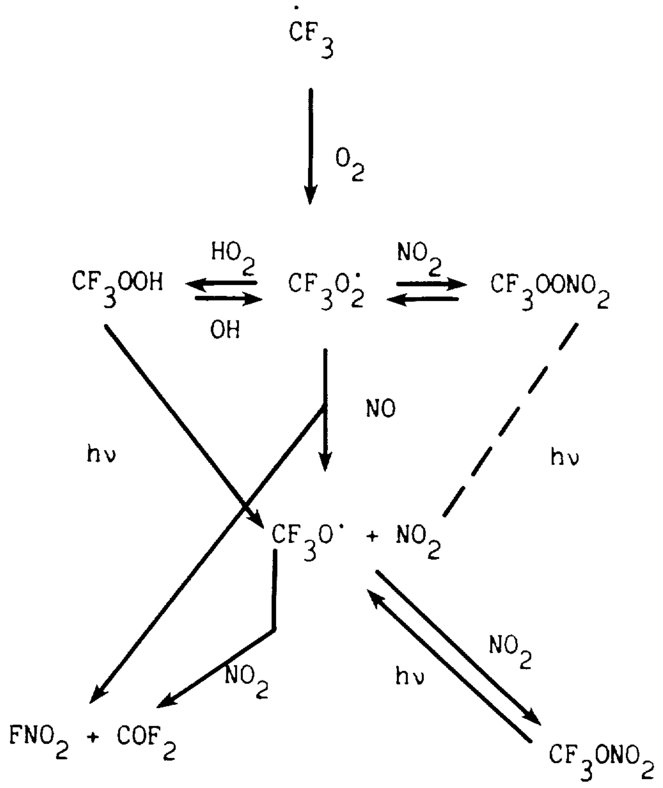
$$CF_3OO^{\cdot} + NO \xrightarrow{M} CF_3ONO$$

to form the nitrite, which is expected to rapidly photolyze back to the $CF_3O^{\cdot}$ radical and NO, and with NO_2

$$CF_3O^{\cdot} + NO_2 \xrightarrow{M} CF_3ONO_2$$

to form the nitrate. The tropospheric chemistry of this nitrate is not known, but unimolecular decomposition to COF_2 + FNO_2, photolysis and wet and/or dry deposition are the likely tropospheric removal pathways.

However, photolysis of CF_3Br in the presence of O_2 gave rise to the formation of COF_2 with a unit formation yield (Withnall and Sodeau, 1986), showing that under the conditions employed the $\dot{C}F_3$ radicals ultimately formed only COF_2. These data then suggest that the $CF_3O_2^{\cdot}$ radicals formed from the $\dot{C}F_3$ radical reaction with O_2 do yield COF_2. Possible tropospheric reactions of the $\dot{C}F_3$ radical are shown schematically below



Clearly, the reactions of the $CF_3O^{\cdot}$ radical under tropospheric conditions need to be investigated, and the formation of $CF_3O^{\cdot}$ from the reaction of $CF_3O_2^{\cdot}$ with NO confirmed. While it may be anticipated that the final product of the tropospheric degradation of the $\dot{C}F_3$ radical is COF_2, the formation of other product species cannot be ruled out.

3. CONCLUSIONS

The expected gas-phase reactions of the haloalkyl radicals formed from the potential alternative fluorocarbons have been outlined and discussed in the Sections above. As noted in the Introduction, only for the $\dot{C}F_2Cl$ radical formed from HCFC-22 are experimental data concerning its tropospheric reactions available. For the remaining radicals formed from the initial OH radical reactions with the HCFCs and HFCs, the reaction sequences operating in the troposphere must to a very large extent be deduced by analogy. This leads to uncertainties concerning the proposed reaction mechanisms, which can only be minimized by experimental investigations of the kinetics and, especially, the products of the individual reaction steps under realistic temperature, pressure and diluent gas conditions. In particular, the experimental investigation of the products of the reactions of the various haloalkoxy ($R\dot{O}$) radicals with NO would remove large areas of uncertainty concerning the ultimate products formed from these HCFCs and HFCs in the troposphere.

Additionally, the absorption cross-sections and photodissociation quantum yields and products (under atmospheric conditions) for the various acetyl halides ($CX_3C(O)Y$) and halogenated acetaldehydes (CX_3CHO) need to be determined. A quantitative understanding of physical removal processes for several of the product species, including the hydroperoxides, peroxynitrates, carbonyl halides, acetyl halides and halogenated acetaldehydes, is also necessary before the lifetimes of these species in the troposphere, the potential for transport of these species to the stratosphere, and the impact of the HFCs and HCFCs on the ecosystem, can be completely assessed.

4. APPENDIX A: TROPOSPHERIC REACTIONS SUBSEQUENT TO ALKYL AND HALOALKYL RADICAL FORMATION

4.1. Alkyl and Haloalkyl ($\dot{R}$) Radicals

Under tropospheric conditions, alkyl and haloalkyl ($\dot{R}$) radicals react rapidly with O_2 to form the corresponding peroxy alkyl ($R\dot{O}_2$) radicals.

$$\dot{R} + O_2 \xrightarrow{M} R\dot{O}_2$$

For the methyl and ethyl radicals and the C_1 haloalkyl radicals, the rate constants at room temperature for these reactions with O_2 are in the fall-off region between second and third-order kinetics below atmospheric pressure. The low and high pressure rate constants k_0 and k_∞ and the factor F at 298 K are given in Table 2, together with calculated rate constants at 298 K and 760 Torr total pressure and at 220 K and 100 Torr total pressure (temperatures and pressures corresponding approximately to the lower and upper levels of the troposphere, respectively). For the C_4 and C_5 alkyl radicals, rate constants have been determined only at 1-4 Torr total pressure, and it is expected that these measured rate constants are close to the high pressure values.

The kinetic data presented in Table 2 show that the rate constants for the C_1 alkyl and haloalkyl radicals are within a factor of $\sim$2-3 of the limiting high-pressure rate constant k_∞ at the temperatures and pressures applicable to the troposphere. The rate constants for the $\geq C_2$ haloalkyl radicals are expected to be closer to the high pressure limit under these conditions and, based upon the data in Table 2, the alkyl and haloalkyl radicals will have bimolecular rate constants for reaction with O_2 of $>5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} throughout the troposphere. Since the O_2 concentration in the troposphere is $\geq 10^{18}$ molecule cm^{-3}, the lifetime of the alkyl and haloalkyl radicals are $<2 \times 10^{-6}$ s and reaction with O_2 is the only tropospheric loss process for alkyl and haloalkyl radicals. It should be noted that, to date, there is no evidence that 1,2-migration of H or halogen atoms occurs following initial OH radical [or Cl atom (Nelson et al., 1984) reaction with the haloalkanes.

Table 2. Low- and high-pressure rate constants k_0 and k_∞ and the broadening coefficient F (at 298 K), together with bimolecular rate constants k at 300 K, 760 Torr total pressure and 220 K, 100 Torr total pressure, for the gas-phase reactions of alkyl and haloalkyl ($R^{\cdot}$) radicals with O_2

				10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})^a		
$R^{\cdot}$	k_0(cm^6 $molecule^{-2}$ s^{-1})	k_∞(cm^3 $molecule^{-1}$ s^{-1})	F (298 K)	300 K 760 Torr	220 K 100 Torr	Reference
$\dot{C}H_3$	8×10^{-31} $(T/300)^{-(3.3 \pm 1)}$	2.2×10^{-12} $(T/300)^{1 \pm 1}$	0.27	1.0	0.76	IUPAC (1989)
$C_2H_5^{\cdot}$	2.0×10^{-28} $(T/300)^{-(3.8 \pm 1)}$	5×10^{-12}	0.7	4.8	4.8	IUPAC (1989)
$CH_3CH_2\dot{C}H_2$		6×10^{-12}		6		IUPAC (1989)
$(CH_3)_2\dot{C}H$		1.5×10^{-11}		15		IUPAC (1989)
$CH_3CH_2CH_2\dot{C}H_2$		$(7.5 \pm 1.4) \times 10^{-12 b}$ (room temperature)				Lenhardt et al. (1980)
$CH_3CH_2\dot{C}HCH_3$		$(1.66 \pm 0.22) \times 10^{-11 b}$ (room temperature)				Lenhardt et al. (1980)
$(CH_3)_3\dot{C}$		$(2.34 \pm 0.39) \times 10^{-11 b}$ (room temperature)				Lenhardt et al. (1980)
$(CH_3)_2CH\dot{C}H_2$		$(2.9 \pm 0.7) \times 10^{-12 b}$ (298 ± 2 K)				Wu and Bayes (1986)
$(CH_3)_3C\dot{C}H_2$		$(1.6 \pm 0.3) \times 10^{-12 b}$ (298 ± 2 K)				Wu and Bayes (1986)
		2.1×10^{-12} $(T/300)^{-2.1 b}$ (266-374 K)				Xi et al. (1988)
$\dot{C}F_3$	1.9×10^{-29} $(T/300)^{-(4.7 \pm 1)}$	1×10^{-11}	0.4-0.5	7.9	8.2	IUPAC (1989)
$\dot{C}FCl_2$	5×10^{-30} $(T/300)^{-(4 \pm 2)}$	6×10^{-12}	0.6	4.7	4.7	IUPAC (1989)
$\dot{C}Cl_3$	1.5×10^{-30} $(T/300)^{-(4 \pm 2)}$	5×10^{-12}	0.25	2.0	2.0	IUPAC (1989)

a Calculated from fall-off expression.

b Rate constants obtained at 1-4 Torr total pressure; expected to be close to the high pressure limit.

For the reactions of alkyl radicals with O_2 in the fall-off region, the activated $RO_2^{\cdot}$ radical can decompose to the alkene and the HO_2 radical

$$\begin{tikzcd} R^{\cdot} + O_2 = & {[RO_2^{\cdot}]^*} \arrow[r] \arrow[d, "M"] & HO_2 + \text{alkene} \\ & RO_2^{\cdot} & \end{tikzcd}$$

in addition to back-decomposition to the reactants (Slagle et al., 1984, 1985; McAdam and Walker, 1987). Hence, at the high pressure limit peroxy radical formation is expected to be the sole reaction process.

4.2. Alkyl Peroxy and Haloalkyl Peroxy ($RO_2^{\cdot}$) Radicals

Under tropospheric conditions, $RO_2^{\cdot}$ radicals are expected to react with NO, NO_2, HO_2 radicals, $RO_2^{\cdot}$ radicals and acyl peroxy ($RCO_3^{\cdot}$) radicals, with the reaction with $RO_2^{\cdot}$ radicals potentially including self-reaction as well as reaction with other alkyl peroxy radicals. The relative importance of these reactions as a loss process for $RO_2^{\cdot}$ radicals depends on the rate constants for the individual reactions and the concentrations of NO, NO_2, HO_2 radicals and the various $RO_2^{\cdot}$ and $RCO_3^{\cdot}$ radicals. These reactions are dealt with below.

A. Reaction with NO. The available rate constant data for the gas-phase reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals with NO, obtained using absolute measurement techniques, are given in Table 3. The rate constants of Adachi and Basco (1979a, 1982) are suspect due to possible interfering absorptions of the product species (Ravishankara et al., 1981). The rate constant of Plumb et al. (1982) for $C_2H_5O_2^{\cdot}$ is similar to that recommended by NASA (1987) and IUPAC (1989) for $CH_3O_2^{\cdot}$, leading to the expectation (Atkinson and Lloyd, 1984; Atkinson, 1989a) that the rate constants for the reactions of alkyl peroxy radicals with NO are identical to that for $CH_3O_2^{\cdot}$:

$$k(RO_2^{\cdot} + NO) = 4.2 \times 10^{-12} e^{180/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ (R = \text{alkyl})$$

The rate constants for the reactions of the C_1 haloalkyl peroxy radicals with NO are approximately a factor of two higher at room temperature.

The reaction of $CH_3O_2^{\cdot}$ with NO proceeds by

$$CH_3O_2^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2$$

(Pate et al., 1974; Ravishankara et al., 1981; Zellner et al., 1986; NASA, 1987), and Plumb et al. (1982) have shown that the reaction of $C_2H_5O_2^{\cdot}$ radicals with NO yields NO_2 with a yield of ≥ 0.80. However, for the larger alkyl peroxy radicals, the reaction pathway

$$RO_2^{\cdot} + NO \rightarrow [ROONO] \rightarrow RONO_2$$

Table 3. Rate constants k at room temperature and temperature-dependent expressions for the gas-phase reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals with NO

$RO_2^{\cdot}$	k(cm³ molecule⁻¹ s⁻¹)	10^{12} x k (cm³ molecule⁻¹ s⁻¹)	at T (K)	Reference
$CH_3O_2^{\cdot}$	$4.2 \times 10^{-12} e^{(180 \pm 180)/T}$	7.6	298	NASA (1987), IUPAC (1989)
$C_2H_5O_2^{\cdot}$		2.66±0.17	Room Temperature	Adachi and Basco (1979a)
		8.9±3.0	298	Plumb et al. (1982)
$(CH_3)_2CHO_2^{\cdot}$		3.5±0.4	Room Temperature	Adachi and Basco (1982)
$(CH_3)_2CO_2^{\cdot}$		>1	298	Anastasi et al. (1978)
$CF_3O_2^{\cdot}$	$1.6 \times 10^{-11} (T/300)^{-1.2}$	16	298	IUPAC (1989)
$CF_2ClO_2^{\cdot}$	$1.6 \times 10^{-11} (T/300)^{-1.5}$	16	298	IUPAC (1989)
$CFCl_2O_2^{\cdot}$	$1.5 \times 10^{-11} (T/300)^{-1.3}$	15	298	IUPAC (1989)
$CCl_3O_2^{\cdot}$	$1.8 \times 10^{-11} (T/300)^{-1.0}$	18	298	IUPAC (1989)

becomes important (see, for example, Atkinson et al., 1987; Harris and Kerr, 1989; Carter and Atkinson, 1989), with the alkyl nitrate yield increasing with the number of carbon atoms at room temperature and atmospheric pressure for the reactions of secondary alkyl peroxy radicals with NO (Atkinson et al., 1982, 1987; Carter and Atkinson, 1989). For a given alkyl peroxy radical the formation of the alkyl nitrate is pressure and temperature dependent, with the formation yield increasing with increasing pressure and decreasing temperature (Atkinson et al., 1987; Harris and Kerr, 1989; Carter and Atkinson, 1989). The calculated yield of ethyl nitrate from the $C_2H_5O_2^{\cdot}$ + NO reaction is ~0.02 at 300 K and 760 Torr total pressure and ~0.006 at 220 K and 100 Torr total pressure. The data of Lesclaux and Caralp (1984) and Dognon et al. (1985) for the reactions of the $CF_3O_2^{\cdot}$, $CF_2ClO_2^{\cdot}$, $CFCl_2O_2^{\cdot}$ and $CCl_3O_2^{\cdot}$ radicals suggest that the major reaction pathway is

$$CX_3O_2^{\cdot} + NO \rightarrow CX_3\dot{O} + NO_2 \ (X = F \text{ and/or } Cl)$$

However, no direct measurements are available concerning whether or not the haloalkyl nitrates are formed in similar yield from the reactions of the haloalkyl peroxy radicals with NO as they are from the alkyl peroxy radical reactions.

B. Reaction with NO_2. The rate constant data obtained by absolute methods for the reactions of alkyl peroxy and haloalkyl peroxy radicals with NO_2 are given in Table 4. The studies of Sander and Watson (1980) and Ravishankara et al. (1980) for $CH_3O_2^{\cdot}$ and of Lesclaux and Caralp (1984), Lesclaux et al. (1986) and Caralp et al. (1988) for the $CX_3O_2^{\cdot}$ radicals (X = F and/or Cl) show that at room temperature

Table 4. Low- and high-pressure rate constants k_0 and k_∞ and the broadening coefficient F (at 298 K), together with bimolecular rate constants k at 300 K, 760 Torr total pressure and 220 K, 100 Torr total pressure, for the gas-phase reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals with NO_2

				10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})[a]		
$\dot{R}$	k_0(cm^6 $molecule^{-2}$ s^{-1})	k_∞(cm^3 $molecule^{-1}$ s^{-1})	F (298 K)	300 K 760 Torr	220 K 100 Torr	Reference
$CH_3O_2^{\cdot}$	2.3×10^{-30} $(T/300)^{-(4.0 \pm 2)}$	8×10^{-12}	0.4	4.1	4.0	IUPAC (1989)
$C_2H_5O_2^{\cdot}$		$(1.25 \pm 0.07) \times 10^{-12}$[b] (room temperature)				Adachi and Basco (1979b)
$(CH_3)_2CHO_2^{\cdot}$		$(5.65 \pm 0.17) \times 10^{-12}$[b] (room temperature)				Adachi and Basco (1982)
$(CH_3)_3CO_2^{\cdot}$		$\geq 5 \times 10^{-13}$ (298 K)				Anastasi et al. (1978)
$CF_3O_2^{\cdot}$	2.7×10^{-29} $(T/300)^{-(5 \pm 2)}$	9×10^{-12} $(T/300)^{-(0.7 \pm 1)}$	0.49	7.6	9.6	IUPAC (1989)
$CF_2ClO_2^{\cdot}$	4.0×10^{-29} $(T/300)^{-(5 \pm 2)}$	1.0×10^{-11} $(T/300)^{-(0.7 \pm 1)}$	0.45	8.4	11	IUPAC (1989)
$CFCl_2O_2^{\cdot}$	5.5×10^{-29} $(T/300)^{-(5 \pm 1)}$	8.3×10^{-12} $(T/300)^{-(0.7 \pm 1)}$	0.42	7.1	9.0	IUPAC (1989)
$CCl_3O_2^{\cdot}$	9.2×10^{-29} $(T/300)^{-(6 \pm 2)}$	1.5×10^{-11} $(T/300)^{-(0.3 \pm 1)}$	0.32	12	14	IUPAC (1989)

a Calculated from fall-off expressions.

b Assumed to be erroneously low due to neglect of absorption of RO_2NO_2 products.

these reactions are in the fall-off regime between second- and third-order kinetics below atmospheric pressure, and this is in agreement with the thermal decomposition data for the peroxynitrates (IUPAC, 1989; see below). The available limiting low- and high-pressure rate constants k_0 and k_∞ and the broadening factor F (at 298 K) are given in Table 4, together with the calculated rate constants at 300 K and 760 Torr total pressure and at 220 K and 100 Torr total pressure. Under tropospheric conditions the bimolecular rate constants for the reactions of the C_1 alkyl peroxy and haloalkyl peroxy radicals with NO_2 are within a factor of ~2 of the high pressure rate constant k_∞, and the rate constants for the C_2 haloalkyl peroxy radicals will be still closer to the high-pressure limit. From the data given in Table 4, the rate constants k_∞ for the reactions of $RO_2^{\cdot}$ radicals with NO_2 are,

$$k_\infty(RO_2^{\cdot} + NO_2) \cong 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

approximately independent of temperature over the range 200-300 K.

These reactions of the alkyl peroxy and haloperoxy radicals with NO_2 proceed solely by addition to form the alkyl and haloalkyl peroxynitrates (Niki et al., 1978, 1979; Edney et al., 1979; Morel et al., 1980; Reimer and Zabel, 1986).

$$RO_2^{\cdot} + NO_2 \overset{M}{\rightleftarrows} ROONO_2$$

C. Reaction with HO_2 Radicals. Absolute rate constants for the reactions of alkyl peroxy and haloalkyl peroxy radicals with the HO_2 radical are available only for $CH_3O_2^{\cdot}$ and $C_2H_5O_2^{\cdot}$, and these data are given in Table 5. The IUPAC (1989) recommended rate constant expressions for these reactions are $k(CH_3O_2^{\cdot} + HO_2) = 1.7 \times 10^{-13} e^{1000/T}$ cm³ molecule⁻¹ s⁻¹ (4.9×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K) and $k(C_2H_5O_2^{\cdot} + HO_2) = 6.5 \times 10^{-13} e^{650/T}$ cm³ molecule⁻¹ s⁻¹ (5.8×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K). The measured rate constants for these reactions are independent of pressure (IUPAC, 1989). Assuming that the rate constants for all $RO_2^{\cdot} + HO_2$ reactions are similar to those for these two reactions, a room temperature rate constant of

$$k(RO_2^{\cdot} + HO_2) \cong 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

and

$$k(RO_2^{\cdot} + HO_2) \cong 3.4 \times 10^{-13} e^{800/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

has been recommended by Atkinson (1989a) for all alkyl peroxy radicals. Clearly, a much wider data base is necessary to test this assumption since, for example, Niki et al. (1980) have obtained evidence from a product study of the Cl atom reactions with CH_3Cl and CH_2Cl_2 that the room temperature rate constant for the reaction of the HO_2 radical with $CH_2ClO_2^{\cdot}$ is significantly slower than the corresponding HO_2 radical reaction rate constant for the $CHCl_2O_2^{\cdot}$ radical.

These reactions have been assumed to proceed by the pathway.

$$RO_2^{\cdot} + HO_2 \rightarrow ROOH + O_2$$

Table 5. Absolute rate constants for the reactions of alkyl peroxy ($RO_2^{\cdot}$) radicals with the HO_2 radical

$RO_2^{\cdot}$	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Reference
$CH_3O_2^{\cdot}$	8.5 ± 1.2	274	Cox and Tyndall (1980)
	6.5 ± 1.0	298	
	3.5 ± 0.5	338	
	3.5[a]	298	McAdam et al. (1987)
	2.9 ± 0.4	298	Kurylo et al. (1987)
	6.8 ± 0.5	228	Dagaut et al. (1988a)
	5.5 ± 0.3	248	
	4.1 ± 0.3	273	
	2.4 ± 0.5	340	
	2.1 ± 0.3	380	
	5.4 ± 1.1	300	Jenkin et al. (1988)
	6.8 ± 0.9	303	
$C_2H_5O_2^{\cdot}$	6.3 ± 0.9	295	Cattell et al. (1986)
	7.3 ± 1.0	248	Dagaut et al. (1988b)
	6.0 ± 0.5	273	
	5.3 ± 1.0	298	
	3.4 ± 1.0	340	
	3.1 ± 0.5	380	

a Revised value as cited by Kurylo et al. (1987), Dagaut et al. (1988a) and Jenkin et al. (1988).

However, Jenkin et al. (1988) observed the formation of HDO from the reaction of $CD_2O_2^{\cdot}$ with the HO_2 radical, and postulated the additional reaction pathway,

$$CD_2O_2^{\cdot} + HO_2 \rightarrow DCDO + HDO + O_2$$

with this channel contributing ~40% of the overall reaction at room temperature.

D. Reaction with Alkyl and Haloalkyl Peroxy ($RO_2^{\cdot}$) and Acyl Peroxy ($RCO_3^{\cdot}$) Radicals. The available absolute rate constant data for the self-reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals and for their reactions with other alkyl peroxy and acyl peroxy radicals are given in Table 6. Clearly, the majority of the data concern the self-reactions of the alkyl peroxy radicals, with the only data for cross-combination reactions being for the reactions of the $CH_3O_2^{\cdot}$ radical with tert-butyl peroxy and acetyl peroxy radicals. Since the tropospheric formation rates of the haloalkyl peroxy radicals being dealt with in this assessment will be low (because of the low rate constants for the reactions of the OH radical with the HCFCs and

HFCs in question), self-reactions of these haloalkyl peroxy radicals will be of minimal importance. It is expected that the dominant $RO_2^{\cdot}$ or $RCO_3^{\cdot}$ radical with which these haloalkyl peroxy radicals will react with will be the $CH_3O_2^{\cdot}$ radical, and the limited data available (Table 6) suggest a rate constant for the reaction of the $CH_3O_2^{\cdot}$ radical with other $RO_2^{\cdot}$ radicals of

$$k(RO_2^{\cdot} + CH_3O_2^{\cdot}) \cong 2 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}$$

with an uncertainty of ~ ± a factor of 5.

Table 6. Rate constants, $k = Ae^{-B/T}$, for the gas-phase combination reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals with $RO_2^{\cdot}$ and $RCO_3^{\cdot}$ radicals

Reaction	10^{13} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{13} x k (298 K) (cm^3 molecule^{-1} s^{-1})	Reference
$CH_3O_2^{\cdot} + CH_3O_2^{\cdot}$	1.7	-220 ± 220	3.6	IUPAC (1989)
$C_2H_5O_2^{\cdot} + C_2H_5O_2^{\cdot}$	1.2	110^{+300}_{-100}	0.86	IUPAC (1989)
$CH_3CH_2CH_2O_2^{\cdot} + CH_3CH_2CH_2O_2^{\cdot}$			3	IUPAC (1989)
$(CH_3)_2CHO_2^{\cdot} + (CH_3)_2CHO_2^{\cdot}$	16	2200 ± 300	0.01	IUPAC (1989)
$(CH_3)_3CO_2^{\cdot} + (CH_3)_3CO_2^{\cdot}$	1700	4775	0.00019	Kirsch et al. (1978)
$CH_3O_2^{\cdot} + (CH_3)_3CO_2^{\cdot}$			1.0 ± 0.5	Parkes (1975)
$CH_2ClCH_2O_2^{\cdot} + CH_2ClCH_2O_2^{\cdot}$	1.1	-1020 ± 170	35.7 ± 5.7	Dagaut et al. (1988c)
$CH_2ClO_2^{\cdot} + CH_2ClO_2^{\cdot}$	3.1	-735 ± 95	37.8 ± 4.5	Dagaut et al. (1988d)
$CH_2FO_2^{\cdot} + CH_2FO_2^{\cdot}$	3.3	-700 ± 100	30.7 ± 6.5	Dagaut et al. (1988d)
$CH_3O_2^{\cdot} + CH_3CO_3^{\cdot}$			110	IUPAC (1989)

These combination reactions of $RO_2^{\cdot}$ radicals can proceed by the reaction channels

$$R_2R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHO^{\cdot} + R_3R_4CHO^{\cdot} + O_2 \tag{a}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOH + R_3R_4CO + O_2 \tag{b}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOOCHR_3R_4 + O_2 \tag{c}$$

with channel (b) not being accessible for tertiary $RO_2^{\cdot}$ radicals. Product data are available for the self-reactions of $CH_3O_2^{\cdot}$, $C_2H_5O_2^{\cdot}$, $(CH_3)_2CHO_2^{\cdot}$ and $(CH_3)_3CO_2^{\cdot}$ radicals (Kirsch and Parkes, 1981; Niki et al., 1981, 1982; Anastasi et al., 1983; IUPAC, 1989). For the primary and secondary $RO_2^{\cdot}$ radicals, the room temperature rate constant ratios k_a/k and k_b/k (where $k = k_a + k_b + k_c$) are both ~0.5, with $k_c < 0.1$. For the reaction of the $(CH_3)_3CO_2^{\cdot}$ radical with the $CH_3O_2^{\cdot}$ radical, Parkes (1975) and Kirsch and Parkes (1981) also proposed that the operative reaction pathways were (a) and (b) above, with $k_a = k_b$ at around room temperature. However, Niki et al. (1980) concluded that reaction pathway (b) was of minor significance for the self-reaction of the $CHCl_2O_2^{\cdot}$ radical, and further product data are required for these $RO_2^{\cdot}$ radical reactions.

For the self-reaction of the tert-butyl peroxy radical, Kirsch and Parkes (1981) determined that $k_c/k = 0.12$ at 298 K, with this ratio decreasing rapidly with increasing temperature.

4.3. Reactions of Alkoxy and Haloalkoxy ($RO^{\cdot}$) Radicals

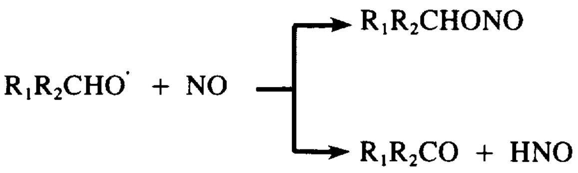
For the C_1 and C_2 haloalkoxy radicals involved in the tropospheric degradation reactions of the HCFCs and HFCs considered in this article, the reactions of concern are with O_2,

$$R_1R_2CHO^{\cdot} + O_2 \rightarrow R_1R_2CO + HO_2$$

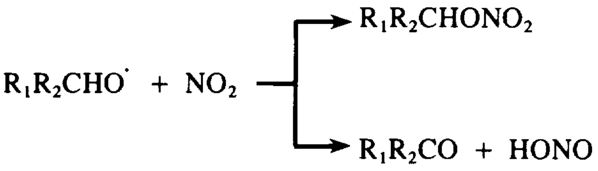
unimolecular decomposition,

$$R_1R_2CH\dot{O} \rightarrow R_1^{\cdot} + R_2CHO$$

and reaction with NO and NO_2.



$$R_1R_2CHO^{\cdot} + NO \rightarrow R_1R_2CHONO$$
$$R_1R_2CHO^{\cdot} + NO \rightarrow R_1R_2CO + HNO$$



$$R_1R_2CHO^{\cdot} + NO_2 \rightarrow R_1R_2CHONO_2$$
$$R_1R_2CHO^{\cdot} + NO_2 \rightarrow R_1R_2CO + HONO$$

A. Reaction with O_2. Absolute rate constants for the reactions of alkoxy radicals with O_2 are available only for the $CH_3O^{\cdot}$, $C_2H_5O^{\cdot}$ and $(CH_3)_2CHO^{\cdot}$ radicals, and the rate constant data obtained are given in Table 7. For the methoxy radical the rate constants of Gutman et al. (1982), Lorenz et al. (1985) and Wantuck et al. (1987) are in good agreement, and Atkinson (1989a) recommended that for temperatures ≤ 300 K (the Arrhenius plot exhibits marked curvature at temperatures >500 K).

$$k(CH_3O^{\cdot} + O_2) = 5.5 \times 10^{-14}\, e^{-1000/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

This recommended temperature expression is that of Lorenz et al. (1985), and is similar to the NASA (1987) and IUPAC (1989) recommendations of $k(CH_3O^{\cdot} + O_2) = 3.9 \times 10^{-14}\, e^{-900/T}\ cm^3\ molecule^{-1}\ s^{-1}$ and $7.2 \times 10^{-14}\, e^{-1080/T}\ cm^3\ molecule^{-1}\ s^{-1}$, respectively. Combining the rate constants of Gutman et al. (1982) at 296 and 353 K for the $C_2H_5O^{\cdot}$ radical with a preexponential factor of $3.7 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ leads to

$$k(RCH_2O^{\cdot} + O_2) = 3.7 \times 10^{-14}\, e^{-460/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

(Atkinson, 1989a). Similarly, the data of Balla et al. (1985) for the $(CH_3)_2CHO^{\cdot}$ radical can be combined with a preexponential factor of $1.8 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ to yield (Atkinson, 1989a)

Table 7. Absolute rate constants, k, for the gas-phase reactions of alkoxy ($RO^{\cdot}$) radicals with O_2

$RO^{\cdot}$	10^{15} x k (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
$CH_3O^{\cdot}$	<2	295	Sanders et al. (1980)
	4.7	413	Gutman et al. (1982)
	6.0	475	
	10.7	563	
	12.7	608	
	$55\ e^{-1000/T}$	298-450	Lorenz et al. (1985)
	1.9^a	298	
	$[1.5 \times 10^5\ e^{-6028/T} + 36\ e^{-880/T}]^b$	298-973	Wantuck et al. (1987)
	2.1	298	
$C_2H_5O^{\cdot}$	8.0	296	Gutman et al. (1982)
	9.8	353	
$(CH_3)_2CHO^{\cdot}$	$15.1\ e^{-196/T}$	294-384	Balla et al. (1985)
	7.8^a	298	

a Calculated from cited Arrhenius expressions.

b Stated fit to data of Gutman et al. (1982), Lorenz et al. (1985) and Wantuck et al. (1987).

$$k(R_1R_2CHO^{\cdot} + O_2) = 1.8 \times 10^{-14}\ e^{-260/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

These rate constant expressions for the $RCH_2O^{\cdot}$ and $R_1R_2CHO^{\cdot}$ alkoxy radicals are assumed to be applicable to haloalkoxy radicals. The reaction rate of primary and secondary $RO^{\cdot}$ radicals with O_2 at 298 K and 760 Torr total pressure of air are then essentially identical at 4.0 x 10^4 s^{-1}.

B. Alkoxy Radical Decomposition. Rate data for the decompositions of the methoxy, ethoxy and the C_1 haloalkoxy radicals are summarized in Table 8, together with the experimentally measured lower limits to the rate constants for several haloalkoxy radicals. The rate expressions for the chloroalkoxy radicals and the $CHF_2O^{\cdot}$ radical are those calculated by Rayez et al. (1987). The experimentally determined lower limits to the decomposition rate constants for the $CF_2ClO^{\cdot}$, $CFCl_2O^{\cdot}$ and $CHCl_2O^{\cdot}$ radicals are in good agreement with the calculated rates. The data in Table 8 show that:

(a) H atom elimination from the C_1 alkoxy radicals is extremely slow ($< 10^{-5}$ s^{-1} at 298 K). When compared to the reaction rate of these species with O_2 of 4 x 10^4 s^{-1} at 298 K and atmospheric pressure, the H atom elimination reactions can be totally neglected. Based upon the rate data for the ethoxy radical, decomposition by H atom elimination can also be totally neglected for the C_2 alkoxy radicals.

(b) For the $CF_2ClO^{\cdot}$, $CFCl_2O^{\cdot}$ and $CCl_3O^{\cdot}$ radicals, decomposition by Cl atom elimination is rapid, and this process will be the dominant loss process for these haloalkoxy radicals in the troposphere. This conclusion is in agreement with the reaction schemes proposed for these radicals by Jayanty et al. (1975),

Table 8. Unimolecular decomposition rate constants, k = $Ae^{-B/T}$, for C_1 and C_2 alkoxy and haloalkoxy ($RO^{\cdot}$) radicals

Reaction	A (s^{-1})[a]	B (K)[a]	k (s^{-1}) at	T (K)	Reference
$CH_3O^{\cdot} \rightarrow HCHO + H$	2.4×10^{13}	14450	2×10^{-8}[b]	298	Batt et al. (1986)
$CH_3CH_2O^{\cdot} \rightarrow HCHO + \dot{C}H_3$	8×10^{13}	10800	0.015[b]	298	Batt (1987)
$CF_3O^{\cdot} \rightarrow COF_2 + F$	5×10^{13}	14300	7×10^{-8}[b]	298	Batt et al. (1986)
$CF_2ClO^{\cdot} \rightarrow COF_2 + Cl$	$\sim 1 \times 10^{14}$	6240[c]	8×10^{4}[b]	298	Rayez et al. (1987)
			$>7 \times 10^{5}$	Room temperature	Carr et al. (1986)
$CFCl_2O^{\cdot} \rightarrow COFCl + Cl$	$\sim 1 \times 10^{14}$	5335[c]	7×10^{4}[b]	253	Rayez et al. (1987)
			$>3 \times 10^{4}$	253	Lesclaux et al. (1987)
$CCl_3O^{\cdot} \rightarrow COCl_2 + Cl$	$\sim 1 \times 10^{14}$	4880[c]	8×10^{4}[b]	233	Rayez et al. (1987)
			$>1 \times 10^{5}$	233	Lesclaux et al. (1987)
$CHCl_2O^{\cdot} \rightarrow HC(O)Cl + Cl$	$\sim 1 \times 10^{14}$	5940[c]	2×10^{5}[b] $>10^{5}$	298 298	Rayez et al. (1987) Niki et al. (1980)
$CH_2ClO^{\cdot} \rightarrow HCHO + Cl$	$\sim 1 \times 10^{14}$	10320[c]	0.1[b]	298	Rayez et al. (1987)
$CHFClO^{\cdot} \rightarrow HC(O)F + Cl$	$\sim 1 \times 10^{14}$	5230[c]	2×10^{-6}[b]	298	Rayez et al. (1987)
$CHF_2O^{\cdot} \rightarrow COF_2 + H$	$\sim 1 \times 10^{14}$	17770[c]	1×10^{-12}[b]	298	Rayez et al. (1987)
$CHFClO^{\cdot} \rightarrow COFCl + H$	$\sim 1 \times 10^{14}$	14800[c]	3×10^{-8}[b]	298	Rayez et al. (1987)
$CH_2ClO^{\cdot} \rightarrow HC(O)Cl + H$	$\sim 1 \times 10^{14}$	14900[c]	2×10^{-8}[b]	298	Rayez et al. (1987)
$CHCl_2O^{\cdot} \rightarrow COCl_2 + H$	$\sim 1 \times 10^{14}$	13340[c]	4×10^{6}[b]	298	Rayez et al. (1987)
$CH_2FO^{\cdot} \rightarrow HC(O)F + H$	$\sim 1 \times 10^{14}$	14540[c]	6×10^{-8}[b]	298	Rayez et al. (1987)

a High-pressure limits.
b Calculated from cited Arrhenius expression.
c Calculated.

Gillespie et al. (1977), Suong and Carr (1982) and Withnall and Sodeau (1986).

(c) For the $CHCl_2O^{\cdot}$ radical, decomposition by Cl atom elimination dominates over reaction with O_2 at room temperature and atmospheric pressure. However, this may not be the case at the lower temperatures and O_2 concentrations encountered in the middle and upper troposphere. In contrast, decomposition of the $CH_2ClO^{\cdot}$ radical is slow and the reaction with O_2

$$CH_2ClO^{\cdot} + O_2 \rightarrow HC(O)Cl + HO_2$$

dominates at room temperature and atmospheric pressure of air (Sanhueza et al., 1976; Niki et al., 1980), and is expected to totally dominate for all tropospheric conditions.

For the C_2 haloalkoxy radicals, Sanhueza et al. (1976) concluded that:

(a) For $CX_3CH_2O^{\cdot}$ radicals (X = F, Cl and/or H), the decomposition pathways are sufficiently endothermic that decomposition does not occur, and hence it is expected that reaction with O_2 will dominate.

(b) For $CX_3CF_2O^{\cdot}$ radicals (X = F, Cl and/or (presumably) H), the C-F bond dissociation energy is sufficiently higher than the C-C bond dissociation energy that C-C bond cleavage occurs.

Thus, for example, as discussed by Sanhueza and Heicklen (1975) and Sanhueza et al. (1976), the dominant reactions for the following haloalkoxy radicals are

$$CFCl_2CFClO^{\cdot} \rightarrow CFCl_2C(O)F + Cl$$

$$CF_2ClCCl_2O^{\cdot} \rightarrow CF_2ClC(O)Cl + Cl$$

$$CCl_3CF_2O^{\cdot} \rightarrow COF_2 + \dot{C}Cl_3$$

$$CF_2ClCF_2O^{\cdot} \rightarrow COF_2 + \dot{C}F_2Cl$$

For tropospheric conditions, the important parameters are the rate constant ratios for the reactions of the alkoxy and haloalkoxy radicals with O_2 and their various decomposition pathways. It is anticipated that the rate constants for these processes will depend on their heats of reaction [since (Table 8) the preexponential factors for the various decomposition pathways appear to be reasonably similar at $\sim 1 \times 10^{14}$ s^{-1}]. Since in most cases the heats of formation of the reactant alkoxy and haloalkoxy radicals are not known with any certainty, it is possible that the differences between the summed heats of formation of the reaction products for the reactions of the various alkoxy and haloalkoxy radicals can be used as a tool in deciding the relative importance of these reaction pathways. Table 9 gives examples of the summed heats of formation of the products for the various reactions of the ethoxy, 2-butoxy, $CH_2ClO^{\cdot}$ and $CH_2ClO^{\cdot}$ radicals. These data in Table 9 show that the H atom elimination pathway is the most endothermic decomposition route (being relatively close to the Cl atom elimination pathway for the $CH_2ClO^{\cdot}$ radical, consistent with Table 8).

The differences in the heats of reaction, $\{[\Delta HO_{2\,reaction} - \Delta H_{decomposition}]\} = \Delta(\Delta H)$, in kcal mol^{-1} (rounded to the nearest kcal mol^{-1}) are then: $C_2H_5O^{\cdot}$, 45; 2-butoxy, 42; $CH_2ClO^{\cdot}$, 48; and $CHCl_2O^{\cdot}$, 30. At room temperature and atmospheric pressure of air, the removal processes of these $RO^{\cdot}$ radicals are: $C_2H_5O^{\cdot}$, reaction with O_2 (Carter and Atkinson, 1985); 2-butoxy, reaction with O_2 and decomposition by C-C bond cleavage in an approximately 60%/40% split (Carter and Atkinson, 1985; Atkinson, 1989a); $CH_2ClO^{\cdot}$, reaction with O_2 (Niki et al., 1980); and $CHCl_2O^{\cdot}$, Cl atom elimination (Niki et al., 1980). Thus, as expected, there is a relation between the reaction pathway and the difference in the heats of reaction between the pathways. For $\Delta(\Delta H) > 43$ kcal mol^{-1}, reaction with O_2 dominates, while for $\Delta(\Delta H) < 40$ kcal mol^{-1}, decomposition by either Cl atom elimination or C-C bond cleavage will dominate. It should be noted that at 298 K, 1 kcal mol^{-1} is equivalent to a factor of ~ 5 in the (reaction with O_2)/decomposition rate constant ratio. This approach of estimating the difference in heats of reaction for the various reaction pathways is used in Section 2 dealing with the specific haloalkoxy radicals to assess the importance of these reaction pathways.

Table 9. Reactions of representative alkoxy and haloalkoxy ($RO^{\bullet}$) radicals: thermochemistries of reactions with O_2, decomposition and H and Cl atom elimination

$RO^{\bullet}$	Reaction	$\Sigma\Delta H_f$ (Products) kcal mol^{-1a}
$CH_3CH_2O^{\bullet}$	$CH_3CH_2O^{\bullet} + O_2 \rightarrow CH_3CHO + HO_2$	-36.1
	$CH_3CH_2O^{\bullet} \rightarrow CH_3CHO + H$	12.5
	$CH_3CH_2O^{\bullet} \rightarrow \dot{C}H_3 + HCHO$	8.8
$CH_3CH_2CH(O)CH_3$	$CH_3CH_2CH(\dot{O})CH_3 + O_2 \rightarrow CH_3CH_2COCH_3 + HO_2$	-53.4
	$CH_3CH_2CH(\dot{O})CH_3 \rightarrow C_2H_5^{\bullet} + CH_3CHO$	-11.6
$CH_2ClO^{\bullet}$	$CH_2ClO^{\bullet} + O_2 \rightarrow HC(O)Cl + HO_2$	-44.7
	$CH_2Cl\dot{O} \rightarrow HC(O)Cl + H$	3.9
	$CH_2ClO^{\bullet} \rightarrow HCHO + Cl$	3.0
$CHCl_2O^{\bullet}$	$CHCl_2O^{\bullet} + O_2 \rightarrow COCl_2 + HO_2$	-49.1
	$CHCl_2O^{\bullet} \rightarrow COCl_2 + H$	-0.5
	$CHCl_2O^{\bullet} \rightarrow HC(O)Cl + Cl$	-19.2

a Heats of formation from IUPAC (1989), except for $\Delta H_f(HC(O)Cl)$ = -48.2 kcal mol^{-1} from Dewar and Rzepa (1983) and $\Delta H_f(CH_3CH_2COCH_3)$ = 56.9 kcal mol^{-1} calculated by the group additivity method of Benson (1976).

For the $CF_3O^{\bullet}$ radical, reaction with O_2 cannot occur and F atom elimination is endothermic by 24 kcal mol^{-1} (Batt and Walsh, 1983; IUPAC, 1989).

C. Reactions with NO and NO_2. Absolute rate constant data are available only for the reactions of NO and NO_2 with the $CH_3O^{\bullet}$ and $(CH_3)_2CHO^{\bullet}$ radicals (Sanders et al., 1980; Balla et al., 1985; McCaulley et al., 1985; Zellner, 1987). For the reaction of the $CH_3O^{\bullet}$ radical with NO, the data of Zellner (1987) yield a high pressure rate constant of $k_{\infty} = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K [IUPAC (1989) recommend 2×10^{-11} cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-400 K, with an uncertainty of ± a factor of 2], with a rate constant for the H atom abstraction route of $\leq 6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Similar data arise from the study of McCaulley et al. (1985) for the reaction of the $CH_3O^{\bullet}$ radical with NO_2, carried out at 0.6-4 Torr total pressure. The rate constants were in the fall-off regime, and the abstraction channel was concluded to have a rate constant of $9.6 \times 10^{-12} e^{-1150/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-473 K (2.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K).

The rate data of Balla et al. (1985) for the reactions of the $(CH_3)_2CHO^{\cdot}$ radical with NO and NO_2 were at the high-pressure limit, with room temperature rate constants of (3-4) x 10^{-11} cm^3 molecule^{-1} s^{-1} and small negative temperature dependencies [$k = 1.22 \times 10^{-11} e^{312/T}$ cm^3 molecule^{-1} s^{-1} for the reaction with NO and $1.5 \times 10^{-11} e^{252/T}$ cm^3 molecule^{-1} s^{-1} for reaction with NO_2].

These absolute rate constant data are in reasonable agreement with the large body of relative rate data (see Atkinson and Lloyd, 1984). Atkinson (1989a) has recently recommended for the reactions of the alkoxy radicals with NO and NO_2 that,

$$k(RO^{\cdot} + NO) = k(RO^{\cdot} + NO_2) = 1.3 \times 10^{-11} e^{300/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with these reactions proceeding essentially entirely by addition,

$$RO^{\cdot} + NO \xrightarrow{M} RONO$$

$$RO^{\cdot} + NO_2 \xrightarrow{M} RONO_2$$

and the H atom abstraction routes being of minor or negligible importance for temperatures ≤ 298 K. In the absence of experimental data, these rate expressions are assumed to be applicable for the corresponding reactions of the haloalkoxy radicals.

The formation of alkyl nitrites, RONO, is balanced by the rapid photolysis of these compounds (see, for example, Taylor et al., 1980).

$$RONO + h\nu \rightarrow RO^{\cdot} + NO$$

Hence, the $R\dot{O}$ radical reaction with NO is of no actual importance for tropospheric purposes.

4.4. Reactions of the Alkyl and Haloalkyl Peroxynitrates ($ROONO_2$)

Under tropospheric conditions, the loss processes of the alkyl and haloalkyl peroxynitrates ($ROONO_2$) which need to be considered are thermal decomposition and photolysis.

A. Thermal Decomposition. Thermal decomposition is expected to be the dominant tropospheric loss process of the alkyl and haloalkyl peroxynitrates ($ROONO_2$),

$$ROONO_2 \overset{M}{\rightleftarrows} RO_2^{\cdot} + NO_2$$

with the $RO_2^{\cdot}$ radical and NO_2 being in thermal equilibrium with the peroxynitrate. For the C_1 peroxynitrates, these thermal decomposition reactions are in the fall-off regime between first- and second-order kinetics under the temperature and pressure conditions applicable to the troposphere. The low- and high-pressure rate constants k_0 and k_∞, respectively, and the broadening factor F (at 298 K) are given in Table 10, together with the calculated unimolecular thermal decomposition rates, k, at 298 K and 760 Torr total pressure and 220 K and 100 Torr total pressure. Data obtained at 700 Torr total pressure for propyl peroxynitrate [a mixture of $CH_3CH_2CH_2OONO_2$ and $(CH_3)_2CHOONO_2$] (Edney et al., 1979) are also included in Table 10, and these rate constants are expected to be close (within a factor of 2) to the high-pressure rate constant k_∞.

For the C_1 haloalkyl peroxynitrates studied, the decomposition rates under tropospheric conditions are within 10-20% of the high-pressure rate constant k_∞, with the lifetimes of these haloalkyl peroxynitrates with respect to thermal decomposition increasing from ~10 s at 298 K to ~10^7 s at 220 K (note that the actual lifetimes of these $ROONO_2$ species depend on the NO_2/NO concentration ratio, and increase as this $[NO_2]/[NO]$ ratio increases, due to the equilibrium between the peroxynitrate, the $R\dot{O}_2$ radical and NO_2). The corresponding lifetimes of the alkyl peroxynitrates, with respect to thermal decomposition, are shorter by approximately one order of magnitude at room temperature and two orders of magnitude at 220 K. The thermal decomposition rate constants are approximately given by

$$k_\infty(\text{haloalkyl peroxynitrate}) \cong 1 \times 10^{15}\, e^{-11000/T}\ s^{-1}$$

$$k_\infty(\text{alkyl peroxynitrate}) \cong 2 \times 10^{15}\, e^{-10300/T}\ s^{-1}$$

Table 10. Low- and high-pressure rate constants k_0 and k_∞ and the broadening factor F at 298 K for the thermal decomposition of alkyl and haloalkyl peroxynitrates, $ROONO_2$, together with calculated rate constants at 298 K and 760 Torr total pressure and 220 K and 100 Torr total pressure

$ROONO_2$	k_0 (cm^3 molecule^{-1} s^{-1})	k_∞ (s^{-1})	F (298 K)	k (s^{-1}) 298 K 760 Torr	k (s^{-1}) 220 K 100 Torr	Reference
CH_3OONO_2	$9 \times 10^{-5}\, e^{-9690/T}$	$1.1 \times 10^{16}\, e^{-10560/T}$	0.4	1.8	5.4×10^{-6}	IUPAC (1989)
$C_3H_7OONO_2$		$3.3 \times 10^{14}\, e^{-9965/T^a}$		1.0^a	7×10^{-6a}	Edney et al. (1979)
$CF_2ClOONO_2$	$5.6 \times 10^{-4}\, e^{-9310/T}$	$1.0 \times 10^{16}\, e^{-11880/T}$	0.4	0.046	3.4×10^{-8}	IUPAC (1989)
$CFCl_2OONO_2$	$3 \times 10^{-3}\, e^{-10570/T}$	$2.1 \times 10^{16}\, e^{-11980/T}$	0.4	0.065	4.3×10^{-8}	IUPAC (1989)
CCl_3OONO_2	$5.6 \times 10^{-4}\, e^{-9310/T}$	$9.1 \times 10^{14}\, e^{-10820/T}$	0.2	0.14	3.6×10^{-7}	IUPAC (1989)

a At 700 Torr total pressure of air; uncertain by at least a factor of 2 because of uncertainties in the rate constant ratio $k(R\dot{O}_2 + NO)/k(R\dot{O}_2 + NO_2)$.

B. <u>Photolysis.</u> The absorption cross-sections of CH_3OONO_2 have been measured over the wavelength range 200-310 nm by Cox and Tyndall (1979), Morel et al. (1980) and Sander and Watson (1980), and for $CFCl_2OONO_2$ and CCl_3OONO_2 over the wavelength range 210-280 nm by Morel et al. (1980). The absorption cross-sections decrease with increasing wavelength above ~240 nm, with cross-sections ≤ 1 x 10^{-19} cm^2 at 280 nm for all three of these peroxynitrates (Morel et al., 1980; Baulch et al., 1982).

Acknowledgments

The author gratefully thanks Ms. Christy J. LaClaire for assistance in the preparation of this manuscript and the reviewers for their helpful comments.

N92-15442

DEGRADATION MECHANISMS OF SELECTED HYDROCHLOROFLUOROCARBONS IN THE ATMOSPHERE: AN ASSESSMENT OF THE CURRENT KNOWLEDGE

Richard A. Cox
Engineering Science Division, Harwell Laboratory
DIDCOT, Oxfordshire, UK, OX11 ORA.

Robert Lesclaux
Laboratoire de Photophysique et Photochimie Moleculaire
Universite de Bordeaux I, 33405 TALENCE Cedex, France.

1. INTRODUCTION

Volatile organic compounds are mainly degraded in the troposphere by attack of OH with abstraction of H atoms or addition to unsaturated linkages. The CFC's (chlorofluorocarbons) do not contain these reactive sites and consequently cannot be degraded in this way in the lower atmosphere. This results in pollution of the stratosphere by these molecules and attendant problems for ozone. The proposed replacements for CFC's, the HCFC's (hydrochlorofluorocarbons) and HFC's (hydrofluorocarbons), contain at least one hydrogen atom in the molecule, which confers on these compounds a much greater sensitivity toward oxidation by OH in the troposphere and in the lower stratosphere, resulting in much shorter atmospheric lifetimes than the CFC's. Consequently the Ozone Depletion Potential and the Atmospheric Warming Potential are reduced substantially compared to the CFC's. We shall examine in this paper all the possible degradation processes of the HCFC's and HFC's proposed to replace the CFC's, with the principal aim of identifying chlorine- and fluorine-containing products which are stable under tropospheric conditions.

2. THE ATMOSPHERIC DEGRADATION PROCESS

The general processes involved in the degradation of organic compounds in the atmosphere are outlined in detail in Appendix I. We summarise here the relevant reactions for halogen substituted alkanes of which the HCFC's and HFC's are typical examples. The atmospheric degradation generally begins in the troposphere by the H-abstraction reaction by OH radicals. In addition, haloalkanes may be degraded by H-abstraction by O^1D atoms in the lower stratosphere and this minor process is included for completeness. The hydrogen abstraction results in the formation of a water molecule and a haloalkyl radical which rapidly combines with oxygen, yielding a haloalkyl peroxy radical.

$$RH + OH \rightarrow R + H \tag{1}$$

$$RH + O(^1D) \rightarrow R + OH \tag{2}$$

$$R + O_2 + M \rightarrow RO_2 + M \tag{3}$$

In addition, $O(^1D)$ atoms can abstract a Cl atom from HCFC's, thereby generating a different peroxy radical

$$R'Cl + O(^1D) \rightarrow R' + ClO \tag{4}$$

$$R' + O_2 + M \rightarrow R'O_2 + M \tag{5}$$

All the studies published to date in the literature show that the oxidation of alkanes or haloalkanes always starts by the formation of a peroxy radical, according to the above mechanisms. It is therefore important to identify in the first place all the potentially important reaction pathways of peroxy radicals, under atmospheric conditions. Current knowledge shows that alkoxy radicals are the principal products formed eventually through these reactions. Alkoxy radicals can react in several ways and a major concern of this review is to examine the details of the possible reactions of these radicals, in order to identify all the stable products formed in this first oxidation sequence. In a further section, the subsequent degradation of these stable products will be discussed and an attempt made to identify their final fate.

DEGRADATION MECHANISMS

Very few studies have been reported in the literature on the oxidation mechanism of HCFC's and HFC's. However, we have now a fairly good understanding of oxidation processes of hydrocarbons, chlorofluoromethanes and some C_2 halocarbons, which allows an extrapolation to HCFC's and CFC's with a fairly good degree of confidence. Nevertheless, because of our lack of knowledge of the thermodynamics or the kinetics of the elementary reactions in HCFC and HFC degradation, there are considerable uncertainties on the reaction rates. Appendix II gives a discussion of the current state of knowledge of the kinetics of the important reactions in the atmospheric degradation of halocarbons.

I - CHEMISTRY OF PEROXY RADICALS DERIVED FROM HCFC's AND HFC's

I-1 - Structure of the peroxy radicals

As a result of a reduced number of hydrogen atoms in the HCFC and HFC molecules which have been considered as alternative compounds for replacement of CFC's, the hydrogen abstraction by OH or $O(^1D)$ leads to a single peroxy radical for each molecule, except for HFC 152a, which may yield two different radicals. Similarly, the chlorine atom abstraction by $O(^1D)$ in HCFC's lead to the formation of a single radical.

The compounds which are considered in this review and the corresponding peroxy radicals are listed in Table I.

Table I : List of compounds and corresponding peroxy radicals

Abstraction of:				H (by OH and O^1D)	Cl (by O^1D)
HCFC	22	$CHClF_2$	→	$CClF_2O_2$	CHF_2O_2
HCFC	123	$CHCl_2CF_3$	→	$CF_3CCl_2O_2$	CF_3CHClO_2
HCFC	124	$CHClFCF_3$	→	CF_3CClFO_2	CF_3CHFO_2
HCFC	141b	CCl_2FCH_3	→	$CCl_2FCH_2O_2$	CH_3CClFO_2
HCFC	142b	$CClF_2CH_3$	→	$CClF_2CH_2O_2$	$CH_3CF_2O_2$
HFC	125	CHF_2CF_3	→	$F_3CF_2O_2$	
HFC	134	CH_2FCF_3	→	CF_3CFHO_2	
HFC	152a	CHF_2CH_3	→	$CHF_2CH_2O_2$	
			→	$CH_3CF_2O_2$	

In the case of HFC 152a, two radicals may be formed, according to the site of the OH attack. No data are available to date for predicting which site of the molecule will preferentially react. However, in both cases, the subsequent reactions lead to formation of CF_2O, as shown in the next section.

I-2 - Reactions of peroxy radicals

Under atmospheric conditions, peroxy radicals principally react with NO, NO_2 and HO_2. Reactions with other peroxy radicals are also possible but, considering the low concentrations of these radicals, they can be neglected.

Reactions with NO

Most small alkylperoxy or halogen substitued alkylperoxy radicals react with NO by a single reaction channel, yielding an alkoxy radical and NO_2:

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6)$$

It can therefore be anticipated with confidence that all peroxy radicals listed in Table I react according to reaction (6) with the formation of an RO radical.

Reactions with NO_2

All peroxy radicals are known to react with NO_2, in a combination reaction forming a peroxynitrate

$$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M \qquad (7, -7)$$

This reaction is generally fast in the troposphere as its rate constant is close to the high pressure limit.

The principal fate of peroxynitrates is the thermal decomposition (-7) into the initial reactants. Photolysis may also occur in the stratosphere and the products are likely to be either $RO_2 + NO_2$ or $RO + NO_3$. Therefore, the only possible product resulting from reaction (7) is again an RO radical.

Reactions with HO_2

In the background troposphere, under conditions of low NO_x concentrations, peroxy radicals react with HO_2 according to reaction (8), forming an hydroperoxide:

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (8)$$

The hydroperoxide is removed from the atmosphere either by physical removal (which is probably rather slow), or by photodissociation into RO + OH. The extent of the alternative pathway for reaction with HO_2,

$$CX_3CH_2O + HO_2 \rightarrow CX_3CHO + H_2O + O_2 \qquad (9)$$

is unknown for halogen substituted RO_2 radicals. The aldehyde produced is the same as that resulting from the RO radical formed via the hydroperoxide, so the nature of the overall degradation products is unaffected.

It can be concluded from this section that the reactions of peroxy radicals in the atmosphere essentially generate RO radicals, other products being of minor importance.

II - ALKOXY RADICALS DERIVED FROM HCFC's AND HFC's

II-1 - General reactions of alkoxy radicals

The RO radicals that we have to consider are those corresponding to peroxy radicals listed in Table I.

Only limited information can be found in the literature on the reactions of these radicals and it is therefore necessary to extrapolate our present knowledge concerning other radicals of this type. RO radicals may undergo three kinds of reactions under atmospheric conditions:

- Reaction with oxygen, for those radicals having at least one H atom on the carbon on the α position from the oxygen atom. These reactions yield a carbonyl compound and HO_2

$$RCXHO + O_2 \rightarrow RCXO + HO_2 \tag{10}$$

(X = H,Cl or F)

- Chlorine atom detachment, yielding a carbonyl compound

$$RCXClO \rightarrow RCXO + Cl \tag{11}$$

This reaction always occur in the case of radicals produced from the oxidation of chlorofluoromethanes.

- Thermal dissociation into a carbonyl compound and a radical.

$$RCX_2O \rightarrow R + CX_2O \tag{12}$$

More details are given in Appendix II concerning these and other reactions of alkoxy radicals. Since most HCFC's and HFC's listed in Table I are C_2 compounds, particular attention is given in Appendix II to the reactions of CX_3CX_2O radicals and the information is used below for establishing the ways radicals relevant to this review react.

II-2 - Reactions of RO radicals produced from HCFC's and HFC's

The fate of the RO radicals corresponding to the peroxy radicals listed in Table I, are now considered in order to predict the carbonyl compounds which are formed under atmospheric conditions. Account is taken of the general properties of the halogenated RO radicals that are reviewed in Appendix II. These properties can be summarised as follows (X = H, Cl or F):

- CX_3CH_2O radicals react with oxygen by hydrogen abstraction;
- CX_3CCl_2O and CX_3CClFO undergo Cl atom detachment;
- CX_3CF_2O, CX_3CHClO and CX_3CHFO undergo a C-C bond cleavage. A small fraction of CX_3CHClO and CX_3CHFO may react with oxygen.
- CF_3O is assumed to yield CF_2O, although the reaction mechanism occuring in the atmosphere is unknown.

HCFC 22 $CHClF_2$

The RO radicals formed are $CClF_2O$ and CHF_2O which can only react by Cl atom detachment and with oxygen, respectively:

$$CClF_2O \rightarrow CF_2O + Cl$$

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

This last reaction is probably fairly slow and reactions of CHF_2O similar to those of CF_3O (see Appendix II) are possible.

Principal product from HCFC 22 : CF_2O

HCFC 123 $CHCl_2CF_3$

The RO radicals formed are CF_3CCl_2O and CF_3CHClO for which Cl atom detachment and C-C bond cleavage, respectively, are the most likely reactions :

$$CF_3CCl_2O \rightarrow CF_3CClO + Cl$$

$$CF_3CHClO \rightarrow CF_3 + CHClO$$

A small fraction of CF_3CHClO may react with oxygen, yielding again CF_3CClO.

Principal products from HCFC 123 : CF_3CClO, CF_2O (from CF_3) and CHClO.

HCFC 124 CF_3CHClF

The RO radicals formed are CF_3CClFO and CF_3CHFO, which undergo the same reactions as in the preceding case :

$$CF_3CClFO \rightarrow CF_3CFO + Cl$$

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

The reaction of CF_3CHFO with oxygen would yield again CF_3CFO.

Principal products from HCFC 124 : CF_3CFO, CF_2O (from CF_3) and CHFO.

HCFC 141b CH_3CCl_2F

The RO radicals formed are CCl_2FCH_2O and CH_3CClFO, reacting with oxygen and by Cl atom detachment, respectively:

$$CCl_2FCH_2O + O_2 \rightarrow CCl_2FCHO + HO_2$$

$$CH_3CClFO \rightarrow CH_3CFO + Cl$$

It can be expected that CCl_2FCHO will react quite rapidly in the troposphere (Appendix II), releasing the CCl_2F radical. However, the $CCl_2FC(O)O_2$ radical formed in the oxidation sequence may react with NO_2 with the formation of the peroxynitrate $CCl_2FC(O)O_2NO_2$, similar to the well known peroxyacetylnitrate (PAN). Like PAN, this molecule is probably thermally stable, particularly in the upper troposphere and no reaction with OH is expected. In addition, photolysis of these peroxynitrates is expected to be very slow and therefore, the residence time is probably long in the troposphere. Thus, the formation of such a molecule may result in enhanced transport of chlorine to the stratosphere.

According to the well established oxidation mechanism of CFC's, the radical CCl_2F will end up as CClFO. It should be pointed out that a C-C bond cleavage in the CCl_2FCH_2O radical would result in the same product. Also, the hydrogen abstraction should be predominent over the Cl abstraction, in the reaction of CH_3CCl_2F with $O(^1D)$ atoms, resulting in minor contribution of the CH_3CFO product.

Principal products from HCFC 141b: CClFO and to a lesser extend CH_3CFO. The peroxynitrate $CCl_2FC(O)O_2NO_2$ should also be considered as a stable product.

HCFC 142b CH_3CClF_2

The RO radicals formed are $CClF_2CH_2O$ and CH_3CF_2O, which undergo reaction with oxygen and C-C bond cleavage, respectively.

$$CClF_2CH_2O + O_2 \rightarrow CClF_2CHO + HO_2$$

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

For the same reasons as in the preceding case, the oxidation of $CClF_2CHO$ will yield CF_2O and the stable peroxynitrate $CClF_2C(O)O_2NO_2$.

Principal products from HCFC 142b : CF_2O and $CClF_2C(O)O_2NO_2$.

HFC 125 CF_3CHF_2

The RO radical formed is CF_3CF_2O, which can only undergo a C-C bond cleavage.

$$CF_3CF_2O \rightarrow CF_3 + CF_2O$$

Principal product from HFC 125 : CF_2O.

HFC 134a CF_3CH_2F

The RO radical formed is CF_3CHFO, which is expected mainly to undergo a C-C bond cleavage, with a possible minor contribution from the reaction with oxygen.

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

$$CF_3CHFO + O_2 \rightarrow CF_3CFO + HO_2$$

Principal products from HFC 134a : CF_2O (from CF_3) and CHFO.

HFC 152a CH_3CHF_2

The RO radicals formed are CHF_2CH_2O and CH_3CF_2O. These radicals react with oxygen and by C-C bond cleavage, respectively.

$$CHF_2CH_2O + O_2 \rightarrow CHF_2CHO + HO_2$$

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

For the same reasons as those given above for other aldehydes, CHF_2CHO will end up as CF_2O.

Principal product from HFC 152a : CF_2O.

III - INVENTORY AND FATE OF THE PRINCIPAL CARBONYL COMPOUNDS PRODUCED IN THE OXIDATION OF THE LISTED HCFC's AND HFC's

The principal carbonyl products obtained as a result of hydrogen and chlorine abstraction from the different HCFC's and HFC's by OH and O(^{1}D) are summarised in Table II.

Table II : Principal carbonyl products obtained from the degradation of the HCFC's and HFC's in the troposphere and the lower stratosphere.

Product obtained from abstraction of :				(by OH and O^1D)	Cl (by O^1D)
HCFC	22	$CHClF_2$	→	CF_2O	CF_2O
HCFC	123	$CHCl_2CF_3$	→	CF_3CClO	CF_2O, CHClO
HCFC	124	$CHClFCF_3$	→	CF_3CFO	CF_2O, CHFO
HCFC	141b	CCl_2FCH_3	→	CClFO	$(CH_3CFO)^a$
HCFC	142b	$CClF_2CH_3$	→	CF_2O	CF_2O
HFC	125	CHF_2CF_3	→	CF_2O	
HFC	134	CH_2FCF_3	→	CF_2O, CHFO	
HFC	152a	CHF_2CH_3	→	CF_2O	
Inventory of products :				CF_2O CHFO CClFO CF_3CClO CF_3CFO	CF_2O CHClO CHFO $(CH_3CFO)^a$
Should also be included in stable products : the peroxynitrates				$CCl_2FC(O)O_2NO_2$ $CClF_2C(O)O_2NO_2$	

[a] : Probably a minor product

The most striking feature is the limited number of the principal carbonyl products obtained, of which CF_2O is obviously the most abundant one. In contrast CH_3CFO is probably a minor product which in addition should be efficiently degraded in the troposphere, due to the presence of the methyl group. The reaction CH_3CFO with OH will form HCOCOF which will further be photolysed into HCO + FCO, FCO ending up as HF + CO. The direct photolysis of CH_3CFO would give CH_3 + CFO.

The other compounds still containing a hydrogen atom are : CHClO and CHFO. In the troposphere, these compounds may undergo photolysis, reaction with OH or hydrolysis. The photolysis should be negligible as the presence of the halogen atom on the carbonyl group shifts the $n \rightarrow \Pi^*$ band to the UV ($\lambda <$ 270 nm), compared to formaldehyde. To our knowledge, no data are available on the kinetics of the reactions with OH and measurements of the rates constants should be performed. Nevertheless, these reactions should be an efficient ^{S}ink for these compounds. Hydrolysis in clouds and rain droplets, yielding HCl or HF + CO, could also be an efficient sink for carbonyl hydrohalides but, as far as we know, the Henry's Law coefficients for these molecules have not been measured and so it is difficult to estimate their propensity for incorporation into the precipitation elements.

The carbonyl products containing chlorine are CClFO, CHClO, CF_3CClO and possibly some small amounts of phosgene, CCl_2O, formed as a side product in the HCFC 123 oxidation (by C-C bond cleavage in CF_3CCl_2O radical). For the same reason given above, the photolysis of such compounds is likely to be negligible in the troposphere but could become significant in the lower stratosphere, particularly for compounds such as CHClO or CF_3CClO. The photolysis rate of this class of compounds, i.e. RCClO, should be carefully investigated in the conditions of upper troposphere/lower stratosphere. In particular, it should be verified that the photolysis of CF_3CClO do not produce CF_3Cl which would be a long lived chlorine carrier in the atmosphere. These compounds are not expected to react with OH, with the exception of CHClO which will be converted to CO and HCl in the troposphere. Reaction with $O(^1D)$ atoms in the lower stratosphere may be significant and an evaluation of this sink could be obtained from models, assuming rate constants for $O(^1D)$ reactions of about 2×10^{-11} $cm_3molecule^{-1}s^{-1}$ (value for CFClO).

The other possible sink of these compounds in the troposphere is hydrolysis in the precipitation elements, but this cannot be quantified in the absence of solubility data.

The halogenated PAN's, $CCl_2FC(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$ may be stable enough result in a transport of chlorine to the stratosphere. Their principal sink in the troposphere is certainly hydrolysis and the efficiency of this process should be investigated.

The other major product molecules are the perfluorocarbonyls : CF_2O and CF_3CFO. Based on laboratory studies, CF_2O has been assumed to be the principal oxidation product of the CF_3 radical. However, the mechanism is not fully established. The reactions of the CF_3 radical with O_2 to give CF_3O_2 and of CF_3O_2 with NO to give CF_3O :

$$CF_3 + O_2\ (+M) \rightarrow CF_3O_2\ (+\ M)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO$$

appear to be well established. CF_3O is also likely to be formed following CF_3O_2 reaction with HO_2 to form CF_3OOH followed by photolysis.

The reaction pathways for CF_3O in the atmosphere are not obvious. This radical is stable with respect to thermal decomposition to CF_2 + F or formation of FO_2 via reaction with oxygen (see Appendix II). It can combine with nitrogen oxides, yielding a nitrite or a nitrate with NO and NO_2 respectively.

$$CF_3O + NO (+ M) \rightarrow CF_3ONO (+ M)$$

$$CF_3O + NO_2 (+ M) \rightarrow CF_3ONO_2 (+ M)$$

However, the nitrate CF_3ONO_2 is not known as a stable molecule and another pathway for this latter reaction could be :

$$CF_3O + NO_2 \rightarrow CF_2O + FNO_2$$

CF_3ONO can only be a temporary reservoir since, by analogy with the methyl derivative, it is expected to be photolysed into the initial reactants. Another possible path for CF_3O is the reaction with other radicals or molecules having weak C-H bonds, such as HO_2 or aldehydes :

$$CF_3O + HO_2 \rightarrow CF_3OH + O_2$$

$$\rightarrow CF_2O + HF + O_2$$

$$CF_3O + RCHO \rightarrow CF_3OH + RCO$$

$$\rightarrow CF_2O + HF + RCO$$

However, the rate constants and products of such reactions are unknown and need to be investigated experimentally. If trifluoromethanol were formed to a significant extent, it could represent a significant sink for fluorine compounds, by precipitation scavenging.

In laboratory experiments, CF_3O is generally converted into CF_2O, probably by heterogeneous reactions. Similar reactions may occur in the atmosphere, particularly in the presence of aqueous droplets and aerosols, but the extent of such heterogeneous processes is difficult to assess. It can nevertheless be anticipated that the principal degradation products of CF_3 are CF_2O and possibly CF_3OH.

As was mentioned in the preceding section, the CHF_2O radical can react with oxygen,

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

but this reaction may be very slow and if so, similar alternative reactions to those of CF_3O should be envisaged.

The only way of degradation of CF_2O and CF_3CFO in the gas phase is photolysis at short wavelengths i.e. above the ozone layer. It is likely that the residence time of such compounds in the stratosphere is quite long but they will be removed in the troposphere by physical processes. Data on the hydrolysis rate should be obtained in order to evaluate the atmospheric lifetime of such compounds.

CONCLUSIONS

- The atmospheric photooxidation of hydrochlorofluorocarbons and hydrofluorocarbons is likely to occur by mechanisms similar to those which have been elucidated for alkanes and chloroalkanes, although virtually no experimenatal data is available to confirm this.

- The final chlorine containing products expected from the HCFC's are HCl, CFClO, CF_3CClO, $CCl_2FC(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$. These compounds are all stable and are expected to be removed only by photolysis in the stratosphere or through precipitation scavenging and hydrolysis. A slow thermal decomposition in the lower troposphere is also expected for the halogenated PAN's.

- The other major product molecules are expected to be HF and the perfluorocarbonyls CF_2O and CF_3CFO. The only loss processes for the carbonyls is photolysis in the upper stratosphere or precipitation scavenging in the troposphere.

- The mechanism of oxidation of CF_3O radicals, which is assumed to produce CF_2O, is not known for atmospheric conditions, and needs further study.

- The atmospheric lifetimes of CF_2O, CFClO, CCl_2O and other perhalogenocarbonyls need to be determined by acquisition of more data on their photochemistry and solubility.

- More information on the chemistry of the formylhalides HCClO and HCFO is required in order to determine their atmospheric lifetimes.

- Further laboratory tests and atmospheric measurements are needed to test the validity of the proposed mechanisms for HCFC and HFC degradation.

APPENDIX I (R.A. COX AND R. LESCLAUX)

Summary of degradation mechanisms of volatile organic compounds in the atmosphere

Volatile organic compounds are removed from the atmosphere predominantly by gas phase photochemically initiated oxidation. A pattern has emerged from the oxidation mechanisms of organics in the atmosphere, as a result of laboratory studies of oxidation of organic compounds under atmospheric conditions, together with knowledge of atmospheric trace gas composition (Atkinson, 1986; Atkinson and Lloyd, 1984; Cox, 1988). This pattern is best illustrated by considering the atmospheric oxidation of a simple hydrocarbon, RH, following attack by OH radicals. The first step involves formation of a peroxy radical by addition of molecular oxygen to the initially formed radical :

$$OH + RH \rightarrow H_2O + R \tag{1}$$

$$R + O_2\ (+\ M) \rightarrow RO_2\ (+\ M) \tag{2}$$

Peroxy radicals are formed quite generally in reaction (2), from organic radicals produced by radical attack or by photolysis.

The next stage involves conversion of the peroxy radical to a carbonyl compound. This may occur by one of several pathways, depending on local atmospheric composition. In the continental boundary layer and in the lower stratosphere/upper troposphere, sufficient nitrogen oxides are normally present for the peroxy radical chemistry to be dominated by their reactions with NO :

$$RO_2 + NO \rightarrow RO + NO_2 \tag{3}$$

Reaction (3) forms an alkoxy radical RO which typically can react with O_2 to give a carbonyl compound R_1R_2CO, and an HO_2 radical :

$$RO + O_2 \rightarrow R_1R_2CO + HO_2 \tag{4}$$

(R_1 and R_2 are H or organic fragment)

In the background middle troposphere where the concentration of nitrogen oxides is very low, the main alternative pathway to reaction (3) is reaction of RO_2 with HO_2 :

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \tag{5a}$$

$$\rightarrow R_1R_2CO + H_2O + O_2 \tag{5b}$$

Reaction (5a) has generally been assumed to be the exclusive channel for the peroxy radical + HO_2 reaction but recent evidence (Jenkin et al. 1998) has shown that, at least in the case of simple hydrocarbon radicals, the alternate channel (5b), forming carbonyl compound and water directly, is significant under atmospheric conditions. It should be noted that this channel can occur only for organic peroxy radicals with an H-C-OO structure.

DEGRADATION MECHANISMS

Carbonyl compounds are producted by subsequent degradation of the hydroperoxide ROOH, either by OH attack or by photolysis, the reaction sequence being :

$$OH + ROOH \rightarrow H_2O + R_1R_2CO + OH \qquad (6)$$

or

$$ROOH + h\nu \rightarrow RO + OH \qquad (7)$$

with subsequent reaction of RO via reaction (4). Simple organic hydroperoxides are photolysed only slowly via the weak tail of their UV absorption bands, which extend into the near UV part of the solar spectrum.

The carbonyl compounds produced in the first stage of atmospheric degradation are further oxidized either by attack of OH (or another radical) or by photodissociation, resulting from absorption in the rather weak near UV bands of these compounds e.g.

$$OH + R_1HCO \rightarrow H_2O + R_1CO \qquad (8)$$

or

$$R_1R_2CO + h\nu \rightarrow R_2 + R_1CO \qquad (9)$$

The acyl radicals form peroxy radicals by addition of O_2 and the acyl peroxy radicals react either with NO or, in low NO_x situations, with HO_2. In the O-atom transfer reaction with NO, the initial product radical, R_1CO_2 rapidly loses CO_2 to form an organic radical of one less C atom than the original radical. This radical forms a new peroxy radical in reaction (2).

$$R_1CO + O_2 \rightarrow R_1CO_3 \qquad (10)$$

$$R_1CO_3 + NO \rightarrow NO_2 + R_1CO \qquad (11)$$

$$R_1CO_2 \rightarrow R_1 + CO_2 \qquad (12)$$

Two parallel reaction pathways occur in the reaction of the simplest acyl peroxy radical, CH_3CO_3, at room temperature (Niki et al. 198 5, Moortgat et al. 1989).

$$CH_3CO_3 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \qquad (13)$$

$$CH_3CO_3 + HO_2 \rightarrow CH_3COOH + O_3 \qquad (14)$$

The first channel is analogous to reaction (5a) but the second channel, in which ozone is formed, has only been observed for acetylperoxy, but may well be general for acylperoxy and substituted acetylperoxy radicals. Degradation of peracid formed in reaction (13) is likely to be via photolysis or by rain out.

Another reaction pathway of general application to peroxy radicals also needs to be considered in conditions where NO_x is at significant concentrations i.e. the addition of NO_2 to form peroxynitrates :

$$RO_2 + NO_2 (+ M) \longleftrightarrow RO_2NO_2 (+ M) \qquad (15)$$

The pernitrates tend to be unstable at ambient temperatures and decompose back to the precursor, leading to no net chemical change via this reaction (Cox and Roffey, 1977). At the lower temperatures prevalent in the upper troposphere the thermal decomposition may become slow enough for the alternate removal process for the peroxynitrates, such as photolysis or reaction with OH, to become dominant (Crutzer, 1979). The rate of thermal decomposition is dependent on the nature of the organic radical, the acyl and the halogen substituted pernitrates, being much more stable than the alkyl derivates.

The above mechanisms have been formulated as a result of studies of the kinetics and products formed in reactions of simple organic radicals. Studies of the oxidation of higher alkanes and simple olefins seem to indicate a generality of behaviour, although the relative rates of some of the steps e.g. decomposition of alkoxy radicals compared to their reaction with O_2, show remarkable sensitivity to structure and lead to mechanistic differences (Batl, 1987). Information on substituted alkyl radicals is much more sparse and elucidation of the mechanisms is more difficult.

APPENDIX II (R.A. COX AND R. LESCLAUX)

Rate constants for selected reactions in the proposed degradation mechanism for hydrochlorofluorocarbons

In this section we examine the available knowledge of the kinetics of the elementary reactions in the general degradation mechanism for halogen substituted organic radicals.

1 - The reaction $CX_3 + O_2 (+ M) \rightarrow CX_3O_2 (+ M)$

The limiting third order rate constants for the association reaction increases with chlorine and fluorine substitution (see Table I)

Table I : Rate constants for combination of CX_3 radicals with oxygen (X = H, Cl or F)

CX_3	$k_0 \times 10^{30}$ $cm^6 molecule^{-2} s^{-1}$ at 298K
CH_3	0.8
CCl_3	1.5
CCl_2F	5.0
CF_3	19.0

Source : IUPAC evaluation, 1989

No experimental data are available for the reaction $CClF_2 + O_2$ or for the halogen substituted C_2 radical with O_2, but it seems likely that halogen substitution (particularly fluorine), enhances the rate of these association reactions, making this the exclusive pathway for the primary radical fragments from HCFC and CFC attack by OH.

2 - The reaction $CX_3O_2 + NO \rightarrow CX_3O + NO_2$

Data are available for the reactions of the halogen substituted methyl radicals with NO. The rate constants are of similar magnitude for X = Cl or F, but are a factor of two larger than the corresponding reactions of CH_3O_2 and $C_2H_5O_2$ (see Table II).

Table II : Rate coefficients for reaction of CX_3O_2 radicals with NO

CX_3O_2	$k \times 10^{11}$ $cm^3 molecule^{-1} s^{-1}$ at 298K
CH_3O_2	0.76
$C_2H_5O_2$	0.88
CF_3O_2	1.6
CF_2ClO_2	1.6
$CFCl_2O_2$	1.5
CCl_3O_2	1.8

Source : IUPAC evaluation, 1989

There are no experimental data for the halogen substituted C_2 radicals, but they are likely to react rapidly with NO, following the pattern of the CX_3O_2 radicals. A reasonable estimate for the C_2 radicals would be a value of 2.0×10^{-11} $cm^3molecule^{-1}s^{-1}$, at tropospheric temperature.

3 - The reaction $CX_3O_2 + NO_2 (+ M) \leftrightarrow CX_3O_2NO_2 (+ M)$

The addition reaction of halogen substituted methyl radicals with NO_2 has been measured at low pressure in the fall-off region and the limiting k_0 (termolecular) and k_{00} (high pressure) rate coefficients have been determined for CF_3O_2, CF_2ClO_2, $CFCl_2O_2$ and CCl_3O_2 reactions (Caralp et al. 1988). Experimental information has been obtained for the reverse decomposition of the peroxynitrates : $CF_2ClO_2NO_2$, $CFCl_2O_2NO_2$ and $CCl_3O_2NO_2$ (Reiner and Zabel, 1986). These peroxynitrates are all more stable than $CH_3O_2NO_2$ indicating that halogen substitution increases the bond energy of the central $O\text{-}ONO_2$ bond. By analogy fully halogenated C_2 peroxynitrates are expected to be more stable than alkylperoxynitrate (which are similar in stability to $CH_3O_2NO_2$).

Under tropospheric conditions it is likely that the C_2 radical addition reactions and corresponding decomposition are near the high pressure limits. The most appropriate parameters suggested for the fully halogenated C_2 radicals are those for CCl_3O_2 reaction with NO_2, which are given in Table III.

Table III : High pressure limit values for $CX_3O_2NO_2$ formation and decomposition

CX_3O_2	Formation $k_{00}/cm^3molecule^{-1}s^{-1}$	Decomposition k_{00}/s^{-1}
CF_2ClO_2	$1.0 \times 10^{-11}(T/300)^{-0.7}$	$1.0 \times 10^{16}\exp(-11880/T)$
$CFCl_2O_2$	$8.3 \times 10^{-12}(T/300)^{-0.7}$	$2.1 \times 10^{16}\exp(-11980/T)$
CCl_3O_2	$1.5 \times 10^{-11}(T/300)^{-0.7}$	$9.1 \times 10^{14}\exp(-10820/T)$

Source : IUPAC evaluation, 1989

The fall-off parameters to allow calculation of the rate cefficients for high altitudes, are given in the NASA evaluation (1987).

4 - The reaction of CX_3O_2 and $C_2X_5O_2$ with HO_2

No information is available on the kinetics and products of these reactions. By analogy with the most recent data for CH_3O_2 (Jenkin et al. 1988) we can expect a rate coefficient of the order of (0.5 - 1.0) $\times 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ with two channels of approximately equal rates :

$$CX_2HO_2 + HO_2 \rightarrow CX_2HOOH + O_2$$

$$\rightarrow CX_2O + H_2O + O_2$$

The second channel will not be possible for halogenated peroxy radical without an α H atom. For C_2 halogenated peroxy radicals a rate coefficient of the order of 1.0×10^{-11} $cm^3molecule^{-1}s^{-1}$ is probably appropriate (c.f. $C_2H_5O_2 + HO_2$ (Cattel et al. 198 6; Dagant et al. 19886).

5 - Decomposition of halogen substituted alkoxy radicals.

There is now very strong evidence that the alkoxy radicals CX_2ClO (where X = Cl or F) are unstable and, under atmospheric conditions, they rapidly eliminate Cl and consequently have only a transitory existence :

$$CX_2ClO \rightarrow CX_2O + Cl$$

This reaction is responsible for the rapid chain reaction occuring in the laboratory photo-oxidation of certain chlorinated methanes CHX_2Cl (Sanhueza and Meicklen, 1975d; Sanhueza, 1977, Lescalux et al. 1987). When X = H, reaction with O_2 can become competitive, particularly in the case of CH_2ClO (e.g. in the oxidation of CH_3Cl) (Sanhueza and Meicklen, 1975d).

$$CH_2ClO + O_2 \rightarrow HO_2 + CHClO$$

For $CHCl_2O$, however, the favoured pathway appears to be dissociation into CHClO + Cl (Sanhueza and Meicklen, 1975d). Quantitative estimates of the rate coefficient for Cl atom elimination have been recently reported for CX_3 radicals (X = Cl or F). The values are given in Table IV.

Table IV - Decomposition of halogen substituted alkoxy radicals.

Radical decomposition	k/s^{-1} (temp)	Ref.
$CCl_3O \rightarrow CCl_2O + Cl$	$> 1 \times 10^5$ (233K)	Lesclaux et al. 1987
$CCl_2FO \rightarrow CFCLO + Cl$	$> 3 \times 10^4$ (253 K)	Lesclaux et al. 1987
$CClF_2O \rightarrow CF_2O + Cl$	$> 7 \times 10^5$ (298 K)	Carr et al. 1986

Reactions of hydrochlorofluoroethoxy radicals

Important information concerning the ways chloro- and chlorofluoro-ethoxy radicals react or decompose, can be obtained from studies of the chlorine atom-initiated oxidation of chloro- and chlorofluoroethylenes which proceeds by a long chain, free radical process. These reactions have been extensively studied, mainly by the groups of Shumacher, Huybrechts and Heicklen (see Muller and Schumacher, 1937a,b; Schumacher and Thurauf, 1941; Huybrechts and Meyers, 1966; Huybrechts et al. 1965; Sanhueza and Meicklen, 1975b,c,e) and the results have been collected by Sanhueza et al. in a review (1976). From these data, some general rules can be drawn on the reactions of such radicals.

i - Chlorine atom detachment

$$CX_3CYClO \rightarrow CX_3CYO + Cl$$

(X and Y = H, Cl or F)

This type of reaction always occurs preferentially if Y = Cl or F, independently of the nature of the CX_3 group. For example, CCl_3CCl_2O, $CHCl_2CCl_2O$, $CClF_2CCl_2O$, $CCl_2FCClFO$, $CClF_2CClFO$ radicals essentially undergo this type of reaction. By studying the photooxidation of methyl chloroform, Nelson et al. (1984), showed that the radical CH_3CCl_2O also dissociates in this way.

ii - C-C bond cleavage

$$CX_3CX_2O \rightarrow CX_3 + CX_2O$$

This reaction always occurs for radicals of the type CX_3CF_2O, independently of the nature of CX_3. The situation is not as clear for CX_3CHFO or CX_3CHClO radicals, since they can either undergo a C-C bond cleavage or react with oxygen. It seems however that the C-C bond cleavage is the most favourable process for these radicals. In a study of Cl atom sensitized oxidation of chlorinated ethanes, in one atmosphere of air, Spence and Hanst (1978) showed that the radicals CCl_3CHClO, $CHCl_2CHClO$, $CH_2ClCHClO$ and CH_3CHClO essentially yield formyl chloride as a result of the C-C bond cleavage. Small amounts of acid chlorides CX_3CClO have, however, been detected, resulting from the reaction with oxygen. The same conclusion was reached in the study of the Cl atom sensitized oxidation of chlorinated ethylenes (Sanhueza et al. 1976). It can be expected that CX_3CHFO radicals react in the same way.

Apparently, the Cl atom detachment from CX_3CClHO has not been observed.

iii - Reaction with oxygen

$$CX_3CXHO \rightarrow CX_3CXO + HO_2$$

Obviously, this reaction preferentially occurs in the cases of radicals of the type CX_3CH_2O, yielding a halogenated acetaldehyde molecule. This has been shown for CCl_3CH_2O (Nelson et al. 1984; Sperce and Henst, 1978) and for CH_2ClCH_2O (Sperce and Henst, 1978). As shown above, the reaction with oxygen seems to be a minor process for CX_3CHXO radicals. However, it will be considered as a possible channel in the compounds relevant to this review. The rate constant for this reaction is assumed to be one tenth of the equivalent reaction for C_2H_5O, taking into account the effect of the halogen atom on the H atom reactivity.

iv - Oxidation of the CF_3O radical

The oxidation of the CF_3O radical is one of the major uncertainties in the mechanism of degradation of perfluorocompounds. This radical is formed in the degradation of CF_3 via CF_2O_2 and the major C-containing product in laboratory systems appears to be CF_2O_2. According to current thermochemical knowledge, the elimination of an F atom either thermally or by reaction with O_2 is too endothermic to be important in the atmosphere :

$$CF_3O + M \rightarrow CF_2O + F + M \qquad \Delta H^0 = +36 \text{ kJ mol}^{-1}$$

$$CF_3O + O_2 \rightarrow CF_2O + FO_2 \qquad \Delta H^0 = +42 \text{ kJ mol}^{-1}$$

Accordingly it has been hypothesized that heteregeneous reactions are responsible for the formation of CF_2O in laboratory systems. It is important therefore to establish whether other homogeneous pathways may occur in the atmosphere.

6 - Photochemical reactions

Halogenated hydroperoxides

Information on the photolysis of halogenated hydroperoxides is sparse. By analogy with the alkyl hydroperoxides, photolysis is likely to be rather slow and to occur via dissociation of the central O-O bond leading to the same alkoxy radical as that produced by reaction of the original peroxy radical with NO. For modeling purposes, it is recommended to use $J(CH_3OOH)$ for the reaction :

$$CX_3OOH + h\nu \rightarrow CX_3O + OH$$

Carbonyl Halides

The absorption spectra of the carbonyl halides, CX_2O, have been determined for CF_2O, CFClO and CCl_2O (Baulch et al. 1980). The molecules absorb only in the deep UV and are virtually unaffected by sunlight in the troposphere. Photolysis leads to elimination of a halogen atom :

$$CX_2O + h\nu \rightarrow CXO + X$$

The fragment radical ClCO is unstable with respect to decomposition to Cl + CO and the same is probably true for FCO, although the thermodynamic stability of this radical is still uncertain.

The photochemistry of CHXO (X = F or Cl) has been investigated in the case of CHFO (Okabe, 1978). It appears that substitution of halogen on the carbonyl carbon atom, X-C = O, has the effect of shifting the $n \rightarrow \Pi^*$ electronic absorption in the C = O group to higher energies (blue shift in wavelength), thus reducing the rate of photoabsorption in the lower part of the atmosphere quite dramatically. Photodissociation rates are therefore likely to be reduced in consequence, although the effect may be modified by changes in the quantum yields, which are not known. These arguments are also expected to apply to fully halogenated carbonyls of the type CX_3CXO.

Halogenated aldehydes

Although there is little information on the photochemistry of the halogenated aldehydes of the type CX_3CHO, there is considerable information on the photochemistry of the halogenated ketones e.g. CX_3COCX_3, which photolyse in the near UV following $n \rightarrow \Pi^*$ excitation (Macket and Phillips, 1962). Since the absorption by aldehydes in the corresponding near UV band is also an $n \rightarrow \Pi^*$,absorption of fully halogenated ketones, $(CF_3)_2CO$, $(CF_2Cl)_2CO$ and $(CCl_3)_2CO$, is shifted up to 20 nm to the red, making these molecules more strongly absorbing in the solar UV troposphere. Moreover, the quantum yields for photodissociation near 300 nm are 0.8 (Whytock and Kutsche, 1988), i.e. substantially higher than for simple aliphatic ketones. Comparing this analogy for aldehydes of the type CX_3CHO, we may expect rather rapid photolysis of these compounds according to the reaction :

$$CX_3CHO + h\nu \rightarrow CX_3 + HCO$$

However, at short wavelength, another photodissociation pathway may occur :

$$CX_3CHO + h\nu \rightarrow CHX_3 + CO$$

A reasonable approximation would be to use the same J value as for HCHO photodissociation via the H + HCO channels for modelling this process in the atmosphere.

A novel process observed in the chloro-substituted ketones is the elimination of a Cl atom rather than C-C bond rupture e.g.

$$CF_2ClCOCF_2Cl + h\nu \rightarrow CF_2ClCOCF_2 + Cl$$

This channel may be open for the (slower) photolysis of CX_3CXO type carbonyls :

$$CX_2ClCXO + h\nu \rightarrow CX_2CXO + Cl$$

7 - Reaction of OH with halogenated peroxides and aldehydes

Halogenated hydroperoxides and aldehydes (containing the -CH0 group) can degrade through OH attack. The reactions can be written as follows :

$$CX_3CHO + OH \rightarrow H_2O + CX_3CO$$

$$CX_3OOH + OH \rightarrow H_2O + CX_3OO$$

For the hydroperoxides, the H-atom attached to the C atom (relative to the peroxy link) are less likely to be abstracted than the H_{00} atom, due to the deactivating effect of the nearby halogen atoms in both C_1 and C_2 fragments. For the rate coefficients the preferred estimates are those for reaction of OH + H_2O_2 reduced by a factor of 2 to compensate for the lower number of abstractable H-atoms. The only halogen substituted aldehyde for which the rate coefficient for OH attack appears to have been measured is chloral, CCl_3CHO, derived from the photo-oxidation of methyl chloroform (Nelson et al. 1984) for which a value of 6.2×10^{-12} $cm^3molecule^{-1}s^{-1}$ was obtained at 298 K. In the same study, the rate coefficient for OH attack on acetyl chloride :

$$OH + CH_3CClO \rightarrow H_2O + CH_2CClO$$

was determined to be 7.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1} showing that the C-ClO group also reduces the rate of H abstraction. Fluorine substitution is also expected to show a similar deactivating effect in analogous fluorocarbonyl compounds.

The rate of the HCFO and HCClO molecules with OH is unknown :

$$OH + HCXO \rightarrow H_2O + CXO$$

A value of approximately 1×10^{-12} $cm^3molecule^{-1}s^{-1}$ is estimated, taking into account the effect of deactivation by the halogen atom for H-abstraction.

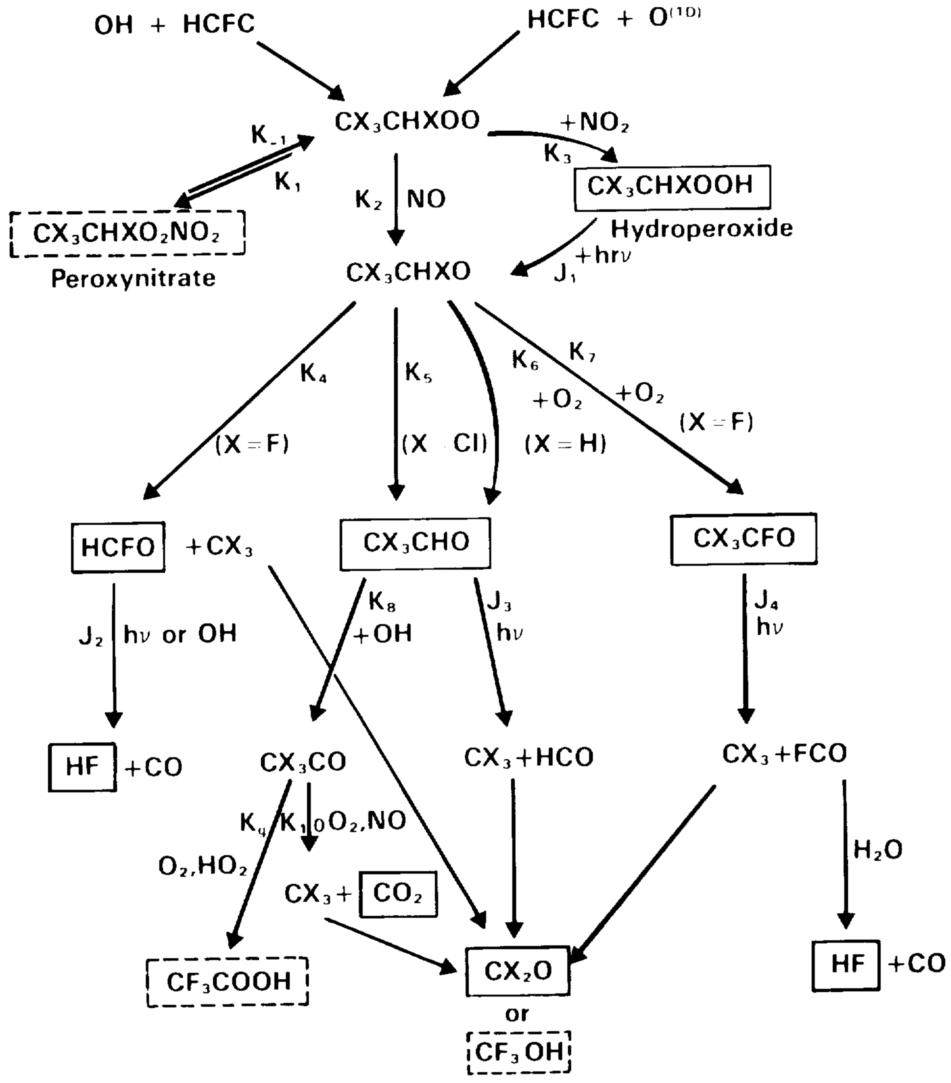
8 - Rainout, washout and dry deposition processes

All oxygenated secondary products from the oxidation of HCFC's and CFC's, hydroperoxides, halogenated aldehydes, carbonyl halides and acid halides (e.g. CX_3CFO), will be subject to removal by solution/hydrolysis in the precipitation elements and also by dry deposition at the earth surface. Knowledge of the solubility and Henry's law constants for these gases is required in order to assess the importance of removal in the precipitation elements for the carbonyl halides CCl_2O, CFClO and CF_2O. Since these molecules are very stable towards gas phase removal, removal by wet and dry deposition probably has an important role in determining their atmospheric lifetime. Recent estimates of the lifetime of phosgene, based on measured concentrations and the estimated source strength (Wilson et al. 1989), are about 2 months.

APPENDIX III (R.A. COX AND R. LESCLAUX)

Recommended rates coefficients for modelling atmospheric degradation of hydrochlorofluorocarbons

A schematic diagram illustrating the degradation pathways of a typical hydrochlorofluocarbon is shown in Figure 1. In order to formulate the basic chemistry, knowledge of the rate coefficients for 10 thermal reactions and 4 photochemical reactions are required. The best estimates of the rate coefficients are summarised in Table A and for the photochemical parameters in Table B.



Minor products shown in "broken" boxes, major products in "full" boxes

Figure 1. Tropospheric Degradation Pathways for typical CFC substrates.

Table A: Rate constants for selective reactions of the degradation mechanism of HCFC's and HFC's

	RO_2+NO_2,M RO_2NO_2+M	RO_2+NO	RO_2+HO_2	$RO \rightarrow CX_3+CX_2O$	$RO \rightarrow CX_3CXO+Cl$	$RO+O_2 \rightarrow CX_3CHO+HO_2$	$RO+O_2 \rightarrow CX_3CXO+HO_2$	$OH+CX_3CHO$	CX_3CO+HO_2	CX_3CO+NO
HCFC's	k_1 & k_{-1}	$k_2 \times 10^{11}$ $cm^3 s^{-1}$	$k_3 \times 10^{11}$ $cm^3 s^{-1}$	k_4	k_5	k_6	k_7	k_8 $cm^3 s^{-1}$	$k_9 \times 10^{11}$ $cm^3 s^{-1}$	$k_{10} \times 10^{11}$ $cm^3 s^{-1}$
HCFC 22										
$CClF_2O_2$	IUPAC*	1.6	1.0***	NA	y[s]	-	-	-	-	-
CHF_2O_2	use k_∞ (CH^3O^2)	1.6	"	NA	-	-	o.1k(CH_3O+O_2)[s]	-	-	-
HCFC 123										
$CF_3CCl_2O_2$	use k_∞ ($CFCl_2O_2$)	1.5	"	-	as $CFCl_2O$[x]	-	-	-	-	-
CF_3CHClO_2	use k_∞ (CF_2ClO_2)	1.6	"	$CF_3+HCClO$		-	-	2.1 x 10^{-12}	-	-
HCFC 124										
CF_3CClFO_2	use k_∞ (CF_2ClO_2)	1.6	"	-	y	-	-	-	-	-
CF_3CHFO_2	" "	1.6	"	CF_3+HCFO[t]	-	-	0.1k(CH_3O+O_2)	-	-	-
HCFC 141b										
$CCl_2FCH_2O_2$	use k_∞(CH_3O_2)	0.9**	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5[z]	1.4[w]
CH_3CClFO_2	use k_∞($CClF_2O_2$)	1.6	"	-	y	-	-	as CH_3CCl_3	-	-
HCFC 142b										
$CClF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	CH_3+CF_2O		-	-	as CH_3CCl_3	-	-
HCF 125										
$CF_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	CF_3+CF_2O[t]	-	-	-	-	-	-
HCFC 134										
CF_3CFHO_2	use k_∞ (CF_2ClO_2)	1.6	"	CF_3+HFCO[t]	-	-	0.1k (CH_3O+O_2)	-	-	-
HCFC 152a										
$CHF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CH_2ClO_2)	1.6	"	CH_3+CF_2O	-	-	-	as CH_3CCl_3	-	-

* IUPAC Data evaluation [10]

** as $C_2H_5O_2$ + NO

*** Estimate based on $C_2H_5O_2$ + HO_2

[s] COF_2 is the product

[t] k = 1 x 10^{16}exp(-8110/T)s^{-1} based on an assumed A factor and a rate constant of 1.5 x $10^4 s^{-1}$ at 298K to fit product yields in chlorocarbon photooxidation : see Appendix II

[u] based on a value of 7.2 x $10^{-14} cm^3 s^{-1}$ for CH_3CClO [24]

[w] assume equal to k(CH_3CO_3 + NO) (IUPAC values [10])

[x] k = 1x10^{13} exp(-4965/T) s^{-1}

[y] k = 1x10^{13} exp(-5000/T) s^{-1} estimate based on data for CCl_3O and CCl_2FO

[z] assume equal to k(CH_3CO_3 → $CX_3C(O)OOH$ + O_2)

Table B : Photochemical reactions

Reaction	J_{value} for atmospheric photoylsis*	
$ROOH + h\nu \rightarrow RO + OH$	J_1	use J (CH_3OOH)
$HCFO + h\nu \rightarrow H + FCO$	J_2	use J (CH_3COCH_3)
$CX_3CHO + h\nu \rightarrow CX_3 + HCO$	J_3	use J ($HCHO \rightarrow H + HCO$)
$CX_3CXO + h\nu \rightarrow CX_3 + XCO$	J_4	use J (CH_3CHO)

* Based on arguments presented in Appendix II

N92-15443

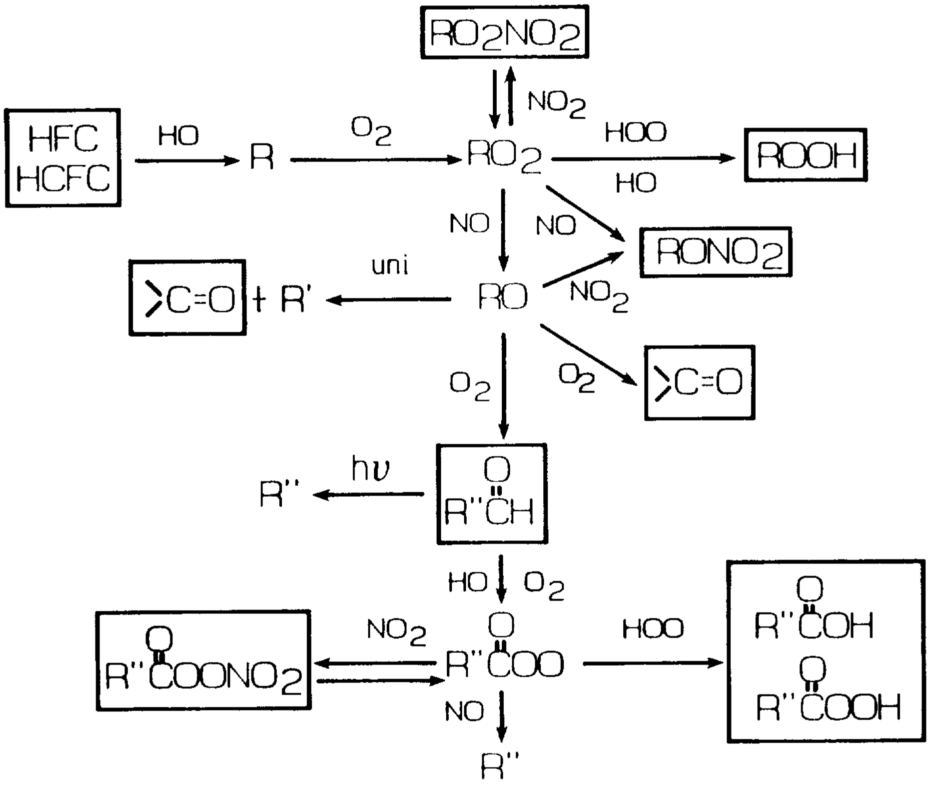
AN ASSESSMENT OF POTENTIAL DEGRADATION PRODUCTS IN THE GAS-PHASE REACTIONS OF ALTERNATIVE FLUOROCARBONS IN THE TROPOSPHERE

Hiromi Niki

Centre for Atmospheric Chemistry
Department of Chemistry
York University
4700 Keele St., North York
Ontario, Canada M3J 1P3

EXECUTIVE SUMMARY

Tropospheric chemical transformations of alternative hydrofluorocarbons (HCFs) and hydrochlorofluorocarbons (HCFCs) are governed by hydroxyl radical initiated oxidation processes, which are likely to be analogous to those known for alkanes and chloroalkanes. A schematic diagram, shown below, illustrates plausible reaction mechanisms for their atmospheric degradation; where R, R' and R'' denote the F- and/or Cl-substituted alkyl groups derived from HCFs and HCFCs subsequent to the initial H atom abstraction by HO radicals. At present, virtually no kinetic data exist for the majority of these reactions, particularly for those involving RO. Potential degradation intermediates and final products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates, as summarized in the attached table. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products shown in this table, there seem to be no significant gas-phase removal mechanisms. Further chemical kinetics and photochemical data are needed to quantitatively assess the atmospheric fate of HCFs and HCFCs, and of the degradation products postulated in this report.



Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC 141B	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
		CCl_2FCH_2O	CCl_2FCHO			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		$CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC 142b	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
		$CClF_2CH_2O$	$CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		$CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC 22	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
HCFC 124	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF 134a	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
		CF_3CHFO	$CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		CFO			$CF(O)OOH$	$CF(O)OONO_2$
HFC 52a	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	CHF_2CHO			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	$CHFO$			
		$CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		CFO		$CF(O)OOH$		$CF(O)OONO_2$
HCF 125	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

1. INTRODUCTION

As part of the AFEAS (Alternative Fluorocarbon Environmental Acceptability Study) program for evaluating all relevant current scientific information to determine the environmental acceptability of the alternative fluorocarbons, the following list of questions concerning their atmospheric degradation via gas-phase chemical reactions will be addressed in this report.

1. How will alternative fluorocarbons degraded in the troposphere after initial hydrogen abstraction by hydroxyl (HO) radicals?
2. What are the intermediate and final products of the gas-phase chemical reactions?
3. What are the most probable gas-phase chemical lifetimes of these products in the troposphere?
4. Is it likely that relatively stable fluorine containing products would be formed?
5. How would the degradation products be removed from the atmosphere via gas-phase chemical reactions?

Alternative fluorocarbons under consideration include all HFCs and HCFCs given, respectively, by the formula $CH_{4-n}F_n$ $(1 \leq n \leq 3)$, $C_2H_{6-n}F_n$ $(1 \leq n \leq 5)$, and $CH_{4-m-n}Cl_mF_n$ $(1 \leq m \leq 2;\ 1 \leq n \leq 2;\ m+n \leq 3)$ and $C_2H_{6-m-n}Cl_mF_n$ $(1 \leq m \leq 4;\ 1 \leq n \leq 4;\ m+n \leq 5)$, but emphasis will be placed on HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The formulas for these fluorocarbons are listed in table 1 along with the expected initial radicals following reaction with HO radicals.

Questions 1 and 2 deal with the formation of fluorine or chlorine-containing molecular products via the gas-phase HO-initiated reactions of HFCs and HCFCs under representative tropospheric conditions, and questions 3-5 with the subsequent removal of these products by either direct photodissociation or reactions with gaseous tropospheric constituents. These topics are discussed in Sections I and II, respectively. Products with sufficiently long lifetimes are eventually removed from the troposphere by processes such as rain out, deposition to the earth's surface or escape into the stratosphere. These heterogeneous removal processes are evaluated elsewhere in the AFEAS program and will not be discussed in this report.

The HO-radical initiated degradation of HFCs and HCFCs in the troposphere takes place via a large number of reactions involving free radical intermediates. A literature review is given in the appendix. Many of these reaction steps have not been determined experimentally. Thus, when judged plausible, available information on analogous reactions and thermochemical data are also utilized (stated as such) in this evaluation.

2. ATMOSPHERIC DEGRADATION MECHANISMS

Listed in Table 1 are all the possible fluorine- and/or chlorine-substituted haloalkyl (R) radicals initially formed from HFCs and HCFCs after H atom abstraction by HO radicals. As discussed later in the Appendix, atmospheric degradation mechanisms of these R radicals appear to be, in large part, analogous to those of the corresponding alkyl radicals, i.e. CH_3 and C_2H_5 (NASA Report, 1987; CODATA, 1982; Kerr and Calvert, 1984; Atkinson, 1986). These reaction steps involve various types of free radicals and molecular products and are illustrated schematically in Figure 1. In this figure, the molecular products

Table 1: List of Alternative Fluorocarbons and Primary Radicals

Compound	m	n	Formula	Primary Radical
HFC				
$CH_{4\text{-}n}F_n$		1	CH_3F	CH_2F
$(1 \le n \le 3)$		2	CH_2F_2	CHF_2
		3	CHF_3	CF_3
$C_2H_{6\text{-}n}F_n$		1	CH_3CH_2F	CH_3CHF; CH_2FCH_2
		2	CH_3CHF_2 (152a)	CH_3CF_2; CHF_2CH_2
			CH_2FCH_2F	CH_2HCHF
		3	CH_3CF_3	CF_3CH_2
			CH_2FCHF_2	CH_2FCF_2; CHF_2CHF
		4	CH_2FCF_3 (134)	CF_3CHF
			CHF_2CHF_2	CHF_2CF_2
		5	CHF_2CF3 (125)	CF_3CF_2
HCFC				
$CH_{4\text{-}m\text{-}n}Cl_mF_n$	1	1	CH_2ClF	$CHClF$
$(1 \le m \le 2)$	2	1	$CHCl_2F$	CCl_2F
$(1 \le n \le 2)$	1	2	$CHClF_2$ (22)	$CFlF_2$
$(2 \le m + n \le 3)$				
$C_2H_{6\text{-}m\text{-}n}Cl_mF_n$	1	1	CH_2ClCH_2F	CH_2ClCHF; CH_2FCHCl
$(1 \le m \le 4)$			CH_3CHClF	CH_3CClF; $CHClFCH_2$
$(1 \le n \le 4)$	1	2	$CHClFCH_2F$	$CHClFCHF$; CH_2FCClF
$(2 \le m + n \le 5)$			$CH_2FCHClF$	CH_2FCClF; $CHClFCHF$
			CH_2ClCHF_2	CH_2ClCF_2; CHF_2CHCl
			CH_3CClF_2	$CClF_2CH_2$
	1	3	$CClF_2CH_2F$	$CClF_2CHF$
			CHF_2CHClF	CHF_2CClF; $CHClFCF_2$
			CH_2FCClF_2	$CClF_2CHF$
			CH_2ClCF_3	CF_3CHCl
	1	4	CF_3CHClF (124)	CF_3CClF
			CCF_2CHF_2	$CClF_2CF_2$
	2	1	CH_3CCl_2F (141b)	CCl_2FCH_2
			$CH_2ClCHClF$	$CH_2ClCClF$; $CHClFCHCl$
	2	2	$CHClFCHClF$	$CHClFCClF$
			CH_2FCCl_2F	CCl_2FCHF
			$CH_2ClCClF_2$	$CClF_2CHCl$
	2	3	$CClF_2CHClF$	$CClF_2CClF$
			CHF_2CCl_2F	CCl_2FCF_2
			$CHCl_2CF_3$ (123)	CF_3CCl_2
	3	1	CCl_3CH_2F	CCl_3CHF
			$CHCl_2CHClF$	$CHCl_2CClF$; $CHClFCClF$
			CH_2ClCCl_2F	CCl_2FCHCl
	3	2	$CCl_2FCHClF$	CCl_2FCClF
			CCl_3CHF_2	CCl_3CF_2
			$CHCl_2CClF_2$	$CClF_2CCl_2$
	4	1	$CHCl_2CCl_2F$	CCl_2FCCl_2
			CCl_3CHClF	CCl_3CClF

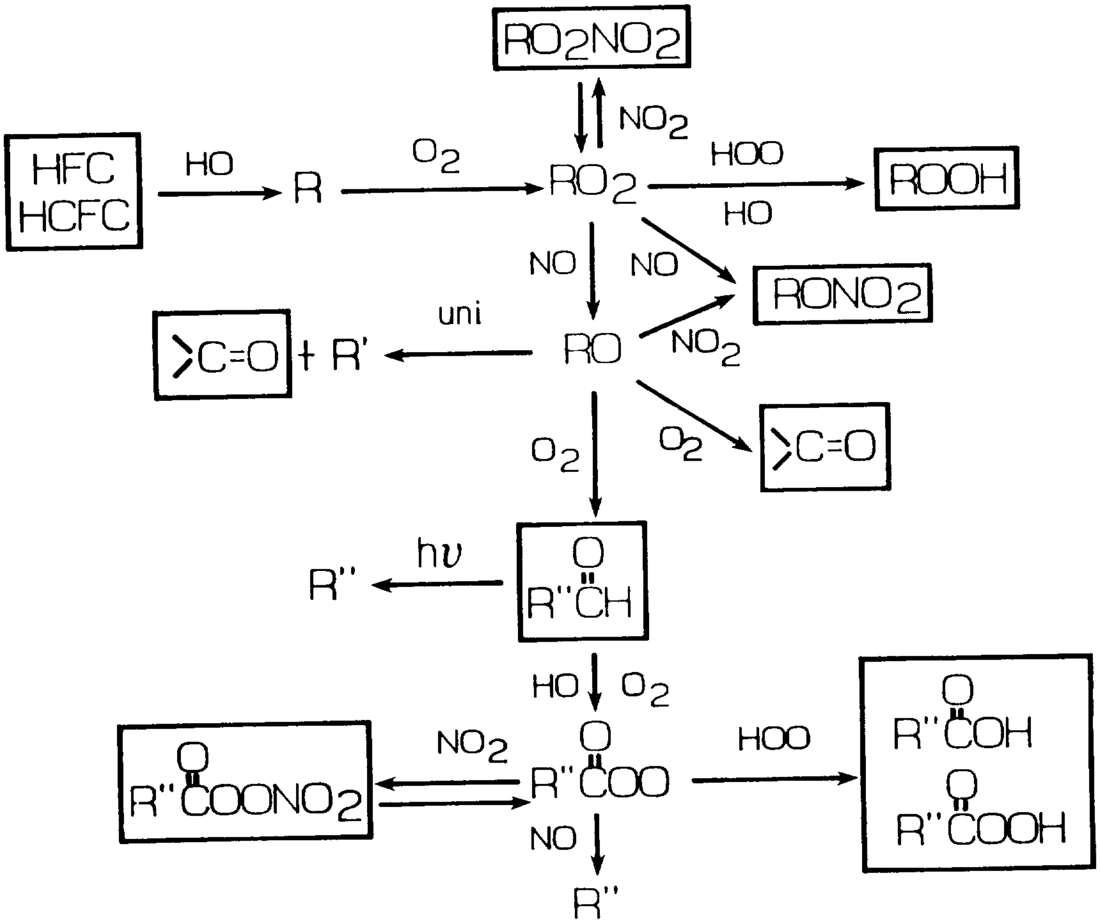


Figure 1: Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

are enclosed in boxes to differentiate them from the free radical intermediates. Note that under tropospheric conditions the initial haloalkyl (R) radicals exclusively add to O_2 to form the corresponding peroxy RO_2 radicals, (reaction 1).

(1a) $$R + O_2 (+M) \rightarrow ROO (+M)$$

The most likely reaction partners for these RO_2 radicals in the troposphere are NO, NO_2 or HOO radicals, (reactions 2a-2c) (See, for example, Logan et al., 1981).

(2a) $$ROO + NO \rightarrow RO + NO_2$$

(2b) $$ROO + NO_2 (+M) \rightarrow ROONO_2 (+M)$$

(2c) $$ROO + HOO \rightarrow ROOH + O_2$$

In reaction 2a, the ROO radicals are converted by NO into the corresponding haloalkoxy RO radicals, while reactions 2b and 2c yield molecular products haloalkylperoxy nitrate $ROONO_2$ and hydroperoxide

ROOH, respectively (Niki et al., 1979, 1980b; Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). Although the $ROONO_2$ products are thermally unstable and readily redissociate back to ROO radicals and NO_2 at temperatures near 300 K, they become sufficiently stable to be the major intermediate products at the colder temperatures encountered in the upper troposphere Simonaitis and Heicklen, 1979. To illustrate, adopting the temperature tabulations in the US standard atmosphere: 288 K ($z = 0$ km), 249 K ($z = 6$ km), and 235 K ($z = 8$ km), the thermal lifetime of CCl_3OONO_2 will be 10 s, 70 min, and 16 hr, respectively Simonaitis and Heicklen, 1979. Also, the haloalkyl hydroperoxides ROOH are the intermediate products which probably react with HO to regenerate ROO radicals, analogous to the HO-reaction of the CH_3OOH produced in the atmospheric oxidation of CH_4 (NASA Report, 1987).

The subsequent fate of the RO radicals appears to vary greatly depending upon the type of the R group, as discussed in detail later. In general, RO radicals are known to lead to the formation of carbonyl compounds, e.g. CF_2O, CClFO, CF_3CFO, CF_3CClO, etc. via unimolecular dissociation, (reaction 3a), and H-atom abstraction by O_2 for those R groups containing hydrogen attached to the oxygenated carbon, (reaction 3b) (Sanhueza, Hisatsune and Heicklen, 1976).

(3a) $$RO \rightarrow {>}C{=}O + R'$$

(3b) $$RO + O_2 \rightarrow {>}C{=}O + HOO$$

where R′ can be either a Cl-atom or a haloalkyl group attached to the oxygenated carbon in the parent R radicals. The R′ radicals, in turn, undergo a series of degradation steps similar to those for the R radicals. However, for CF_3O radicals, neither the unimolecular dissociation nor the O2-reaction are thermochemically feasible, and bimolecular reactions with other reactive atmospheric species such as NO_2, O_2, or HOO are likely to be operative, (reactions 3c - 3e).

(3c) $$CF3O + NO_2\ (+M) \rightarrow CF_3ONO_2\ (+M)$$

(3d) $$CF_3O + O_3 \rightarrow CF_3OO + O_2$$

(3e) $$CF_3O + HOO \rightarrow CF_3OH + O_2$$

Among the carbonyl products, those containing aldehydic hydrogen [-CHO] group probably undergo both photodissociation, (reaction 4a), and bimolecular reaction with HO-radicals to yield peroxycarbonyl radicals, (reactions 4b - 4c).

(4a) $$R'CHO + h\nu \rightarrow R'' + CHO$$

(4b) $$R'CHO + HO \rightarrow R'CO + H_2O$$

(4c) $$R'CO + O_2\ (+M) \rightarrow R''C(O)OO\ (+M)$$

where R″ represents a haloalkyl group. The R″C(O)OO radicals then react with NO, NO_2 and HOO to form R″ radicals, peroxy nitrates $R''C(O)OONO_2$, and acids R″C(O)OOH, R″C(O)OH, (reactions 5a - 5c), in a manner analogous to $CH_3C(O)OO$ (NASA Report, 1987; CODATA, 1984).

(5a) $$R''C(O)OO + NO \rightarrow R'' + CO_2 + NO_2$$

(5b) $$R''C(O)OO + NO_2\ (+M) \rightarrow R''C(O)OONO_2\ (+M)$$

(5c) $$R''C(O)OO + HOO \rightarrow R''C(O)OOH + O_2\ (\text{or } R''C(O)OH + O_3)$$

The peroxy nitrates $R''C(O)OONO_2$ are thermally unstable, but can persist in colder regions of the troposphere because of the strong temperature dependence of reaction 5b, analogous to the behavior of $CH_3C(O)OONO_2$ (PAN) (NASA Report, 1987; CODATA, 1982, 1984), i.e. 3 days at 288 K (0 km); 1 month at 262 K (4 km); 1 yr at 249 K (6 km); 15 yrs at 235 K (8 km). However, the long lifetime probably will not be realized because of the possibility of photodissociation. Notably, while there is no evidence for the existence of the H-substituted carbonylperoxy nitrate $HC(O)OONO_2$, presumably due to thermal instability of its precursor radicals HC(O)OO, the corresponding fluorine- and chlorine-substituted peroxy nitrates, $FC(O)OONO_2$ and $ClC(O)OONO_2$ produced via reaction 5b, have been observed in the laboratory, and their thermal dissociation lifetimes appear to be comparable to that of PAN (Edney, Spence and Hanst, 1979).

Summarized in Table 2 are the fluorine- and/or chlorine-containing free radicals and molecular products to be expected in the atmospheric degradation of those HFCs and HCFCs that are of particular interest to the AFEAS assessment, i.e. HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The molecular products include carbonyls, acids, hydroxides and nitrates formed via the reactions illustrated in Figure 1. These products are listed for each alternative fluorocarbon in the consecutive order of occurrence during the course of their degradation. Listed in the 3rd column to the left of the products appearing in each row are their free radical precursors. The H-containing carbonyl products indicated by asterisks are the precursors for those radicals indicated also by asterisks. It can be noted from Table 2 that some free radical precursors and molecular products, particularly fluorinated carbonyls such as CHFO, CF_2O and CClFO, are common to degradation of many of the HFCs and HCFCs. The expected carbonyl products from all the C1- and C_2-HFCs and HCFCs are listed in Table 3.

3. GAS-PHASE CHEMICAL LIFETIMES IN THE TROPOSPHERE

As already indicated in the preceding section, the atmospheric reactivity of various fluorine- and/or chlorine-containing molecular products can be assessed in terms of three different types of gas-phase chemical reaction, i.e. thermal decomposition, photolysis, and bimolecular reaction with atmospheric species, particularly HO radicals.

Thermal decomposition is important for the peroxy nitrates, $ROONO_2$ and $RC(O)OONO_2$, listed in Table 2. In colder regions of the troposphere, the acylperoxy nitrates $RC(O)OONO_2$ have thermal lifetimes longer than one year and can be considered "stable," while haloalkylperoxy nitrates $ROONO_2$ are short-lived (<1 day) intermediate products. Notably, these peroxy nitrates are present in the troposphere at concentrations equal to or greater than those determined by the equilibrium with their precursors ROO and NO_2, and they can persist significantly longer than predicted solely from their dissociation rate constants.

Solar radiation in the troposphere contains photons in the near-UV (≤ 295 nm) region which are energetically capable of dissociating various atmospheric compounds (NASA Report, 1987). However, the

Table 2: Degradation Products in the Tropospheric Oxidation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC 141B	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
		CCl_2FCH_2O	$*CCl_2FCHO$			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		$*CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC 142b	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
		$CClF_2CH_2O$	$*CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		$*CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC 22	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
HCFC 124	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF 134a	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
		CF_3CHFO	$*CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		$*CFO$			$CF(O)OOH$	$CF(O)OONO_2$
HFC 52a	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	$*CHF_2CHO$			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	$*CHFO$			
		$*CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		$*CFO$		$CF(O)OOH$		$CF(O)OONO_2$
HCF 125	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

Table 3: List of Alternative Fluorocarbons and Carbonyl Radicals

Compound	m	n	Formula	Carbonyl Radical
HFC				
$CH_{4-n}F_n$		1	CH_3F	$CHFO$
$(1 \leq n \leq 3)$		2	CH_2F_2	CF_2O
		3	CHF_3	
$C_2H_{6-n}F_n$		1	CH_3CH_2F	$CHFO$, CH_3CFO, CH_2FCHO
$(1 \leq n \leq 5)$		2	CH_3CHF_2 (152a)	$CHFO$, CF_2O, CHF_2CHO
			CH_2FCH_2F	$CHFO$, CH_2FCFO
		3	CH_3CF_3	CF_3CHO
			CH_2FCHF_2	$CHFO$, CF_2O, CHF_2CFO
		4	CH_2FCF_3	$CHFO$, CF_3CFO
			CHF_2CHF_2	CF_2O
		5	CHF_2CF_3	CF_2O
HCFC				
$CH_{4-m-n}Cl_mF_n$	1	1	CH_2ClF	$CHFO$
$(1 \leq m \leq 2)$	2	1	$CHCl_2F$	$CClFO$
$(1 \leq n \leq 2)$	1	2	$CHClF_2$ (22)	CF_2O
$(2 \leq m+n \leq 3)$				
$C_2H_{6-m-n}Cl_mF_n$	1	1	CH_2ClCH_2F	$CHFO$, $CHClO$, CH_2FCHOH, CH_2ClCFO
$(1 \leq m \leq 4)$			CH_3CHClF	$CClFO$, CH_3CFO, $CHClFCHO$
$(1 \leq n \leq 4)$	1	2	$CHClFCH_2F$	$CHFO$, $CClFO$, $CHClFCFO$, CH_2FCFO
$(2 \leq m+n \leq 5)$			$CH_2FCHClF$	$CHFO$, $CHClFCFO$, CH_2FCFO, CH_2FCFO
			CH_2ClCHF_2	$CHClO$, CF_2O, CHF_2CHO
			CH_3CClF_2	CF_2O, $CClF_2CHO$
	1	3	$CClF_2CH_2F$	$CHFO$, CF_2O, $CClF_2CFO$
			CHF_2CHClF	$CHFO$, CF_2O, $CClFO$, CHF_2CFO
			CH_2FCClF_2	$CHFO$, CF_2O, $CClF_2CFO$
			CH_2ClCF_3	$CHClO$, CF_3CHO
	1	4	CF_3CHClF	CF_3CFO
			CCF_2CHF_2	CF_2O
	2	1	CH_3CCl_2F	$CClFO$, CCl_2FCHO
			$CH_2ClCHClF$	$CHFO$, $CClFO$, CH_2ClCFO, $CHClFCHO$
	2	2	$CHClFCHClF$	$CClFO$, $CHClFCFO$
			CH_2FCCl_2F	$CHFO$, $CClFO$, CCl_2FCFO
			$CH_2ClCClF_2$	$CHClO$, $CClF_2CHO$
	2	3	$CClF_2CHClF$	CF_2O, $CClFO$, $CClF_2CFO$
			CHF_2CCl_2F	CF_2O, $CClFO$
			$CHCl_2CF_3$	CF_2CClO, CCl_2O
	3	1	CCl_3CH_2F	$CHFO$, CCl_2O, CCl_3CFO
			$CHCl_2CHClF$	$CHFO$, $CHClO$, $CHCl_2CFO$, $CHClFCClO$
			CH_2ClCCl_2F	$CHClO$, $CClFO$, CCl_2FCHO
	3	2	$CCl_2FCHClF$	$CCLFO$, CCl_2CFO
			CCl_3CHF_2	CF_2O, CCl_2O
			$CHCl_2CClF_2$	CF_2O, CCl_2O, $CClF_2CClO$
	4	1	$CHCl_2CCl_2F$	$CClFO$, CCl_2O, CCl_2FCClO
			CCl_3CHClF	$CClFO$, CCl_2O, CCl_3CFO

data for UV absorption cross sections and quantum yields required for determining photodissociative lifetimes are not available for the majority of the fluorine-containing products listed in Table 2. Carbonyl compounds such as CF_2O, CClFO and CCl_2O Mare known to lack absorptions in the near-UV region and thus, are photochemically inactive in the troposphere (NASA Report, 1987). On the other hand, those RCHO compounds with R = haloalky group are known to absorb UV at wavelengths longer than 300 nm (Calvert and Pitts; 1967), but their quantum yields for the formation of R + HCO and RH + CO under atmospheric conditions have not been determined. In the absence of the necessary information, all the carbonyls listed in Table 2 should be regarded as being potentially photochemically stable. The haloalkyl acids also appear to be photochemically inactive, since the first UV absorption bands of the organic acids generally lie below 250 nm (Calvert and Pitts; 1967). The onset of absorption for the ROOH compounds listed in Table 2 is likely to occur at wavelengths longer than 295 nm, by analogy to H_2O_2 and CH_3OOH (NASA Report; 1987). The latter peroxides can decay photochemically in the troposphere, splitting the O-O bond, at noon photolysis rates of approximately 1 day-1 and thus, short photochemical lifetimes are also expected for the haloalkyl hydroperoxides. There appears to be no information on the photochemical properties of the haloalkyl-substituted $RC(O)OONO_2$ compounds, although they are not expected to be strong absorbers in the near-UV region. The UV spectrum of even the most common compound of this type, i.e. PAN (R = CH_3), is not sufficiently well-characterized to exclude significant photolysis in the middle and upper troposphere.

Reaction with HO radicals can be responsible, at least in part, for the subsequent degradation of various hydrogen-containing products listed in Tables 2 and 3, depending on their HO-radical reactivity. Among the aldehydic products RCHO, all those containing R = haloalkyl group probably react rapidly with HO radicals. For instance, a room temperature rate constant of 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the HO + CCl_3CHO reaction (Logan et al.; 1981; Crutzen, 1982; WMO Report; 1985) combined with the global average HO concentration of 5×10^5 molecule cm^{-3} (Crutzen, 1982) gives a lifetime of about 12 days. Although not firmly established experimentally, halogen-substitution for the aldehydic products RCHO (R = F or Cl atom) should greatly reduce their reactivity towards HO radicals [cf. Appendix], and their corresponding atmospheric lifetimes are likely to be as long as several months. For the carbonyls and other products containing hydrogen in the haloalkyl groups only, rate constants for H-abstraction are expected to be comparable to those for the corresponding haloalkanes, leading to lifetimes typically longer than one year. The HO-reactivity of the haloalkyl-substituted acidic products RC(O)OH is expected to be similar to that of HC(O)OH and $CH_3C(O)OH$ (Atkinson, 1985), and their estimated atmospheric lifetimes are about a month or longer. On the other hand, the HO-group in a peroxy acid RC(O)OOH is expected to be much less reactive towards HO radicals due to internal hydrogen-bonding to the C=O group. It remains to be determined whether H abstraction from the HO groups in haloalkyl-substituted alcohols and hydroperoxides will occur at rates comparable to those of their alkyl counterparts. For comparison, room temperature rate constants for the H abstraction from the CH_3 groups of CH_3OH and CH_3OOH are approximately 1×10^{-13} and 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, i.e. lifetimes of 8 months and 5 days, respectively. Among the $RONO_2$ and $RC(O)OONO_2$ compounds listed in Table 2, only $CHF_2C(O)OONO_2$ formed from HFC-152a contains hydrogen. This compound is expected to react with HO radicals more slowly than $CH_3C(O)OONO_2$ [PAN]. The rate constant for PAN is 1.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K, corresponding to a lifetime of approximately 6 months.

The preceding semi-quantitative discussion concerning atmospheric reactivity of various degradation products suggests that F- and/or Cl-substituted alkyl compounds generally have substantially longer lifetimes than their alkyl counterparts. There appear to be no known gas-phase reactions for the removal of fully halogenated carbonyls and nitrates.

4. SUMMARY

Tropospheric gas-phase degradation mechanisms and products of alternative fluorocarbons have been assessed based on available laboratory data. The fluorine- and/or chlorine-substituted haloalkyl radicals formed from HFCs and HCFCs after H atom abstraction by HO radicals appear to undergo atmospheric transformations largely analogous to those of the corresponding alkyl radicals. The molecular products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products there seem to be no significant gas-phase removal mechanisms.

5. ACKNOWLEDGEMENTS

The author wishes to thank J. Herron for helpful discussions concerning thermochemistry. G. Yarwood and and C. Francis are acknowledged for their assistance in the preparation of this manuscript.

APPENDIX: LITERATURE REVIEW OF THE RELEVANT GAS-PHASE REACTIONS

This review focuses primarily on aspects of the literature information which are not included in the kinetic data evaluation reports published by the NASA and CODATA panels (NASA Report, 1987; CODATA, 1982, 1984). Some of the studies cited are highly qualitative but provide important information for the present assessment. It is not intended as recommendation for modeling purposes.

$HO + RH \rightarrow R + H_2O$ (RH = HFC and HCFC)

The rate constants for these reactions appear to be well established (NASA Report, 1987). For those C_2 -fluorocarbons containing H atoms attached to both the A- and B-carbon atoms, H-atom abstraction from either carbon can occur, but the product distribution is largely unknown. The only available experimental value is that for CH_3CH_2F; 85% ± 4% for abstraction from the A-carbon ($HO + CH_3CH_2F \rightarrow H_2O + CH_3CHF$) (Singleton, Paraskevopoulos and Irwin; 1980). Empirical correlations between the rate constant and C-H bond energy do not work well for predicting product distributions (Atkinson, 1985). Recommendations based on transition-state-theory calculations and the above-mentioned single experimental measurement at room temperature are also available for extrapolation to other temperatures and to other fluorocarbons (Cohen and Westberg, 1988). In the present assessment, all possible primary radicals and their reaction products are considered, as indicated in Tables 1-3.

$R + O_2 + M \rightarrow RO_2 + M$

Limiting high pressure rate constants of $>10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} have been reported for R = CF_3 (Ryan and Plumb, 1982), CCl_2F (Caralp and Lesclaux, 1983; Caralp, Dognon and Lesclaux, 1984), and CCl_3 (Cooper et al., 1980; Ryan and Plumb, 1984). These rate constants are comparable to those for R = CH_3 (NASA Report, 1987; CODATA, 1982, 1984). Similar values are expected for all the R species listed in Table 1. Under tropospheric conditions, these addition reactions seem likely to be the exclusive reaction path for R radicals.

$RO_2 + NO \rightarrow RO + NO_2$

The rate constants for R = CF_3, CF_2Cl, $CFCl_2$, and CCl_3 are recommended by the NASA panel report are based on existing experimental data (Caralp, Dognon and Lesclaux, 1984; Ryan and Plumb, 1984; Lesclaux and Caralp, 1984; Dognon, Caralp and Lesclaux, 1985; Plumb and Ryan, 1982). The room-temperature rate constants of 1.5-1.7 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} are comparable to the NASA-recommended value of 7.6 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for R = CH_3 (NASA Report, 1987). In these reactions NO_2 has been shown to be the major nitrogen-containing product (Ryan and Plumb, 1984). Some of the RO_2 radicals may yield $RONO_2$ as well as $RO + NO_2$ upon reaction with NO under atmospheric conditions, analogous to the alkyl radicals ($\geq C_4$) (Carter and Atkinson, 1985). Thus, in the present assessment, both possibilities are indicated in Figure 1 and Tables 2-3.

$RO_2 + NO_2 (+M) \rightarrow RO_2NO_2 (+M)$

These reactions appear to be highly competitive with reaction 2a under tropospheric conditions. For

R = CCl_3, the ratio of rate constants k_{2b}/k_{2a} = 0.68 has been reported at 1 atmosphere, independent of temperature (Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). For R = $CFCl_2$, a high pressure limit of k_{2b} = 6.0 (± 1.0) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} has been determined based on extrapolation from the data obtained at the diluent O_2 pressures of 1-12 torr. The unimolecular rate constants for the thermal dissociation of the haloalkyl and alkylperoxy nitrates are probably all similar, e.g. k_{-2b} = $10^{15.56 \pm 1.00}$ exp[(-11 000 + 600/T] s^{-1} for R = CCl_3 (Simonaitis and Heicklen, 1979).

ROO + HOO → ROOH + O_2

By analogy to ROO = CH_3OO (NASA Report, 1987; CODATA, 1982, 1984), the HOO-reactions of haloalkyl-substituted ROO radicals are probably competitive with reactions 2a and 2b. No kinetic data are available for these reactions. For R = CH_2Cl and $CHCl_2$, there is IR spectroscopic evidence for the formation of ROOH products (Niki et al., 1980b). However, the possibility of an alternative mechanism to form $>C=O$ + H_2O + O2 via formation of an adduct [ROOOOH] complex formation has not been entirely ruled out. The products, haloalkyl hydroperoxides, are intermediate products which are likely to react further with HO radicals to regenerate ROO radicals, in analogy to the reaction of CH_3OOH (NASA Report, 11987; CODATA, 1982, 1984).

Reactions Involving RO Radicals

The atmospheric reactions of the haloalkoxy RO radicals are less well established. Product studies have been carried out at room temperature and atmospheric pressure of air for the following RO radicals; CH_2ClO + O_2 → CHClO + HO_2 (Simonaities and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $CHCl_2O$ → CHClO + Cl (Simonaitis and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $CF_{3-x}Cl_xO$ → $CF_{3-x}Cl_{x-1}O$ + Cl ($1 \leq x \leq 3$) (Jayanty, Simonaitis and Heicklen, 1975; Gillespie, Garraway and Donovan, 1977; Suong and Carr, 1982); CCl_3CCl_2O → (CCl_3CClO + Cl)/(CCl_3 + CCl_2O) = 6.0 (Mathias et al., 1974; Hybrechts, Olbregts and Thomas, 1967); $CHCl_2CCl_2O$ → ($CH_2ClCClO$ + Cl)/($CHCl_2$ + CCl_2O) >6.0 (Hybrechts and Meyers, 1966; Bertrand et al., 1968); CH_2ClCCl_2O → ($CH_2ClCClO$ + Cl)/(CH_2Cl + CCl_2O) <50 (Sanhueza and Heicklen, 1975b); $CHCl_2CHClO$ → ($CHCl_2CHO$ + Cl)/($CHCl_2$ + CHClO) <50 (Sanhueza and Heicklen, 1975c); $CH_2ClHCHClO$ → ($CH_2ClHCHO$ + Cl)/(CH_2ClH + CHClO) >10 (Sanhueza and Heicklen, 1975c); $CClF_2CCl_2O$ → ($CClF_2CClO$ + Cl)/($CClF_2$ + CCl_2O) >10 (Simonaitis and Heicklen, 1979); CF_2ClCF_2O → CF_2Cl + CF_2O (Simonaitis and Heicklen, 1979). Some general trend in the degradation mechanisms can be inferred from these studies (Simonaitis and Heicklen, 1979), i.e.

* The strong C-F bonding is not broken during the course of the degradation.

* H atom abstraction by O_2 is the dominant reaction for those R radicals containing two H atoms attached to the oxygenated carbon atom, and also for one carbon RO containing only H and F atoms.

* For R = R''CHFO where R'' is a haloalkyl group, the predominant reaction is unimolecular decomposition.

* For those R groups containing one H and one or more Cl attached to the oxygenated carbon atom, the ROO radicals may predominantly undergo unimolecular dissociation by either breaking the C-Cl

and/or C-C bond depending upon the exothermicity of these two channels. In this assessment, both possibilities are included for all these ROO radicals.

For R = CF_3O, the O_2-reaction $CF_3O + O_2 \rightarrow CF_2O + FO_2$ and the unimolecular dissociation $CF_3O \rightarrow CF_2O + F$ are endothermic by 29 and 22 kcal/mole (Herron, 1989), respectively, so other bimolecular reactions such as those with NO_2, HOO or O_3 are likely to occur, as indicated in the text.

Reactions Involving RCHO (R = F, Cl or haloalkyl group)

Although no data seem to be available, both photodissociation and HO-reaction may play a role in the atmospheric removal of the RCHO compounds. Note that if UV absorption spectra of HCFO and HCClO resemble those of CF_2O and CCl_2O rather than that of HCHO (NASA Report, 1987), these RCHO compounds cannot photodissociate in the troposphere. Also, F- or Cl-substitution should greatly reduce their reactivity towards HO radicals analogous to the Cl-atom reaction of HCHO and HCClO (Sanhueza and Heicklen, 1975a; Niki et al., 1980a). On the other hand, those RCHO compounds with R = haloalky group are known to absorb UV at wavelength longer than 300 nm (Calvert and Pitts, 1967), but the quantum yields for the formation of R + HCO and RH + CO under atmospheric conditions have not been determined. The HO-reactions of these RCHO compounds and their subsequent reactions are probably analogous to that of CH_3CHO (NASA Report, 1987; CODATA, 1982,1984), but their HO-rate constants are probably much smaller than 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for CH_3CHO at 298 K. For instance, a room temperature value of 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} has been determined for CCl_3CHO (Nelson, Treacy and Sidebottom, 1984). This value may be used as an upper limit for estimating the atmospheric lifetimes of the RCHO compounds in this assessment.

The F, Cl or haloalkyl-substituted RC(O)OO radicals are expected to undergo reactions with NO, NO_2 and HOO,(reactions 5a - 5c), analogous to $CH_3C(O)OO$ radicals (NASA Report, 1987; CODATA, 1982,1984). Except for the IR spectroscopic observation of $FC(O)OONO_2$ and $ClC(O)OONO_2$ and the thermal dissociation of $ClC(O)OONO_2$ (Edney, Spence and Hanst, 1979), no quantitative data are available on the kinetics of these reactions. The rate constants for the reaction $ClC(O)OONO_2 \rightarrow ClC(O)OO + NO_2$ have been determined over the temperature range of 293.7 to 300.3 K in air at 1 atm pressure to be $10^{16.8 \pm 1.5}$ exp(-27.7 ± 2.3 kcal/mol) s^{-1} (Edney, Spence and Hanst, 1979). This expression is comparable to the rate expression of 1.12×10^{16} exp(-13330/T) for R = CH_3 (CODATA, 1982,1984).

N92-15444

ATMOSPHERIC DEGRADATION MECHANISMS OF HYDROGEN CONTAINING CHLOROFLUOROCARBONS (HCFC) AND FLUOROCARBONS (HFC)

Reinhard Zellner

Institut für Physikalische Chemie und Elektrochemie
Universität Hannover
Callinstrasse 3 A, 3000 Hannover, FRG

EXECUTIVE SUMMARY

The current knowledge of atmospheric degradation of hydrogen containing chlorofluorocarbons [HCFC 22 ($CHClF_2$), HCFC 123 ($CHCl_2CF_3$), HCFC 124 ($CHClFCF_3$), HCFC 141b ($CFCl_2CH_3$), HCFC 142b (CF_2ClCH_3)] and fluorocarbons [HFC 125 (CHF_2CF_3), HFC 134a (CH_2FCF_3), HFC 152a (CHF_2CH_3)] is assessed. Except for the initiation reaction by OH radicals there are virtually no experimental data available concerning the subsequent oxidative breakdown of these molecules. However, from an analogy to the degradation mechanisms of simple alkanes, some useful guidelines as to the expected intermediates and final products can be derived. A noteable exception from this analogy, however, appears for the oxi-radicals. Here, halogen substitution induces new reaction types (C-Cl and C-C bond ruptures) which are unknown to the unsubstituted analogues and which modify the nature of the expected carbonyl products. Based on an evaluation of these processes using estimated bond strength data, the following simplified rules with regards to the chlorine content of the HCFC's may be deduced:

- HCFC's containing one chlorine atom such as 22 and 142b seem to release their chlorine content essentially instantaneous with the initial attack on the parent by OH radicals. For HCFC 124 such release is apparently prevented.

- HCFC's such as 123 and 141b with two chlorine atoms are expected to release only one of these instantaneously. The second chlorine atom may be stored in potentially long-lived carbonyl compounds such as CF_3CClO or $CClFO$.

1. INTRODUCTION

According to current knowledge volatile organic compounds are removed from the atmosphere predominantly by gas phase oxidation processes. These are always initiated photochemically, either by direct photolysis or - more importantly - by photochemically generated species such as OH, O(^{1}D), HO_2, Cl, NO_3 and O_3. Due to the high energies of the first electronic absorption bands of saturated hydrocarbons and their halogen containing analogues, direct photodissociation is only possible in the middle and upper stratosphere where solar photon fluxes become sufficiently intense below 270 nm.

Among the photochemically generated oxidants, the OH radical is by far the most important species. It is present at all altitudes from ground to well above the stratopause with a maximum density of several 10^7 cm^{-3} during the daytime near 40 km. Due to its photochemical origin and due to the spatial variation of its main source and sink species (O_3, H_2O, NO, CO), OH is highly variable in space and time; the globally and annually averaged concentration is normally assumed to be $\sim$5 x 10^5 cm^{-3}.

OH is important not only because of its concentration level but also because of its reactivity. Due to the strong HO-H bond, it reacts readily in an exothermic reaction with all saturated hydrocarbons by H-atom abstraction. Only the atoms O(^{1}D) and Cl are capable of performing similar abstraction processes. In general the reactions of these species have higher rate coefficients than those of the OH radical, their importance however is limited to those regions of the atmosphere (> 30 km) where sufficient concentrations of these species prevail.

Conventional CFC's owe their long tropospheric lifetime and effective stratospheric chlorine injections - as expressed by their ozone depletion potential (ODP) - to their stability against OH attack in the troposphere. Reactions such as $CX_3Cl + OH \rightarrow CX_3 + HOCl$ are endothermic and have not been observed in the laboratory (DeMore et al. 1987). Hydrogen containing HCFC's and HFC's on the contrary may be degraded by initial OH attack in the troposphere and hence are expected to have correspondingly lower ODP values. The most relevant question with regard to the environmental acceptability of this class of compounds is

- What is the flux of chlorine across the tropopause relative to CFC 11 and per unit mass emitted?

An answer to this question can only be found by addressing to the following problem areas:

- Reactivity towards OH, the global distribution of tropospheric OH and its temporal evolution

- Other potential tropospheric sinks (i.e. solubility, hydrolysis)

- Tropospheric lifetime and fate of oxidation intermediates.

In this review an attempt is being made to delineate the current knowledge of the tropospheric oxidation mechanisms of HCFC's and HFC's with particular view to assessing their ultimate role as chlorine sources in the stratosphere. Since some of the mechanistic details remain speculative at the present time, we will first highlight what is known about the tropospheric oxidation of simple hydrocarbons and on which some of the analogies presented later are based.

2. THE OXIDATION MECHANISM OF SIMPLE HC'S IN THE TROPOSPHERE

Following the initial attack of HC's (alkanes) by OH radicals, viz.

(1) $$OH + RH \rightarrow H_2O + R$$

the subsequent oxidation of the alkyl radicals (R) under tropospheric conditions is known to proceed by the general sequence:

$$\text{alkyl} \xrightarrow{(a)} \text{alkylperoxi} \xrightarrow{(b)} \text{alkoxi} \xrightarrow{(c)} \text{carbonyl compound} \xrightarrow{(d)} \text{oxidized fragments}$$

The rates of these individual steps, including the oxidation of the carbonyl compound are generally faster than that of reaction (1) such that the initial OH attack is rate determining and the lifetime of the hydrocarbon is given by the space and time average of $(k_1 [OH])^{-1}$. Other potential loss processes of hydrocarbons in the troposphere (i.e. reactions with HO_2 and O_3, photolysis, hydrolysis) are unimportant.

a. R/RO_2 conversion

Step (a) of the above sequence reflects the universal conversion of alkyl radicals to alkylperoxi radicals, viz.

(2) $$R + O_2 (+M) \rightarrow RO_2 (+M)$$

This reaction is extremely fast under all tropospheric conditions. Due to the relatively high R-O_2 bond strength (> 25 kcal/mol), reaction (2) is not reversible and RO_2 is the only form in which R exists in perceivable levels in the troposphere. Alternative interactions between R and O_2 leading to an unsaturated HC and HO_2, viz.

(2^1) $$R'CH_2 + O_2 \rightarrow R'_{-H} = CH_2 + HO_2$$

account for less than 0.1% ($R' = CH_3$) of the overall reaction and can safely be discarded for the simpler HC's.

b. RO_2/RO conversion

Unlike step (a), the conversion mechanism of alkylperoxi radicals to alkoxi radicals - step (b) - depends on the ambient conditions.

(i) RO_2/NO_x interactions:

In the continental boundary layer as well as in the upper troposphere/lower stratosphere, sufficient nitrogen oxides are normally present for the alkylperoxi radical chemistry to be dominated by the fast reaction with NO, viz.

(3) $$RO_2 + NO \rightarrow RO + NO_2$$

The rate constants for this process at 298 K are of the order of 8 x 10^{-12} cm^3/s for R = CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7 (Atkinson et al., 1989). However, with the exception of R = CH_3, the interaction between RO_2 and NO may also proceed in recombination forming alkylnitrates,

$$RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M) \tag{3'}$$

The importance of this process increases somewhat with chain length and amounts to < 1.5%, 2% and 4.4% for R = C_2H_5, n-C_3H_7 and i-C_3H_7, respectively.

Under conditions where RO_2 radicals interact predominantly with NO_x another reaction pathway of general application also needs to be considered: the recombination between RO_2 and NO_2 to form peroxinitrates, viz.

$$RO_2 + NO_2\ (+M) \Longleftrightarrow RO_2NO_2\ (+M) \tag{4,-4}$$

Similiar to (3') this reaction terminates the hydrocarbon oxidation chain. Its rate coefficients are well established for the smaller peroxiradicals with values near10^{-11} cm^3/s in the high pressure limit. However, peroxinitrates have a relatively low bond strength and tend to be unstable at the temperatures of the lower troposphere. For instance, $CH_3O_2NO_2$ has a thermal lifetime of < 1 s at 298 K. Only at the lower temperatures of the upper troposphere and lower stratosphere peroxinitrates are more persistent and removal pathways other than thermal decomposition (i.e. photolysis, reaction with OH) may become important. It should be noted that halogen and acyl substitution tends to make peroxinitrates considerably more stable. The lifetimes of $CF_2ClO_2NO_2$ and $CH_3C(O)O_2NO_2$ (PAN) for instance, at 298 K are 20 s and 28 min, respectively, in the high pressure limit (Atkinson et al., 1989). Since these lifetimes will be further enhanced at all pressures prevailing in the troposphere, peroxinitrate formation from these radicals is clearly an important process.

Taking peroxinitrates as relevant temporary reservoir species of HC oxidation intermediates, the question arises whether and how the oxidation chain may be continued other than by the "do-nothing" sequence (4,-4)? It appears that there is at present insufficient knowledge to assess alternatives such as photolysis or reactions with OH. One may speculate that the photolysis products of RO_2NO_2 may be $RO_2 + NO_2$ or $RO + NO_3$ which would correspond to "do-nothing" or the standard RO_2/RO conversion of step (b), respectively. The OH reactions of RO_2NO_2 except for PAN (Wallington et al., 1984; leBras, 1988), have apparently not been investigated. Assuming that their mechanisms occur by α - hydrogen abstraction, viz.

$$OH + R'CH_2O_2NO_2 \rightarrow H_2O + R'CHO_2NO_2$$

these processes may provide direct access to the carbonyl compound since the product radical is expected to decompose readily to $R'CHO + NO_3$.

(ii) RO_2/HO_2 interactions:

In the background middle troposphere where the concentration of NO_x is very low, RO_2 can only be removed in mutual interactions or in reaction with other free radicals such as OH, HO_2 or Cl. Considerations of the concentration levels of each of these species suggest that HO_2 will be the dominant oxidant of RO_2 leading primarily to the formation of hydroperoxides, viz.

(5) $$RO_2 + HO_2 \rightarrow ROOH + O_2$$

The rate constant of this type of reaction is only well established by direct techniques for $R = CH_3$ ($k = 6.3 \times 10^{-12}$ cm^3/s at 298 K). However, there is evidence of a still larger reactivity of $R = CH_3CO$ (Moortgat et al., Veret et al., private communications). Recent product studies performed on reaction (5) ($R = CH_3$) also suggest that there may be an alternative reaction channel forming formaldehyde + H_2O directly, viz.

(5') $$CH_3O_2 + HO_2 \rightarrow CH_2O + H_2O + O_2$$

Whereas (5') as well as the subsequent oxidation of the hydroperoxide by OH

(6) $$OH + ROOH \rightarrow H_2O + R_1R_2CO + OH$$

both produce carbonyl compounds directly (thereby circumventing the alkoxi oxidation stage) alkoxi radicals are formed in the competitive photolysis of ROOH, viz.

(7) $$ROOH + h\nu \rightarrow RO + OH$$

This process however is slow in the troposphere since simple hydroperoxides absorb only weakly in the actinic range of the solar spectrum (Molina and Arguello, 1979). It should be noted that hydroperoxides resulting from simple organics are expected to be highly soluble in water and their formation may therefore provide an efficient route of heterogenous removal via rain out. Whether peroxiradicals themselves may also undergo this pathway is presently open to speculation.

c. RO/carbonyl compound conversion

The dominant oxidation pathway of simpler alkoxi radicals is by direct abstraction of the α -H-atom in reaction with O_2, viz.

(8) $$RO + O_2 \rightarrow R_1R_2CO + HO_2$$

The rate coefficient for this type of reaction is relatively small ($k = 1.9 \times 10^{-15}$ cm^3/s at T = 298 K for $R = CH_3$ (DeMore et al., 1987) and 1.1×10^{-14} cm^3/s at T = 298 K for $R = C_2H_5$ (Gutman et al., 1982; Hartmann et al., 1989). However due to the atmospheric O_2 content, the "lifetime" of RO radicals with respect to this process is <0.2 ms. For RO radicals with a chainlength $\geq C_4$, alternative reaction pathways (isomerization, decomposition) forming hydroxyalkyl radicals and carbonyl compounds + alkyl radical are also important (Balla et al., 1985, Dobe et al., 1986).

d. Carbonyl compound/oxidized fragment conversion

It is apparent from the above discussion that carbonyl compounds are the primary oxidation products of any HC oxidation in the atmosphere. Apart from the decomposition routes possible for larger RO radicals, the number of carbon atoms of the parent HC has been conserved. However, carbonyl compounds are further oxidized, mainly in reaction with OH. In case of an aldehyde, R_1HCO, this oxidation occurs almost exclusively by abstraction of the weakly-bonded carbonyl-H-atom leading to the formation of an acyl radical, viz.

(9) $$OH + R_1HCO \rightarrow H_2O + R_1CO$$

The subsequent oxidation of this radical occurs in the sequence

$$R_1CO + O_2 \rightarrow R_1C(O)O_2$$

$$R_1C(O)O_2 + NO \rightarrow R_1C(O)O + NO_2$$

$$R_1C(O)O \rightarrow R_1 + CO_2$$

leading eventually to the split of the α -C-C bond and the formation of CO_2.

Acylperoxiradicals of the type $R_1C(O)O_2$ also tend to react readily with NO_2 to form relatively stable acylperoxinitrates, viz.

$$R_1C(O)O_2 + NO_2 \rightarrow R_1C(O)O_2NO_2$$

The kinetics of formation and decay of the simplest of these species, PAN ($CH_3C(O)O_2NO_2$), are well documented (Atkinson et al., 1989).

Carbonyl compounds have weak near UV (230 - 340 nm) absorption bands arising from the "forbidden" $n — \pi^*$ singlet-singlet transition. The band maxima appear around 280 - 290 nm with absorption coefficients near 6 x 10^{-20} cm^2 (Calvert and Pitts, 1967). Therefore photolysis is a minor but non negligible alternative pathway of degradation. The photolysis products are alkyl + acyl radicals, i.e.

(10) $$R_1R_2CO + h\nu \rightarrow R_1 + R_2CO$$

both of which will be further oxidized according to the mechanisms delineated above.

3. THE OXIDATION MECHANISMS OF SIMPLE HYDROGEN CONTAINING HCFC's AND HFC's

3.1. General considerations

In light of the above discussion and in view of additional evidence, the following similarities/differences of the atmospheric oxidation of partially halogenated alkanes can be formulated

- Due to the hydrogen content the initial oxidative attack will be by OH radicals. Compared to CH_4 the reactivity of individual C-H bonds in partially halogenated methanes, including $CHClF_2$, is increased by increasing F and Cl substitution due to a corresponding reduction of the C-H bond strength. An exception being CF_3H, with a C-H bond strength about 1.5 kcal/mol larger than CH_4. The same increase of reactivity applies to F and Cl substituted ethanes, again except when one of the carbon atoms represents a CF_3 group (McMillen and Golden, 1982). Note, however, that the overall reactivity towards OH, as expressed by the rate coefficient, also depends on the number of abstractable H atoms in the molecule. The results for k_{OH}-values are documented elsewhere in this report.
- The fully or partially halogenated alkyl radicals will add O_2 to form the corresponding peroxi radicals. Direct kinetic measurements which are available only for CCl_3, CCl_2F and CF_3 (Atkinson et al., 1989; Caralp et al., 1986) indicate that halogen substitution enhances the rates of these association processes

(for instance k (CF_3 + O_2) / k (CH_3 + O_2) $\simeq$ 22). Moreover, since the thermochemistry is expected to be similar for the substituted and unsubstituted case reactions, peroxi radical formation will be the exclusive pathway of oxidation of the halogenated alkyl radicals.

- Halogenated peroxi radicals will be reduced to the corresponding oxi radicals in reactions with NO. The limited direct evidence available for CCl_3O_2, $CFCl_2O_2$, CF_2ClO_2, CF_3O_2 suggests that these reactions have rate constants in the order $\sim 1.6 \times 10^{-11}$ cm^3/s at 298 K, i.e. a factor of two larger than the corresponding reaction of CH_2O_2 (Atkinson et al., 1989; Dognon et al., 1985). An alternative formation of nitrates from the recombination of halogenated RO_2 with NO is uncertain; for the C_1 case it is most probably unimportant. The recombination of halogenated peroxi radicals with NO_2 occurs with similar rate coefficients to those of the unsubstituted radicals, i.e. k $\cong 10^{-11}$ cm^3/s in the high pressure limit (Atkinson et al., 1989). The pernitrates formed, however, are considerably more stable in the halogenated series (Caralp et al., 1988a) with an increase of the RO_2 -NO_2 bond strength of approximately 4.3 kcal/mol.
- Reactions of halogenated RO_2 with HO_2 have apparently not yet been studied. However, there appears to be no reason to assume that they would not occur and that hydroperoxides will be the products in complete analogy to the unsubstituted systems. Since the RO_2/HO_2-interactions, however, are in competition with the RO_2/NO_x-interactions and since the latter are faster in the substituted cases, we expect reactions between halogenated RO_2 and HO_2 to be generally less important.
- As a result of modified bond strengths, halogenated oxi radicals present new types of reactions. Whereas simple alkoxi radicals such as CH_3O and C_2H_5O only react with O_2 (to form aldehyde + HO_2) and not by C-H or C-C bond rupture, the latter reaction is induced upon halogen substitution. As a result, C-Cl and C-C bond dissociations may become competitive events, even when there are remaining H atoms in the oxi radical (Betrand et al., 1971). Fluorine subsitution in the α-position does not significantly affect the C-Cl bond strength, but it tends to make C-C bonds more stable (McMillen and Golden, 1982). These processes are considered in more detail in the subsequent section.

3.2. Discussion of specific examples

In the following we will discuss the possible atmospheric degradation pathways of a number of specific HCFC's and CFC's in the light of the above principles. The available kinetic information from laboratory studies is too weak to make a firm assessment except perhaps for the more simple cases, i.e. $CHClF_2$.

For the sake of brevity we will condense the initiation reactions as long as they are expected to follow the general pattern of HC oxidation, i.e. we will use the symbol

$$\text{——}\,\mathrm{OX}\,\longrightarrow$$

to indicate the sequence: H atom abstraction by OH/O_2 addition/reduction with NO, and will concentrate on the subsequent fate of the oxi radicals. This is done because from the reactions of these radicals the largest differences compared to the hydrocarbon system and between the individual substituted cases are to be expected. It must be understood, though, that in each case presented, additional products such as peroxinitrates and hydroperoxide which arise as chain termination steps from the interactions of peroxi radicals with NO_2 and HO_2 will also occur. They are listed together with the carbonyl compounds in the individual lists of expected products.

As a general rule we have used thermochemical arguments as a guideline of discussing the atmospheric fate of the individual oxi radicals. This has two substantial shortcomings:

- The thermodynamic data base is derived using group additivity rules (Benson, 1976; see appendix). Although this leads generally to acceptable accuracy it is expected to be less reliable for halogen substituted compunds due to polar effects, in particular for F-substitution (Chen et al., 1975). As a consequence the calculated enthalpies of reaction, which in cases comprising fluorinated compounds are the difference between large numbers, may even be uncertain with regards to the sign of their values.
- There is no direct way to relate enthalpies of reaction to a kinetic quantity such as an activation energy. However, we may assume that intrinsic activation barrieres for C-C or C-Cl fission in a radical are small such that the likelihood of these processes to occur will be governed by thermochemistry.

(i) HCFC 22: CHF_2Cl

$$CHF_2Cl \text{ —— } OX \longrightarrow CF_2ClO$$

followed by:

$$CF_2ClO \rightarrow CF_2O + Cl \qquad \Delta H_R = -30 \text{ kcal/mol}$$

There is evidence from various laboratory studies (Carr et al., 1986; Sanhueza, 1977; Hauteclogue, 1980; Lesclaux et al., 1987; Zellner), mainly performed on the photo-oxidation of CHX_3 type compounds, which indicate that a Cl atom is readily released from CX_3O. A rate coefficient of 7×10^5 s^{-1} at 298 K has been determined for CF_2ClO (Carr et al., 1986). The alternative dissociation pathway

$$CF_2ClO \rightarrow CFClO + F$$

is endothermic by 10 kcal/mol and can safely be discarded. The thermal decay rate of CF_2ClO under atmospheric conditions is comparable to the rate of reaction of CH_3O with O_2. It ensures the rapid transformation of CHF_2Cl to CF_2O with accompanied release of the Cl atom and negligible build-up of CF_2ClO.

CF_2O is considered to be stable with regards to reaction with any of the tropospheric oxidants. However, it is very susceptible to hydrolysis (yielding CO_2 and HF) and is therefore most likely to be removed from the troposphere by this pathway. In the stratosphere CF_2O may be degraded by reaction with $O(^1D)$, viz.

$$CF_2O + O(^1D) \rightarrow CO_2 + F_2$$

($k = 2.2 \times 10^{-11}$ cm^3 (Atkinson et al., 1989)) or by photolysis. However, its UV absorption is very weak even at 220 nm ($\sigma \sim 5 \times 10^{-22}$ cm^2 (DeMore et al., 1987).

Summary of expected products from CHF_2Cl:

Carbonyl compounds: CF_2O
Others: $CF_2ClO_2NO_2$, CF_2ClOOH

(ii) HCFC 123: $CHCl_2CF_3$

$$CHCl_2CF_3 \xrightarrow{OX} CF_3CCl_2O$$

followed by:

$$CF_3CCl_2O \rightarrow CF_3CClO + Cl \qquad \Delta H_R = -3 \text{ kcal/mol}$$

There is no direct evidence that this reaction occurs. It is suggested on the basis of its exothermicity. The alternative dissociation pathway

$$CF_3CCl_2O \rightarrow CF_3 + CCl_2O \qquad \Delta H_R = +2 \text{ kcal/mol}$$

is thermodynamically less favourable and therefore not expected to be competitive with the α -Cl-elimination. The subsequent fate of trifluoroacetylchloride (CF_3CClO) is uncertain. In the troposphere it is not expected to react with OH. Similarly, on the basis of the CCl_2O/CH_2O analogy its photolysis is expected to be slower than that of CH_3CHO. However, CF_3CClO is known to be highly soluble and easily hydrolyzed with trifuoroacetic acid as a product (Beilstein, 1960). Therefore we may expect the lifetime of CF_3CClO to be determined by wash-out or by transport to the ocean. There is therefore little potential for chlorine transport into the stratosphere.

Summary of expected products from $CHCl_2CF_3$:

Carbonyl compounds: CF_3CClO
Other products: $CF_3CCl_2O_2NO_2$, CF_3CCl_2OOH.

(iii) HCFC 124: $CHFClCF_3$

$$CHFClCF_3 \xrightarrow{OX} CF_3CFClO$$

followed by:

$$CF_3CFClO \rightarrow CF_3 + CFClO \qquad \Delta H_R = -4 \text{ kcal/mol}$$

C-C bond fission of CF_3CFClO seems to be the most favourable reaction of this radical. The altemative α - Cl - elimination

$$CF_3CFClO \rightarrow CF_3CFO + Cl \qquad \Delta H_R = +4 \text{ kcal/mol}$$

is thermodynamically less likely and may not be competitive with the former. Therefore we expect the Cl-atom of $CHFClCF_3$ to be stored in $CFClO$.

The atmospheric fate of CFClO is presently not well known. It must be considered stable with regards to reaction with any of the tropospheric oxidants and its photolysis is very slow in the troposphere (DeMore et al., 1987). However, CFClO may be subject to hydrolysis (yielding CO_2, HF and HCl) and is expected to be removed from the troposphere by this pathway.

The subsequent oxidation of the CF_3 radical in the troposphere is highly speculative. It is expected to undergo the normal oxidation chain producing CF_3O radicals. However, there is no apparent thermodynamically allowed pathway for decomposition or reaction with O_2 of this radical. Therefore, CF_3O may be expected to react with other trace gases such as NO or HO_2, viz.

$$CF_3O + NO \rightarrow CF_3ONO$$

$$CF_3O + HO_2 \rightarrow CF_3OH + O_2$$

Summary of expected products from $CHFClCF_3$:

Carbonyl compounds: CFClO, (CF_3CFO)
Other products: $CF_3CFClO_2NO_2$, $CF_3CFClOOH$
(CF_3ONO, CF_3OH)

(iv) HCFC 141b: CCl_2FCH_3

$$CCl_2FCH_3 \text{ —— OX} \longrightarrow CCl_2FCH_2O$$

followed by:

$$CCl_2FCH_2O + O_2 \rightarrow CCl_2FCHO + HO_2 \qquad \Delta H_R = -32 \text{ kcal/mol}$$

Due to the remaining α - atoms the CCl_2FCH_2O radical is expected to react predominantly with O_2 to produce a perhalogenated acetaldehyde in accordance with the standard hydrocarbon oxidation chain. Chlorine release from the oxi radical is not possible. Moreover, β - scission of CCl_2FCHO, viz

$$CCl_2FCH_2O \rightarrow CCl_2F + CH_2O \qquad \Delta H_R = +7 \text{ kcal/mol}$$

is endothermic and may therefore not be competitive with the O_2 reaction.

The subsequent fate of the aldehyde will most likely be degradation via initial OH attack to yield CO_2 + CCl_2F (CClFO), viz.

$$CCl_2FCHO \text{ —— OX} \longrightarrow CCl_2FC(O)O$$

$$CCl_2FC(O)O \rightarrow CCl_2F + CO_2$$

$$CCl_2F + O_2 \rightarrow CCl_2FO_2$$

$$CCl_2FO_2 + NO \rightarrow CCl_2FO + NO_2$$

$$CCl_2FO \rightarrow CClFO + Cl$$

Due to the higher OH reaction rate of the aldehyde compared to the initial HCFC, this sequence corresponds essentially to the release of one chlorine atom instantaneous with the degradation of the HCFC. The second one is being stored in CClFO, the fate of which has been discussed under (iii). It may be worthy of note that β-scission of the oxiradical will produce the same products.

Summary of expected products from CCl_2FCH_3:

Carbonyl compounds: CCl_2FCHO, CClFO, (CH_2O)
Other products: $CCl_2FCH_2O_2NO_2$, CCl_2FCH_2OOH,
$CCl_2FC(O)O_2NO_2$ (from the oxidation of CCl_2FCHO),
$CCl_2FO_2NO_2$, CCl_2FOOH (from the oxidation of CCl_2FCHO)

(iv) HCFC 142b: $CClF_2CH_3$

$$CClF_2CH_3 \text{ —— OX} \longrightarrow CClF_2CH_2O$$

followed by:

$$CClF_2CH_2O + O_2 \rightarrow CClF_2CHO + HO_2 \qquad \Delta H_R = -29 \text{ kcal/mol}$$

In complete analogy to Cl_2FCH_2O we expect $CClF_2CH_2O$ to react predominantly with O_2 to form perhalogenated acetaldehyde. Chlorine release from $CClF_2CH_2O$ is not possible. Moreover, the β- scission reaction

$$CClF_2CH_2O \rightarrow CClF_2 + CH_2O \qquad \Delta H_R = +10 \text{ kcal/mol}$$

is more endothermic than in the 141b case and hence may be entirely negligible.

The subsequent oxidation of $CClF_2CHO$ will lead to $CClF_2 + CO_2$; whereupon $CClF_2$ radicals will oxidize to CF_2O. As a consequence we expect the release of the chlorine content of HCFC 142b instantaneous with the initial OH attack. However, since HCFC 142b has a relatively long tropospheric lifetime (~ 28 years), some of this degradation will always occur in the stratosphere.

Summary of expected products from $CClF_2CH_3$:

Carbonyl compounds: $CClF_2CHO$, CF_2O, (CH_2O)
Other compounds: $CClF_2CH_2O_2NO_2$, $CClF_2CH_2OOH$
$CClF_2C(O)O_2NO_2$, $CClF_2O_2NO_2$, $CClF_2OOH$
(from the oxidation of $CClF_2CHO$).

(vi) HFC 125: CHF_2CF_3

$$CHF_2CF_3 \text{ —— OX} \longrightarrow CF_3CF_2O$$

followed by:

$$CF_3CF_2O \rightarrow CF_3 + CF_2O \qquad \Delta H_R = -23 \text{ kcal /mol}$$

The perfluorinated oxi radical CF_3CF_2O is expected to be thermally unstable with respect to C-C bond fission. The alternative elimination of an F-atom to yield CF_3CFO is endothermic by ~ 25 kcal/mol and can safely be discarded. The subsequent atmospheric fates of CF_3 and CF_2O have been discussed above (compare (iii) and (i)).

Summary of expected products from CHF_2CF_3:

Carbonyl compounds: CF_2O
Other products: $CF_3CF_2O_2NO_2$, CF_3CF_2OOH,
(CF$_3$ONO, CF$_3$OH)

(vii) HFC 134a: CH_2FCF_3

$$CH_2FCF_3 \text{ —— OX} \longrightarrow CF_3CHFO$$

followed by:

$$CF_3CHFO + O_2 \rightarrow CF_3CFO + HO_2 \qquad \Delta H_R = -38 \text{ kcal/mol}$$

and, alternatively,

$$CF_3CHFO \rightarrow CF_3 + CHFO \qquad \Delta H_R = 8 \text{ kcal/mol}$$

Due to the hydrogen content of CF_3CHFO this radical is expected to react readily with O_2 yielding perfluoroacetylfluoride. The alternative C-C bond fission is sufficiently exothermic to be expected as a competitive reaction pathway. Thermal elimination of an H atom from CF_3CHFO on the other hand is endothermic (+ 11 kcal/mol) and can safely be discarded.

The product CF_3CFO is not expected to react with any of the tropospheric oxidants, nor to be subject to photolysis. However, in analogy to CF_2O and CF_3CClO it may readily hydrolyze yielding CF_3OOH and HF as products. Therefore its removal rate from the troposphere may be determined by the rate of wash-out or by transport to the ocean surface.

The atmospheric fate of the CF_3 product has been discussed above (cf (iii)). For the second product resulting from this channel, CHFO, we expect both photolysis and reaction with OH as possible degradation pathways, viz.

$$\begin{aligned} CHFO + h\nu &\rightarrow CFO + H \\ &\rightarrow CO + HF \\ OH + CHFO &\rightarrow CFO + H_2 \end{aligned}$$

The consecutive reactions of the CFO radical are highly uncertain. Due to the strong C-F bond we must expect other reactions than for CHO and propose the following sequence

$$\begin{aligned} CFO + O_2 &\rightarrow FC(O)O_2 \\ FC(O)O_2 + NO_2 &\rightarrow FC(O)O_2NO_2 \end{aligned}$$

$$FC(O)O_2 + NO \rightarrow FC(O)O + NO_2$$

$$FC(O)O + HO_2 \rightarrow FC(O)\,OH + O_2$$

with fluorinated formic acid as a product, which may further stabilize by HF elimination.

Summary of expected products from CH_2FCF_3:

Carbonyl compounds: CF_3CFO, $CHFO$,
Other products: $CF_3CHFO_2NO_2$, $CF_3CHFOOH$,
$FC(O)O_2NO_2$, $FC(O)OH$ (from the oxidation of CHFO)

(viii) HFC 152a: CH_2CH_3

There are two different initial oxidation pathways, viz.

(a) $$CHF_2CH_3 \xrightarrow{OX} CHF_2CH_2O$$

(b) $$\text{OX} \text{ —— } CH_3CF_2O \longrightarrow$$

arising from α-and β-H-abstraction from the parent by OH radicals. Apparently, the relative rates of these processes have not been directly measured. However, there is indirect evidence from reactions of OH and Cl radicals with fluorinated alkanes (Martens et al., 1976, Tschuikow-Roux et al., 1985, Singleton et al., 1980) that suggest preferential attack of the α-(fluorinated) position yielding predominantly CH_3CF_2O (channel b) despite the statistical advantage of the β-position. However, in the subsequent presentation we will still consider the possible final products arising from both types of oxi radicals.

For CHF_2CH_2O we expect the reaction with O_2 as the most likely pathway of its subsequent removal, viz.

$$CHF_2CH_2O + O_2 \rightarrow CHF_2CHO + HO_2 \qquad \Delta H_R = -29 \text{ kcal/mol}$$

The alternative C-C-bond fission

$$CHF_2CH_2O \rightarrow CHF_2 + CH_2O \qquad \Delta H_R = +11 \text{ kcal/mol}$$

is sufficiently endothermic to be safely discarded. The product, difluoro-ace-taldehyde, will readily oxidize to yield CO_2 and CF_2O as final products, viz.

$$CHF_2CHO \xrightarrow{OX} CHF_2C(O)O$$

$$CHF_2C(O)O \rightarrow CHF_2 + CO_2$$

$$CHF_2 + O_2 \rightarrow CHF_2O_2$$

$$CHF_2O_2 + NO \rightarrow CHF_2O + NO_2$$

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

The oxi-radical formed in channel (b) on the hand is expected to undergo rapid C-C-bond fission, viz.

$$CH_3CF_2O \rightarrow CH_3 + CF_2O \qquad \Delta H_R = -24 \text{ kcal/mol}$$

eventually leading to CO_2 + CF_2O, the same products as expected from CHF_2CH_2O. As a consequence the relative Initiation rate (α- or β-H -atom abstraction) does not modify the main product distribution. It will influence, however, products such as pernitrates and hydroperoxides.

Summary of expected products from CHF_2CH_3:

Carbonyl compounds: CHF_2CHO, CF_2O,
Other products: $CHF_2CH_2O_2NO_2$, CHF_2CH_2OOH,
$CH_3CF_2O_2NO_2$, CH_3CF_2OOH,
$CHF_2C(O)O_2NO_2$, $CHF_2O_2NO_2$ (from the oxidation of CHF_2CHO)
CHF_2OOH (from the oxidation of CHF_2CHO)

4. SUMMARY AND RECOMMENDATIONS

- The mechanisms of the tropospheric degradation of HCFC's such as 22 and 142b suggest that their chlorine content will be released essentially instantaneous with the initial attack of the HCFC by OH. For HCFC 124 this release is prevented due to competitive C-C bond fission.

- HCFC's such as 123 and 141b with two chlorine atoms are expected to release only one of these instantaneously. The second chlorine atom may be stored in relatively long-lived species such as CF_3CClO or CClFO.

- The photochemistry of compounds such as CF_3CClO and CClFO should be investigated in order to assess their potential for chlorine release in the stratosphere.

- The effect of Cl atom release on the chemistry of the troposphere should be assessed.

- The experimental data base is too weak to allow firmer assessment of the degradation mechanism of HCFC's and HFC's. A large uncertainty arises for the reactions of the oxi radicals. Even the thermodynamic data base is too speculative to draw more substantiated conclusions. It is absolutely essential to initiate direct experimental studies in order to validate these assessments.

APPENDIX TABLE: Summary of standard enthalpies of formation used in the present evaluation: (in units of kcal/mol). Calculated quantities are underlined.

Radicals		Carbonyl compounds	
F	18.9 a)	CH_2O	- 26 a)
Cl	28.9 a)	CHFO	- $\underline{88.9}$ f)
HO_2	2.5 b)	CF_2O	-152 a)
CH_3	35.1 b)	CFClO	-102 k)
CHF_2	- 59 b)	CCl_2O	- 52.6 a)
CF_3	-112 a, b)	CHF_2CHO	$\underline{-127}$ l)
CF_2Cl	- 64 b)	$CFCl_2CHO$	$\underline{-90}$ m)
$CFCl_2$	- 23 b)	CF_2ClCHO	$\underline{-131}$ m)
CCl_3	18.5 a)	CF_3CFO	$\underline{-235}$ n)
CF_3O	$\underline{-145}$ c), -157 d)	CF_3CClO	$\underline{-198}$ o)
CF_2ClO	- 93 e), - $\underline{97}$ f)		
$CFCl_2O$	- $\underline{49}$ g), - $\underline{49}$ f)		
CF_3CF_2O	$\underline{-241}$ h)		
CF_3CHFO	$\underline{-193}$ i)		
CHF_2CH_2O	$\underline{-96}$ j)		
CH_3CF_2O	$\underline{-93}$ j)		
CF_3CFClO	$\underline{-210}$ j)		
CF_3CCl_2O	$\underline{-166}$ j)		
CF_2ClCH_2O	$\underline{-100}$ j)		
$CFCl_2CH_2O$	$\underline{-56}$ j)		

a) Benson, 1976
b) McMillen and Golden, 1982
c) Calculated from bond additivity rules (Benson, 1976) using [C-(F)} (O)] ~ $[C\text{-}(F)_3(C)] = -158.4$ and a correction for the oxi group of $[O\text{-}(C)] = +13.6$ as derived from $\Delta H_f(CH_3O) = [C\text{-}(H)_3(O)] + [O\text{-}(C)] = 3.5$
d) Batt, 1977
e) Calculated using $[C\text{-}(F)_2(Cl)(O)] \sim (C\text{-}(F)_2(Cl)(C)] = -106.3$ (Benson, 1976)
f) MNDO-calculation from Rayez et al., 1987
g) Calculated from $\Delta H_f(CF_2ClO)$ using a correction for F/Cl-exchange as derived from ΔH_f's for substituted CX_3 radicals
h) Calculated using $[C\text{-}(F)_3(C)] = -158.4$, $[C\text{-}(F)_2(C)(O)] \sim [C\text{-}(F)_2(C)_2] = -97$ (Benson, 1976) and a correction for the oxi group of $[O\text{-}(C)] = +14.3$ as derived from $\Delta H_f(C_2H_5O) = -4$ and the corresponding group contributions.
i) Calculated as for h) and with $[C\text{-}(H)(F)(O)] = -49$ (Benson, 1976)
j) Calculated according to h) with group contributions from Benson, 1976
k) JANAF Tables, 1979
l) Calculated from $[C\text{-}(CO)(F)_2(Cl)] = -102$ and a correction for substitution of Cl by H according to Benson, 1976 and $[CO\text{-}(C)(H)] = -26.9$
m) Calculated as for l) and by applying a correction for F exchange by Cl
n) Calculated from $[C\text{-}(CO)(F)_3] = -158$ (Benson, 1976) and $[CO\text{-}(C)(F)] = -77$, where the latter was obtained from [CO-(C)(Cl)] (see o.)) and a correction for Cl/F exchange.
o) Calculated from $[C\text{-}(CO)(F)_3] = -158$ (Benson, 1976) and $[CO\text{-}(C)(Cl)] = -40$, where the latter was obtained from the experimental ΔH_f for CH_3COCl (-60.5 (Pritchard and Skinner, 1950)) and $[C\text{-}(CO)(Cl)_3] = -20.7$ (Benson, 1976)

VII. LIQUID PHASE PROCESSES

Possible Atmospheric Lifetimes and Chemical Reaction Mechanisms for Selected HCFCs, HFCs, CH_3CCl_3, and their Degradation Products Against Dissolution and/or Degradation in Seawater and Cloudwater

Paul H. Wine

and

W. L. Chameides
Georgia Tech Research Institute and School of Geophysical Sciences
Georgia Institute of Technology
Atlanta, GA 30332

EXECUTIVE SUMMARY

The rates at which eight potential alternative HCFCs and HFCs and methyl chloroform (CH_3CCl_3) can be removed from the atmosphere by dissolution and reaction in the oceans and in cloudwater have been estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the aqueous phase. The HCFCs and HFCs considered are $CHCl_2CF_3$ (HCFC-123), $CFCl_2CH_3$ (HCFC-141b), CF_2ClCH_3 (HCFC-142b), CHF_2Cl (HCFC-22), $CHFClCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), and CHF_2CF_3 (HFC-125).

Cloudwater is found to be of no importance as an atmospheric sink for any of the above compounds. Best-estimate lifetimes for all eight HCFCs and HFCs toward removal in the oceans are greater than 77 years, with only HCFC-22, HCFC-123, and HCFC-141b having lifetimes shorter than 200 years. The most reactive of the nine species considered toward removal in the oceans is methyl chloroform with a best-estimate lifetime of 42 years and a minimum reasonable lifetime of 22 years. Important removal mechanisms for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b in seawater are hydrolysis and reaction with hydrated electrons. Improved hydrolysis kinetics data and Henry's law solubility data for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b would help to reduce the uncertainties in the aqueous phase removal rates of these species, as would improved estimates of the hydrated electron concentration in seawater.

Gas phase degradation products of the eight HCFCs and HFCs include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates. Although handicapped by the total absence of Henry's law solubility data for any of the compounds of interest and the limited availability of relevant kinetic data, an assessment of the rates and mechanisms of aqueous phase removal of the gas phase degradation products has been carried out.

The species X_2CO, HXCO, CH_3CXO, CF_3OH, CX_3OONO_2, and ROOH (X = F or Cl, R = halo-substituted methyl or acetyl) are all expected to be removed from the atmosphere on time scales limited by transport to cloudy regions or the marine boundary layer (i.e. about 1 month); aqueous phase reactions of these species result in the formation of chloride, fluoride, and carbon dioxide, as well as formic, acetic, and oxalic acids. The species CX_3CXO, CX_3CX_2OOH, $CX_3CX_2OONO_2$, $CX_3C(O)OONO_2$, and $CX_3C(O)OOH$ are also expected to be removed from the atmosphere rapidly, and their aqueous phase reactions result in the formation of halo-substituted acetates, $CX_3C(O)O^-$.

The species $CX_3C(O)OH$ are very acidic and, as a result, are highly soluble in cloudwater. These acids are expected to be rapidly removed from the atmosphere by rainout. However, the aqueous phase species $CX_3C(O)O^-$ are expected to be resistant to chemical degradation. Trichloroacetate can thermally decompose on a time scale of 2-10 years to yield carbon dioxide and chloroform. In fresh water, the reaction of $CCl_3C(O)O^-$ with the hydrated electron is also expected to occur on a time scale of a few years. The species $CFCl_2C(O)O^-$, $CF_2ClC(O)O^-$, and $CF_3C(O)O^-$ may have very long aqueous phase lifetimes. The longest lived species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.

One possible gas phase degradation product about which very little is known is CF_3ONO_2. This compound has never been observed, and may be thermally unstable. If CF_3ONO_2 is thermally stable, then it may have a long lifetime toward aqueous phase removal. Henry's law solubility data and hydrolysis kinetics data for CF_3ONO_2 are needed before its aqueous phase removal rate can be assessed with any degree of confidence.

N92-15445

POSSIBLE ATMOSPHERIC LIFETIMES AND CHEMICAL REACTION MECHANISMS FOR SELECTED HCFCs, HFCs, CH_3CCl_3, AND THEIR DEGRADATION PRODUCTS AGAINST DISSOLUTION AND/OR DEGRADATION IN SEAWATER AND CLOUDWATER

P.H. Wine and W.L. Chameides

Georgia Tech Research Institute and School of Geophysical Sciences
Georgia Institute of Technology
Atlanta, GA 30332

PRECEDING PAGE BLANK NOT FILMED

1. INTRODUCTION

For a wide variety of atmospheric species including CO_2, HNO_3, and SO_2, dissolution in seawater or cloudwater followed by hydrolysis or chemical reaction represents a primary pathway for removal from the atmosphere (Peters, 1983; Liss, 1983; Chameides and Davis, 1982). In order to determine if this mechanism can also remove significant amounts of atmospheric chlorofluorocarbons (HCFCs), fluorocarbons (HFCs), and their degradation products, an investigation was undertaken as part of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). In this investigation, the rates at which $CHCl_2CF_3$ (HCFC-123), CCl_2FCH_3 (HCFC-141b), $CClF_2CH_3$ (HCFC-142b), $CHClF_2$ (HCFC-22), $CHClFCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), CHF_2CF_3 (HFC-125), and CH_3CCl_3 can be dissolved in the oceans and in cloudwater were estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the ocean or cloudwater. The ability of cloudwater and rainwater to remove gas phase degradation products of these compounds was also considered as was the aqueous phase chemistry of the degradation products. The results of this investigation are described below.

2. OCEANIC REMOVAL OF HCFCs AND HFCs

The exchange of gases between the atmosphere and ocean is typically simulated with the "stagnant film" model (Danckwerts, 1970). In this model, transfer from the atmosphere to the ocean is assumed to be limited by the rate at which the gas can diffuse (via molecular diffusion) through a thin film of air residing directly above the ocean-atmosphere boundary and a thin film of seawater residing below the boundary. Under these conditions, ϕ_o, the steady state flux of a species from the atmosphere to the ocean (in molecules $cm^{-2}\ s^{-1}$) is given by (Liss, 1983)

$$\phi_o = \{C_A - [I]_o/(HRT)\} \frac{1}{\left[r_A + r_S/(HRT\ N_A\ 10^{-3})\right]} \tag{1}$$

where r_A and r_S are the transfer resistances (in s cm^{-1}) of the atmospheric and oceanic film, respectively, H is the species Henry's or solubility constant (M atm^{-1}), $R = 1.36 \times 10^{-22}$ atm cm^3/molecule/K is the gas constant, T is temperature (assumed to be 285K), N_A is Avogadro's number, C_A is the species' concentration (in molecules cm^{-3}) at the bottom of the atmospheric mixed layer, and $[I]_o$ is the species concentration (in M or moles per liter) at the top of the oceanic mixed layer. It can be shown by solving the one-dimensional diffusion equation that the transfer resistances in Eqn. [1] are given by the thicknesses of the films divided by the molecular diffusion coefficient; in the case of r_A one would use a gas-phase diffusion coefficient of about 0.01 $cm^2\ s^{-1}$, while for r_S an aqueous-phase diffusion coefficient of about 10^{-5} $cm^2\ s^{-1}$ would be used (Danckwerts, 1970). For conditions typical of the ocean, r_A is about 1.25 s cm^{-1}, while r_S is about 170 s cm^{-1} (Liss, 1983). For the HCFCs and HFCs under consideration here, $H \leq 0.2$ M $atm^{-1}$and thus

$$r_S/(HRT\ N_A\ 10^{-3}) \approx 7/H > 35 >> r_A \tag{2}$$

It follows, therefore, that the oceanic resistance, r_S, dominates for these compounds and Eqn. [1] can be represented by

$$\phi_o = \{HRT\ N_A\ 10^{-3}/r_S\}\ \{C_A - [I]_o/(HRT)\} \tag{3}$$

In order to evaluate Eqn. [3], the species' concentration, $[I]_0$, at the bottom of the oceanic stagnant layer must be defined. This can be accomplished by considering the downward transport of the species through the wave-mixed surface layer of the ocean, which typically extends from the surface (i.e., the bottom of the stagnant ocean film) to the beginning of the main thermocline at about 80 m depth. Following Johnson (1981), the one-dimensional form of the continuity equation for the species in this mixed layer is given by

$$[I]/\ t = -\, k[I] + \ /\ z\,(D\ \ [I]/\ z) \tag{4}$$

where [I] is the species' concentration in the layer, t is time, k is the species' pseudo first-order loss rate due to hydrolysis or chemical reaction, z is depth below the surface, and D is the eddy diffusion coefficient used to parameterize the effect of turbulence on vertical transport. The value of D assumed in our calculations is 40 $cm^2\ s^{-1}$ (Johnson, 1981).

Assuming that [I] tends to zero as z gets large, the steady state solution of [4] yields the following form for ϕ_0 (Johnson, 1981):

$$\phi_0 = (Dk)^{1/2}\,[I]_0\,N_A\,10^{-3} \tag{5}$$

Equating [3] and [5], it follows that

$$[I]_0 = (HRT)\,C_A/\{1 + r_S\,(Dk)^{1/2}\} \tag{6}$$

and substituting [6] into [5] yields a closed form for ϕ_0; i.e.,

$$\phi_0 = (Dk)^{1/2}\,N_A\,10^{-3}\,HRT\,C_A/\{1 + r_S\,(Dk)^{1/2}\} \tag{7}$$

Substituting for R, N_A, and T, Eqn [7] reduces to

$$\phi_0 = (H\,C_A/0.04)\,\{r_S + 1/(Dk)^{1/2}\}^{-1} \tag{8}$$

Table 1. Atmospheric Lifetimes (in years) Against Oceanic Loss as a Function of Solubility (H) and First-Order Loss Coefficient in Ocean (k)

	H (M atm^{-1})							
	0.001	0.005	0.01	0.02	0.04	0.06	0.08	0.1
k(s^{-1})								
10^{-11}	73,200	14,600	7,320	3,600	1,830	1,230	916	732
10^{-10}	23,300	4,670	2,330	1,170	583	389	292	233
10^{-9}	7,550	1,510	755	377	189	126	94	75
10^{-8}	2,560	511	256	128	64	43	32	25
10^{-7}	978	196	98	49	24.5	16	12	9.8

If the species is well-mixed in the atmosphere, it follows from [8] that τ_0, the species' atmospheric lifetime against dissolution in the ocean, is given by

$$\tau_0 = (H_A\ 0.04/f/H)\ \{r_S + 1/(Dk)^{1/2}\} \tag{9}$$

where H_A = 8 km is the atmospheric scale height and f = 0.7 is the fraction of the earth's surface covered by ocean. Values of τ_0 calculated from Eqn. [9] for H varying from 0.001 to 0.1 M atm^{-1} and k varying from 10^{-11} to 10^{-7} s^{-1} are listed in Table 1. It should be noted that Eqn. [9] is only valid for values of H and k such that τ_0 >30 - 60 days. Once the calculated ϕ_0 falls below this value, the assumption used in the above derivation that the species is well-mixed in the atmosphere is no longer valid. In this case, the actual atmospheric lifetime for removal in the oceans will be limited by the time required to transport the species to the marine boundary layer (i.e., about 30 to 60 days).

The values for H and k used to calculate τ_0 for the HFCs and HCFCs of interest in this work are listed in Table 2. For all species except CH_3CCl_3, values for H in seawater were assumed to be 80% of their pure water Henry's law coefficient at a temperature of 285K. Pure water values for H (see Figure 1) were taken from McLinden AFEAS, 1989 (this report) for all species considered except CH_3CCl_3. The Henry's law coefficients for CH_3CCl_3 in pure water and seawater were obtained from the results of Gossett (1987). He found that H = 5.8 x 10^{-8} exp (4130/T) M atm^{-1} in pure water and that addition of .75M

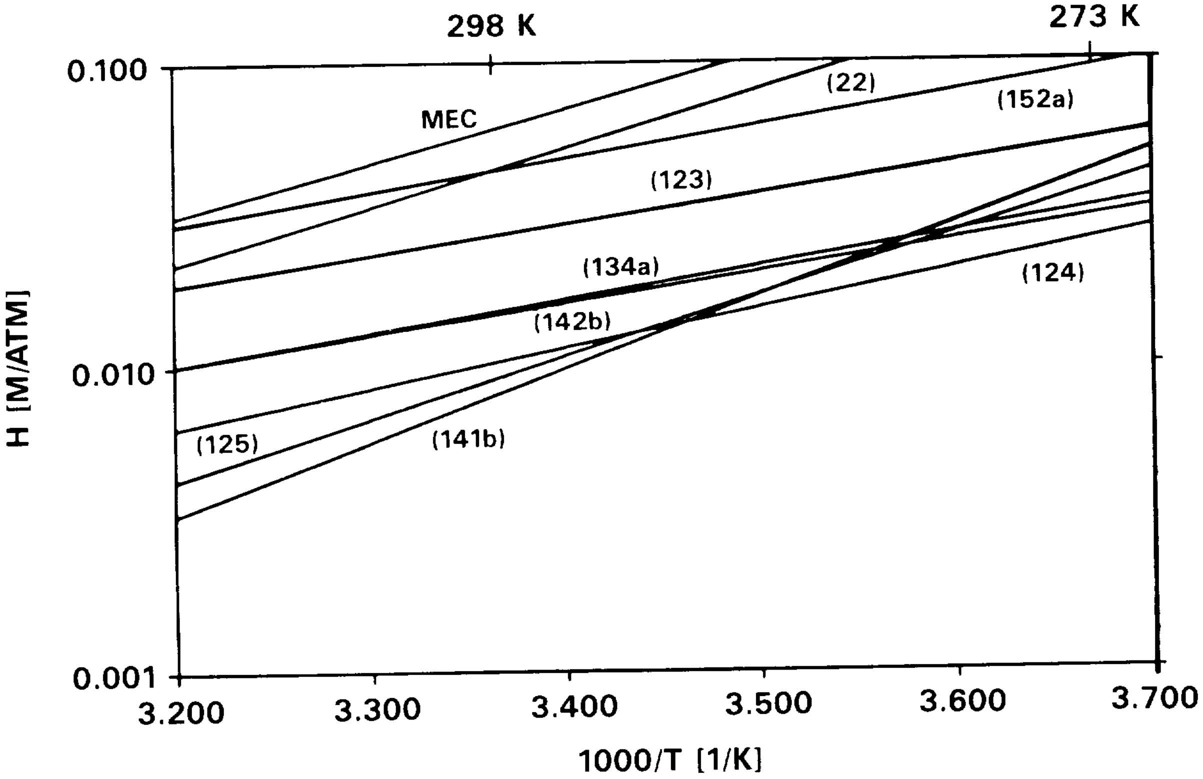


Figure 1. Henry's Law solubilities in pure water for selected HFCs, HCFCs, and CH_3CCl_3 (MEC) as a function of temperature.

Table 2. Solubilities, Pseudo First-Order Loss Rates, and Lifetimes Against Oceanic Removal For Selected HFCs and HCFCs

Species	H(M/atm)	Pseudo First Order Loss Rates (s^{-1})				Lifetime (years)	
		k_h	k_e	k_{OH}	k	b.e.	min
CH_3CCl_3	0.08	4×10^{-9}	1.4×10^{-9}	1.6×10^{-11}	5.4×10^{-9}	42	22
CF_3CHF_2(125)	<0.015	$<10^{-10}$	$<10^{-11}$	4×10^{-12}	$<10^{-10}$	>1500	>700
CF_3CH_2F(134a)	0.02	$<10^{-10}$	$<10^{-11}$	1.2×10^{-11}	$<10^{-10}$	>1100	>530
CH_3CHF_2(152a)	0.05	$<10^{-10}$	$<10^{-11}$	4×10^{-11}	$<10^{-10}$	>460	>210
CF_3CHClF(124)	0.015	10^{-9}	10^{-9}	1.6×10^{-11}	2×10^{-9}	360	170
CH_3CClF_2(142b)	0.02	10^{-9}	10^{-9}	4×10^{-12}	2×10^{-9}	270	130
CF_3CHCl_2(123)	0.03	10^{-9}	10^{-9}	4×10^{-11}	2×10^{-9}	180	85
CH_3CFCl_2(141b)	0.015 - 0.07	10^{-9}	10^{-9}	1×10^{-11}	2×10^{-9}	77-360	36
$CHClF_2$(22)	0.085	3×10^{-10}	3×10^{-10}	6×10^{-12}	6×10^{-10}	110	45

T is assumed to be 285K
b.e. = Lifetime calculated with H and k listed in Table
min = Lifetime calculated with maximum H value listed and k enhanced by a factor of 5

KCl resulted in a 40% decrease in H (the ionic strength of seawater is approximately 0.75M). Gossett's result in pure water at 298K is in excellent agreement with an estimate by Lyman (1985) which was based on solubility and vapor pressure data, but a factor of two larger than an earlier measurement reported by Dilling (1977). While the values for the Henry's law solubilities of most of the species were judged to be known to within about 15%, McLinden AFEAS 1989 has noted the possibility of a significant error in the Henry's Law solubilities cited for CF_3CHF_2 and CH_3CFCl_2. To account for this possibility as well as other unknown systematic errors, we have adopted a range of H-values for CF_3CHF_2 and CH_3CFCl_2. (See Table 2).

Three processes were considered to determine the pseudo first-order loss rate, k, for the compounds of interest. These were hydrolysis, indicated by k_h in Table 2, reaction with hydrated electrons, indicated by k_e in Table 2, and reaction with OH, indicated by k_{OH} in Table 2. The total loss rate is thus given by

$$k = k_h + k_e + k_{OH} \tag{10}$$

The hydrolysis rates in Table 2 for $CHClF_2$ and for CH_3CCl_3 were obtained from McLinden AFEAS, 1989 and Ellenrieder and Reinhard (1988), respectively. New unpublished results (Gerkens and Franklin, 1989) verify the CH_3CCl_3 hydrolysis rate in Table 2 and provide improved temperature dependence data.

The other hydrolysis rates were assumed to be intermediate between that of CH_3CCl_3 and $CHClF_2$ for those species which contain at least one Cl atom (i.e., 10^{-9} s^{-1}) and less than 10^{-10} s^{-1} for those species which do not contain any Cl. It should be noted that the k_h values listed in Table 2 are based on data obtained from fresh water and that the actual hydrolysis rates in seawater may be significantly different. For instance, ionic strength effects have the potential to increase or decrease the hydrolysis rates by as much as 50% (Neely, 1985). In the case of the fluorinated compounds, hydrolysis can be enhanced by perhaps an order of magnitude or more because the large levels of Cl^- ions in seawater can catalyze hydrolysis of fluorocarbons via nucleophilic substitution of Cl for F followed by hydrolysis of the chlorocarbon (Zafiriou, 1975). In order to indicate the possible impact of these effects on our results, sensitivity calculations will be presented in which our estimated values for k are arbitrarily increased by a factor of 5. It should be noted, however, that it does not appear possible for Cl^- catalysis to cause any of the HFCs to have an "effective" hydrolysis rate faster than that of CF_3CHClF, because nucleophilic substitution of OH for Cl is expected to be considerably faster than nucleophilic substitution of Cl for F.

The values for k_e in Table 2 were obtained by assuming an average hydrated electron level in the mixed layer of the ocean of 1×10^{-19} M. This estimate for the concentration of hydrated electrons in the oceans is based on: 1. the observations of Zepp et al. (1987a) which implied a diurnally averaged abundance of free electrons at the surface of fresh water lakes and rivers of about 5×10^{-18} M from the irradiation of dissolved organic matter; 2. the fact that dissolved organic matter is about 10 times less abundant in the ocean than in fresh water (Stumm and Morgan, 1970); and 3. the assumption that free electrons will decrease with increasing depth with a scale depth of 15m due to the attenuation of sunlight in the ocean. (Note that the upper limit for e^- in seawater of 10^{-15} M reported by Swallow (1969) seems much too high based on current information). Second-order rate constants for the reaction of CH_3CCl_3 and $CHClF_2$ with hydrated electrons were taken to be 1.4×10^{10} M^{-1} s^{-1} and 3×10^9 M^{-1} s^{-1}, respectively, based on the observations of Lal et al. (1988) and Salih et al. (1976). Rate constants for the other HFCs and HCFCs which contain Cl atoms were assumed to be intermediate between that of CH_3CCl_3 and $CHClF_2$, i.e. 10^{10} M^{-1} s^{-1} for species containing Cl atoms (cf., Balkas et al., 1971; Anbar and Hart, 1965; Balkas, 1972; Afanassiev et al., 1979; Salih, et al., 1976; Hart et al., 1964; Bullock and Cooper, 1970), and less than 10^8 M^{-1} s^-1 for those species which contain no Cl atoms.

The values of k_{OH} listed in Table 2 were estimated assuming a seawater OH concentration of 4×10^{-19} M (Zepp et al., 1987b; Zafiriou and True, 1979). For CH_3CCl_3, a second-order aqueous-phase rate constant for the OH reaction of 4×10^7 M^{-1} s^{-1} (Lal et al., 1988) was adopted. The second-order rate constants for the other HFCs and HCFCs were assigned values based on their gas phase rate constants relative to the gas phase OH + CH_3CCl_3 rate constant. Comparison of the aqueous phase rate constants reported by Lal, et al. (1988) with known gas phase rate constants for the same reactions seems to justify this procedure.

The resulting lifetimes obtained from Eqn [9] for each of the HFCs and HCFCs considered here are listed in Table 2. Note that two sets of lifetimes are listed in the Table: the 'best estimate' for the values of H and k obtained in the manner described above, and a minimum lifetime obtained from the maximum value estimated for H and a k enhanced by a factor of 5 over the value listed in the Table. With the exception of CH_3CCl_3 and CH_3CFCl_2, it appears likely that the lifetimes for HFCs and HCFCs against removal by dissolution in the oceans are of the order of 100 years or more indicating that this process is unlikely to be of significance. In the case of CH_3CCl_3 and CH_3CFCl_2, however, oceanic removal could be non-negligible depending on the exact Henry's law solubilities and loss rates of these species in seawater. There is also a possibility that the same may be true of $CHClF_2$ and CF_3CHCl_2. Further research to better define the Henry's Law coefficients and loss rates for these species in seawater might prove to be a useful endeavor.

3. REMOVAL OF HCFCs AND HFCs IN CLOUDWATER

The removal of HCFCs and HFCs by dissolution and chemical degradation in cloudwater appears to be much smaller than the rate of removal in the oceans. To illustrate this fact, consider the removal by cloudwater of CH_3CCl_3, probably the most readily removed of all the compounds considered here. As discussed above, CH_3CCl_3 probably has a Henry's law solubility in cloudwater ($T \geq 273K$) of ≤ 0.2 M atm^{-1}. Its pseudo first-order rate of removal in cloudwater is probably controlled by reaction with aqueous-phase OH radicals; given a second-order, aqueous-phase rate constant against reaction with OH of 4×10^7 M^{-1} s^{-1} (Lal et al., 1988) and a cloudwater OH concentration of about 2×10^{-13} M (Chameides, 1984; Jacob, 1986), we estimate a k-value for CH_3CCl_3 in cloudwater of about 8×10^{-6} s^{-1}. Assuming an average column content of liquid water in the atmosphere of about 10^{-4} L cm^{-2} (Junge, 1963) and assuming gas-aqueous-phase equilibration, (appropriate for $H \leq 10^3$ M atm^{-1}, cf., Xing and Chameides, 1989) it follows that RC, the rate of loss of the species in cloudwater (in molecules cm^{-2} s^{-1}), is given by

$$RC = X\ (0.2\ \text{M atm}^{-1})\ (10^{-4}\ \text{L cm}^{-2})\ N_A\ 8 \times 10^{-6}\ \text{s}^{-1} \qquad (11)$$

where X is the species volume mixing ratio. If we further assume that the species is well-mixed in the atmosphere, Eqn. [11] implies an atmospheric lifetime, τ_c, against removal by cloudwater of

$$\tau_c = X\ (2.5 \times 10^{19}\ \text{molec cm}^{-3})\ H_A/RC \approx 5{,}000\ \text{years} \qquad (12)$$

Even longer lifetimes are obtained as H and k are decreased for the other HFCs and HCFCs.

4. DEGRADATION PRODUCTS OF HYDROLYSIS AND HYDRATED ELECTRON REACTIONS

Hydrolysis of C_2 halocarbons can proceed via either substitution or elimination mechanisms, while only the substitution pathway is available for C_1 halocarbons. Primary halocarbons generally hydrolyze predominantly by the substitution pathway, with elimination becoming more important for branched halocarbons (Roberts and Caserio, 1965). For CH_3CCl_3, hydrolysis is known to yield 70-80% $CH_3C(O)OH$ (the substitution product) and 20-30% $H_2C=CCl_2$ (the elimination product) (Ellenrieder and Reinhard, 1988; Gerkens and Franklin, 1989). Product information is not available for the other halocarbons of interest in this assessment.

The haloethylenes formed via elimination are resistant to hydrolysis and relatively insoluble in water (see, for example, Gossett, 1987). Degradation of these compounds is expected to occur rapidly in the gas phase following volatilization from the aqueous phase.

Hydrolysis via the substitution pathway is a multistep process which involves formation of unstable intermediates such as α-haloalcohols and acid halides. Probable intermediate and end products are summarized in Table 3. The expected stable products are: $HC(O)OH$ from $CHClF_2$; $CH_3C(O)OH$ from CH_3CFCl_2 and CH_3CF_2Cl; CF_3CHO from CF_3CHCl_2, CF_3CHF_2 and CF_3CHFCl; CF_3CH_2OH from CF_3CH_2F;

Table 3. Probable Reaction Pathways for Hydrolysis of the Halocarbons of Interest via Substitution Mechanisms

$$CH_3CCl_3 \xrightarrow{H_2O} CH_3CCl_2OH \xrightarrow{-HCl} CH_3CClO \xrightarrow{H_2O} CH_3C(O)OH$$

$$\text{NET: } CH_3CCl_3 + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 3Cl-$$

$$CHClF_2 \xrightarrow{H_2O} CHF_2OH \xrightarrow{-HF} HCFO \xrightarrow{H_2O} HC(O)OH$$

$$\text{NET: } CHClF_2 + 2H_2O \rightarrow HC(O)OH + 3H^+ + 2F^- + Cl^-$$

$$CF_3CHCl_2 \xrightarrow{H_2O} CF_3CHClOH \xrightarrow{-HCl} CF_3CHO$$

$$\text{NET: } CF_3CHCl_2 + H_2O \rightarrow CF_3CHO + 2H^+ + 2Cl-$$

$$CH_3CFCl_2 \xrightarrow{H_2O} CH_3CFClOH \xrightarrow{-HCl} CH_3CFHO \xrightarrow{H_2O} CH_3C(O)OH$$

$$\text{NET: } CH_3CFCl_2 + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 3H^+ + 2Cl- + F-$$

$$CH_3CF_2Cl \xrightarrow{H_2O} CH_3CF_2OH \xrightarrow{-HF} CH_3CFO \xrightarrow{H_2O} CH_3C(O)OH$$

$$\text{NET: } CH_3CF_2Cl + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 2F- + Cl-$$

$$CF_3CHFCl \xrightarrow{H_2O} CF_3CHFOH \xrightarrow{-HF} CF_3CHO$$

$$\text{NET: } CF_3CHFCl + H_2O \rightarrow CF_3CHO + 2H^+ + Cl- + F-$$

$$CF_3CH2F \xrightarrow{Cl-} CF_3CH_2Cl \xrightarrow{H_2O} CF_3CH_2OH$$

$$\text{NET: } CF_3CH_2F + H_2O \rightarrow CF_3CH_2OH + H^+ + F-$$

$$CH_3CHF_2 \xrightarrow{Cl-} CH_3CHFCl \xrightarrow{H_2O} CH_3CHFOH \xrightarrow{-HF} CH_3CHO$$

$$\text{NET: } CH_3CHF_2 + H_2O \rightarrow CH_3CHO + 2H^+ + 2F-$$

$$CF_3CHF_2 \xrightarrow{Cl-} CF_3CHFCl \xrightarrow{H_2O} CF_3CHFOH \xrightarrow{-HF} CF_3CHO$$

$$\text{NET: } CF_3CHF_2 + H_2O \rightarrow CF_3CHO + 2H^+ + 2F-$$

CH_3CHO from CH_3CHF_2. The fluorine containing end product CF_3CH_2OH is expected to be volatilized from the ocean to the gas phase where it would be oxidized by OH radicals. The recent work of Betterton and Hoffmann (1988) suggests that the other fluorine containing end product, CF_3CHO, will have a large effective Henry's law solubility (10^5 - 10^6 M atm^{-1}) due to efficient hydration,

$$CF_3CHO + H_2O \rightarrow CF_3CH(OH)_2 \qquad (R1)$$

The gem-diol species $CF_3CH(OH)_2$ is expected to be relatively stable in seawater. The lifetime of $CF_3CHO \rightleftarrows CF_3CH(OH)_2$ in seawater may be limited by oxidation of the small equilibrium concentration of $CF_3CHO(g)$ via reaction with OH radicals.

The reactions of hydrated electrons with halocarbons result in the formation of halo-substituted peroxy radicals.

$$RX + e^- \rightarrow R + X^- \qquad (R2)$$

$$R + O_2 \rightarrow RO_2 \qquad (R3)$$

As mentioned in an earlier section, (R2) proceeds at a diffusion controlled rate for most chlorocarbons, but is considerably slower for fluorocarbons. Attack of chlorofluorocarbons by e^- will always result in removal of a chlorine atom. Haloperoxy radicals are strong oxidizing agents which, in seawater, are expected to undergo electron transfer reactions with resultant production of halohydroperoxides. The aqueous phase chemistries of haloperoxy radicals and halohydroperoxides are considered in some detail in later sections of this report.

5. ALTERNATIVE DEGRADATION PATHWAYS

In addition to hydrolysis and reaction with hydrated electrons, a number of other halocarbon degradation pathways are operative in selected environments such as anoxic contaminant groundwaters, surface waters with high concentrations of metal ion reductants, and regions of high biological activity. These pathways are discussed in a recent review by Vogel, et al. (1987). They include metal catalyzed hydrogenolysis and dihalo-elimination, nucleophilic substitution of SH^- for X^-, and enzyme catalyzed hydrolysis and halogenation reactions. It seems unlikely that the above processes will make significant contributions to the global removal rate of HCFCs, HFCs, and CH_3CCl_3 from the atmosphere, although research aimed at quantifying their contribution would be worthwhile.

6. AQUEOUS PHASE REMOVAL OF GAS PHASE DEGRADATION PRODUCTS

Several assessments of potential gas phase degradation products have been prepared as part of the Alternative Fluorocarbons Environmental Acceptability Study. The degradation products include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates. Our attempt to assess the lifetimes of the above compounds toward aqueous phase removal is somewhat hampered by the total absence of Henry's law solubilities for any of the compounds of interest. An Appendix is attached to this report which contains tables of Henry's law solubilities for non-halo-substituted analogs, vapor pressure data, acid-base equilibria, and one-electron redox potentials. These data were used extensively in our evaluation. Possible aqueous phase removal rates and degradation mechanisms for each class of gas phase products are considered below.

Acid Halides

Acid halides are known to hydrolyze rapidly. For Cl_2CO, F_2CO, and ClFCO, substitution of OH for X (X = Cl, F) produces a halohydroxycarbonyl which rapidly eliminates HX to yield the end product CO_2. Hydrolysis of the other acid halides of interest, (i.e., HCXO, CH_3CXO, CX_3CXO) proceeds by a single step substitution route to give the corresponding carboxylic acid.

Kinetic data for acid halide hydrolysis in water solvent are rather sparse. Bunton and Fendler (1966) studied the kinetics of CH_3CFO hydrolysis in water as a function of temperature and pH. They obtained the result $k_h = 2.9 \times 10^7 \exp(-6290/T)\ s^{-1}$ independent of pH over the range 2.8-6.8, i.e. $k_h = 0.0051\ s^{-1}$ at 280K and $0.023\ s^{-1}$ at 300K. Hudson and Moss (1962) used stop-flow techniques to investigate the kinetics of CH_3CClO hydrolysis at 300K in 75.6% H_2O - 24.4% dioxan; they measured $k_h = 292\ s^{-1}$, a rate which is expected to be even faster in pure H_2O solvent. Swain and Scott (1953) measured the relative rates of hydrolysis of CH_3CClO and CH_3CFO in 75% acetone - 25% water at 298K and found that CH_3CClO was 7700 times more reactive, in agreement with the reactivity trend suggested by the above-mentioned absolute rate measurements. Ugi and Beck (1961) studied the hydrolysis kinetics of a series of acid chlorides in 10.9 vol % H_2O + 89.1 vol % acetone at 298K and obtained the following rate constants in units of s^{-1}: CH_3CClO, 0.0011; $ClCH_2CClO$, 0.020; $Cl_2CHCClO$, 3.1; Cl_3CClO, >10; Cl_2CO, 1.02. Substitution of Cl for H on the alkyl carbon dramatically increases the rate of hydrolysis, presumably because the electron withdrawing power of Cl results in stabilization of the transition state for water attack on the carbonyl carbon. Substitution of F for H on the alkyl carbon should increase the hydrolysis rate even more dramatically. Based on the above information it seems clear that, with the possible exception of HFCO, all acid halides of interest will hydrolyze more rapidly than CH_3CFO. Hence, the kinetic data of Bunton and Fendler (1966) for CH_3CFO hydrolysis provide a useful lower limit rate coefficient for assessing the maximum lifetime of acid halides toward uptake and hydrolysis in the ocean and in cloudwater.

For temperatures typical of cloudwater and surface seawater, it seems safe to assume that k_h will be greater than $10^{-3}\ s^{-1}$ for all acid halides of interest. Using the 285K effective Henry's law solubility for acetaldehyde of 45 M atm^{-1} (Snider and Dawson, 1985; Betterton and Hoffmann, 1988) as a guide, it also seems safe to assume that $H > 10$ M atm^{-1} for all acid halides of interest, particularly since electron withdrawing substituents such as Cl and F are known to increase the solubility of carbonyls (Betterton and Hoffmann, 1988). On the basis of the formulations described above, these lower limit values for k_h and H imply upper limit lifetimes for the acid halides against removal in the ocean and removal in cloudwater of the order of a month and 2 years, respectively. It should be noted that the maximum lifetime for removal of acid halides by hydrolysis in the ocean is transport limited, and would be only one or two months even if the above lower limits for k_h and H were reduced by a factor of ten each. Hence, there seems to be very little chance that (apparently) important gas phase degradation products such as ClFCO and CF_3CClO (R.A. Cox, AFEAS, 1989 (this report)) will survive in the atmosphere long enough to represent significant sources of stratospheric chlorine.

CF_3OH

In the condensed phase, CF_3OH is known to be unstable toward elimination of HF (Seppelt, 1977),

$$CF_3OH \rightarrow CF_2O + HF \qquad (R4)$$

(R4) probably also occurs in the gas phase. If not, it will occur very rapidly upon uptake of CF_3OH into cloudwater or seawater. Henry's law solubilities for aliphatic alcohols are typically an order of magnitude larger than those of the corresponding aldehydes (Snider and Dawson, 1985). Hence, conversion of CF_3OH to CO_2 + 3HF via HF elimination and subsequent hydrolysis of CF_2O will be as fast as CF_2O hydrolysis if HF elimination occurs in the gas phase and faster if HF elimination occurs in the aqueous phase.

Peroxyacetylnitrates

Both hydrolysis and Henry's law data are available for PAN. At 285K, $H \approx 7$ M atm^{-1} and $k_h \approx 1 \times 10^{-4}$ s^{-1} (Lee, 1984; Holdren, et al., 1984). Based on our earlier discussions, these values suggest a lifetime of about 10 years for PAN removal by cloudwater and of the order of a month for removal in the ocean. Holdren, et al. (1984) have shown that the PAN hydrolysis rate is independent of pH over the range 4.0 - 5.6, and that nitrate is produced as a product. Hence, the hydrolysis reaction is probably

$$CH_3C(O)OONO_2 + H_2O \rightarrow CH_3C(O)OOH + NO_3^- + H^+. \qquad (R5)$$

In the absence of experimental data, it seems reasonable to assume that removal of $CF_nCl_{3-n}C(O)OONO_2$ by hydrolysis in seawater and cloudwater will proceed at a rate somewhat faster than that for PAN due to stabilization of the transition state for water attack on the carbonyl carbon by the electron withdrawing nature of Cl and F. The hydrolysis products are expected to be halo-substituted peroxy acids and nitrate. Lifetimes toward hydrolysis in seawater and cloudwater on the order of a few weeks and few years, respectively seem likely.

Despite the rapid removal rate estimated above, ocean hydrolysis may not be an important atmospheric removal mechanism for the halogenated peroxyacetylnitrates. The marine boundary layer is typified by relatively warm temperatures, low NO_x levels, and high HO_x levels. Under such conditions, conversion of peroxyacetylnitrates to peroxyacetic acids should occur in the gas phase, i.e.

$$CF_nCl_{3-n}C(O)OONO_2 + M \rightarrow CF_nCl_{3-n}C(O)OO + NO_2 + M \qquad (R6)$$

$$CF_nCl_{3-n}C(O)OO + HO_2 \rightarrow CF_nCl_{3-n}C(O)OOH + O_2 \qquad (R7)$$

The stoichiometry of PAN hydrolysis in alkaline solution is (Nicksic, et al., 1967; Stephens, 1967)

$$CH_3C(O)OONO_2 + 2OH^- \rightarrow CH_3C(O)O^- + NO_2^- + O_2 + H_2O \qquad (R8)$$

At a typical seawater pH of 8.1 it is not clear what the relative contributions of (R5) and (R8) to PAN hydrolysis will be. However, since peroxyacetic acid is known to hydrolyze rapidly to acetic acid and H_2O_2 (Lind and Kok, 1986), acetate is produced in either case. Similarly, the long-lived halogen-containing products of $CF_nCl_{3-n}C(O)OONO_2$ hydrolysis are expected to be halo-substituted acetates, although halo-substituted peroxyacetates may be produced as intermediates with lifetimes of hours to days. The chemistry of peroxyacetates is discussed in more detail in a later section.

CF_3ONO_2

It has been suggested in the literature (Hohorst and DesMarteau, 1974) that CF_3ONO_2 is thermally unstable in condensed phases.

$$CF_3ONO_2 \rightarrow CF_2O + FNO_2 \qquad (R9)$$

(R9) may also occur in the gas phase.

If CF_3ONO_2 turns out to be thermally stable, then in the absence of Henry's law solubility data and hydrolysis data, we assume that CF_3ONO_2 will behave similarly to CH_3ONO_2 (methyl nitrate). The Henry's law solubility of CH_3ONO_2 is nearly identical to that of PAN (Lee, et al., 1983). Robertson, et al. (1982) studied the hydrolysis kinetics of isopropylnitrate and three other secondary nitrates in water. Because the observed rates were very slow at room temperature, Robertson, et al.'s experiments were carried out at elevated temperature; the temperature range covered for isopropylnitrate was 340-369K. Extrapolation of Robertson, et al.'s results to lower temperatures suggests $k_h \sim 2 \times 10^{-7}\ s^{-1}$ at 300K and $5 \times 10^{-9}\ s^{-1}$ at 280K. Baker and Easty (1952), have studied the kinetics of neutral hydrolysis (H_2O nucleophile) of methyl-, ethyl-, and isopropylnitrate in 60% ethanol/40% water at 60.2°C; they obtain the relative reactivities methyl:ethyl:isopropyl = 2.0:1.1:4.8. Alkaline hydrolysis (OH^- nucleophile) was found to be about 100 times faster than neutral hydrolysis, but the neutral reaction is expected to dominate under atmospheric conditions. The above results suggest that at 285K, a typical seawater temperature, k_h for methylnitrate is about $4 \times 10^{-9}\ s^{-1}$.

Clearly, removal of CF_3ONO_2 by hydrolysis in cloudwater will be of no importance as an atmospheric loss process. For $H = 1 - 10\ M\ atm^{-1}$ and $k_h = (1 - 10) \times 10^{-9}\ s^{-1}$, the lifetime of CF_3ONO_2 toward hydrolysis in seawater will be in the range 0.1 - 10 years. Measurements of H and k_h for CF_3ONO_2 in seawater would clearly be worthwhile.

It is well established that neutral hydrolysis of simple primary and secondary alkyl nitrates proceeds via an S_N2 mechanism to yield the corresponding alcohol (Baker and Easty, 1952; Robertson, et al., 1982). Hence, while the CF_3ONO_2 hydrolysis rate is highly uncertain and could be quite long, the degradation mechanism can be predicted with a reasonable degree of certainty:

$$CF_3ONO_2 + H_2O \rightarrow CF_3OH + NO_3^- + H^+ \qquad (R10)$$

$$CF_3OH \rightarrow CF_2O + H^+ + F^- \qquad (R4)$$

$$CF_2O + H_2O \rightarrow CO_2 + 2H^+ + 2F^- \qquad (R11)$$

Peroxynitrates

No quantitative solubility or hydrolysis rate data is available for alkylperoxynitrates (which are thermally unstable) or the halo-substituted species. The synthesis and characterization of CF_3OONO_2 is reported in the literature (Hohorst and DesMarteau, 1974). Thermal decomposition of CF_3OONO_2 is found to be rather slow in the liquid phase, but hydrolysis to $CF_3OOH + NO_3^-$ is rapid. The Henry's law solubilities of the halo-substituted peroxynitrates are probably similar to those of the peroxyacetylnitrates and the alkylnitrates, i.e. $1 - 10\ M\ atm^{-1}$.

AQUATIC MECHANISMS

The above information suggests that the lifetime of halo-substituted peroxynitrates in the atmosphere will be short. In the marine boundary layer, gas phase conversion to halo-substituted alkylhydroperoxides via a mechanism analogous to (R6) and (R7) will occur if the lifetime toward unimolecular decomposition is of the order of 10^6s or less. Otherwise, removal will be dominated by dissolution and hydrolysis in seawater.

Peroxyacids

Lind and Kok (1986) have determined the Henry's law solubility of peracetic acid to be exp(6171/T - 14.55)M atm^{-1} (i.e. 1790 M atm^{-1} at 280K). These authors have also observed that peracetic acid hydrolyzes to acetic acid and hydrogen peroxide, with the hydrolysis reaction going to completion in a day or two, (i.e. $k_h \sim 10^{-5}\ s^{-1}$ at 298K). The negative log of the acid dissociation constant (pKa) for peracetic acid is 8.2 (Koubek, et al., 1963). The halogenated peracetic acids will be more acidic than peracetic acid itself. We estimate that the pKa for trichloroperacetic acid will be in the range 6-7, while the pKa for trifluoroperacetic acid will be in the range 5-6. Hence, the halogenated peroxyacids will be partially dissociated in cloudwater, and almost completely dissociated in seawater. For reasons discussed above in conjunction with acid halide and peroxyacetylnitrate hydrolysis, halogenated peroxyacids are expected to hydrolyze considerably more rapidly than alkylperoxyacids.

Based on the above information, we estimate that under cloudwater conditions, pH $\sim$ 5 and T $\sim$ 280K, reasonable values for H and k_h for the halogenated peroxyacetic acids are $(1\text{-}5) \times 10^3$ M atm^{-1} and $(1\text{-}100) \times 10^{-5}\ s^{-1}$, respectively, with the fluorinated species expected to be the most reactive. Under seawater conditions, pH $\sim$ 8.1 and T $\sim$ 285K, the effective Henry's law solubilities of the halogenated peroxyacetic acids are expected to be quite large. Reasonable estimates for $CCl_3C(O)OOH$ and $CF_3C(O)OOH$ are 3×10^4 M atm^{-1} and 3×10^5 M atm^{-1}, respectively. Assuming that the unprotonated acid hydrolyzes about as efficiently as the protonated acid, we estimate that $k_h \sim (2\text{-}200) \times 10^{-5}\ s^{-1}$ with $CF_3C(O)OO^-$ expected to be the most reactive species. The above parameters suggest that the lifetimes of the halogenated peroxyacids toward hydrolysis in cloudwater and the ocean are quite short; probably of the order of a week to a month and limited by the rate of transport to cloudy regions and/or the marine boundary layer.

The products of peroxyacid hydrolysis are expected to be the corresponding acids (Lind and Kok, 1986), i.e.,

$$CF_nCl_{3-n}C(O)OOH + H_2O \rightarrow CF_nCl_{3-n}C(O)OH + H_2O_2 \qquad (R12)$$

$$CF_nCl_{3-n}C(O)OO^- + H_2O \rightarrow CF_nCl_{3-n}C(O)O^- + H_2O_2 \qquad (R13)$$

Acids

The halo-substituted acetic acids are very acidic species. The pKa's for $CF_3C(O)OH$ and $CCl_3C(O)OH$ are 0.25 and 0.64, respectively (Lange, 1979). Hence, these species are almost totally deprotonated in environmental aqueous phase systems. Taking 10^3 M atm^{-1} as a reasonable lower limit Henry's law solubility for $CF_nCl_{3-n}C(O)OH$ at 280 - 285K, effective Henry's law solubilities are $> 10^7$ M atm^{-1} in cloudwater, $> 10^9$ M atm^{-1} in freshwater lakes and rivers, and $> 10^{10}$ M atm^{-1} in seawater.

As discussed in detail below, we expect the halo-acids to be resistant to chemical degradation. The combination of low reactivity and high solubility suggests that the principal fate of atmospheric halo-acids will be rainout. Rainout of highly soluble species has been modelled in some detail by Giorgi and Chameides (1985), who showed that the rainout rate depends not only on the average rainfall, but also on the period of the storm cycle. The difference between rainout rates calculated for continuous light rainfall versus a short period of heavy rain followed by a long dry period is about an order of magnitude with continuous light rainfall resulting in more rapid rainout. A typical rainout rate for $CF_nCl_{3-n}C(O)OH$ is estimated to be 10^{-6} s^{-1}, or about 12 days.

Once the halo-acids are deposited into freshwater or seawater, they may undergo a number of reactions. These include reaction with hydrated electrons, oxidation-decarboxylation, thermal decarboxylation, hydrolysis, and microbial degradation. Probable rates and mechanisms for these reactions are discussed below.

The rate coefficient for the reaction

$$e^- + CCl_3C(O)O^- \rightarrow CCl_2C(O)O^- + Cl^- \qquad (R14)$$

is known to be 8.5 x 10^9 M^{-1} s^{-1} (Anbar and Hart, 1965). As discussed previously in this report, estimated hydrated electron concentrations in freshwater and seawater are 10^{-18} M and 10^{-19} M, respectively. Hence, the lifetime of $CCl_3C(O)O^-$ toward removal via (R14) is estimated to be 3.7 years in freshwater and 37 years in seawater. $CF_3C(O)O^-$ is expected to be at least 100 times less reactive with e^- than is $CCl_3C(O)O^-$, while $CF_2ClC(O)O^-$ and $CFCl_2C(O)O^-$ will react at intermediate rates. The radical products of (R14) and its analogs will rapidly add O_2 to form peroxy radicals,

$$CX_2C(O)O^- + O_2 \rightarrow OOCX_2C(O)O^- \qquad (R15)$$

Halo-substituted peroxy radicals are known to be strong oxidizing agents (Packer, et al., 1980; Monig, et al., 1983; Alfassi, et al., 1987; Huie, et al., 1987; Lal et al., 1988). For example, Huie and Neta (private communication) have found that the reactions

$$CX_3OO + I^- \rightarrow CX_3OO^- + I \qquad (R16)$$

proceed rapidly with k ~ 10^8 M^{-1} s^{-1} for X = Cl and F. Kinetics studies of CCl_3OO, $OOCCl_2(O)O^-$, and $OOCF_2C(O)O^-$ reactions with a number of antioxidants have shown that $OOCCl_2(O)O^-$ and $OOCF_2C(O)O^-$ are about equally reactive, but both are 3 - 10 times less reactive than CCl_3OO (Packer, et al., 1980). A typical iodide concentration in seawater is 10^{-7} M, suggesting that the lifetime of $OOCX_2C(O)O^-$ toward reduction by I^- is about one second. Analogous reactions are also expected to proceed rapidly in freshwater due to the availability of good reducing agents such as, for example, NO_2^-. The probable chemistry of $^-OOCX_2C(O)O^-$ and their protonated species $HOOCX_2C(O)O^-$ is discussed in the next section.

It is known that strong oxidizing agents can undergo the following reaction with acetate:

$$X + CH_3C(O)O^- \rightarrow X^- + CH_3C(O)O \rightarrow CH_3 + CO_2 \qquad (R17)$$

The sulfate radical, for example, is known to react with acetate at a moderate rate (k = 3.7 x 10^6 M^{-1} s^{-1} in the zero ionic strength limit) (Wine, et al., 1989) to produce CO_2 (Madhavan, et al., 1978). The one electron redox potential (E^0) is 2.41 volts (versus the normal hydrogen electrode) for the $CH_3C(O)O/CH_3C(O)O^-$ couple and 2.52 volts for the SO_4^-/SO_4^{2-} couple (Eberson, 1982). Substitution of electron withdrawing substituents such as Cl and F on the alkyl carbon are expected to significantly increase E^0. Hence, it appears that SO_4^-, one of the strongest oxidizing agents found in environmental aqueous systems, is not capable of oxidizing $CF_nCl_{3-n}C(O)O^-$. Another possibility worth considering is oxidation of the halo-acetates by valence band holes in colloidal metal oxide particles which can be generated photolytically in surface natural waters. For example, the bandgaps of TiO_2 and ZnO are 3.0 volts (Morrison, 1980) and 3.4 volts (Bahnemann, et al., 1987), respectively. Because the electron donor (i.e. $CF_nCl_{3-n}C(O)O^-$) must interact with the hole within nanoseconds after the hole is created in order to compete with rapid electron-hole recombination (Rothenberger, et al., 1985), the oxidation process can only occur for donors which are adsorbed to the particle surface. Kormann, et al. (1989), using relatively high concentrations of donor and metal oxide, have found that chloroacetates can be degraded with quantum yields in the range of 3% for TiO_2 and 0.1% for ZnO at $pH = 5$. Improved knowledge of particle size distributions and concentration profiles in natural waters, rates of adsorption and desorption of the haloacetates to particle surfaces, and degradation quantum yields as a function of wavelength are needed before the potential importance of haloacetate oxidation by valence band holes in semiconductor particles can be assessed with any degree of confidence.

Thermal decarboxylation of halo-substituted acetic acids at elevated temperatures are a well-known set of organic reactions, which are discussed in most undergraduate organic chemistry textbooks (see, for example, Roberts and Caserio, 1965). Verhoek (1934) studied the kinetics of CCl_3COO^- thermal decarboxylation in aqueous solution over the temperature range 50 - 90°C; measured rate coefficients varied from $6.2 \times 10^{-7}\ s^{-1}$ at 50°C to $3.1 \times 10^{-4}\ s^{-1}$ at 90°C. Extrapolation of Verhoek's results to 285K, a typical surface seawater temperature, suggests that $k \sim 3.7 \times 10^{-9}\ s^{-1}$ (lifetime ~86 years). At 300K, however, the lifetime of $CCl_3C(O)O^-$ toward thermal decarboxylation appears to be only about 2 years. Clearly, thermal decarboxylation in the tropical oceans could be an important removal process for $CCl_3C(O)O^-$. The thermal decarboxylation kinetics of $CF_3C(O)O^-$ (Auerbach, et al., 1950), $CCl_2FC(O)O^-$ (Hine and Duffey, 1959a) and $CF_2ClC(O)O^-$ (Hine and Duffey, 1959b) have also been studied in aqueous solution. Extrapolation of available data suggests that at $T \leq 300K$ all three reactions have rate coefficients of less than $10^{-10}\ s^{-1}$. The more fluorine atoms on the alkyl carbon, the slower the reaction proceeds. For $CCl_3C(O)O^-$, $CCl_2FC(O)O^-$, and $CF_3C(O)O^-$, the mechanism of the thermal decarboxylation reaction is

$$CX_3C(O)O^- \rightarrow CO_2 + CX_3^- \rightarrow CHX_3 \qquad \text{(R18)}$$

For $CClF_2C(O)O^-$, Hine and Duffey (1959b) have shown that the detailed mechanism is somewhat different

$$CClF_2C(O)O^- \rightarrow CO_2 + Cl^- + CF_2 \qquad \text{(R19}$$

In seawater the CF_2 radical should react with chloride, then protonate to form $CHClF_2$:

$$CF_2 + Cl^- \rightarrow CF_2Cl^- \rightarrow CHF_2Cl \qquad \text{(R20)}$$

Very little information is available concerning hydrolysis of trihaloacetic acids. It appears that S_N2 attack by H_2O does not compete with thermal decarboxylation, at least over the temperature regime where the overall reaction rate is convenient for experimental determination. Hine and Duffey (1959b) did observe oxalic acid as a minor product of $CF_2ClC(O)O^-$ degradation in aqueous solution and attributed its production to a hydrolysis reaction:

$$CClF_2C(O)O^- + H_2O \rightarrow HOCF_2COO^- + H^+ + Cl^- \quad (R21)$$

$$HOCF_2C(O)O^- \rightarrow OFCC(O)O^- + H^+ + F^- \quad (R22)$$

$$OFCC(O)O^- + H_2O \rightarrow HO(O)CC(O)O^- + H^+ + F^- \quad (R23)$$

In seawater oxalic acid exists primarily in the singly protonated form with a smaller but significant concentration of the fully protonated acid.

It is known that enzymes found in soil microorganisms and higher plants can cleave the C-X bonds in a number of haloacetates, including $CH_2FC(O)O^-$, $CH_2ClC(O)O^-$ and $CHCl_2C(O)O^-$, by catalyzing hydrolysis (Goldman, 1969). It seems reasonable to expect that plant and/or microbial enzymes can remove fluorine atoms from $CF_nCl_{3-n}C(O)O^-$ as well. Further research is needed to establish the rates of $CF_nCl_{3-n}C(O)O^-$ degradation via biological processes in natural environments such as soils, vegetation, fresh water, and seawater.

In summary, it appears that $CCl_3C(O)O^-$ can react at appreciable rates in natural waters with hydrated electrons and by thermal decarboxylation; the lifetime of $CCl_3C(O)O^-$ toward removal by these processes is probably a few years. The other chlorofluoroacetates are more stable toward chemical removal. The most stable species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than those suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.

Hydroperoxides

Lind and Kok (1986) have determined the Henry's law solubility of CH_3OOH to be exp(5607/T - 13.41) M atm^{-1} (i.e. 746 M atm^{-1} at 280K). These authors have also observed that CH_3OOH hydrolyzes to methanol and hydrogen peroxide; the lifetime of CH_3OOH toward hydrolysis appeared to be a month or two at 298K. The pKa for CH_3OOH is 11.5 (Lange, 1979). However, the halogenated hydroperoxides are expected to be considerably more acidic. Bernstein, et al.,(1971) report a pKa of 6.4 for CF_3OOH, suggesting that this species is > 90% protonated in cloudwater but > 90% unprotonated in seawater. Although no Henry's law data is available for the halogenated hydroperoxides, the vapor pressure of CF_3OOH is known to be about 2 atmospheres at 298K (Bernstein, et al., 1971) whereas the vapor pressure of CH_3OOH is only 54.2 Torr at 298K (G.L. Vaghjiani, private communication). Hence, it seems likely that the Henry's law solubility of CF_3OOH is smaller than that of CH_3OOH.

If photolysis, rates for halogenated hydroperoxides in the gas phase are similar to those of H_2O_2 and CH_3OOH, then gas phase photolysis will be the dominant atmospheric sink for these species ($\tau \approx$ 1-2 weeks). However, it is possible that the UV spectra of halogenated hydroperoxides are blue-shifted from the spectra of H_2O_2 and CH_3OOH, in which case gas phase photolysis could be very slow and aqueous phase removal could become important.

The halogenated hydroperoxides' lifetimes against dissolution in cloudwater and photolysis or reaction with OH radicals is likely to be slow. For a Henry's law solubility of 300 M atm^{-1}, a relatively fast photolysis rate in cloudwater of 2×10^{-6} s^{-1}, and a rate constant for reaction with aqueous-phase OH of 1×10^{7} M^{-1} s^{-1}, we estimate a cloudwater removal lifetime using equations [11] and [12] of the order of years.

With regard to photolysis it is interesting to note that hydroperoxides photolyze via rupture of the O-O bond to give an alkoxy radical and an OH radical. In solution, chlorinated alkoxy radicals are thermally unstable and would be expected to rapidly eliminate a Cl atom to form an acid halide which, as discussed above, would rapidly hydrolyze. Totally fluorinated alkoxy radicals such as CF_3O should react rapidly either by electron transfer, i.e.

$$CF_3O + O_2^-, NO_2^-, \ldots \rightarrow CF_3O^- + O_2, NO_2, \ldots \rightarrow CF_3OH \qquad (R24)$$

or by hydrogen abstraction, i.e.

$$CF_3O + HO_2, \ldots \rightarrow CF_3OH + O_2, \ldots \qquad (R25)$$

As discussed above, CF_3OH rapidly eliminates HF to produce CF_2O, which rapidly hydrolyzes to CO_2 + HF. On the other hand, in the case of OH attack on the hydroperoxides, we expect that the products will undergo rapid reactions in solution regenerating hydroperoxide (see above).

In seawater, reactions of the type

$$X^- + ROOH \rightarrow X + RO + OH^- \qquad (R26)$$

can compete with photodissociation as a removal mechanism for hydroperoxides. The species X can be halide ions or transition metal ions. It is worth noting that the reactions where X = I^- and Fe^{2+} are used for quantitative analysis of peroxides (Siggia and Hanna, 1979). While quantitative kinetic data for X^- + ROOH reactions seem to be available only for hydrogen peroxide (i.e. R = H), it is worth noting that all hydroperoxides are known to react rapidly with iodide (Siggia and Hanna, 1979). Parameters relevant to the assessment of the importance of reactions of I^-, Br^-, Cl^-, Cu(I), and Fe(II) with H_2O_2 as peroxide destruction mechanisms in seawater are given in Table 4. It should be noted that complexation with OH^- and Cl^- leads to complicated speciation patterns for the transition metal ions. The dominant reacting Cu(I) and Fe(II) species are not the bare metal ions, but $CuCl_2^-$ and $Fe(OH)^+$ (Moffett and Zika, 1987a). The results presented in Table 4 suggest that reaction with Fe(II) is the dominant sink for H_2O_2 in seawater, since photolysis in surface water and hydrolysis are expected to proceed at rates on the order of 10^{-7} s^{-1} each.

To estimate the lifetime of halogenated hydroperoxides toward chemical or photochemical removal in seawater, we assume that they undergo reactions with X^-, hydrolysis, and photolysis at rates similar to those observed for H_2O_2, i.e. $k \approx 10^{-4}$ s^{-1}. The Henry's law solubilities for the halogenated hydroperoxides under seawater conditions ($T \sim 285K$, $\mu \sim 0.75$ M) are estimated to lie in the range 50 - 500 M atm^{-1}. For the above range of values for k and H, it is likely that hydroperoxide removal in seawater will be of the order of 1 month and be limited by transport to the marine boundary layer. Reduction of k by a factor of 100 would have no effect on the (transport limited) lifetime.

Table 4. Sinks for H_2O_2 in Seawater via the Reaction $X^- + H_2O_2 \rightarrow X + OH + OH^-$

	$k(M^{-1}\ s^{-1})^{(a)}$	[X](M)	$k(s^{-1})$	References
I^-	0.26	1×10^{-7}	2.6×10^{-8}	1
Br^-	4.4×10^{-6}	8×10^{-4}	3.5×10^{-9}	2
Cl^-	$1.7 \times 10^{-8(b)}$	0.54	9.2×10^{-9}	2
$Cu(I)^{(c)}$	70	1×10^{-10}	7.0×10^{-9}	3,4
$Fe(II)^{(d)}$	3×10^{4}	5×10^{-9}	1.5×10^{-4}	5,6

(a) T = 285K
(b) highly uncertain
(c) the reactive species in seawater is thought to be $CuCl_2^-$
(d) the reactive species in seawater is thought to be $Fe(OH)^+$

1. Liebhafsky and Mohammed, 1933
2. Mohammed and Liebhafsky, 1934
3. Moffett and Zika, 1987a
4. Moffett and Zika, 1987b
5. Hong and Kester, 1986
6. Landing and Westerlund, 1988

X^- + ROOH reactions and photolysis lead to the production of haloalkoxy radicals which decay via mechanisms discussed above in conjunction with the cloud chemistry of hydroperoxides. Hydrolysis is expected to produce haloalcohols; these compounds rapidly eliminate HX to form acid halides which, in turn, rapidly hydrolyze via mechanisms discussed earlier.

As discussed in an earlier section, reactions of the hydrated electron with haloacetic acids results in the production of acid hydroperoxides, i.e. $HOOCF_nCl_{2-n}C(O)O^-$. These species are expected to be degraded via mechanisms completely analogous to those described above for haloalkyl hydroperoxides. The end products are expected to be oxalic acid (HOOCCOOH), HF, and HCl.

7. SUMMARY

The rates at which eight potential alternative HCFCs and HFCs and methyl chloroform (CH_3CCl_3) can be removed from the atmosphere by dissolution and reaction in the oceans and in cloudwater have been estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the aqueous phase. The HCFCs and HFCs considered are $CHCl_2CF_3$ (HCFC-123), $CFCl_2CH_3$ (HCFC-141b), CF_2ClCH_3 (HCFC-142b), CHF_2Cl (HCFC-22), $CHFClCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), and CHF_2CF_3 (HFC-125).

Cloudwater is found to be of no importance as an atmospheric sink for any of the above compounds. Best-estimate lifetimes for all eight HCFCs and HFCs toward removal in the oceans are greater than 77 years, with only HCFC-22, HCFC-123, and HCFC-141b having lifetimes shorter than 200 years. The most reactive of the nine species, considered toward removal in the oceans is methyl chloroform, with a best-estimate lifetime of 42 years and a minimum reasonable lifetime of 22 years. Important removal mechanisms for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b in seawater are hydrolysis and reaction with hydrated electrons. Improved hydrolysis kinetics data and Henry's law solubility data for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b would help to reduce the uncertainties in the aqueous phase removal rates of these species as would improved estimates of the hydrated electron concentration in seawater.

Gas phase degradation products of the eight HCFCs and HFCs include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates.

Although handicapped by the total absence of Henry's law solubility data for any of the compounds of interest and the limited availability of relevant kinetic data, an assessment of the rates and mechanisms of aqueous phase removal of the gas phase degradation products has been carried out.

The species X_2CO, $HXCO$, CH_3CXO, CF_3OH, CX_3OONO_2, and $ROOH$ (X = F or Cl, R = halo-substituted methyl or acetyl) are all expected to be removed from the atmosphere on time scales limited by transport to cloudy regions or the marine boundary layer (i.e. about 1 month); aqueous phase reactions of these species result in the formation of chloride, fluoride, and carbon dioxide, as well as formic, acetic, and oxalic acids. The species CX_3CXO, CX_3CX_2OOH, $CX_3CX_2OONO_2$, $CX_3C(O)OONO_2$, and $CX_3C(O)OOH$ are also expected to be removed from the atmosphere rapidly, and their aqueous phase reactions result in the formation of halo-substituted acetates, $CX_3C(O)O^-$.

The species $CX_3C(O)OH$ are very acidic and, as a result, are highly soluble in cloudwater. These acids are expected to be rapidly removed from the atmosphere by rainout. However, the aqueous phase species $CX_3C(O)O^-$ are expected to be resistant to chemical degradation. Trichloroacetate can thermally decompose on a time scale of 2-10 years to yield carbon dioxide and chloroform. In fresh water, the reaction of $CCl_3C(O)O^-$ with the hydrated electron is also expected to occur on a time scale of a few years. The species $CFCl_2C(O)O^-$, $CF_2ClC(O)O^-$, and $CF_3C(O)O^-$ may have very long aqueous phase lifetimes. The longest lived species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.

One possible gas phase degradation product about which very little is known is CF_3ONO_2. This compound has never been observed, and may be thermally unstable. If CF_3ONO_2 is thermally stable, then it may have a long lifetime toward aqueous phase removal. Henry's law solubility data and hydrolysis kinetics data for CF_3ONO_2 are needed before its aqueous phase removal rate can be assessed with any degree of confidence.

8. ACKNOWLEDGMENTS

The authors would like to thank the reviewers, M.R. Hoffmann and D.D. DesMarteau, for a number of constructive comments which greatly improved the quality of this assessment. They would also like to acknowledge L. Clever, D. Creed, R.E. Huie, E.M. Perdue, A.R. Ravishankara, E.S. Saltzman, G.J. Vaghjiani, O.C. Zafiriou, and R.G. Zepp for helpful discussions concerning various aspects of this work, and R.P. Thorn for assistance with the literature search.

In preparing this assessment the authors made use of information from a number of other AFEAS reports. Authors of these reports were R. Atkinson, R.A. Cox, R.F. Hampson, M.J. Kurylo,R. Lesclaux, D.C. McCune, M.O. McLinden, H. Niki, S.P. Sander, L.H. Weinstein, and R. Zellner.

APPENDIX
(R.H. WINE AND W.L. CHAMEIDES)

Tables of Relevant Physical Constants

AI	Henry's law solubilities
AII	Vapor Pressures
AIII	Acid-base equilibrium constants
AIV	One-electron redox potentials

Table AI. Henry's Law Solubilities

Species	(M atm^{-1}) 5°C	 25°C	Reference
HOOH	360000	74000	1
CH_3OOH	850	220	1
$CH_3C(O)OOH$	2100	470	1
HCOOH	1500	3700	2
CH_3COOH	41000	8700	3
CH_3CHO	49	13	4
CH_3OH	720	220	4
CH_3ONO_2		3(22°C)	5
$CH_3C(O)OONO_2$	12	2.9	6
CH_2CCl_2	0.096	0.039	7

1. Lind and Kok, 1986
2. Latimer, 1952
3. Jacob and Wofsy, 1988
4. Snider and Dawson, 1985
5. Lee, et al., 1983
6. Lee, 1984
7. Gossett, 1987

Table AII. Vapor Pressure of Selected Compounds

	Vapor Pressure (Torr)		
Species	**0°C**	**30°C**	**Reference**
HFCO	1590	2420	1
Cl_2CO	563	1670	1
CH_3CClO	90.4	353	1
CCl_3CClO	4.72	27.0	1
CH_3OOH	10.9	70	2
CF_3OOH	444	1670	3
CF_3COOH	2.90	14.3	1
CCl_3COOH	0.0043	0.130	1
CH_3OH	29.1	162	1
CH_2CH_2OH	12.2	79.2	1
CF_3CH_2OH	13.7	93.5	1

1. Lange, 1979
2. G.L. Vaghjiani, private communication
3. Bernstein, et al., 1971

Table AIII. Acid-Base Equilibrium Constants

Equilibrated Species	pKa	Reference
$CO_2 \cdot H_2O/HCO_3^-$	6.35	1
HCO_3^-/CO_3^{2-}	10.33	1
HCl/Cl^-	$^-6.1$	1
HF/F^-	3.18	1
$HC(O)OH/HC(O)O^-$	3.75	1
$CH_3C(O)OH/CH_3C(O)O^-$	4.76	1
$CCl_3C(O)OH/CCl_3C(O))^-$	0.64	1
$CF_3C(O)OH/CF_3C(O)O^-$	0.25	1
$CH_3C(O)OOH/CH_3C(O)OO^-$	8.20	1
$ClCH_2C(O)OOH/ClCH_2C(O)OO^-$	7.2	2
CH_3OOH/CH_3OO^-	11.5	2
CF_3OOH/CF_3OO^-	6.4	3
$CH_3CH_2OH/CH_3CH_2O^-$	15	4
$CF_3CH_2OH/CF_3CH_2O^-$	12.37	4
HO_2/O_2^-	4.69	5

1. Lange, 1979
2. Richardson, 1983
3. Bernstein, et al., 1971
4. Ballinger and Long, 1960
5. Bielski, 1978

Table AIV. One-Electron Redox Potentials

Couple	E^0(volts)*	Reference
F/F^-	3.6	1
Cl/Cl^-	2.41	2
Br/Br^-	1.93	2
I/I^-	1.33	3
NO_2/NO_2^-	1.03	4
NO_3/NO_3^-	2.3	1
OH/OH^-	1.89	2
SO_4^-/SO_4^{2-}	2.52	5
SO_3^-/SO_3^{2-}	0.63	6
$CH_3C(O)O/CH_3C(O)O^-$	2.41	7
HO_2/HO_2^-	0.8	1
O_2/O_2^-	$^-$0.2	1
CO_3^-/CO_3^{2-}	1.59	8
Fe^{3+}/Fe^{2+}	0.771	9
$Fe(OH)^{2+}/Fe(OH)^+$	0.304	9
Cu^{2+}/Cu^+	0.153	9
$CuCl_2/CuCl_2^-$	0.567	9

*in water, versus the normal hydrogen electrode

1. Berdnikov and Bazhin, 1970
2. Schwarz and Dodson, 1984
3. Stanbury, et al., 1980
4. Wilmarth, et al., 1983
5. Eberson, 1982
6. Huie and Neta, 1984
7. Eberson, 1963
8. R.E. Huie, private communication
9. Moffett and Zika, 1987a

VIII. OZONE DEPLETION POTENTIALS

Relative Effects on Stratospheric Ozone of Halogenated Methanes and Ethanes of Social and Industrial Interest

D. A. Fisher, Charles H. Hales and **David L. Filkin**
E. I. du Pont de Nemours & Company
Wilmington, DE

Malcolm K. W. Ko and **N. Dak Sze**
Atmospheric And Environmental Research, Inc.
Cambridge, MA

Peter S. Connell and **Donald J. Wuebbles**
Lawrence Livermore National Laboratory
Livermore, CA

Ivar S. A. Isaksen and **Frode Stordal**
Institute for Geophysics
University of Oslo
Oslo, Norway

EXECUTIVE SUMMARY

Ozone Depletion Potentials (ODPs) have been defined and calculated in order to allow estimates of the relative effects of halocarbons on stratospheric ozone. Models using representations of homogeneous atmospherics chemical processes have estimated relative effects on global ozone. These estimates indicate that the ODPs of the hydrohalocarbons are generally one-tenth or less those of the CFC-11 and -12. The reduction in ODP that might be expected due to replacement of uses of a CFC by a hydrohalocarbon can be estimated by taking the ratio of the ODP of the hydrohalocarbon to the ODP of the CFC it might replace. For example, the reduction in ODP in replacing uses of CFC-12 by HCFC-22 is (0.049 ± .015)/(.93) = .053 ± .015. Of course, the relative quantities of the compound required in the use application must also be taken into account.

Although the values of ODPs reported here agree reasonably well among models, uncertainties in the values still exist due to the uncertainties in modeled chemistry and dynamics. Since reaction with OH dominates the chemistry of the HCFCs, uncertainties in the model calculated OH values remain a major source of uncertainty for both lifetimes and ODPs of these compounds. Uncertainties for some compounds may be reduced with new laboratory data on the ultraviolet absorption properties and the rate constants with hydroxyl for the HCFCs and HFCs.

Sensitivity analyses reveal that the global ODP values are affected to only a minor degree by the levels of N_2O, CH_4, CO_2, CO, and Brx used in model calculations. Latitudinal relative effects on ozone depletion depend on the species - species with high altitude sinks show more latitudinal dependency than CFC-11. Those species destroyed in the lower stratosphere have latitudinal effects equivalent to CFC-11. Seasonal variation of relative ozone depletions are second order.

Another major uncertainty centers on the potential effects of heterogeneous chemistry in the lower stratosphere, particularly near the poles in winter-time. While these effects are believed to cause the Antarctic spring-time ozone decreases, they are not included in any of the model calculations of ODPs. Due to the cold stratospheric temperatures, polar stratospheric clouds become activation sites for chlorine compounds (by-products from the decomposition of the chlorocarbons) resulting in increased chlorine catalytic loss for ozone. Since ODP is defined relative to CFC-11, the effect of including heterogeneous chemistry will have little effect on the local ODP value compared to values determined assuming only homogeneous chemistry. However, polar contribution to global ozone loss would be greater such that global ODP values would be more heavily weighted by the polar values. Thus, species with large, positive latitudinal gradients in ODP would have global ODPs that are fractionally increased. On the other hand, inclusion of stronger polar dynamics would affect both the transport and the distribution of chlorine species and would directly impact both the local and global ODP values.

Upper bounds are placed on the local effects by a chlorine loading potential, i.e. the relative amount of chlorine added to the stratosphere by a given gas. A less conservative estimate derived from the relative values of Cly in the lower polar stratosphere in spring indicates that the potential effect can be substantially less than the Chlorine Loading Potential but would be above the homogeneous chemisty ODP value. The geographic extent of the heterogeneous effect on global ODP outside of the polar vortex is impossible to estimate at the present time.

Time-dependent Relative Ozone Depletions and Relative Chlorine Loading for HCFCs have values above the ODP and CLP values derived from steady-state calculations. For longer lived CFCs, the time-dependent values are always less than the ODP and CLP values.

Range of Ozone Depletion Potentials (ODP) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs by CH_3CCl_3 observed lifetime (6.3 years).

Species	1-D Models*	2-D Models**
CFC-11	1.0	1.0
CFC-12	0.9-1.0	0.9
CFC-113	0.8-0.9	0.8-0.9
CFC-114	0.6-0.8	0.6-0.8
CFC-115	0.4-0.5	0.3-0.4
HCFC-22	0.4-0.05	0.04-0.06
HCFC-123	0.013-0.016	0.013-0.022
HCFC-124	0.016-0.018	0.017-0.024
HFC-125	0	0
HFC-134a	0	0
HCFC-141b	0.07-0.08	0.09-0.11
HCFC-142b	0.05-0.06	0.05-0.06
HFC-134a	0	0
HFC-152a	0	0
CCl_4	1.0-1.2	1.0-1.2
CH_3CCl_3	0.10-0.12	0.13-0.16

* 1-D models from AER, LLNL and DuPont.

** 2-D models from AER, LLNL, University of Oslo, and DuPont.

N92-15446

RELATIVE EFFECTS ON STRATOSPHERIC OZONE OF HALOGENATED METHANES AND ETHANES OF SOCIAL AND INDUSTRIAL INTEREST

Donald A. Fisher, Charles H. Hales and David L. Filkin
E. I. du Pont de Nemours & Company

Malcolm K. W. Ko and N. Dak Sze
Atmospheric and Environmental Research, Inc.

Peter S. Connell and Donald J. Wuebbles
Lawrence Livermore National Laboratory

Ivar S.A. Isaksen and Frode Stordal
Institute for Geophysics
University of Oslo

ABSTRACT

Four atmospheric modeling groups have calculated relative effects of several halocarbons (CFCs -11, 12, 113, 114, and 115; HCFCs 22, 123, 124, 141b, and 142b; and HFCs 125, 134a, 143a, and 152a, carbon tetrachloride; and methyl chloroform) on stratospheric ozone. Effects on stratospheric ozone were calculated for each compound and normalized relative to the effect of CFC-11. These models include the representations for homogeneous physical and chemical processes in the middle atmosphere but do not account for either heterogeneous chemistry or polar dynamics which are important in the spring time loss of ozone over Antarctica.

Relative calculated effects using a range of models compare reasonably well. Within the limits of the uncertainties of these model results, compounds now under consideration as functional replacements for fully halogenated compounds have modeled stratospheric ozone reductions of 10% or less of that of CFC-11. Sensitivity analyses examined the sensitivity of relative calculated effects to levels of other trace gases, assumed transport in the models, and latitudinal and seasonal local dependencies. Relative effects on polar ozone are discussed in the context of evolving information on the special processes affecting ozone especially during polar winter-springtime. Lastly, the time dependency of relative effects have been calculated.

1. INTRODUCTION

Concern over the global environmental consequences of fully halogenated chlorofluorocarbons (CFCs) has sparked development of replacement compounds. A systematic evaluation of potential environmental effects of replacement chemicals is clearly important. The two major environmental considerations for these chemicals are possible changes in stratospheric ozone and global clinmate. This paper will deal with estimation of potential effects on stratospheric ozone.

The candidates under intensive development are composed of either carbon, hydrogen and fluorine (hydrofluorocarbons or HFCs) or carbon, hydrogen, chlorine and fluorine (hydrochlorofluorocarbons or HCFCs). For simplicity, both classes of compounds are referred to as hydrohalocarbons. Because they contain hydrogen, the hydrohalocarbons are far more reactive with atmospheric hydroxyl radicals than CFCs. This destruction mechanism leads to significantly shorter atmospheric lifetimes for these compounds (e.g. Makide and Rowland, 1981) compared to those of the CFCs. The shorter atmospheric lifetime is a primary factor in the reduced potential of HCFCs and HFCs to affect both stratospheric ozone and global warming.

This paper examines the calculated effects of several one and two carbon halocarbons on stratospheric ozone. Estimation of each compound's effect on stratospheric ozone will be quantified as a relative Ozone Depletion Potential (or ODP). Estimates of relative potentials to enhance global warming (Halocarbons Global Warming Potential or HGWP) will be discussed in a subsequent publication (Fisher et al. 1989b).

Computer models have long been used to estimate the relative effects of trace gases on stratospheric ozone. Early reports were made in terms of an efficiency factor for different chemicals [Wofsy and McElroy (1974), Donahue et al. (1976), and Robbins and Stolarski, (1976)]. The concept of a relative Ozone Depletion Potential was introduced in 1981 (Wuebbles, 1981) and was adopted as a quick reference for estimating the relative potential of these trace gases to reduce stratospheric ozone. Several papers have reported model results as ODPs: Wuebbles (1983), Hammitt et al. (1987), Rognerud et al. (1988). Regulation of fully halogenated CFCs under the Montreal Protocol is based on the concept of ODP in order to establish relative weighting factors for each chemical.

ODP values for sixteen gases have been calculated by four atmospheric modeling groups; Atmospheric and Environmental Research, Inc. (AER), Du Pont Central Research (Du Pont), Lawrence Livermore National Laboratory (LLNL), and the University of Oslo. Each of these models is described in the literature [ko et al. (1984 & 1985), Kinnison et al. (1988), Miller et al. (1981), Miller et al. (1981a), Rognerud et al. (1988), Stordal et al. (1985), Sze and Ko (1981), Wuebbles (1983), and Wuebbles et al. (1988). The halocarbons considered in this study, their chemical formulate, and their IUPAC names are listed in Table 1.

This paper will describe a clearer definition of ODP, as well as examine the basis for selecting its definition, present calculated results from several models, and examine the differences and uncertainties in model results.

2. DEFINITION BASIS

Ozone Depletion Potential (ODP) has traditionally been defined as the ratio of model calculated ozone depletions under steady state conditions. More specifically, it is defined as the ratio of calculated ozone column change for each mass unit of a gas emitted into the atmosphere relative to the calculated depletion

Table 1 Compounds Examined in this Study

HALOCARBON	FORMULA	IUPAC NAME
CFC-11	CCl_3F	METHANE, TRICHLOROFLUORO-
CFC-12	CCl_2F_2	METHANE, DICHLORODIFLUORO-
CFC-113	CCl_2FCClF_2	ETHANE, 1,1,2-TRICHLORO-1.2.2-TRIFLUORO-
CFC-114	$CCClF_2ClF_2$	ETHANE, 1.2-DICHLORO-1,1.2.2-TETRAFLUORO-
CFC-115	$CClF_2CF_3$	ETHANE, CHLOROPENTAFLUORO-
HCFC-22	$CHClF_2$	METHANE, CHLORODIFLUORO-
HCFC-123	CF_3CHCl_2	ETHANE, 2.2-DICHLORO-I,I,I-TRIFLUORO-
HCFC-124	CF_3CHClF	ETHANE, 2-CHLORO-1,1,1,2-TETRAFLUORO-
HFC-125	CF_3CHF_2	ETHANE, PENTAFLUORO-
HFC-134a	CF_3CH_2F	ETHANE, 1,1,1,2-TETRAFLUORO-
HCFC-141b	CCl_2FCH_3	ETHANE, 1,1-DICHLORO-1-FLUORO-
HCFC-142b	$CClF_2CH_3$	ETHANE, 1-CHLORO-1.1-DIFLUORO-
HFC-143a	CF_3CH_3	ETHANE, 1,1,1-TRIFLUORO-
HFC-152a	CHF_2CH_3	ETHANE, 1,1-DIFLUORO-
CARBON-TETRACHLORIDE	CCl_4	METHANE, TETRACHLORO-
METHYL CHLOROFORM	CCl_3CH_3	ETHANE, 1,1,1-TRICHLORO-

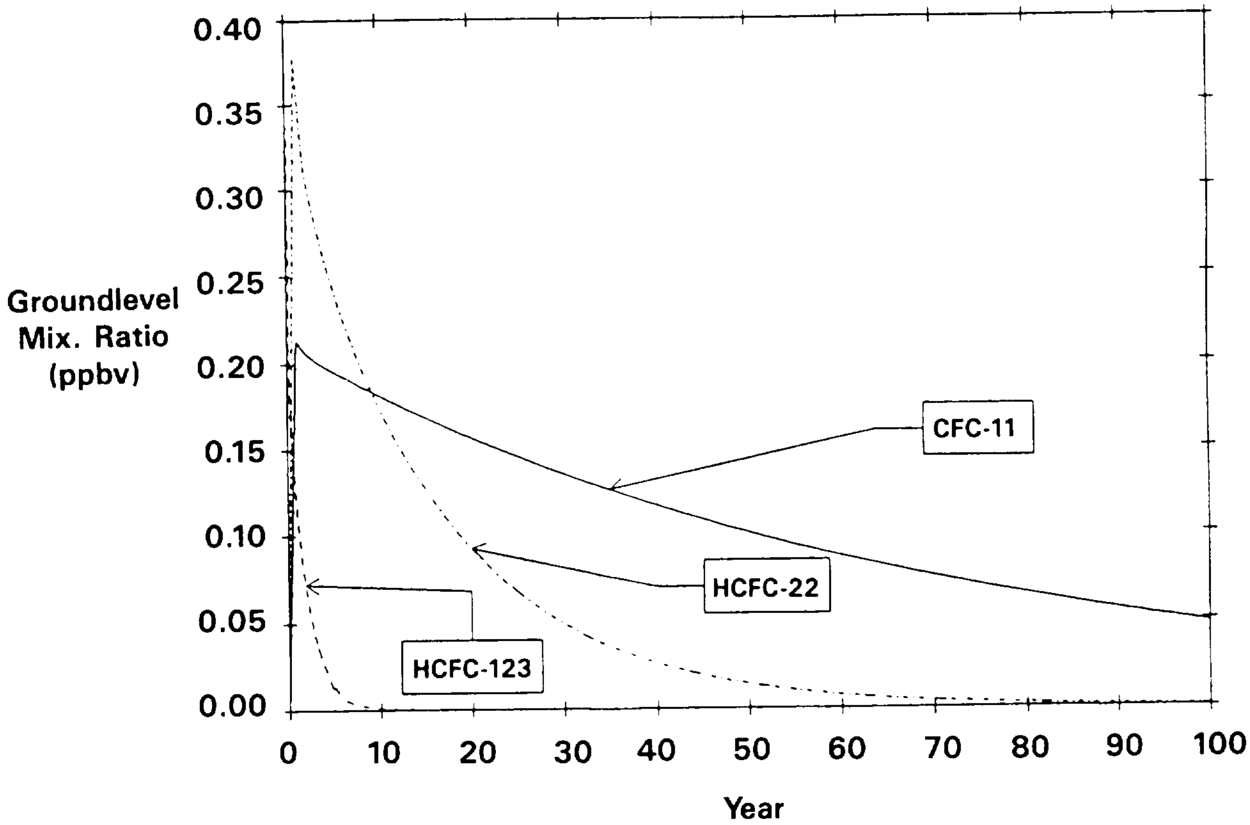


Figure 1. Calculated Tropospheric Mixing Ratio of Specified Gas Following a Pulsed Input of 5.0x10**9 kg. (DuPont 1-D Model)

for the reference gas CFC-11. Column ozone is the total amount of ozone between the Earth's surface and space, or mathematically, it is the vertical integral of ozone concentration (molecules/cubic cm.) through the entire atmosphere. Defined in this manner, ODP is a useful measure of the potential for each compound to affect stratospheric ozone since:

(1) It provides a measure of the cumulative chronic effect on ozone for each unit released into the atmosphere (more discussion below).

(2) The ODP yields a single value for each compound rather than a time varying multitude of values.

(3) It provides an estimate of the calculated effect of a compound compared to the maximum calculated effect of CFC-11 on an equal mass basis.

(4) Calculations are easy and inexpensive, especially using models designed to calculate steady state ozone changes directly rather than through a time step approach.

The first reason for choosing this definition, and perhaps the most critical, is that it estmates the cumulative chronic effect on atmospheric ozone of each unit released. This effect is illustrated by the follow-

C-4

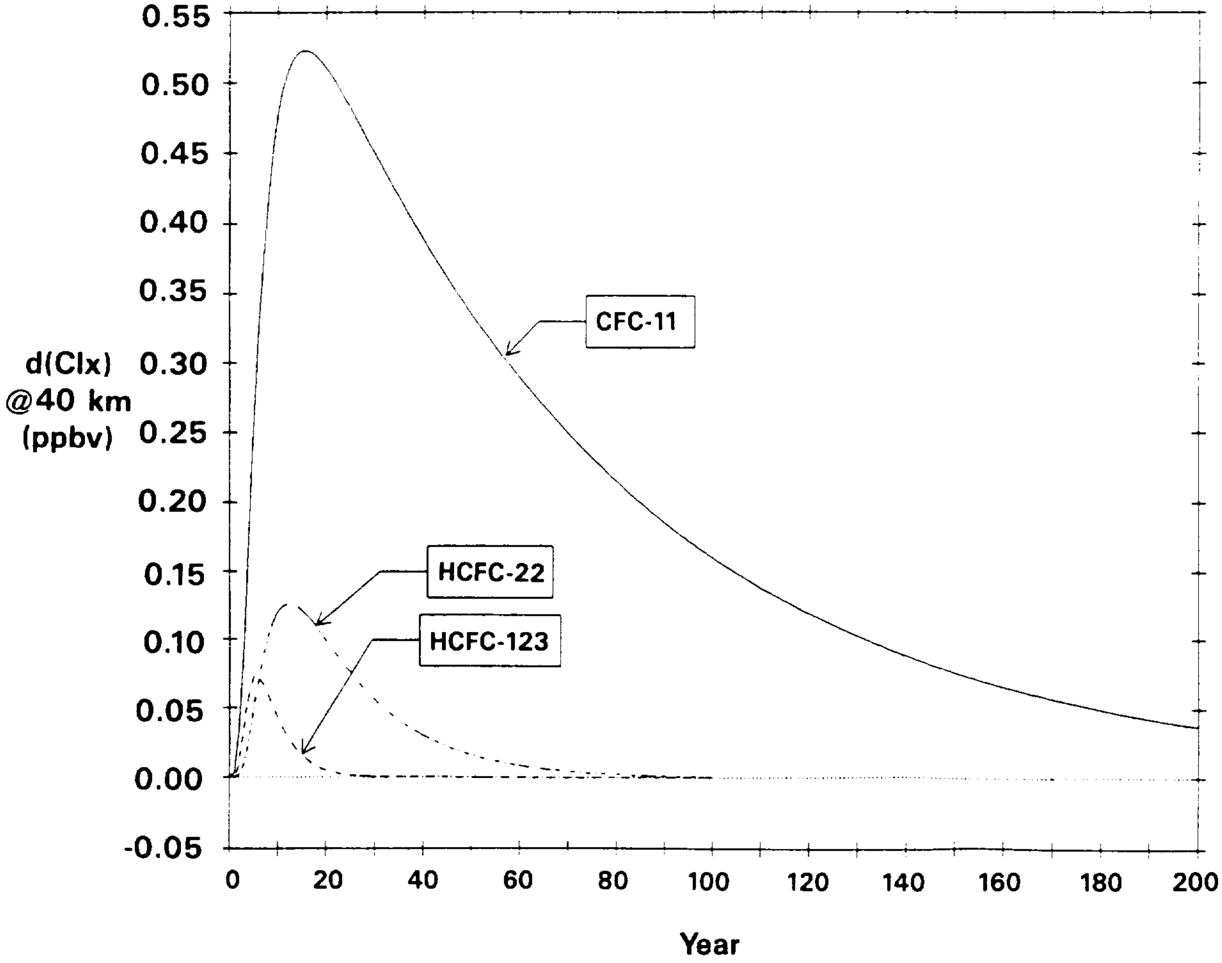
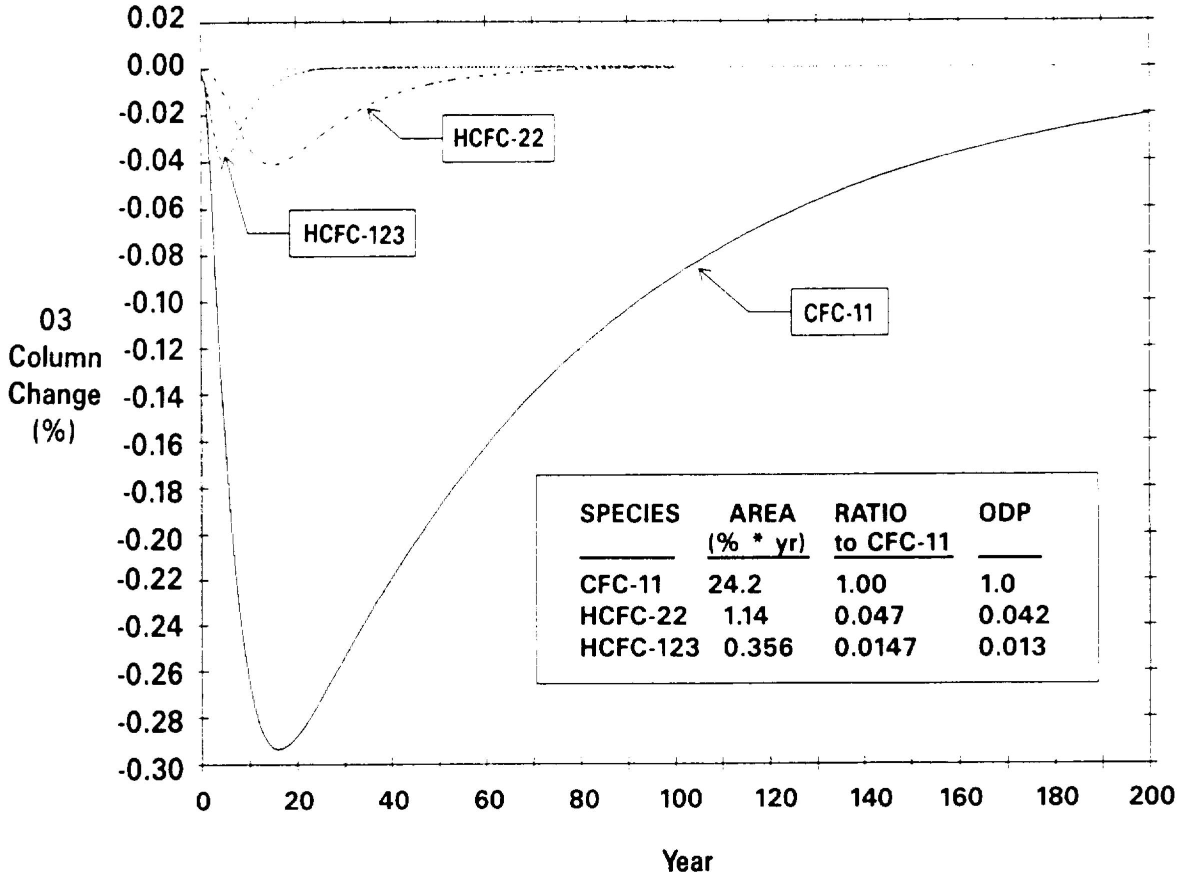


Figure 2. Calculated Change in Inorganic Chlorine at 40 km Following a Pulsed Input of 5.0x10**9 kg of Specified Gas. (DuPont 1-D Model)

ing test performed using the Du Pont one dimensional model to determine relative effects of a given release of HCFC-123, HCFC-22, and CFC-11. This test assumed that a quantity (5x109 kg) of each halocarbon was emitted into the atmosphere during the first model year. Subsequent model years had zero modeled emissions and the transient atmospheric responses were calculated.

Transient results from the model are shown in Figures 1 to 3. Figure 1 shows the calculated tropospheric concentration of each gas, peaking at the year of the release, and then diminishing over time as a result of chemical reaction in the atmosphere. The decay time constant (on an exponential scale) corresponds to the calculated lifetime of the gas.

Figure 2 shows the calculated change of inorganic chlorine level at 40 km for each of the cases. Inorganic chlorine concentration (total of Cl, ClO, OCLO, Cl_2O_2, HCl, HOCl, and $ClONO_2$), is an important parameter in the stratospheric chemistry since rate of chlorine catalysis of ozone destruction, among other factors, is directly related to its magnitude. Differences in inorganic chlorine concentrations for the these



SPECIES	AREA (% * yr)	RATIO to CFC-11	ODP
CFC-11	24.2	1.00	1.0
HCFC-22	1.14	0.047	0.042
HCFC-123	0.356	0.0147	0.013

Figure 3. Calculated Column Ozone Change Following a Pulsed Input of 5.0x10**9 kg of Specified Gas. (DuPont 1-D Model)

compounds are due to three factors: (1) The weight percent of chlorine in each species is somewhat different ranging from 71% in CFC-11 to 41% of HCFC-22. (2) Location of decomposition of the species is important. HCFCs -123 and -22 are mainly destroyed in the troposphere such that only a fraction of the chlorine reaches the stratosphere as inorganic products. CFC-11, on the other hand, passes through the troposphere unreacted, such that all the chlorine is transported to the stratosphere where it eventuallv is broken down (primarily through photolysis) to inorganic chlorine. (3) Once in the stratosphere, compounds break down at different altitudes resulting in different levels of inorganic chlorine.

Figure 3 shows the change in column ozone for all cases. As seen in the insert table, the cumulative effects (time integrated) from emissions of 5×10^9 kg of each halocarbon are closely, proprotional to the ODP values for each chemical. Appendix A discusses the mathematical relationships that exist between the ODP calculated based on steady state perturbations and this transient problem. In summary, this test validates ODP as a measure of the cumulative effect on stratospheric ozone for each mass unit emitted to the atmosphere.

Just as valuable as knowing the applicability of ODP, we also should recognize the limitations of the ODP definition in order to not extend interpretation beyond its valid scope. For instance, since ODP is defined at steady state, it is not representative of relative transient effects, especially during the early years of emissions. This fact is illustrated in Figure 4 showing the tropospheric concentration of two compounds following the onset of a constant emission level of each. One of the compounds has a 100 year lifetime (comparable to lifetimes of CFCs) and the other compound has a 5 year lifetime (comparable to lifetimes of hydrohalocarbons). We see that the ratio of the relative atmosphere concentration ratio does not approach steady state until about 400 years. Since the ODPs are based on steady state relative effects which are (nearly) proportional to CFC concentrations, the calculated relative effects for short-lived compounds during the approach to steady state are larger than indicated by the ODP value. This is simply because the effect from the short-lived species has reached its full strength whereas the effect from the long-lived species is still short of its steady state value. Further discussion on these transient effects will be covered in a later section of this paper.

3. DEFINITIONS

In order to make the ODP definition consistent among models the following criteria were selected:

1) Depletion level-the calculations are based on emission rates of each compound required to give a modeled ozone depletion of approximately 1%. This value of depletion was selected in order to yield results large enough to avoid the noise level inherent with numerical models, yet small enough to remain in the linear perturbation region.

2) Trace gas levels-changing concentrations of other trace gases affect calculated tropospheric OH levels [Sze (1977) and Chameides et al. (1977)] and future depletions. However, we chose to base the calculations on current levels of CO_2, CH_4, CO and N_2O due to the uncertainties in future concentrations. The constant concentration assumption was chosen for clarity and simplicity.

3) Chlorine levels-since the long lived CFCs are present in today's atmosphere and will affect chlorine chemistry over the time scales that hydrohalocarbons might be used, backcground halocarbon concentrations were assumed constant at current levels (3.0 ppbv in the stratosphere with the exception of Oslo which used a background amount of 5.2 ppbv. Prior calculations with the Oslo model indicate little effect on the derived ODPs from the assumed chlorine background).

4) Bromine chemistry-current levels of bromine compounds were included in the model chemistrv where appropriate.

Using the above provisions, the ODPs were then calculated as:

$$\text{ODP} = \frac{\dfrac{\text{Calculated Steady State 03 depletion due to Compound X}}{\text{Emission rate of compound X to give depletion of 1\%}}}{\dfrac{\text{Calculated Steady State 03 depletion due to CFC-11}}{\text{Emission rate of CFC-11 to give depletion of 1\%}}}$$

CFC-11 is used as the reference gas consistent with previous work (Wuebbles 1981).

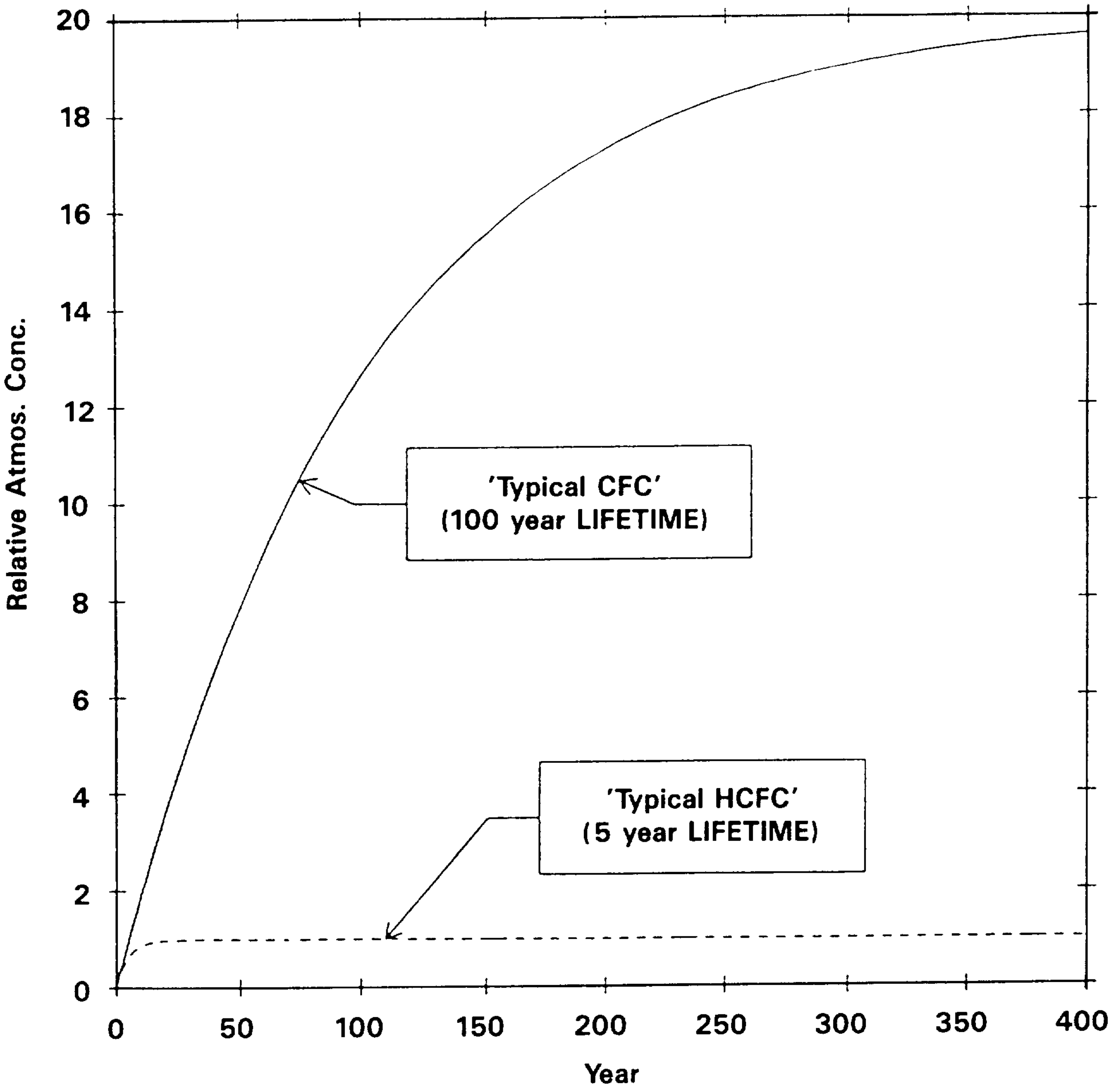


Figure 4. Atmospheric Concentrations of Halocarbons with 5- and 100- Year Lifetimes.

4. MODEL CALCULATIONS

Atmospheric chemistry models use mathematical expressions to describe the chemical reaction rates, transport, and photolysis processes that determine the chemical fate of the halocarbons. Figure 5 illustrates a generalized image of the chemical life cycle of halocarbons in the atmosphere. Each compound enters the atmosphere at ground level and, in general, is removed by a combination of chemical processes: reaction with hydroxyl (OH) in the troposphere and the stratosphere, reaction with excited state oxygen in the stratosphere, and photolytic breakdown by ultraviolet light in the stratosphere. Laboratory measurements indicate that CFCs (e.g. CFC-ll,-12,-113,- 114 and -115) are primarily destroyed by ultraviolet light in the stratosphere and to a lesser degree, reaction with excited atomic oxygen; reaction with hydroxyl radical is inconsequential. Hydrohalocarbons are removed by all three processes, but the predominant mechanism is reaction with OH in the troposphere. The reaction of the hydrohalocarbons with hydroxyl radicals leads to appreciably shorter atmospheric lifetimes and reduced ODPs compared to the CFCs. Additionally, the HFCs have no calculated effect on ozone because they contain no chlorine and current theory indicates that fluorine released in their destruction will rapidly be converted to hydrogen fluoride, which has no effect on ozone.

Reaction rate constants and photolysis cross sections required as model input were obtained from a number of sources. When available, rate data recently reevaluated by Hampson et al.(1989), Hampson (1989), and Molina (1989) have been used. The secondary data source was the most recent evaluation of rate data by the NASA Panel (DeMore et al. 1987). In the absence of these recommendations, some reaction rate parameters were obtained from the open literature [Davidson et al (1978), Hubrich and Stuhl (1980)]. Some data were only available from unpublished sources (Magid 1988). Finally, no photolysis measurements could be found for HFC-125 and HFC-143 so photolytic destruction was assumed zero. Since photolysis is generally of little consequence for the hydrogenated halocarbons, this is a reasonable assumption. Table 2 lists reference sources, and when possible, the values for each kinetic parameters. All models utilize their "best" representations for transport and radiation processes, generally derived from first principles as well as fitting to key observed values for trace species.

Both one- and two-dimensional models have been used for these evaluations. One dimensional models calculate the altitudinal variation of the relevant atmospheric chemical processes at an average point on the surface of the earth with an average temperature profile. These models all share the advantage that they are easy to operate and evaluate. Two-dimensional (2-D) models on the other hand allow examination of calculated effects over the full range of latitudes and seasons. As such, their added complexity, is offset by better representation of nonlinear characteristics of global stratospheric transport and radiative processes. Ozone changes calculated by 2-D models are averaged with respect to both latitude and seasons before calculation of the ODP values.

The calculated atmospheric lifetime of each gas species provides a key comparison for modeled results. Table 3 shows a comparison of lifetime values calculated by the models.

ODP values are reported in Table 4. Note that the HFCs (molecules without chlorine) have zero calculated effect on ozone and therefore ODP = 0. Each of the ODP is reported to 2 figures, in reality, the results are credible to less than two significant figures due to uncertainties in model input parameters.

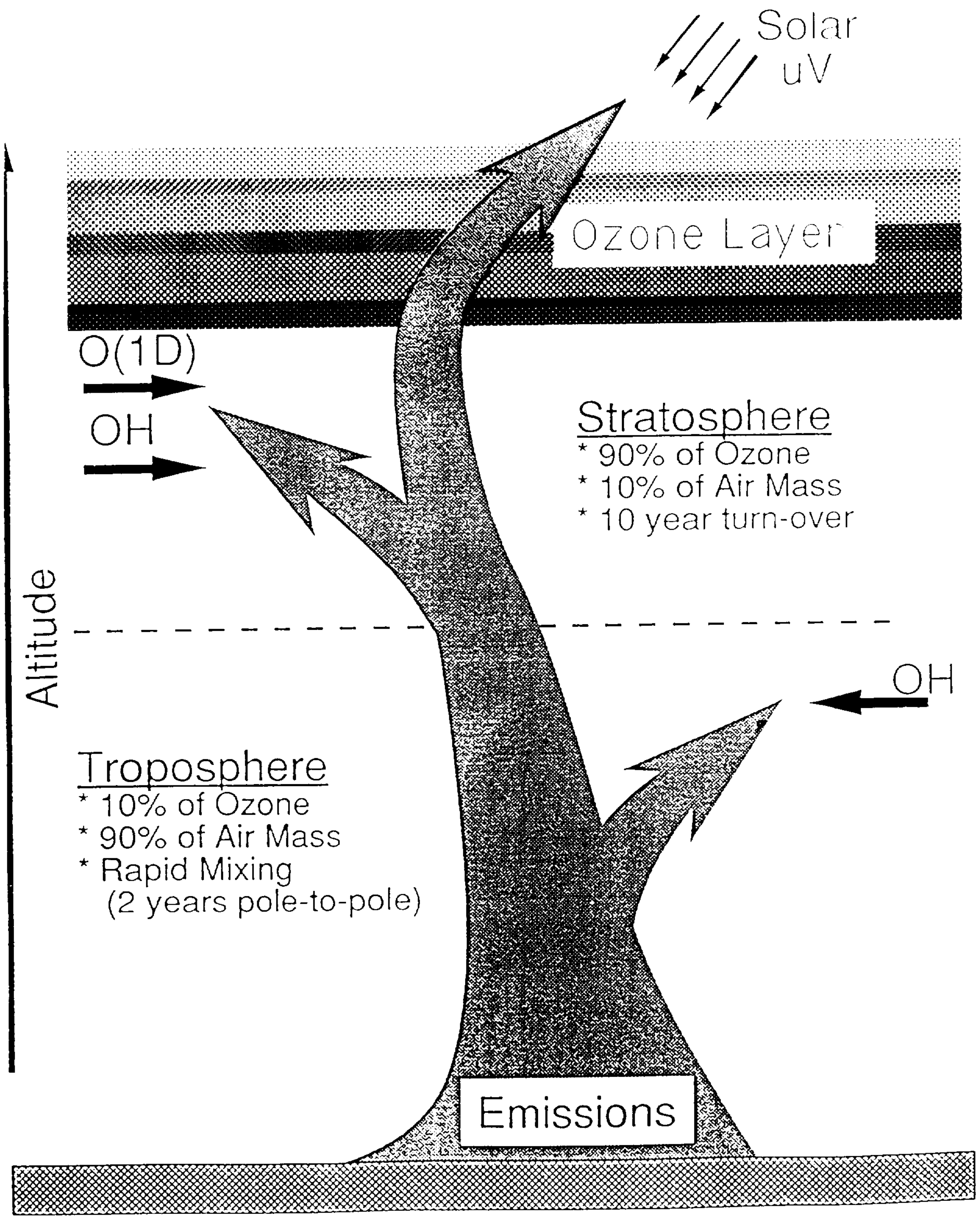


Figure 5. Generalized Chemical Lifecycle of a Halocarbon in the Atmosphere.

Table 2 Chemical Rate Data Used in ODP Calculations

		OH Reactions			O(^{1}D) Reactions		
Species	Photolysis UV X-Section	Reaction A	Rate(*) E/R	Refer.	Reaction Rate (**)	Branching Ratio (#	Refer. (##)
CFC 11	JPL p130	—	—	—	2.3(-10)	.75	JPL
CFC 12	JPL p131	—	—	—	1.4(-10)	.86	JPL
CFC113	H&S (1980)	—	—	-	2.0(-10)	.80	Dav.
CFC 114	H&S (1980)	—	—	—	1.6(-10)	.80	Dav.
CFC 115	H&S (1980)	—	—	—	.89(-10)	.80	Dav.
HCFC 22	JPL p133	1.2(-12)	1650	Hamp	1.0(-10)	1.	Hamp
HCFC 123	Molina	6.4(-13)	850	Hamp	2.3(-10)	1.	Hamp
HCFC 124	Molina	6.6(-13)	1250	Hamp	1.0(-10)	1.	Hamp_a
HFC 125	—	3.8(-13)	1500	Hamp	0.5(-10)	1.	Hamp
HFC 134a	Allied	1.7(-12)	1750	Hamp	0.5(-10)	1.	Hamp_a
HCFC 141b	Molina	2.7(-13)	1050	Hamp	1.5(-10)	1.	Hamp_a
HCFC 142b	Molina	9.6(-13)	1650	Hamp	1.4(-10)	1.	Hamp
HFC 143a	—	2.6(-13)	1500	Hamp	0.6(-10)	1.	Hamp
HFC 152a	Allied	1.5(-12)	1100	Hamp	1.0(-10)	1.	Hamp_a
Carbon Tet.	JPL p129	—	—	—	3.3(-10)	.86	JPL
Methyl Chloro.	JPL p167	5.0(-12)	1800	JPL	3.18(-10)	80	Dav.

* Reaction Rate Constant of form: k = A exp[-E/(RT)], where A and k have the units of cm**3/(molecule sec).

** Reaction rate constant with units cm**3/(molecule sec).

\# Fraction of O(^{1}D) disappearances proceeding through reaction channel, remainder pass through quenching channel to O(3p) and no reaction with the halocarbon.

\#\# Measurements reported in Davidson et al. were used. Data for remaining gases generated using the estimation formula developed in that reference. Branching ratios of 0.8 were assumed values.

Reference Key:

Allied	—Magid (1988)
Dav.	—Davidson et al.(1978)
Hamp	—Hampson, Kurylo, and Sander (1989)
Hamp_a	—Hampson (1989)
H&S	—Hubrich and Stuhl (1980)
Molina	—Molina (1989)
JPL	—DeMore et al. (1987)

Table 3 Lifetimes (Years)

	1-D Model Results			2-D Model Results			
Species	**LLNL**	**AER**	**Du Pont**	**Oslo**	**LLNL**	**AER**	**Du Pont**
CFCII	80.	60.	71.	60.	52.	47.	46.
CFC12	154.	125.	154.	105.	101.	95.	118.
CFC113	96.	96.	117.	101.	79.		
CFC114	209.	260.	319.	236.	197.		
CFC115	680.	690.	548.	522.	393.	399.	
HCFC22	20.	20.0	16.	17.	15.	24.	12.7
HCFC123	1.9	2.1	1.6	1.7	1.5	2.4	1.2
HCFC124	8.4	8.8	6.9	7.4	6.5	10.	5.3
HFC125	37.	37.	25.	27.	43.	19.	
HFC134a	21.	21.	16.	15.	24.	12.5	
HCFC141b	8.9	9.4	7.8	8.0	6.9	11.	5.8
HCFC142b	25.	25.	19.	21.0	19.	28.	15.1
HFC143a	54.	52.	42.	40.			
HFC152a	2.1	2.3	1.7	1.5	2.7	1.3	
CCl_4	73.	53.	61.	52.2	47.	40.	40.
CH_3CCl_3	7.4	7.4	6.0	6.3	5.8	7.9	4.7

Differences in calculated tropospheric hydroxyl concentrations account for many of the lifetime differences. Several factors could contribute to the differences in the calculated concentrations of tropospheric OH. First, there is inadequate information on the distributions of a number of gases (e.g., CO, O_3 and NO_x) that play critical roles in the determination of tropospheric OH levels. Different modeling groups are likely using different boundary conditions for these gases. Second, there are uncertainties in many tropospheric processes, especially in rates for key reactions.

However, hydrohalocarbon lifetimes are generally consistent among the models. The sensitivity of calculated lifetimes to chemical rate information is most pronounced in the case of HFC-143a. Because its UV absorption spectrum was unreported, reaction with hydroxyl radical was the only modelled loss process. Its recommended OH reaction rate constant is the slowest of the hydrohalocarbons, so its calculated lifetime is long. Inclusion of photolysis will impact the chemical lifetime of this species.

Analysis of data for atmospheric CH_3CCl_3 may provide a reasonable though indirect check on the calculated lifetime of CH_3CCl_3 and therefore the global average concentration of OH. Based on the observed trends of CH_3CCl_3 and the estimated emission data, analysis indicates a globally averaged CH_3CCl_3 atmospheric lifetime of 6.3 ± 1.1 years [Prinn et al. (1987, NASA (1988)], compared with model calculated values which range from 4.7 to 7.8 years (see table 3 for the various models). The deduced average OH from CH_3CCl_3 data, while useful for placing important constaints on theoretical models, must be

Table 4 Ozone Depletion Potentials

	1-D Model Results			2-D Model Results			
Species	**LLNL**	**AER**	**Du Pont**	**Oslo**	**LLNL**	**AER**	**Du Pont**
CFC11	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CFC12	1.0	0.92	1.0	0.92	0.87	0.88	0.89
CFC113	0.82	0.83	0.89	0.86	0.76		
CFC114	0.76	0.63	0.79	0.82	0.56		
CFC115	0.43	0.36	0.45	0.40	0.27	0.37	
HCFC22	0.053	0.057	0.042	0.046	0.043	0.071	0.032
HCFC123	0.016	0.019	0.013	0.013	0.016	0.027	0.013
HCFC124	0.019	0.021	0.016	0.018	0.017	0.030	0.013
HFC125	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HFC134a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HCFC141b	0.081	0.092	0.066	0.089	0.081	0.14	0.065
HCFC142b	0.059	0.056	0.053	0.056	0.045	0.077	0.035
HFC143a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HFC152a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
CCl_4	1.1	1.16	1.1	1.2	1.1	0.95	1.2
CH_3CCl_3	0.11	0.14	0.092	0.14	0.12	0.20	.11

interpreted as an appropriate density and temperature-weighted average characteristic to CH_3CCl_3. Since the concentration of OH is expected to fluctuate appreciably in both time and space, using globally averaged OH deduced from CH_3CCl_3 to calculate lifetimes for other HCFCs may not necessarily be accurate, particularly for those HCFCs with lifetimes substantially different from that of CH_3CCl_3. The approach used here is to calculate tropospheric OH based on chemical models rather than adopt a single OH value derived from CH_3CCl_3 data.

Table 5 Scaled by Methyl Chloroform Lifetime of 6.3 years

	1-D Model Results			2-D Model Results			
Species	**LLNL**	**AER**	**Du Pont**	**Oslo**	**LLNL**	**AER**	**Du Pont**
HCFC22	0.045	0.049	0.044	0.046	0.047	0.057	0.043
HCFC123	0.013	0.016	0.013	0.013	0.017	0.022	0.017
HCFC124	0.016	0.018	0.017	0.018	0.019	0.024	0.017
HCFC141b	0.069	0.078	0.069	0.089	0.089	0.11	0.088
HCFC 142b	0.051	0.048	0.055	0.056	0.050	0.062	0.047
CH_3CCl_3	0.094	0.12	0.096	0.14	0.13	0.16	0.149

However, as a way to examine differences in ODPs due to differences in model calculated OH, the calculated ODPs can be scaled using the ratio of measured lifetime for methylchloroform of 6.3 years (NASA 1988) to the calculated lifetimes from each of the models. This normalization leads to a more consistent set of ODP values as shown in Table 5. This set of calculations indicate that the HCFCs have ozone depletion potentials one-tenth or less of CFC-11 and that the values calculated bv different modeling groups agree fairly well.

5. SENSITIVITY STUDIES

The above globally averaged ODP values are derived from model calculations assuming present day atmospheric gas concentrations conditions using "best" representations of transport processes. To check the importance of these assumptions, additional calculations have been carried out to test the sensitivity of the relative effects to 1) levels of other trace gases, 2) seasonal and latitudinal dependencies and 3) assumed stratospheric transport processes.

Sensitivity of ODPs to Other Trace Gas Levels

ODP values have all been based on calculated ozone changes in a modeled atmosphere assuming present day amounts of CFCs, CO_2, CH_4, CO, N_2O, Brx and other trace gases. Because it is important to quantify the effects of possible changes in the future trace gas concentrations on ODPs, calculations were performed to determine the sensitivity of the ODPs to trace gas concentration changes that may occur within the next century if current trends continue.

Trace gas concentrations were varied from current concentrations as shown in Table 6. These concentrations were changed both individually and as an ensemble in the sensitivity calculations. Calculated chances in ozone for tested CFCs and HCFCs are relative to an atmosphere including the assumed trace gas perturbation.

Two models were used to detemine the sensitivity of atmospheric lifetimes and Ozone Depletion Potentials to trace gas concentrations. Calculations with the AER 1-D model assumed a background stratospheric chlorine content of 3 ppbv. Calculations with the Oslo 2-D model used a background chlorine amount of 5.2 ppbv. Prior calculations with the Oslo model indicate little effect on the derived ODPs from the assumed chlorine background amount.

Table 6 Change in Ground Level Trace Gas Concentrations Assumed in Sensitivity Studies

Trace Gas	Normal	Perturbed
CO_2	340 ppmv	680 ppmv
CH_4	1.6 ppmv	3.2 ppmv
CO	100 ppbv	200 ppbv
N_2O	300 ppbv	360 ppbv
Brx	20 pptv	40 pptv

Table 7 Sensitivity of Calculated Lifetimes to Changes in Trace Gas Values (based on AER 1-D results)

LIFETIMES (years)

	CFC-11	CFC-12	HCFC-22	HCFC-123
Present day atmosphere	60	125	20	2.1
CO_2 (340 → 680 ppmv)	61	128	20	2.1
CH_4 (4.6 → 3.2 ppmv)	60	126	23	2.5
CO (100 → 200 ppbv)	60	125	25	2.7
N_2O (300 → 360 ppbv)	59	123	20	2.1
CH_3Br (20 → 40 pptv)	59	125	20	2.1
All changes combined	60	127	26	2.9

Table 7 shows the calculated changes in atmospheric lifetimes of CFC-11, CFC-12, HCFC-22 and HCFC-123 for the various sensitivity calculations. The largest effects are evident for the HCFCs in the cases where CH_4 and CO concentrations are perturbed. Both CH_4 and CO strongly influence tropospheric HO_X chemistry, therefore OH concentration, and consequently the primary destruction of the HCFCs are affected resulting in the expected impact on atmospheric lifetimes. The relatively minor changes in lifetimes of the CFCs are primarily a result of increased photolysis rates for the trace gas perturbed atmospheres.

Table 8 presents ODPs resulting from these calculations. For both the AER 1-D model and the Oslo 2-D model, the largest sensitivity in the ODP for CFC-12 occurs for the assumed concentration change in N_2O. As expected, ODPs for the HCFCs are affected most by chances in CH_4 and CO levels.

Table 8 Sensitivity of Ozone Depletion Potentials to Changes in Trace Gas Values

1. AER 1-D Model

	CFC-11	CFC-12	HCFC-22	HCFC-123
Present day atmosphere	1.0	0.92	0.057	0.019
CO_2 (340 → 680 ppmv)	1.0	0.93	0.051	0.018
CH_4 (1.6 → 3.2 ppmv)	1.0	0.93	0.069	0.023
CO (100 → 200 ppbv)	1.0	0.93	0.070	0.024
N_2O (300 → 360 ppbv)	1.0	1.01	0.071	0.019
CH_3Br(20 → 40 pptv)	1.0	0.92	0.055	0.019
All changes combined	1.0	0.95	0.076	0.026

2. Oslo 2-D model (all calculations with 5.2 ppbv Cly)

	CFC-12	HCFC-22	HCFC-123	HCFC-124
Present day atmosphere	0.92	0.046	0.013	0.018
CO_2 (340 → 600 ppmv)	0.94	0.049	0.016	
CH_4 (1.6 → 3.2 ppmv)	0.93	0.058	0.016	
N_2O (300 → 360 ppbv)	0.97	0.042	0.015	
Brx (18 → 33 pptv)	0.91	0.051	0.016	0.020
All changes combined	0.96	0.062	0.018	0.020

The calculated sensitivities to background trace gas concentrations can be explained as follows. First, changes in atmospheric lifetimes will affect the ODP in that as the lifetime increases/decreases, more/less of the CFC or HCFC is accumulated in the atmosphere at steady state for the same mass emitted. Secondly, the response of ozone to increases in chlorine can be different in the future atmosphere. However, this change in response will only affect the ODP estimates if the response of individual CFCs or HCFCs are different from that of CFC-11.

In conclusion, both lifetimes and derived ODPs are moderately sensitive to significant changes in background trace gas concentrations. However, for the scenarios examined, the range in sensitivity of the ODPs is well within the overall uncertainty range for model-determined ODP values. Possible systematic errors, perhaps due to missing chemistry or other processes, may provide a much more significant impact on the derived ODP values.

Sensitivity of ODPs with Latitude and Season

The ODPs derived from two-dimensional model results are analyzed in this section in terms of the variations of the ODP values as a function of latitude and season. These values were determined by comparing ozone changes calculated for each gas relative to changes calculated for the same mass of CFC-11 at all latitudes of the earth and seasons of the year in an approach analogous to the globally-averaged ODPs.

Figures 6 through 13 show results from the four two-dimensional modeling groups. Figure 6 shows

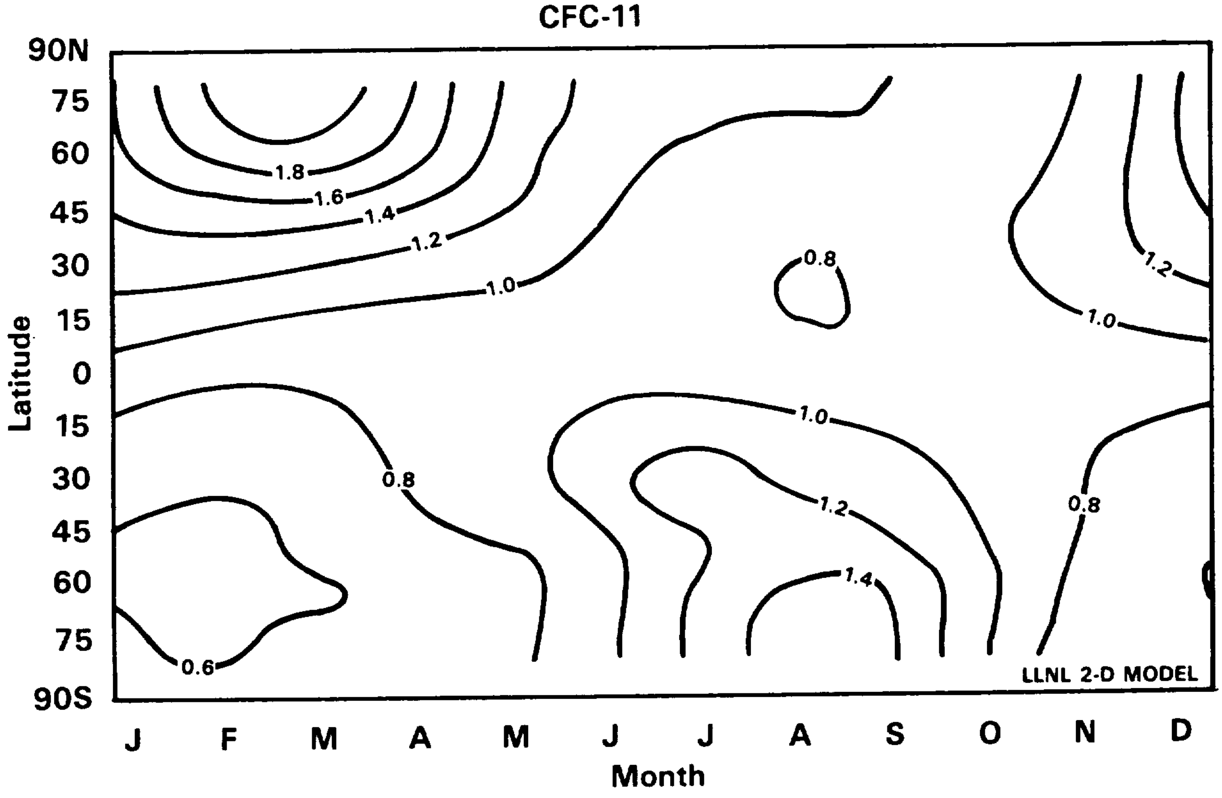


Figure 6. Calculated Latitudinal and Seasonal Steady-State Ozone Change from Emission of CFC-11 (LLNL 2-D).

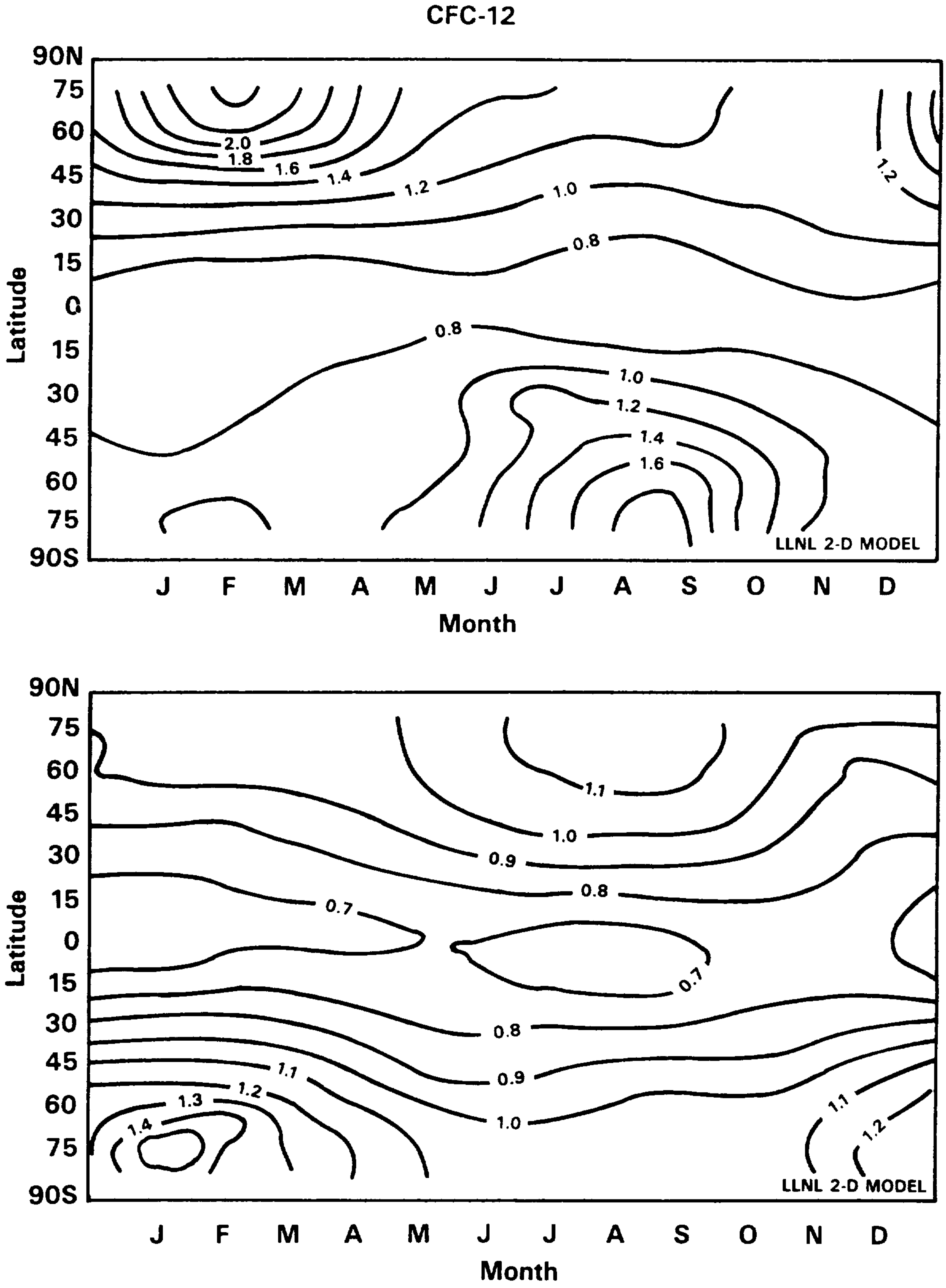
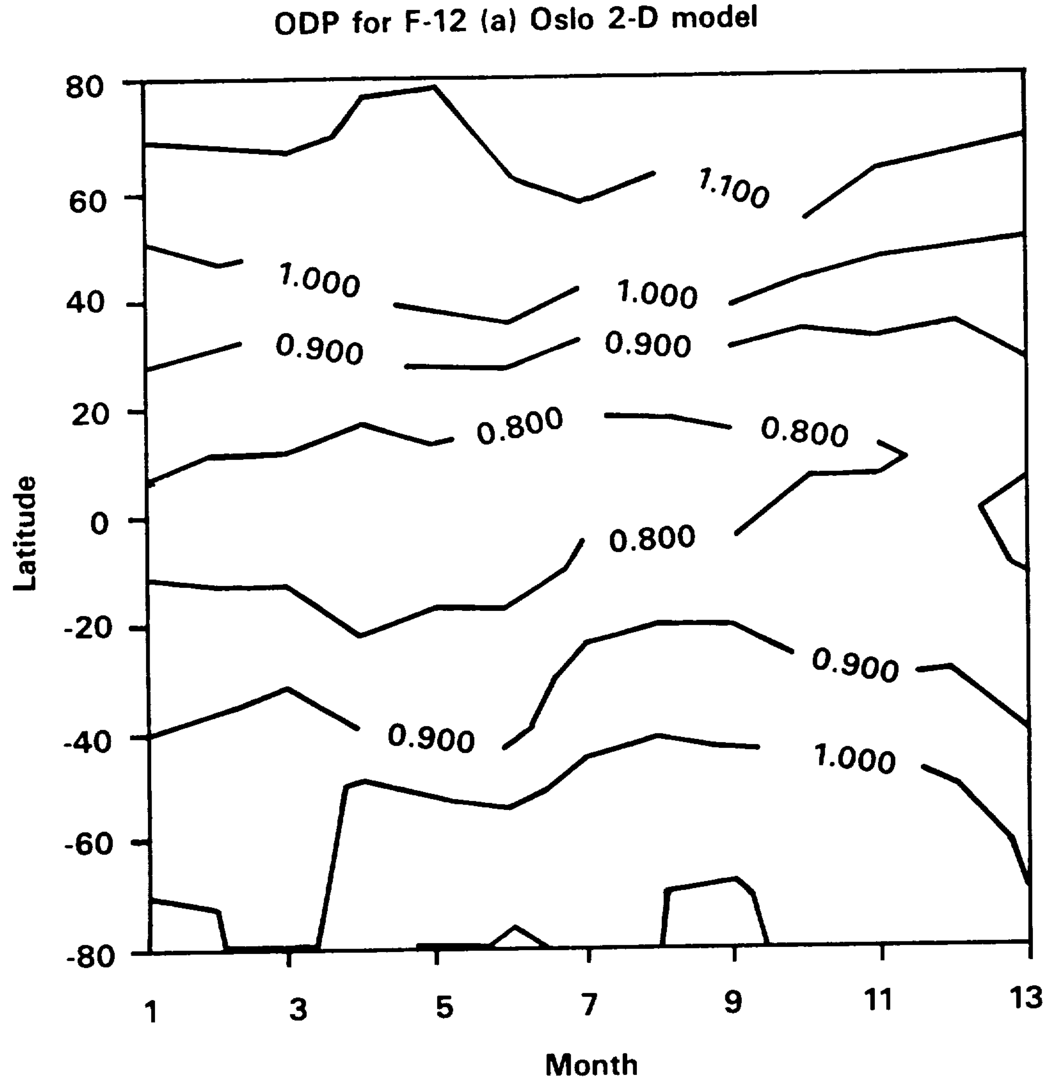


Figure 7A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of CFC-12 (LLNL 2-D).

the calculated change in total ozone as a function of latitude and season for CFC-11 perturbation as calculated in the LLNL 2-D model; this calculation, designed with assumed emissions to give a global ozone decrease of 1 %, acts as the comparison reference for the following discussion of latitudinal/seasonal ODPs. Consistent with previous 2-D model analyses of CFC effects on ozone (e.g., WMO, 1986), the largest changes in ozone occur at the poles in late winter to early spring. Figures 7 through 13 give the calculated latitude/season variations in ODPs from the four models (when available) for the following species: CFC-12, HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b and methyl chloroform. Also for each case, the calculated changes in total ozone are shown for the LLNL model assuming emission rates sufficiently large to give an approximate 1 % global ozone decrease; as with CFC-11, maximum changes in total ozone are calculated to occur near the poles in late winter for all species.

Once the calculated changes are compared relative to CFC-11 and adjusted for differences in assumed emission rates, the resulting values indicate a generally variable dependency on latitude and generally weaker



ODP for F-12 (a) Oslo 2-D model

Figure 7B. Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (Oslo 2-D).

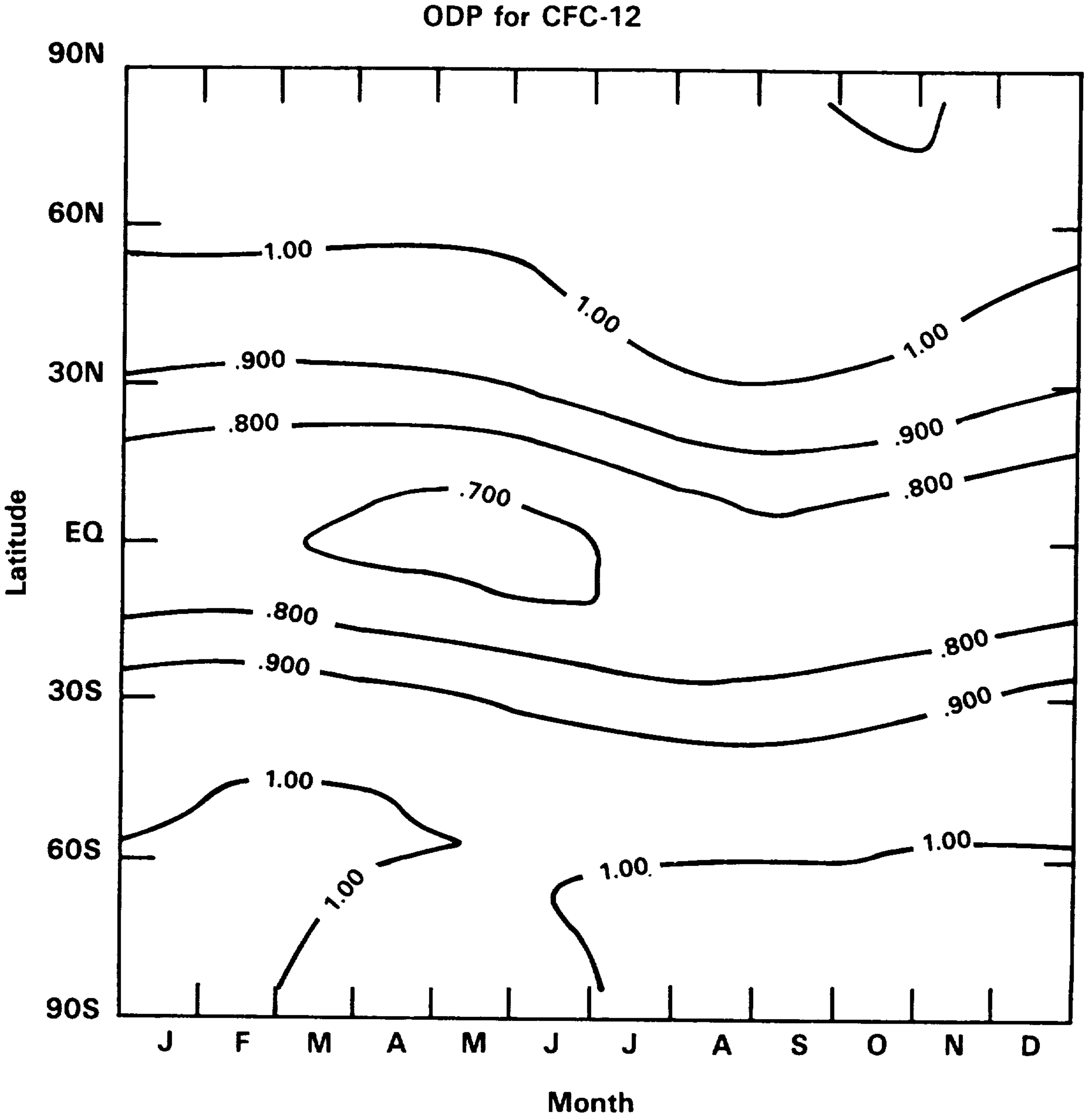


Figure 7C. Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (AER 2-D).

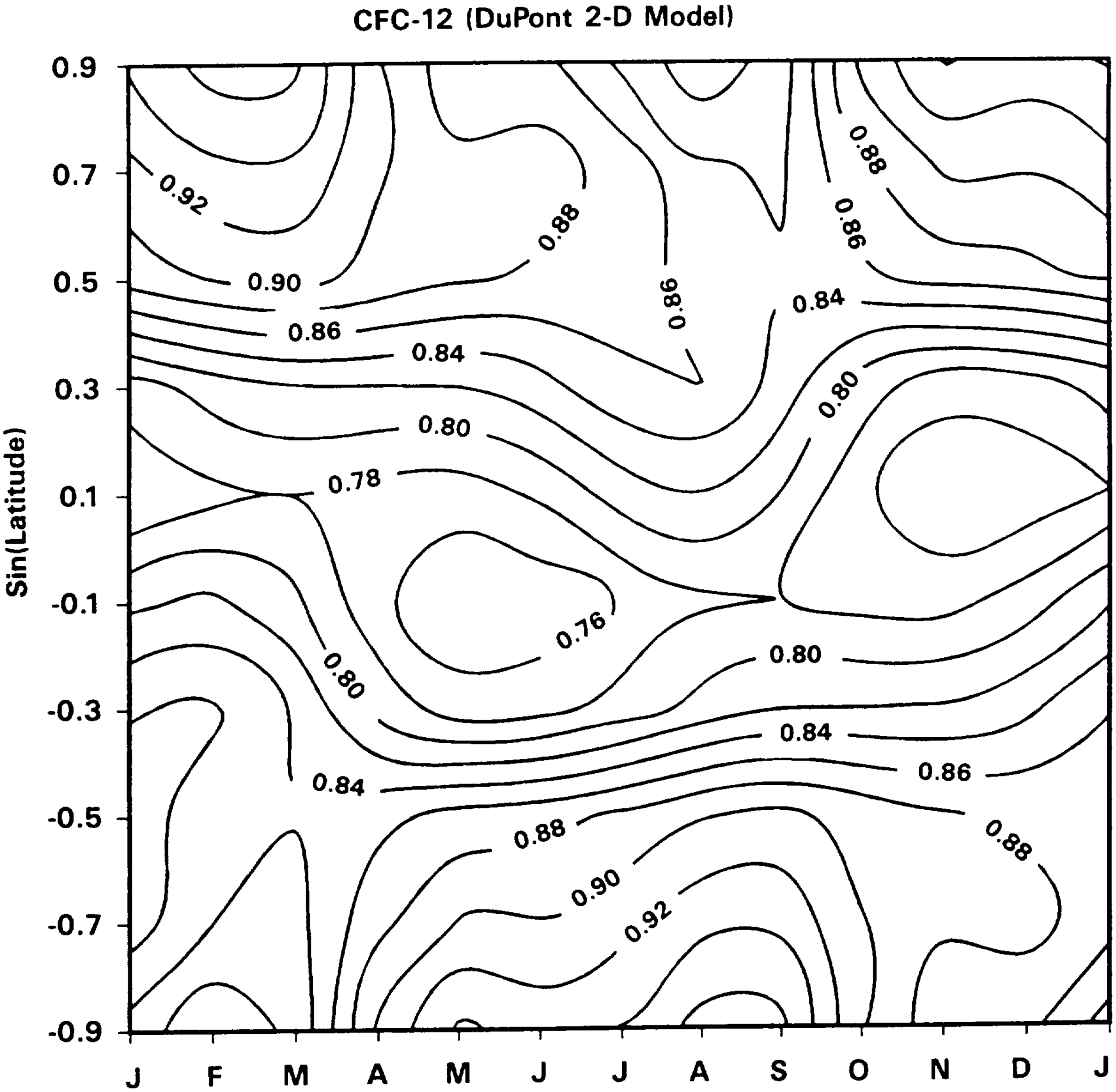


Figure 7D. Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (DuPont 2-D).

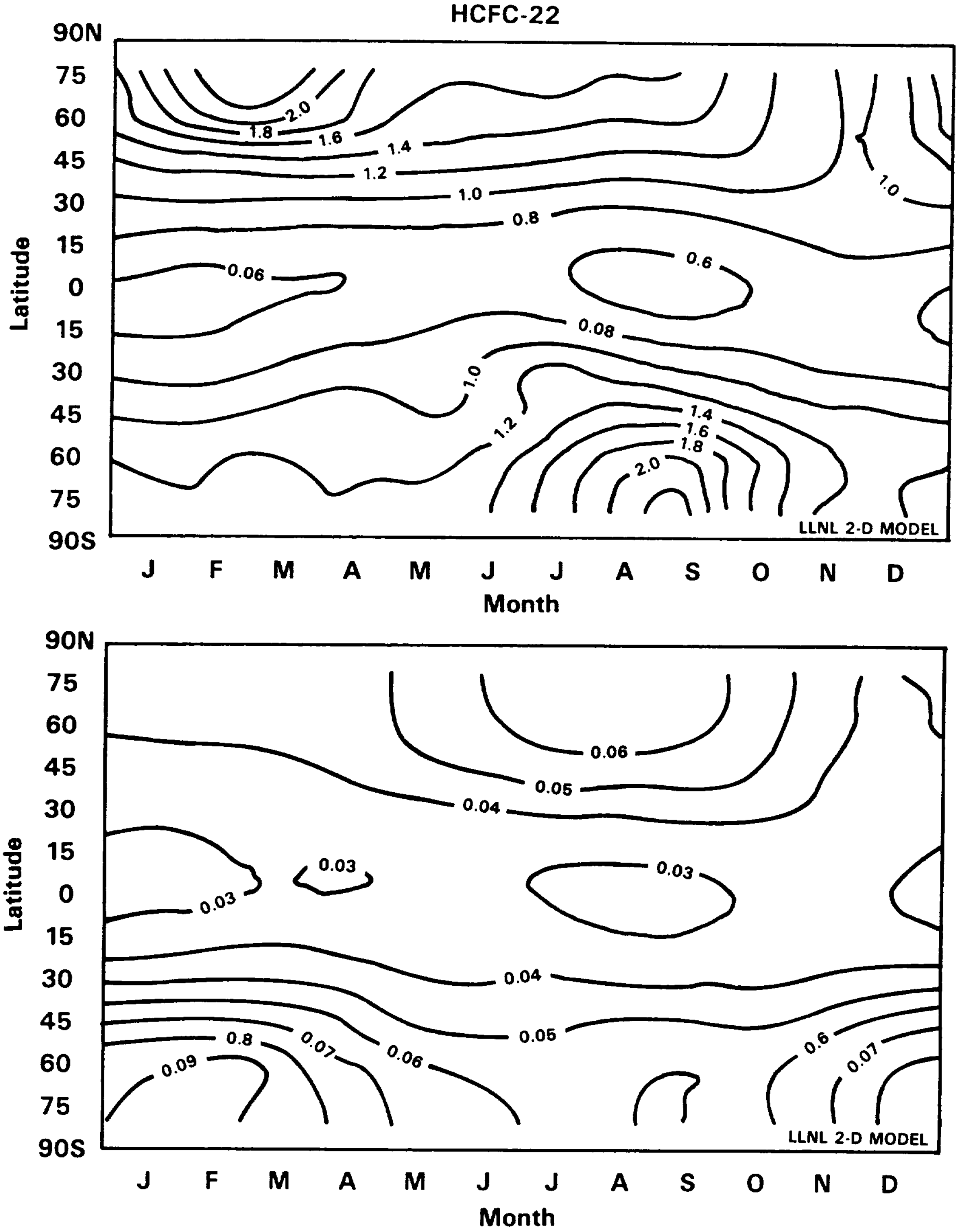


Figure 8A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-22 (LLNL 2-D).

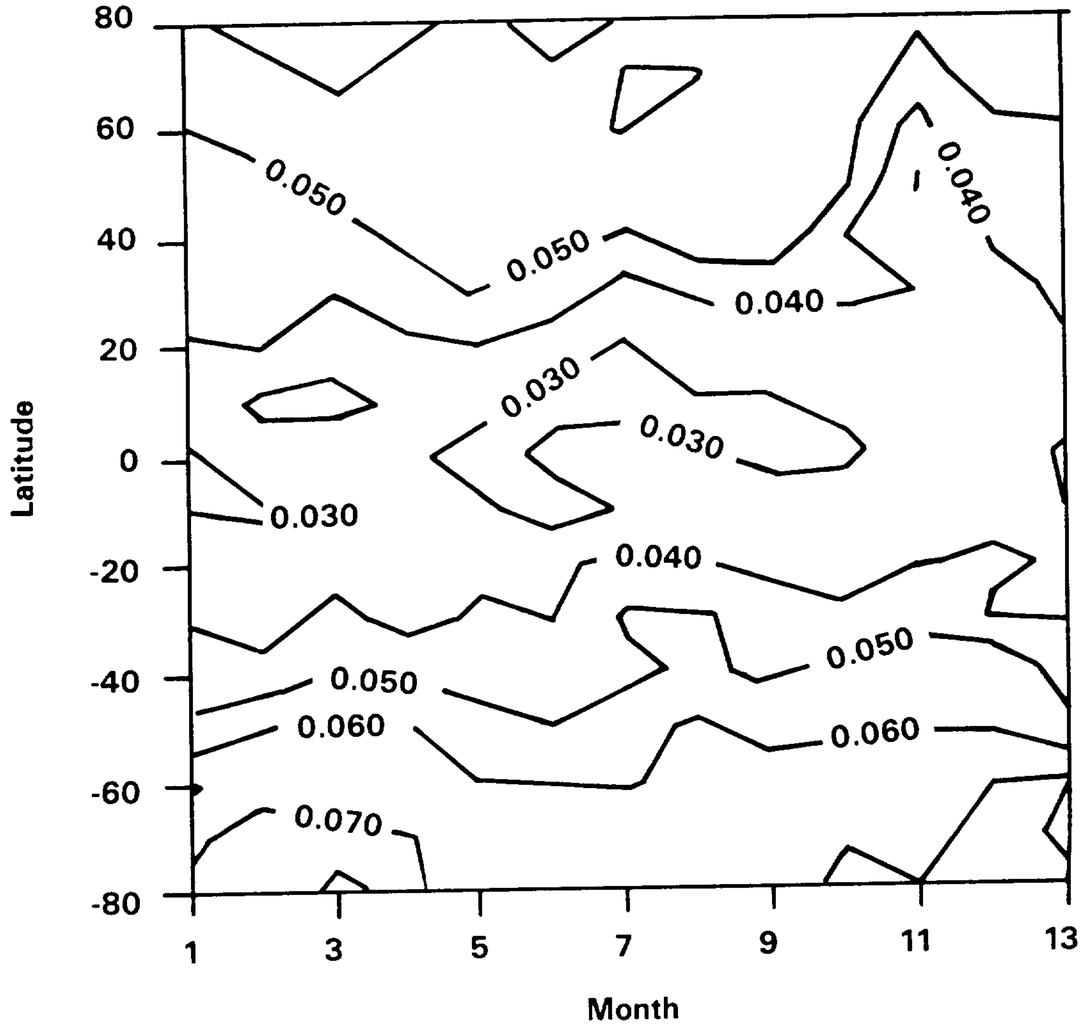


Figure 8B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 2 of Transport Sensitivity Study] (AER 2-D).

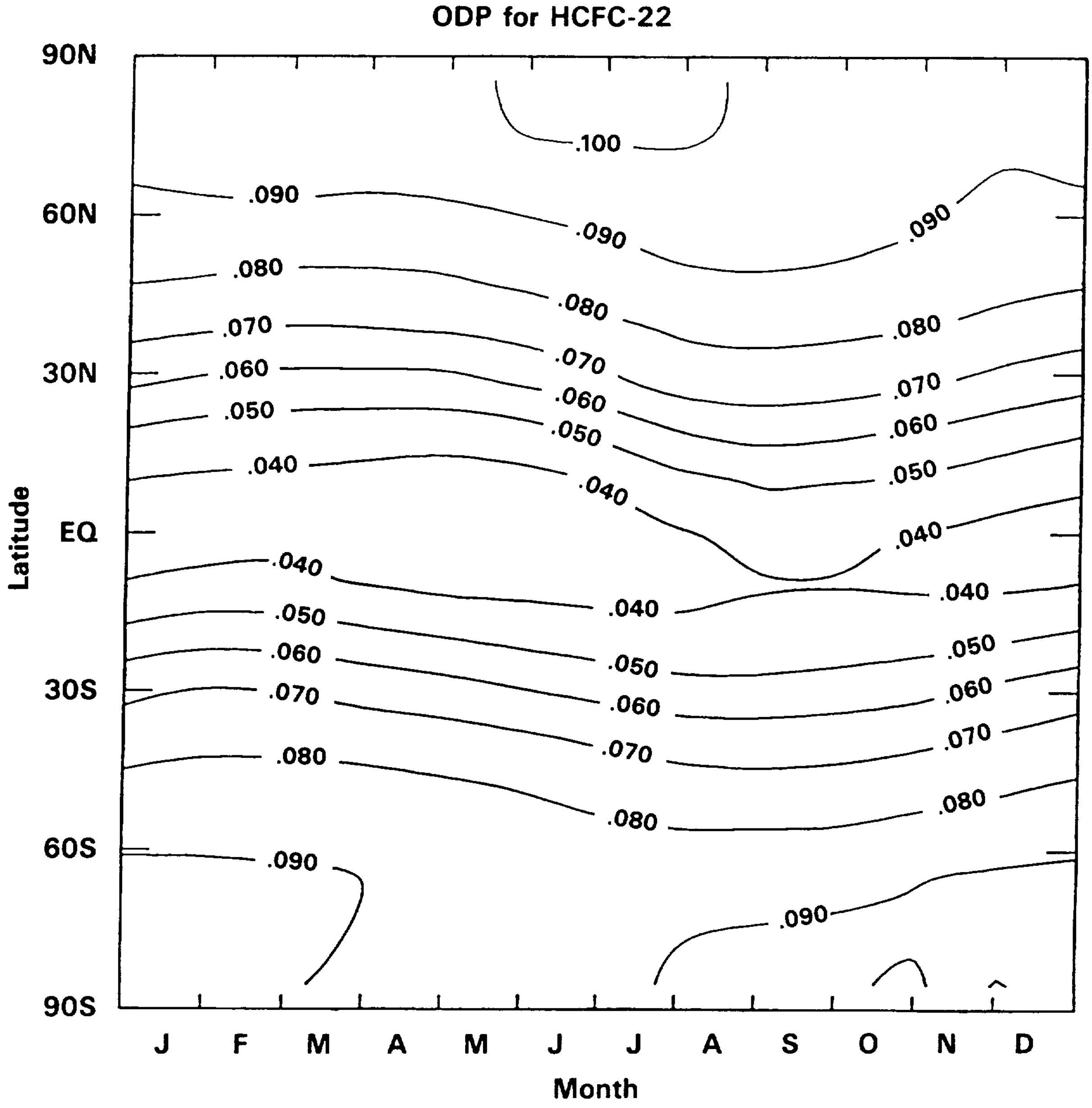


Figure 8C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 (AER 2-D).

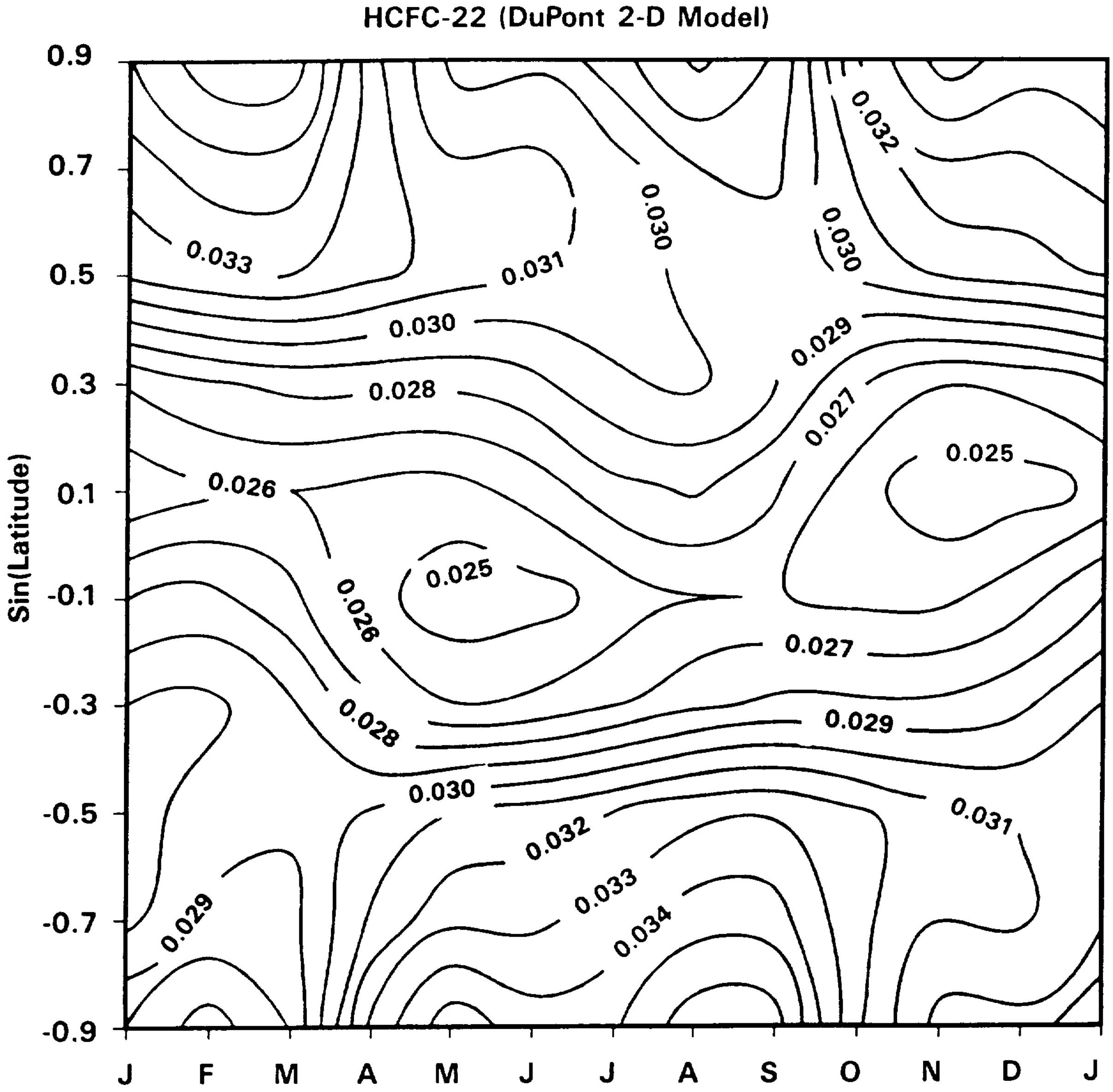


Figure 8D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 (DuPont 2-D).

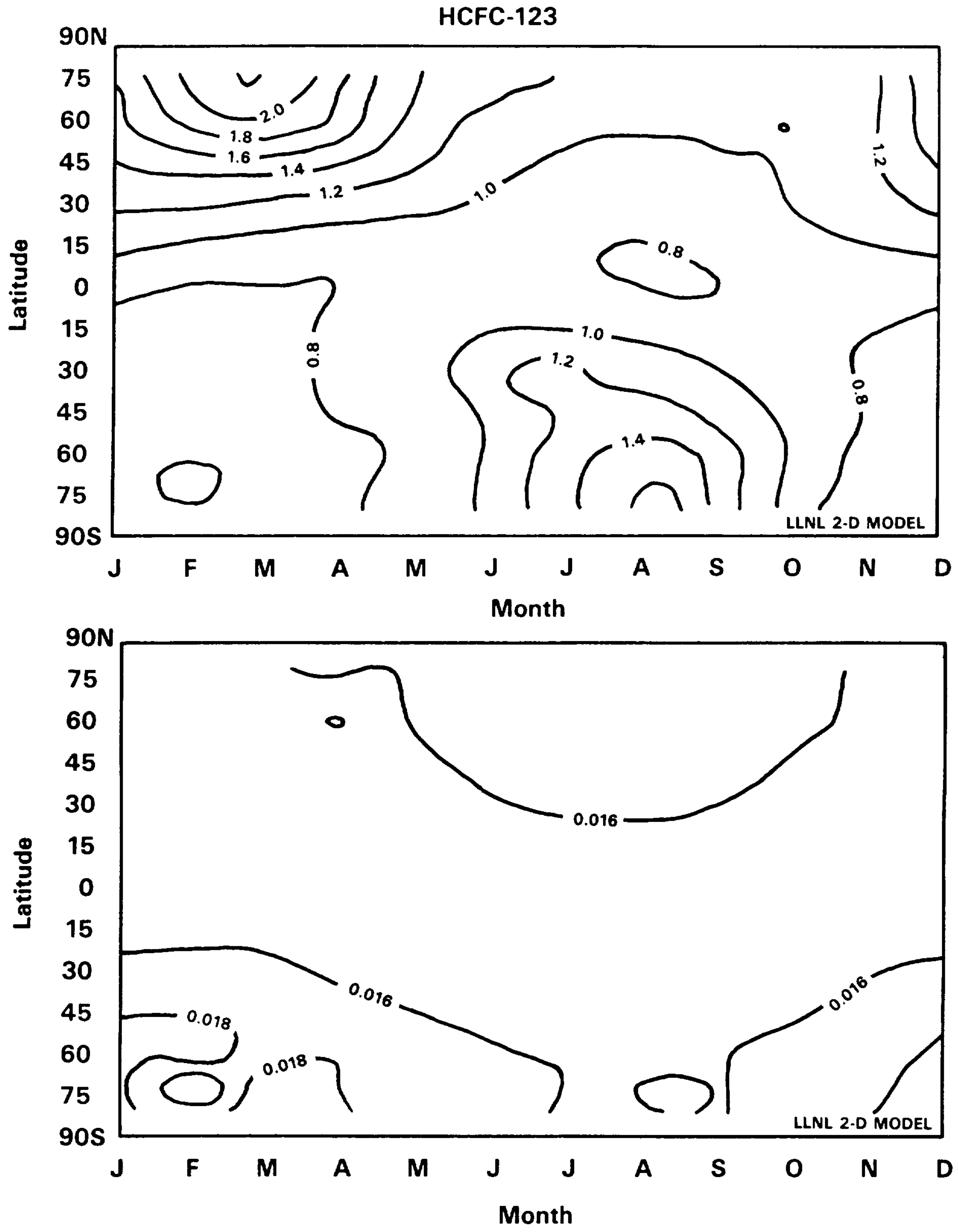


Figure 9A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-123 (LLNL 2-D).

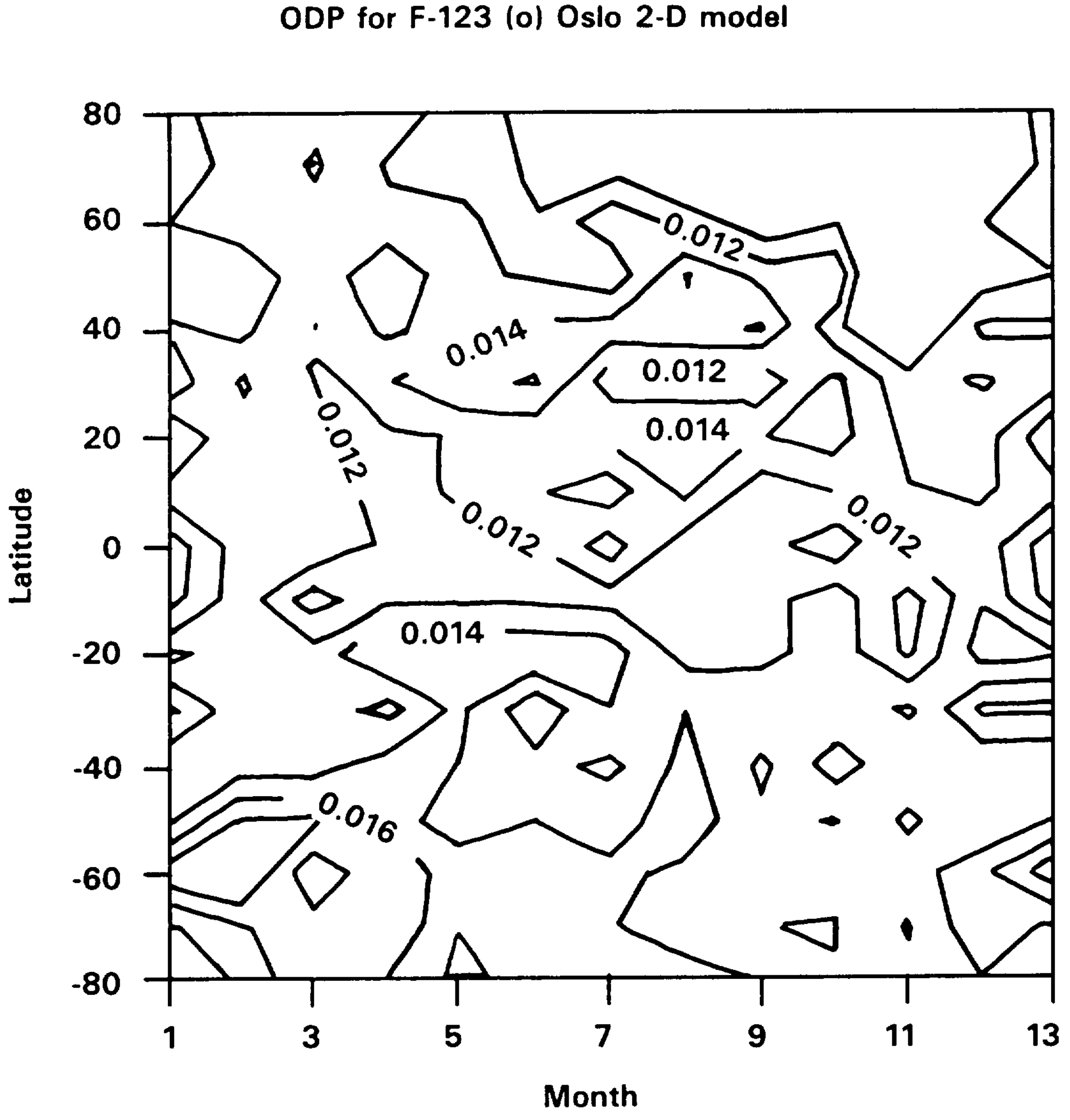
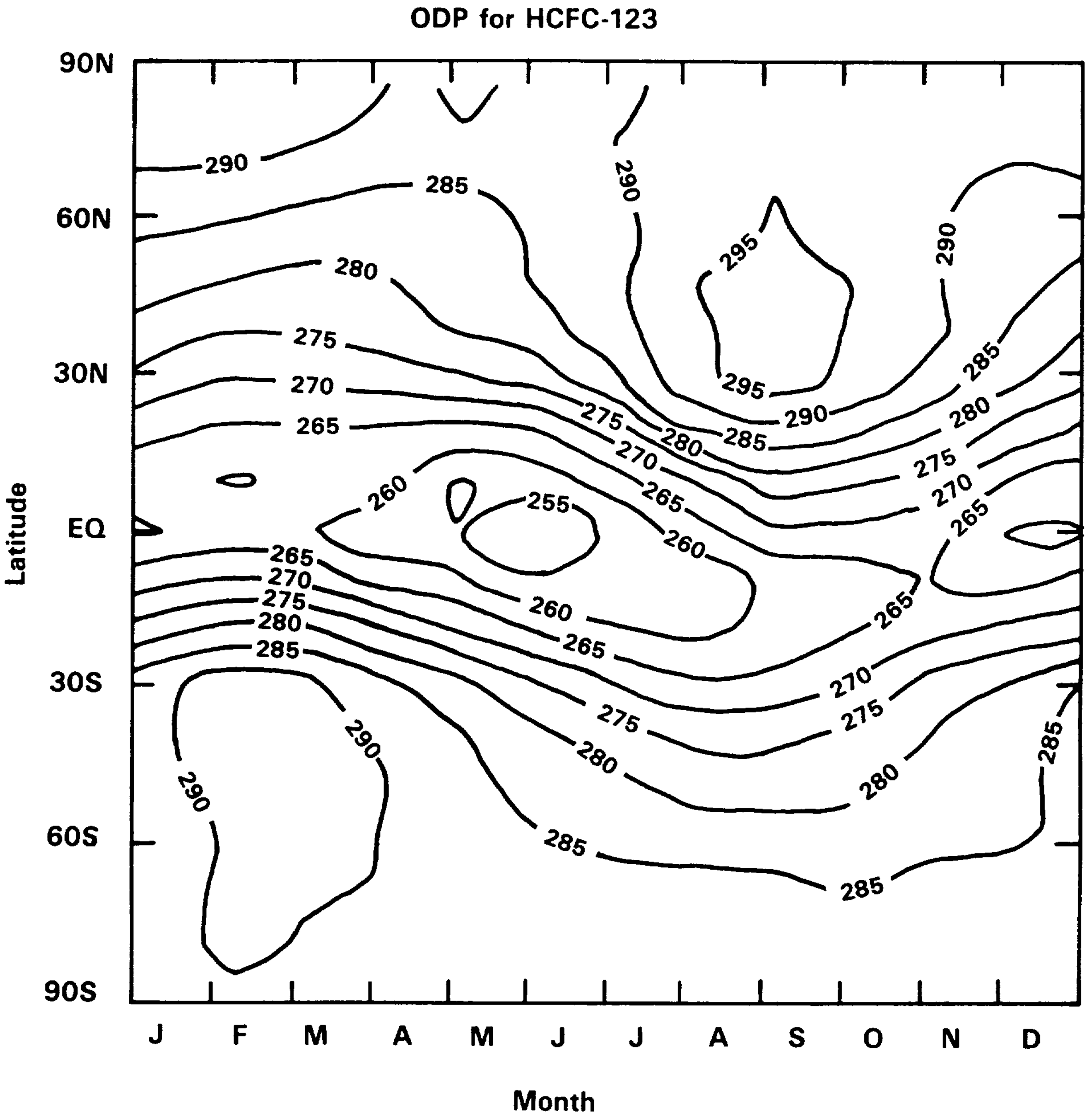


Figure 9B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (Oslo 2-D).



Please Note:
Contours Labels are Multiplied by 1,000

Figure 9C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (AER 2-D).

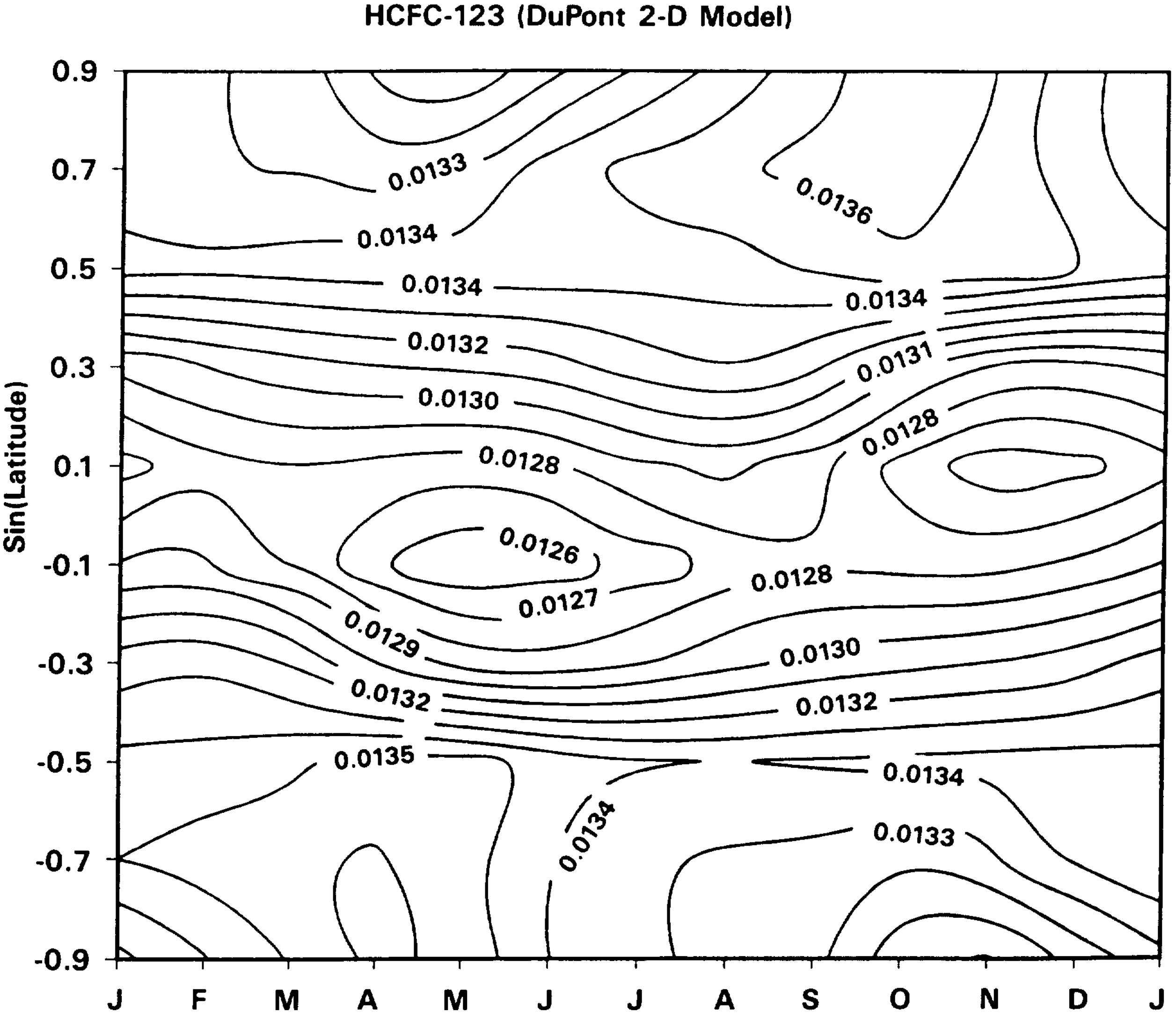


Figure 9D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (DuPont 2-D).

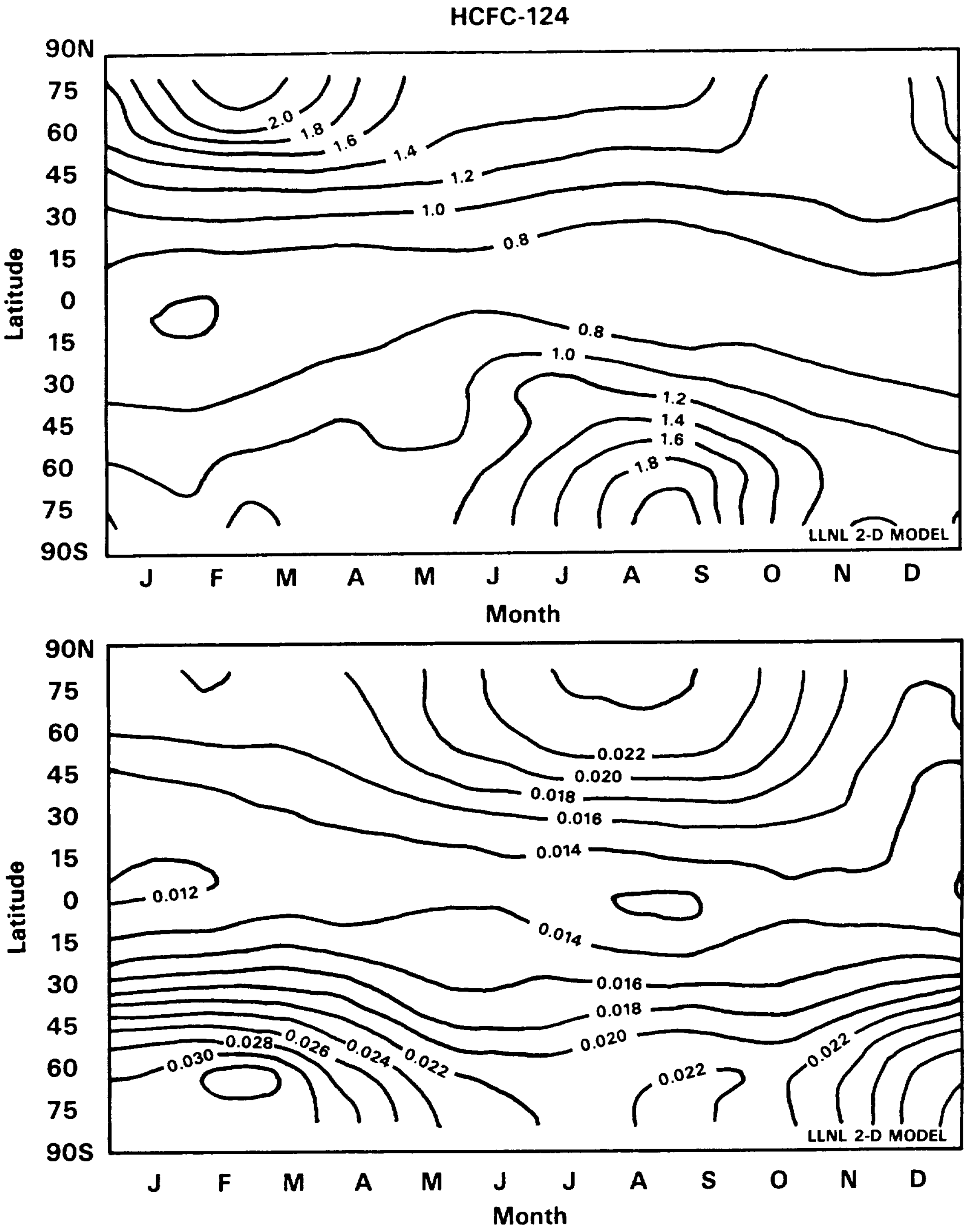
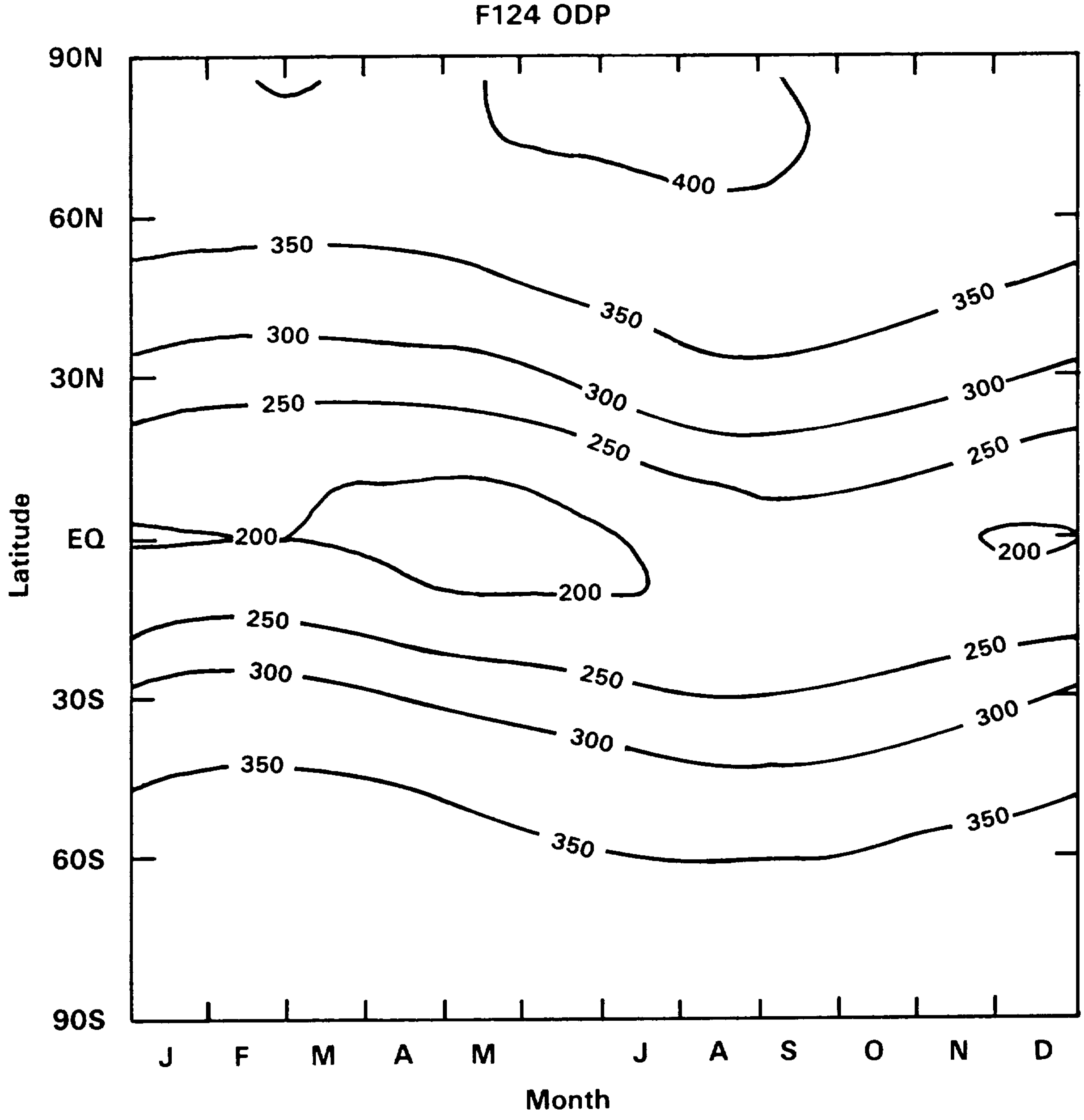


Figure 10A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-124 (LLNL 2-D).



Please Note:
Contours are ODP X 10,000

Figure 10B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124 (AER 2-D).

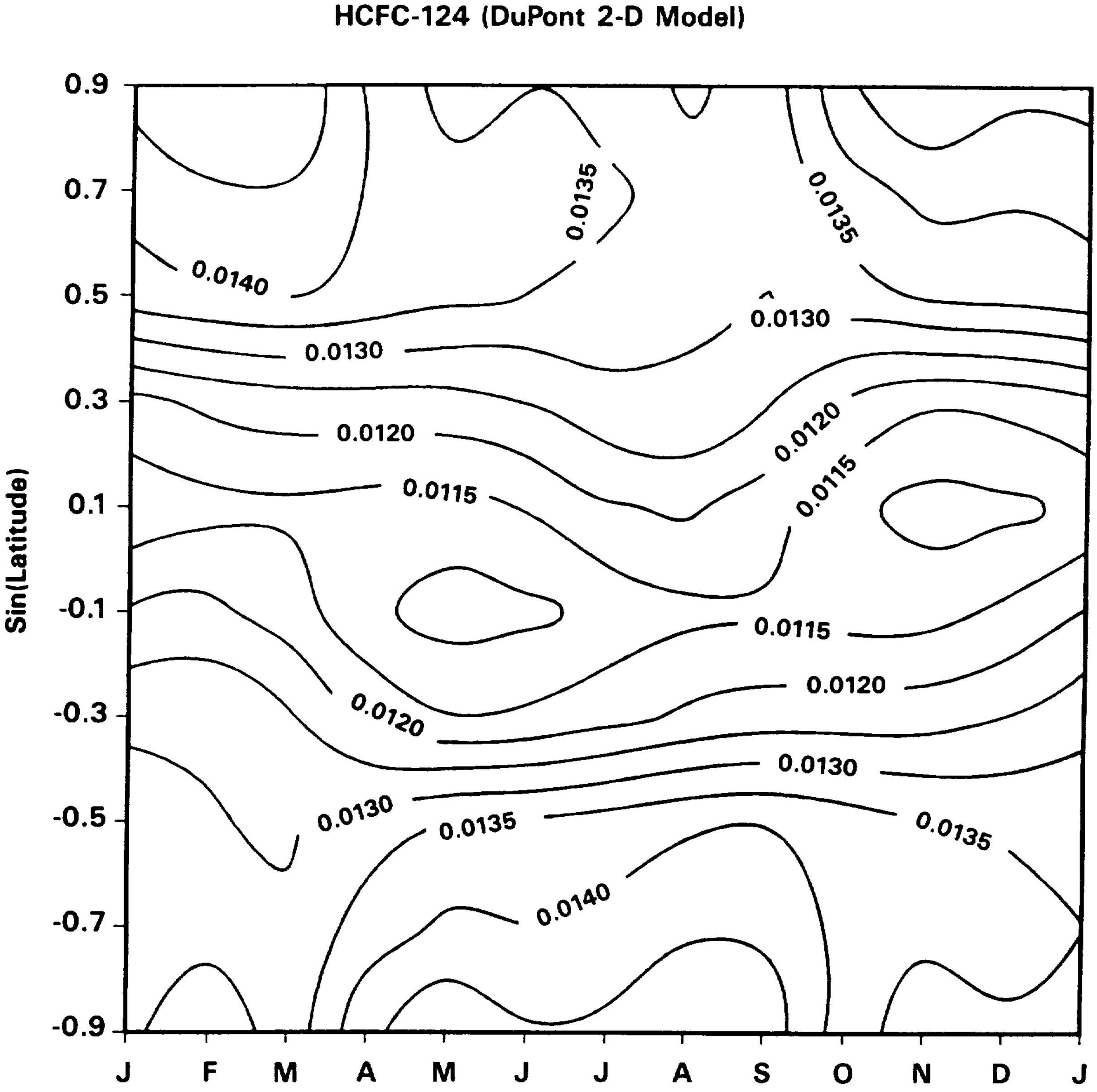


Figure 10C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124 (DuPont 2-D).

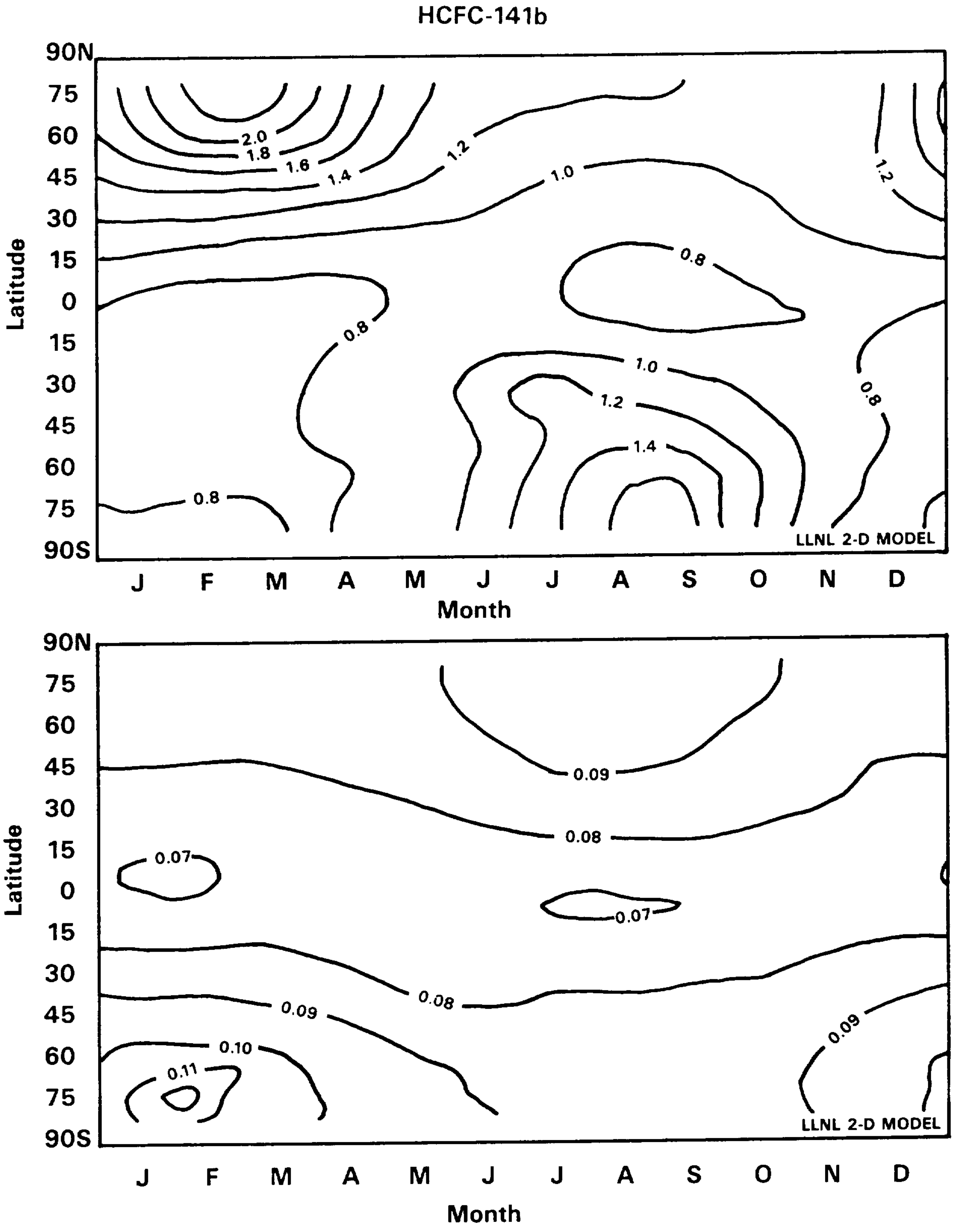

HCFC-141b

Figure 11A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-141b (LLNL 2-D).

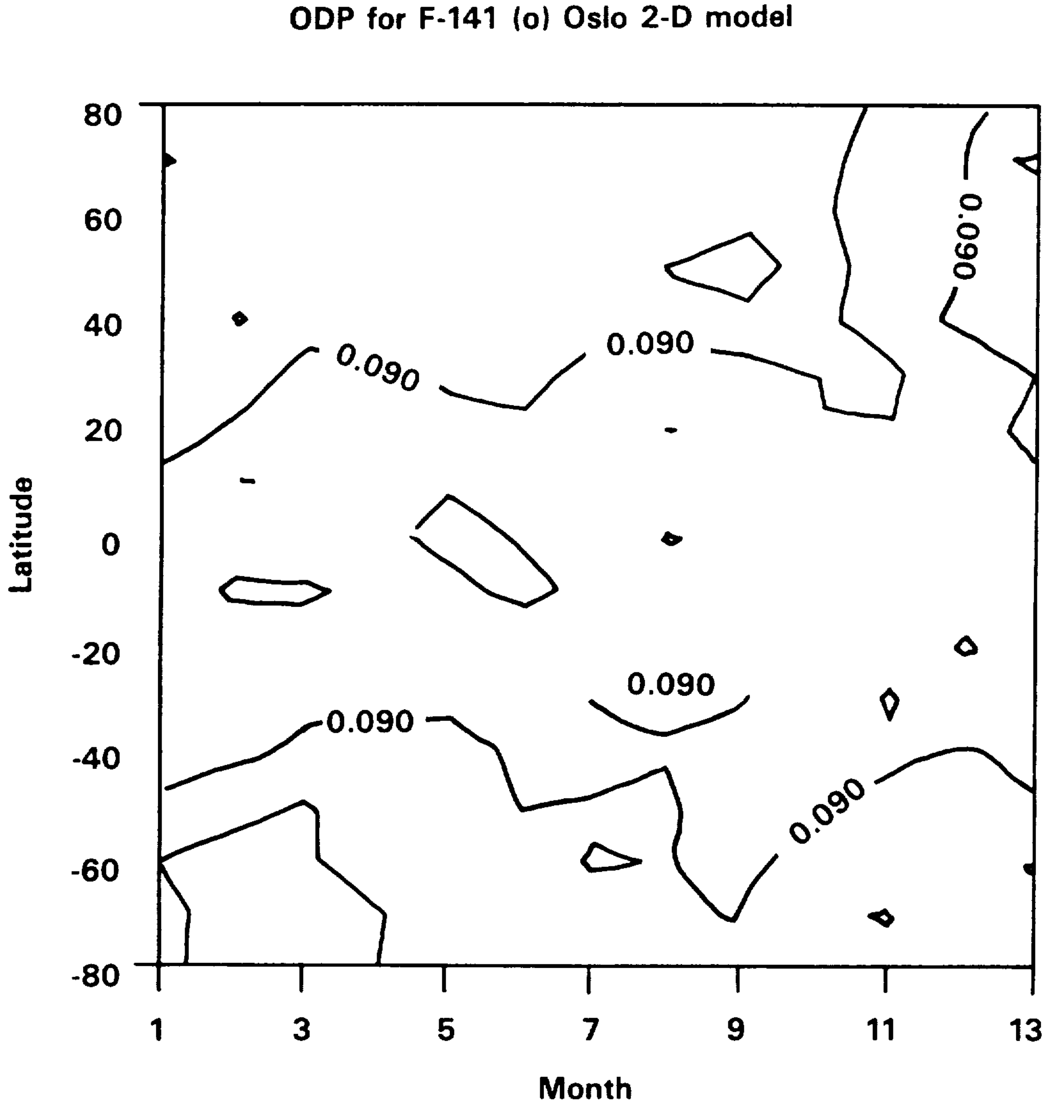


Figure 11B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (Oslo 2-D).

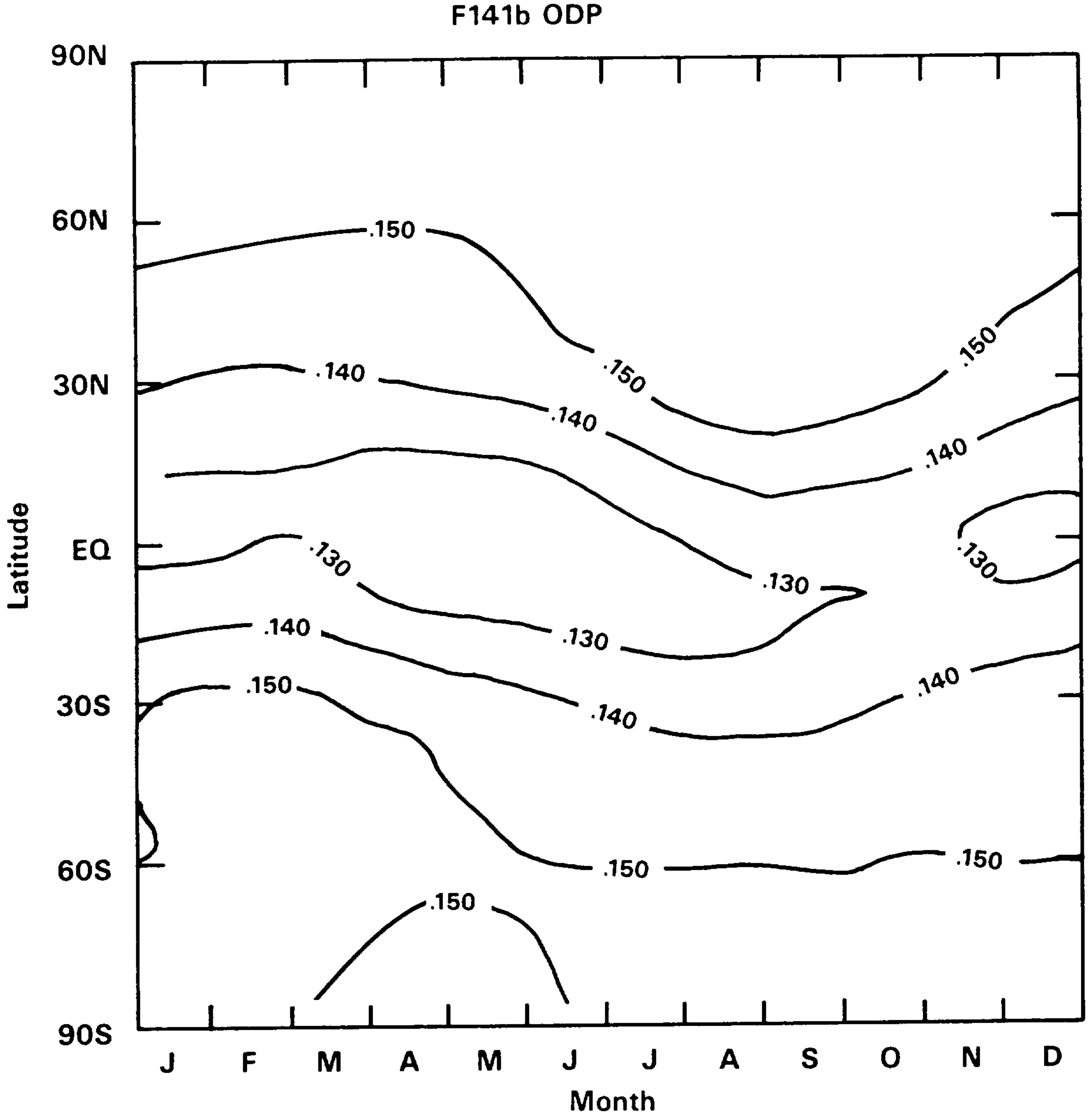


Figure 11C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (AER 2-D).

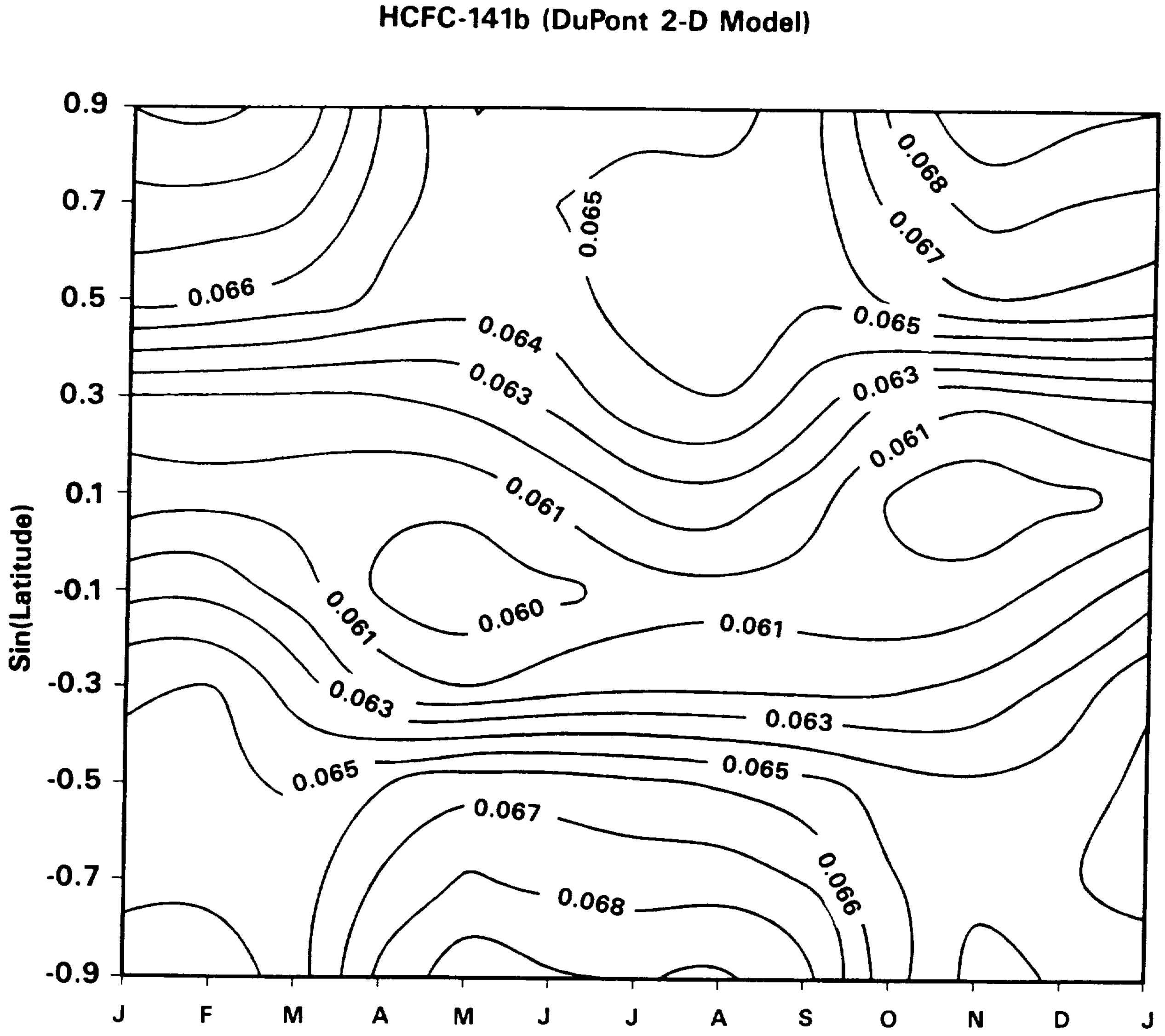


Figure 11D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (DuPont 2-D).

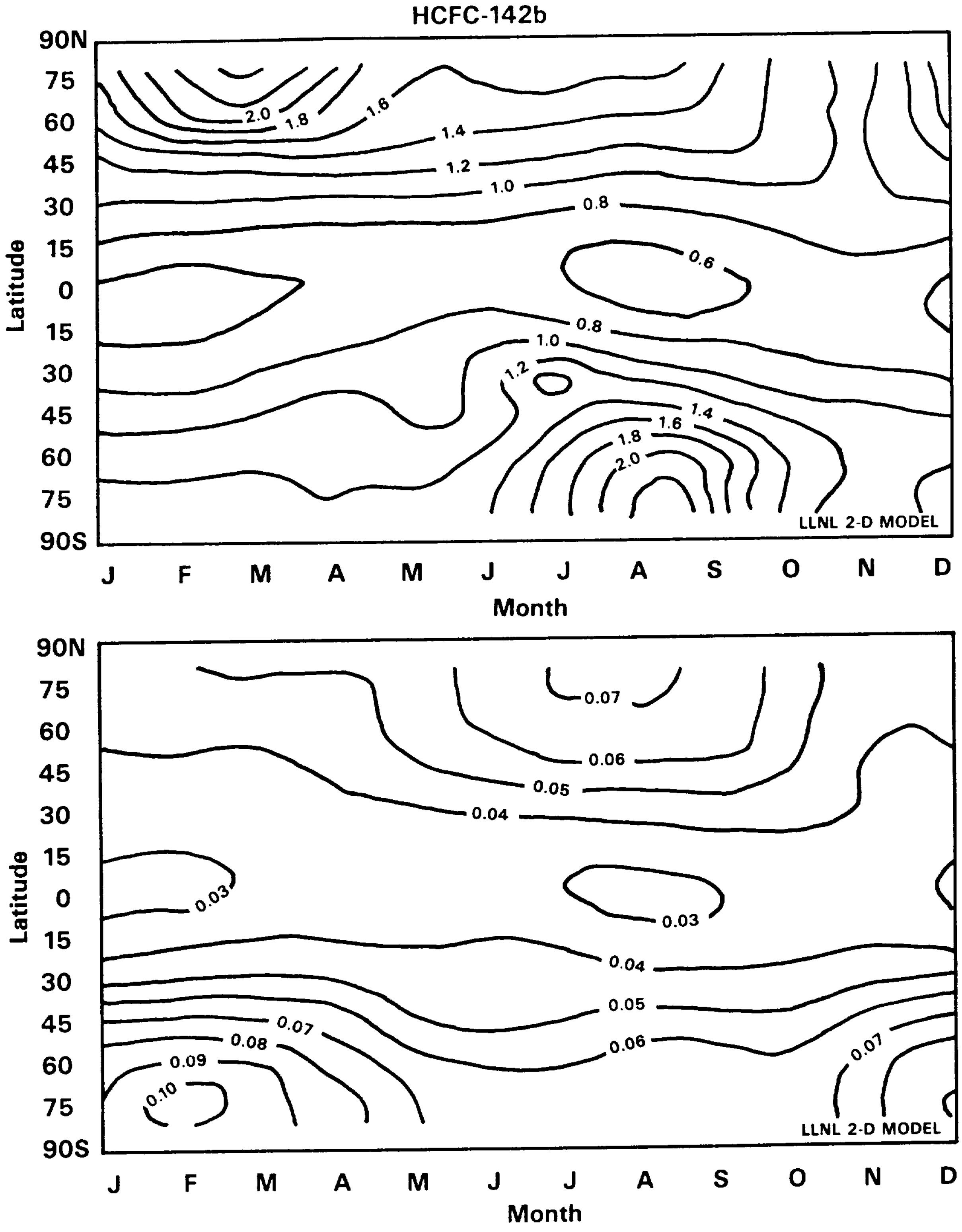


Figure 12A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Depletion from Emission of HCFC-142b (LLNL 2-D).

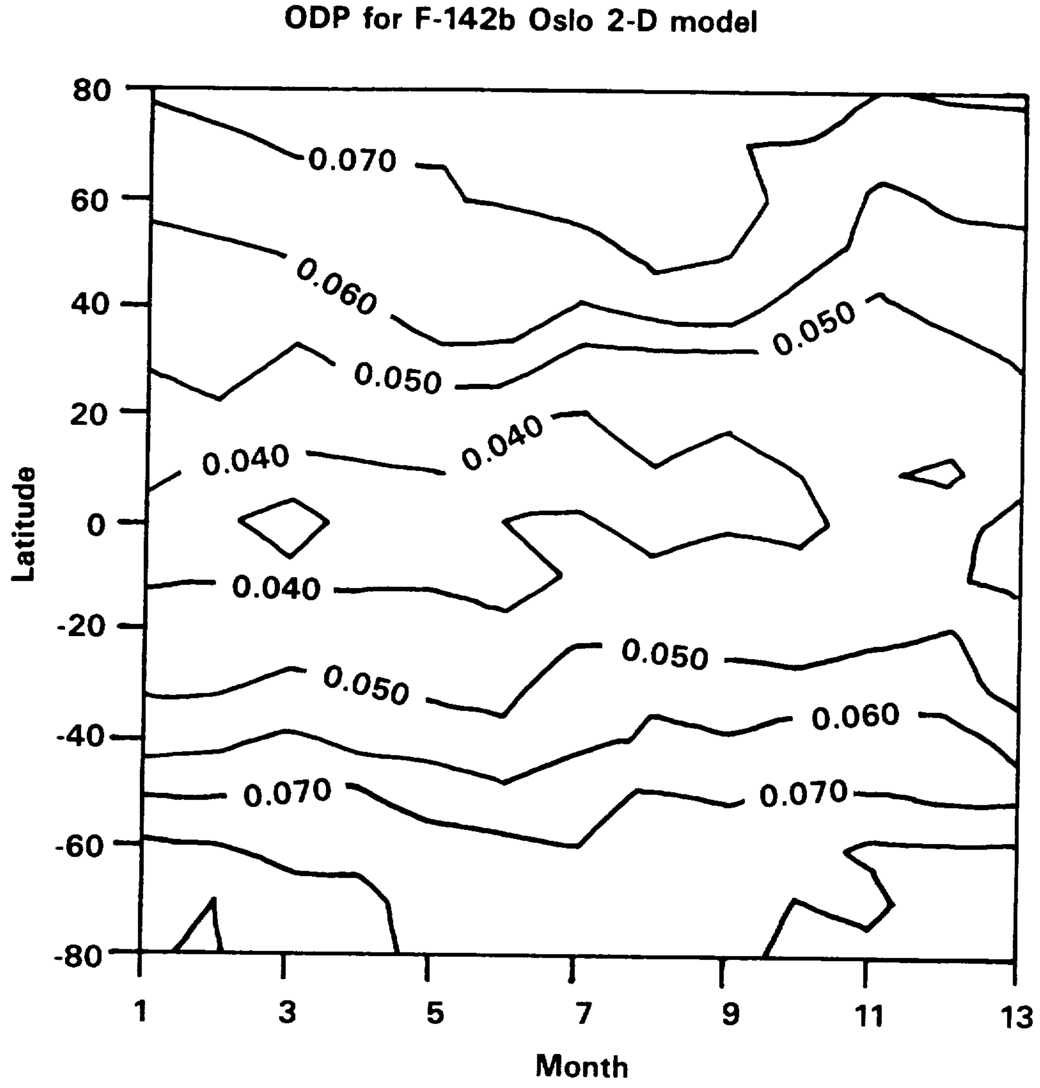


Figure 12B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-142b (Oslo 2-D).

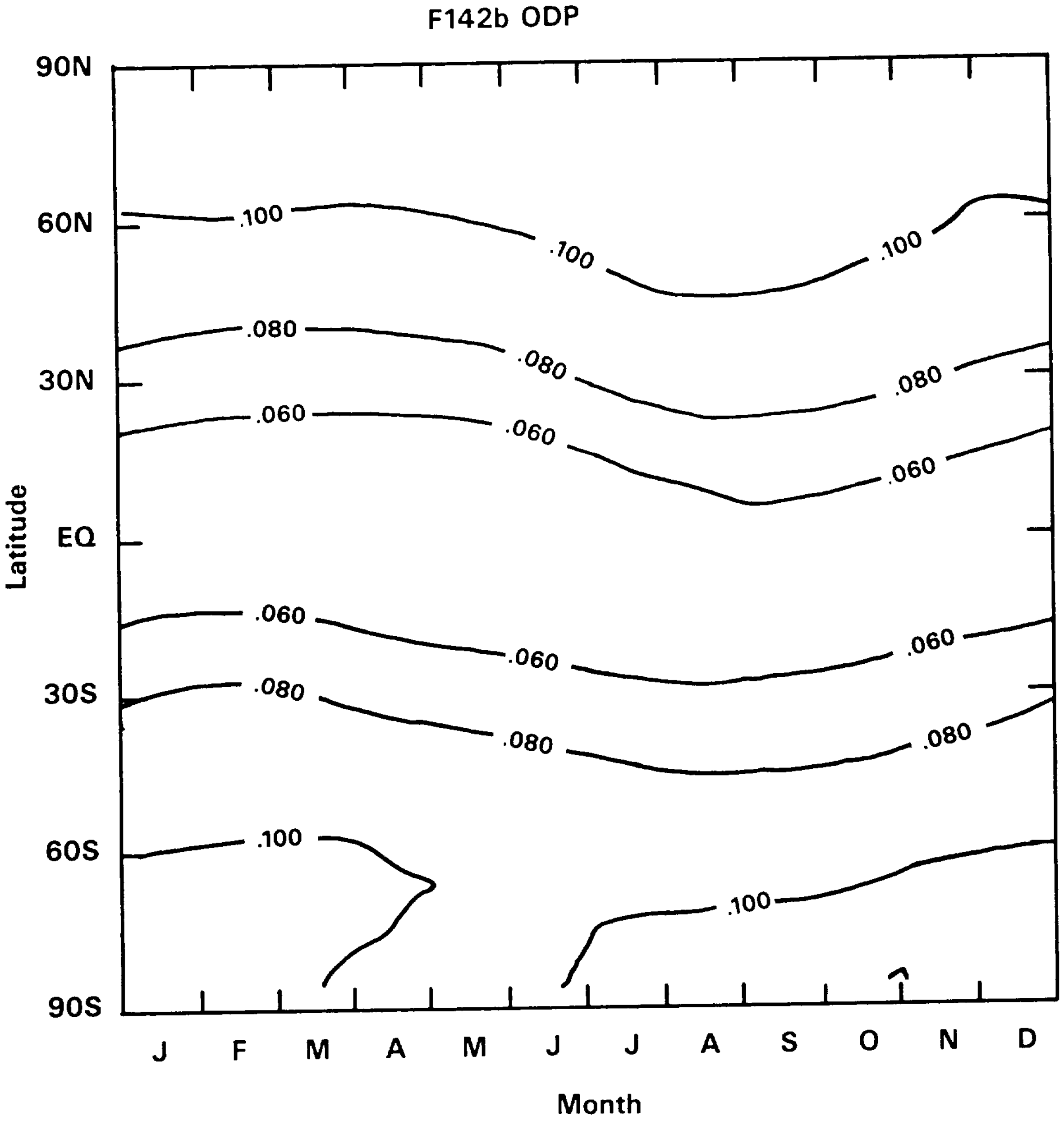


Figure 12C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-142b (AER 2-D).

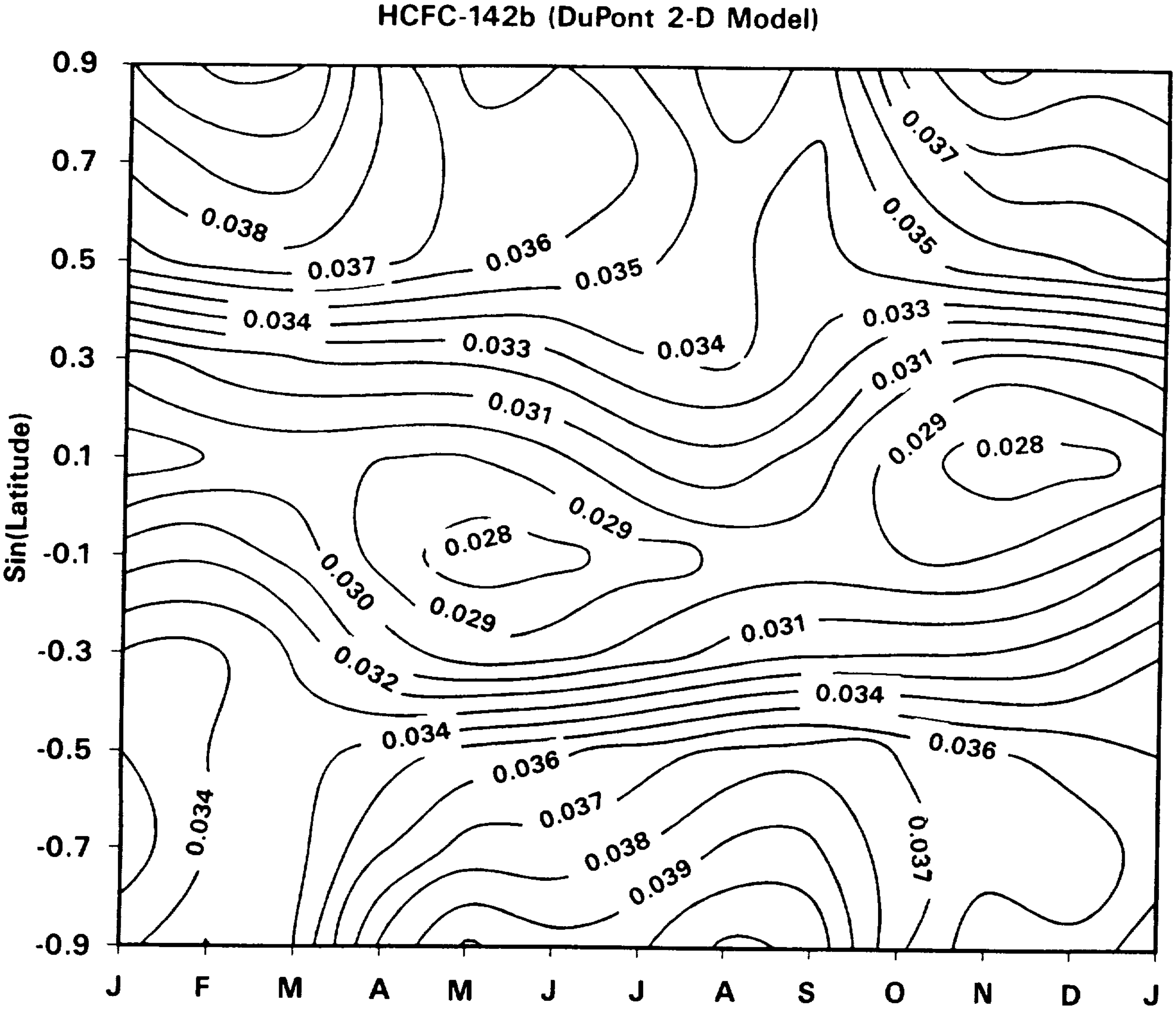


Figure 12D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124b (DuPont 2-D).

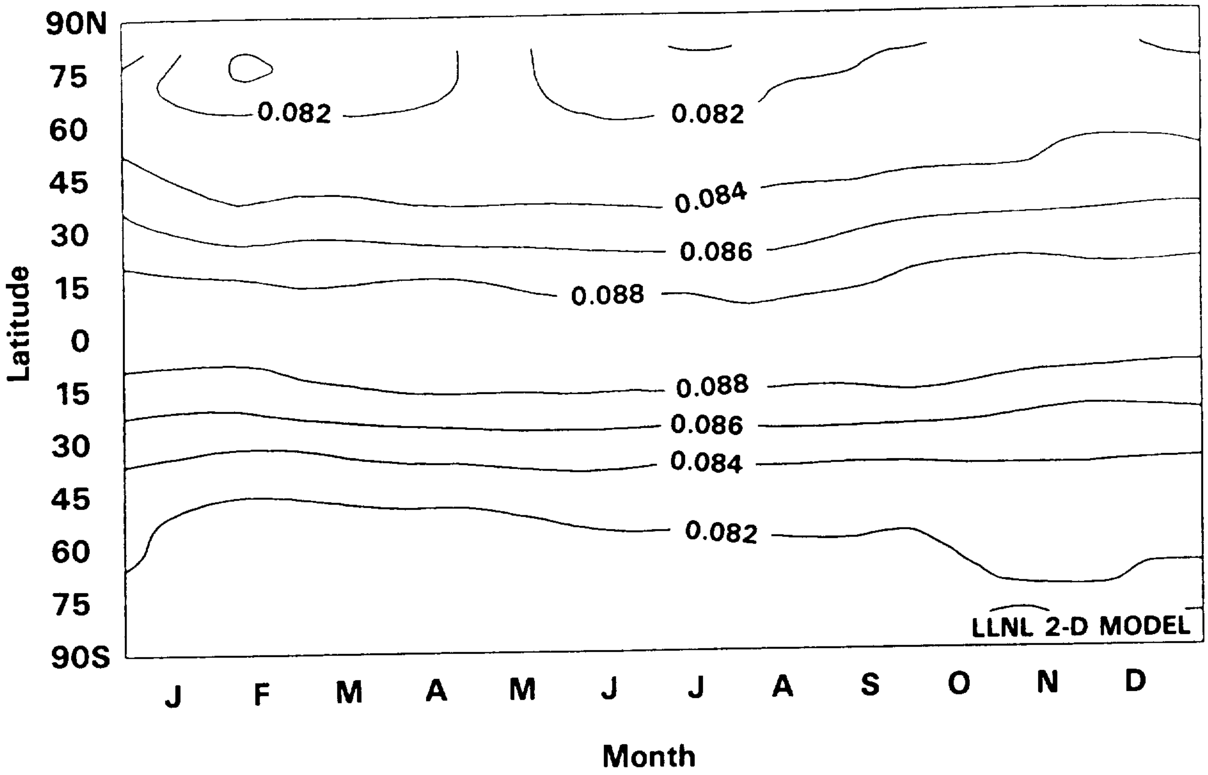


Figure 13A. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (LLNL 2-D).

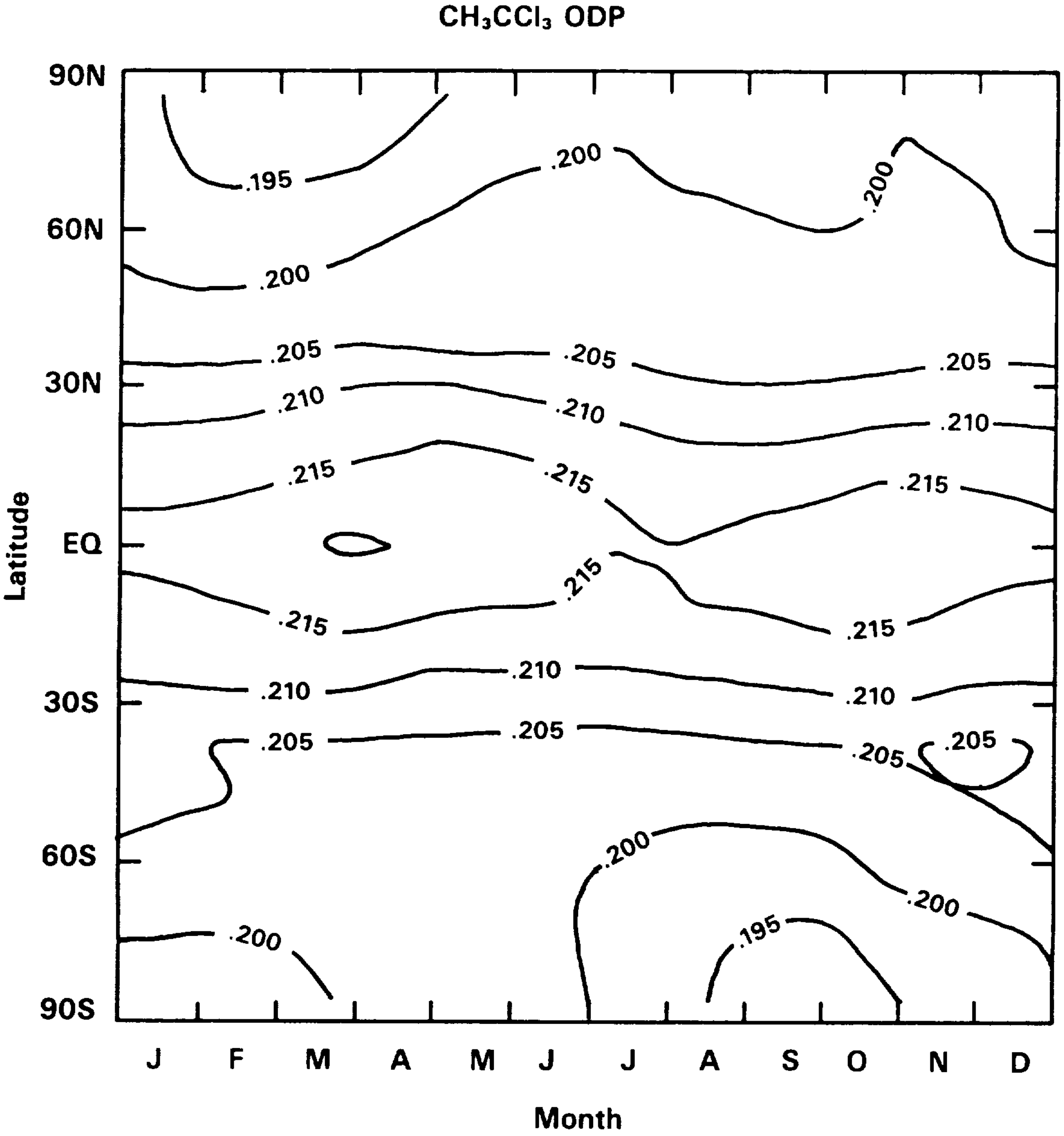


Figure 13B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (AER 2-D).

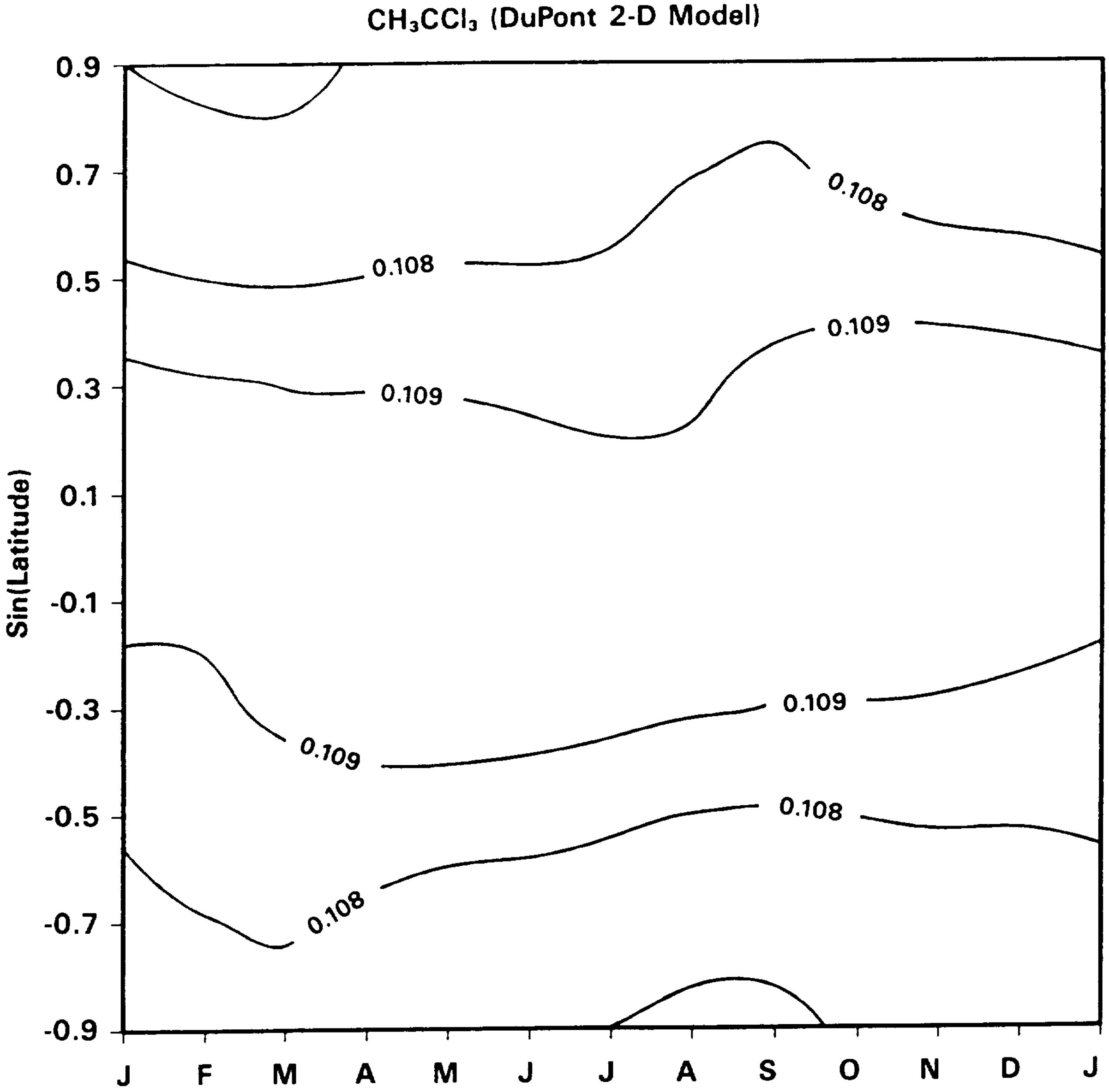


Figure 13C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (DuPont 2-D).

seasonal variations. In particular, the ODPs for CFC-12, HCFC-22, HCFC-124, and HCFC-142b have strong latitudinal variations, with the ODP increasing from lower tropical values to higher polar values by as much as a factor of three. Other species, such as HCFC-123, HCFC-141b, and CH3CC3 show little variation with latitude or season. The results from the four models are in good general agreement regarding this pattern, although the LLNL model shows slightly more seasonal response for some species than the other models, particularly at high latitudes in the Southern Hemisphere.

The strong latitudinal ODP variation of some species, in contrast to the weak variation determined for others, warrants further discussion. The distinguishing difference between the species categories is based on differences in the distributions of chlorine atoms which, in turn, depend on the altitudes for destruction of the respective species. Compounds that do not survive transport to the upper stratosphere for dissociation, and are therefore similar to CFC-11, show very little variation in their ODP with latitude and season. HCFC-123 is an example of such a species. On the other hand, species that persist into the upper stratosphere, (even if the dominant removal is at lower altitudes) show stronger latitudinal dependencies. CFC-12 and HCFC-22 are two examples that show a significant latitudinal dependency. CFC-12 is primarily dissociated at higher altitudes than CFC-11. HCFC-22, on the other hand, is primarily destroyed in the troposphere and lower stratosphere by reaction with OH radical, yet models predict that a fraction survives transport to the upper stratosphere and is dissociated through reaction with OH and $O(^1D)$ resulting in high altitude Cly generation.

The resulting strong variations of ODPs with latitude occur in response to latitudinal differences in upper stratospheric chemistry on ozone destruction and the resultant effects of transport on both the ClO_x produced and on the ozone being destroyed. The extent of these variations depends on the treatment and the strength of the modeled transport. It is not surprising, therefore, to find differences in the ODP variations with latitude and season between models.

Sensitivity of ODP to Modeled Transport

The question can next be raised as to the sensitivity of ODP values to model parameters - primarily, transport processes. Model transport parameterization is a source of significant uncertainty in 2-D models. Modelers have used a combination of theoretical and empirical basics to derive expressions for circulation and dispersive fields for species transport in their models. As such, models yield good agreement of predicted profiles for key trace gases relative to measured values at low- and mid-latitudes. However, agreement at high latitudes is generally not as good. Modeled polar chemical profiles are keenly dependent on the representation of transport utilized in this region. Therefore, transport of chemical species is a source of significant uncertainties in atmospheric modeling.

Changing the model transport parameters would affect the ODP directly in three ways. First, the ODP values can change because of changes in lifetimes. Lifetime for CFC-11 is sensitive to the strength of the circulation in the stratosphere while the lifetime of HCFC-22, which is dominated by removal in the troposphere, is less sensitive. Second, changing transport parameters would affect the distribution of chlorine atoms in the stratosphere. The responses of each species differ according to where the chlorine atoms are released. Finally, change in transport can also affect the response of ozone to chemical perturbations.

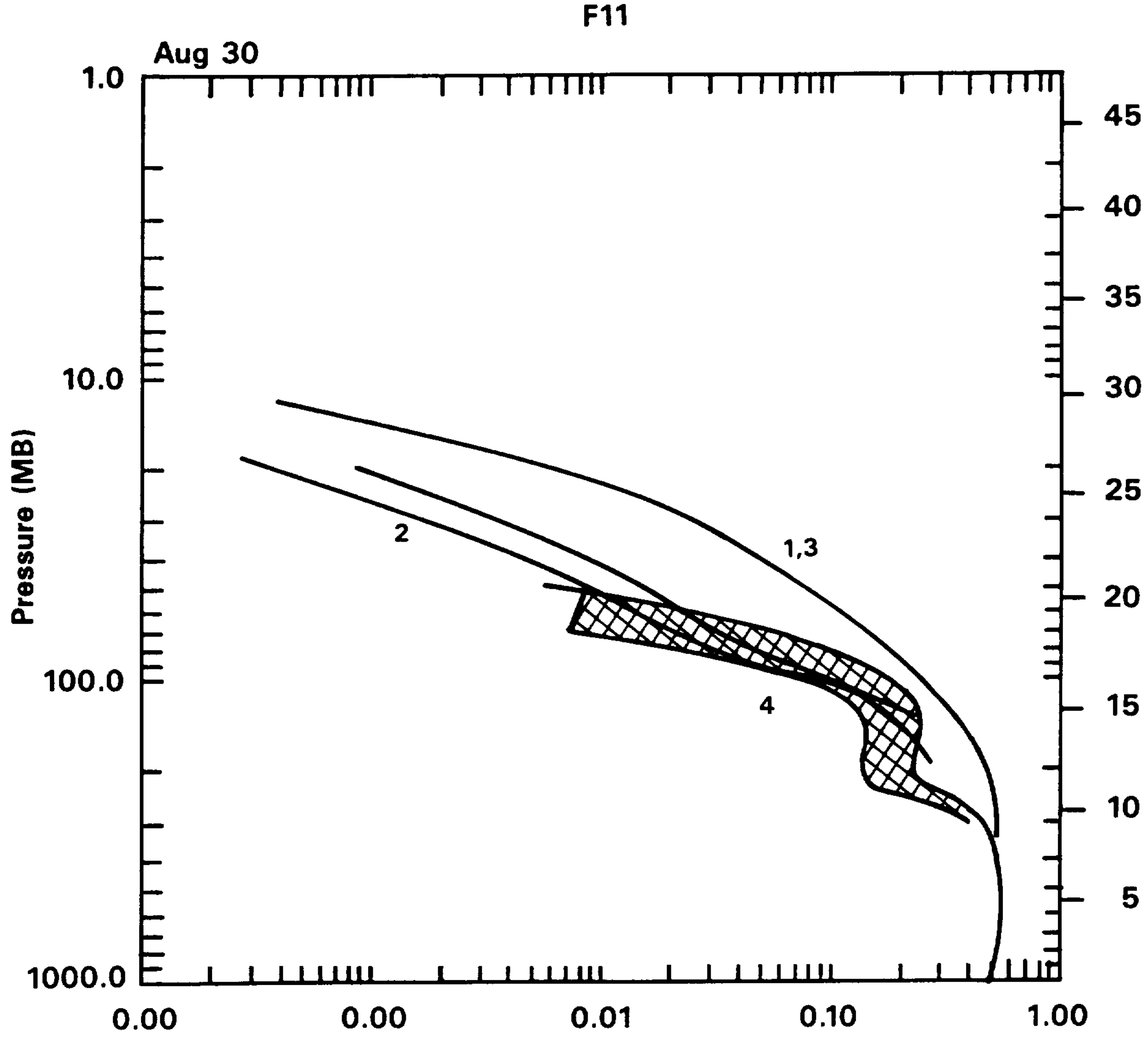


Figure 14. Calculated CFC-11 Profiles from Transport Sensitivity Study at 75 Deg. South at Equinoc (AER-2D). AAOE Measurements Indicated by Cross Hatch Area.

Four sets of calculations were performed using different circulations and Kyy (latitudinal eddy diffusivity) values to define transport within the AER 2-D model. Calculated effects of CFC-1-1 and HCFC-22 were determined in each case. These cases are designated by:

	Circulation	Kyy
case 1	standard	standard (3x10^9 cm^2 s^{-1})
case 2	standard	small (1x10^8 cm^2 s^{-1})
case 3	weak	standard (3x10^9 cm^2 s^{-1})
case 4	weak	small (1x10^8 cm^2 s^{-1})

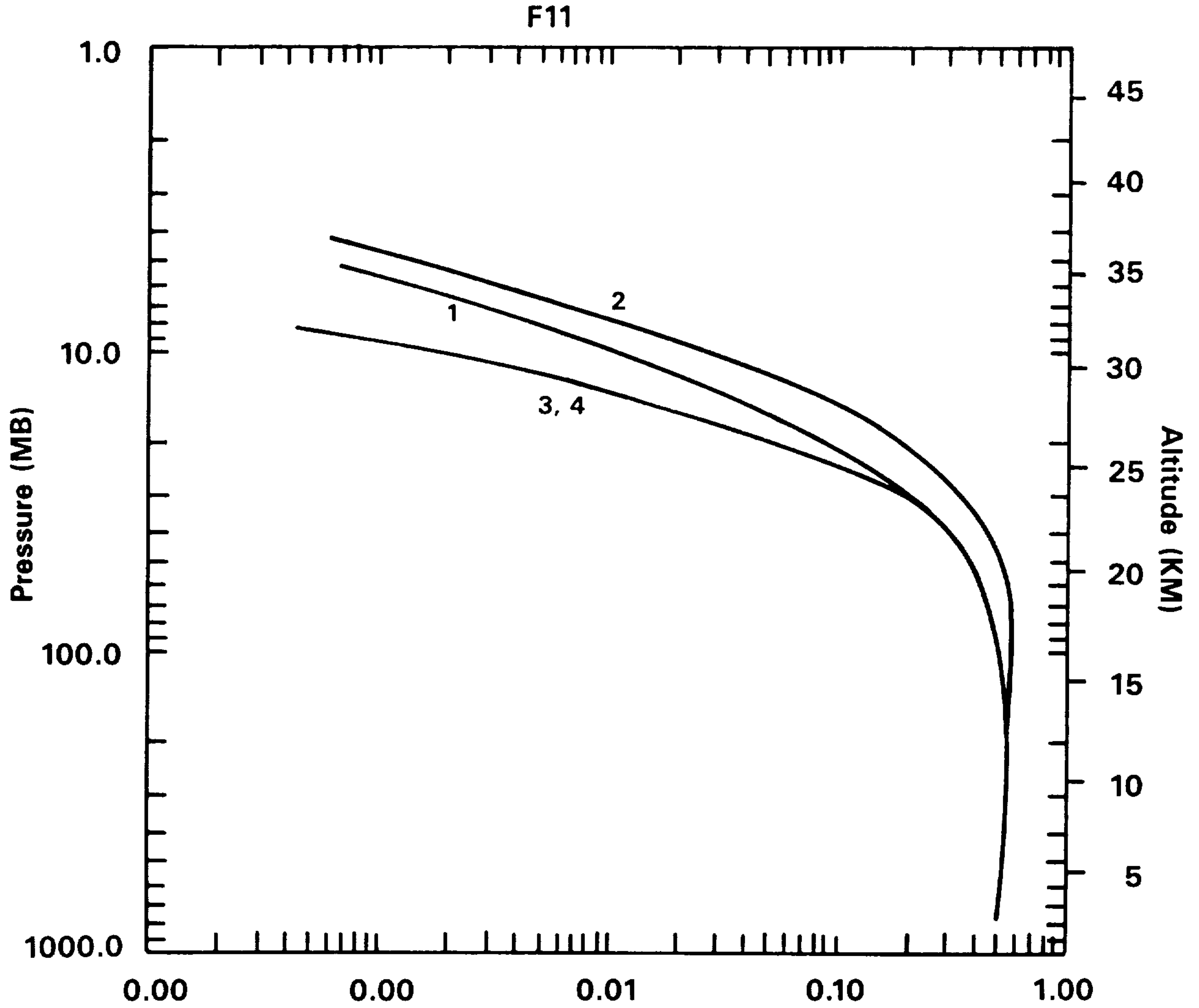


Figure 15. Calculated CFC-11 Profiles from Transport Sensitivity Study at Equator at Equinox (AER-2D).

The weak circulation for cases 3 and 4 is chosen to test the response of ODP for CFC-22 if a large portion of the CFC-22 is dissociated in the upper stratosphere. The circulation is adjusted so that the CFC-22 molecules spend more time in the upper stratosphere resulting in 90% dissociation of the molecules. Adopting smaller Kyy values for cases 2 and 4 represents an attempt to obtain lower concentrations for species such as N_2O, CFC-11 and CFC-12 in the polar lower stratosphere more in line with the observations obtained in the polar vortices during the Antarctic Airborne Ozone Experiment (AAOE) campaign. For simplicity, we have adopted the smaller value globally and year round. Clearly, if the smaller values are restricted to the high latitudes and limited to certain seasons, the response could be somewhat different. Finally, a more definitive test might be to utilize a transport scheme with stronger down-welling in the winter polar vortices.

Figure 14 shows calculated profiles of CFC-11 from the 4 cases for August at 75 deg. S compared to

Table 9 Results of Transport Sensitivity Study (AER 2-D Model)

	Case 1	Case 2	Case 3	Case 4
CFC-11 lifetime	47 years	34 years	51 years	44 years
HCFC-22 lifetime	24 years	22 years	24 years	23 years
ODP	.07	.035	.055	.034
CLP	.27	.35	.25	.28
CEF	.26	.10	.22	.12

the AAOE measurements. The profiles at equinox for the equator are shown in Figure 15. The cases with small Kyy predict CFC-11 profiles that are in better agreement with observations at polar latitudes. At the same time, the concentration at the equator calculated under case 2 is large compared to case 1. Corresponding graphs for HCFC-22 are shown in Figures 16. Figures 17 shows the calculated column abundances of O_3 for the four cases. The results from cases 2 and 4 are distinctly different from observations with high columns predicted at high latitudes. Table 9 summaries the calculated lifetimes and ODP values from the cases. Calculated lifetime of CFC-11 depends heavily on the transport field whereas the lifetime of HCFC-22 is less dependent. The ODP values for HCFC-22 for these cases reflects the impact of transport on the CFC-11 destruction process. Figure 18B shows that while there is an increase in ODP values at high latitudes for case 2 relative to case 1, the decrease at the tropics more than compensates for it in the global ODP value. Corresponding results for cases 3 and 4 are shown in Figures 18C and 18D. More discussion and analysis of these results as they relate to polar observations will follow in the next section.

In summary, the analysis presented here represents an attempt to quantify the sensitivity of the calculated ODP to model parameterization of transport. It is difficult to draw a definitive conclusion based on these limited number of simulations. Our attempts here to increase the ODP at high latitudes by using smaller Kyy lead to much smaller ODP at the tropics because of decreased eddy transport. We cannot be certain that there may not be other combinations of circulation and Kyy that would change the ODP results significantly. Our results did show that the same change in circulation would also have significant effects on the model simulated ozone and other trace gas profiles. Comparison of these simulated results with available observations would provide a way to validate the ODP values.

6. UNCERTAINTIES CONCERNING "OZONE HOLE" EFFECTS

None of the above Ozone Depletion Potential calculations consider the potential effects of heterogeneous chemistry in the lower stratosphere, particularly within the circulation vortex occurring at either pole during late winter and early springtime. Available observations indicate that the observed Antarctic ozone destruction is occurring as a result of heterogeneous reactions occurring on the surfaces of polar stratospheric clouds where free chlorine can be converted to activated forms that result in efficient chlorine-based catalyzed ozone destruction. Under these conditions, chlorine-induced ozone loss in the late winter- early spring- polar stratosphere is related to the total amount of available chlorine at the height of the polar stratospheric clouds, below approximately 25 km. Currently, inclusion of such effects in ODP calculations is prema-

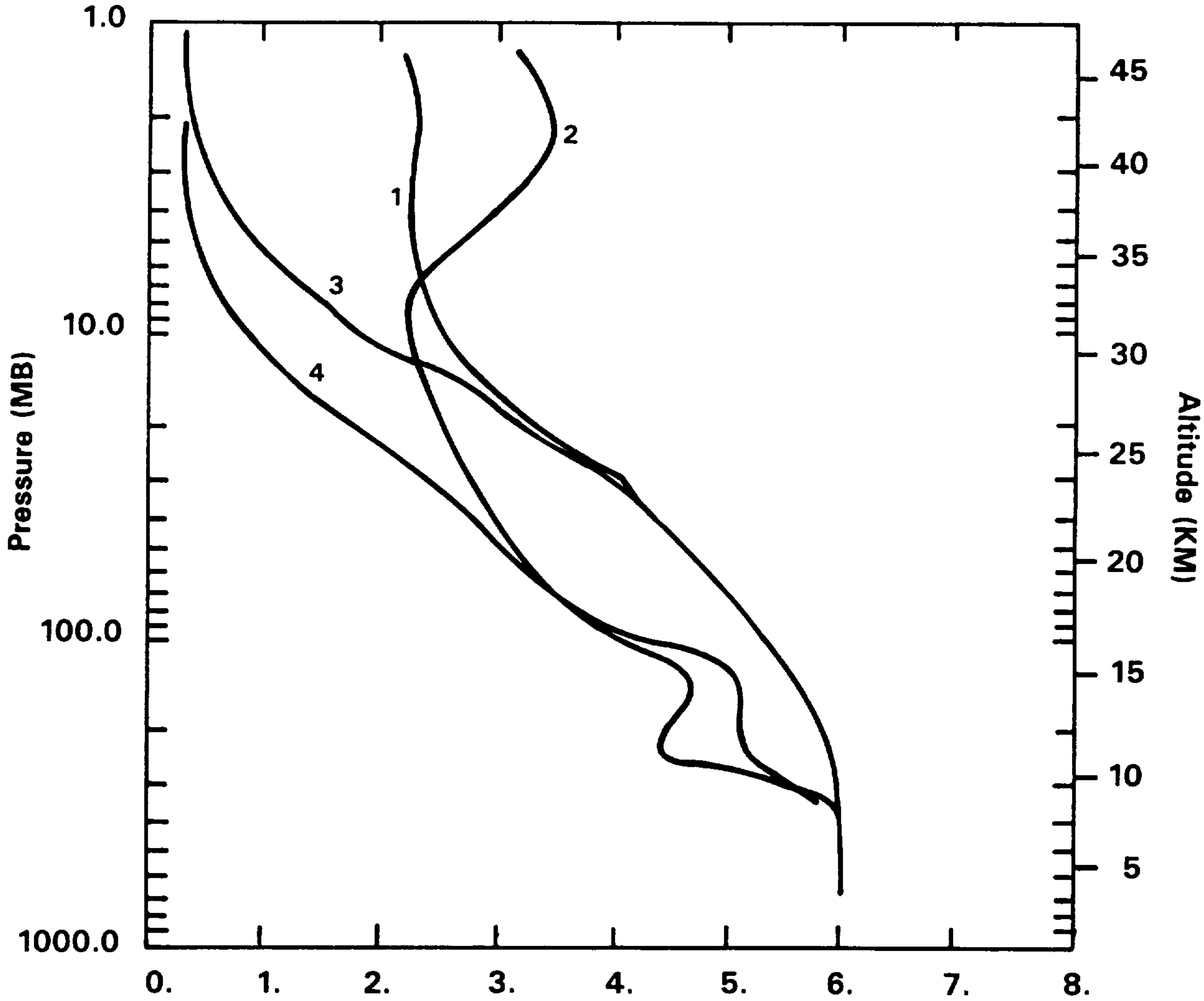


Figure 16A. Calculated HCFC-22 Profiles from Transport Sensitivity Study at 75 Deg. South Equinox (AER-2D).

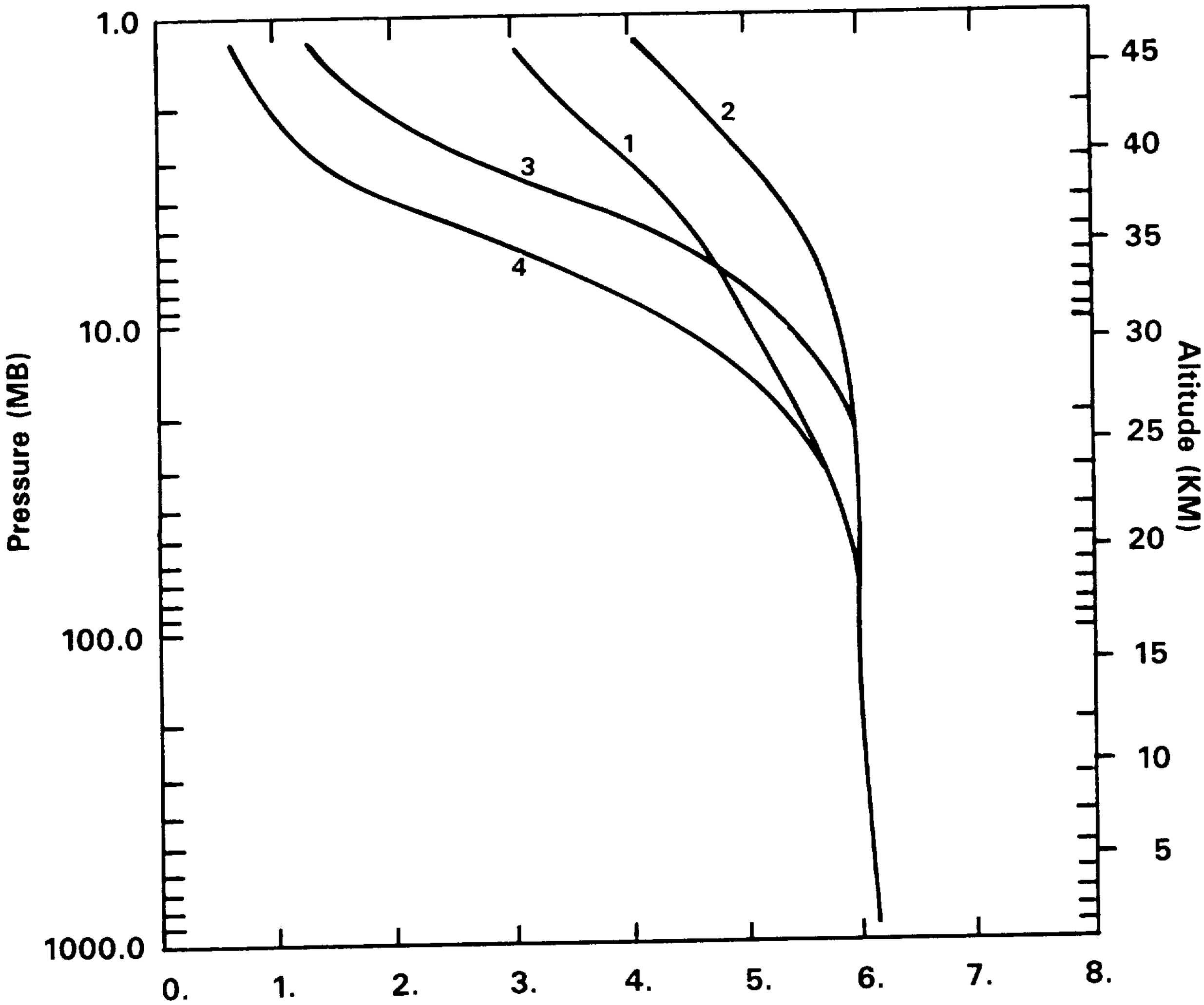


Figure 16B. Calculated HCFC-22 Profiles from Transport Sensitivity Study at the Equator at Equinox (AER-2D).

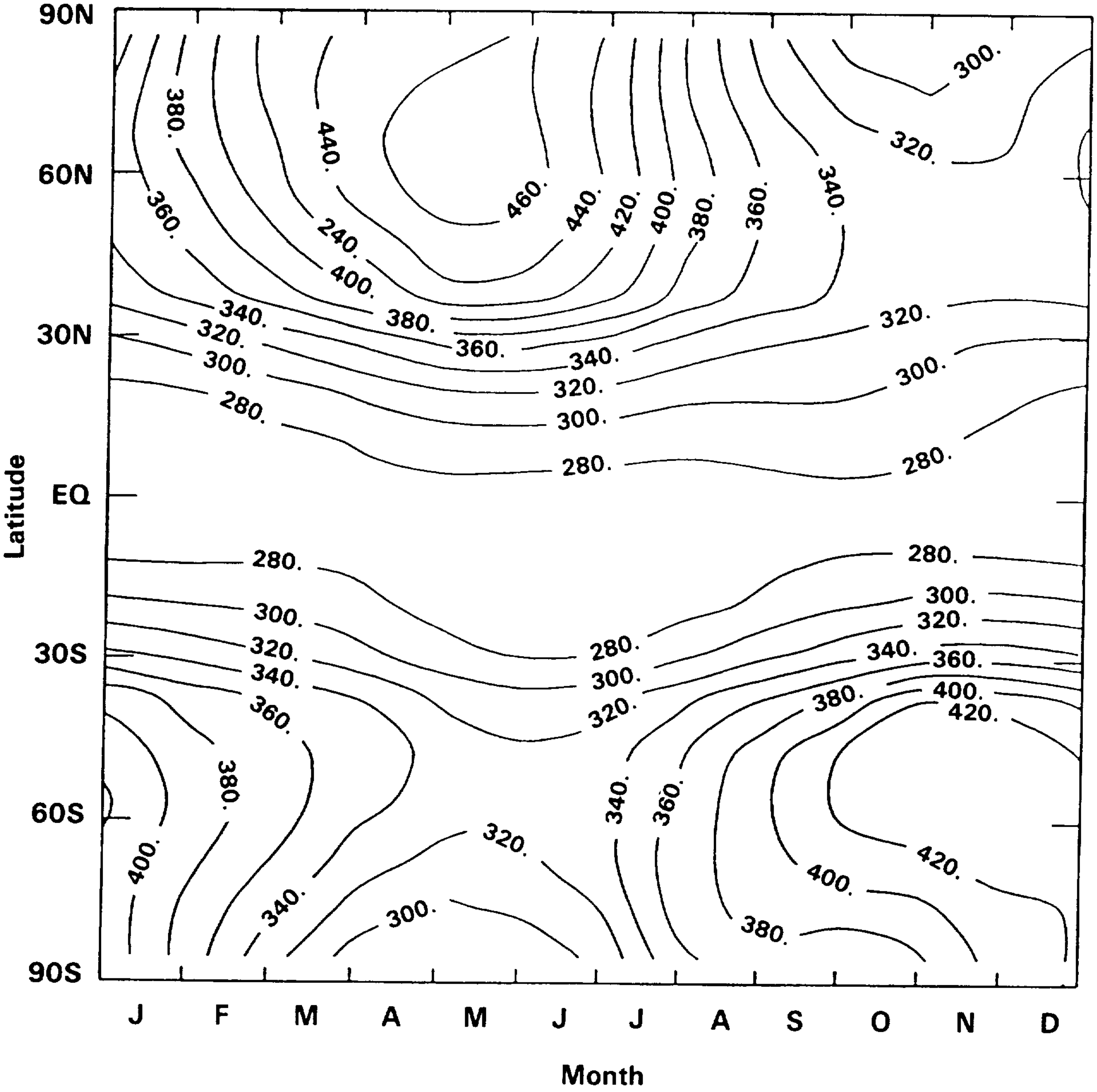


Figure 17A. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 2 of Transport Sensitivity Study] (AER-2D)

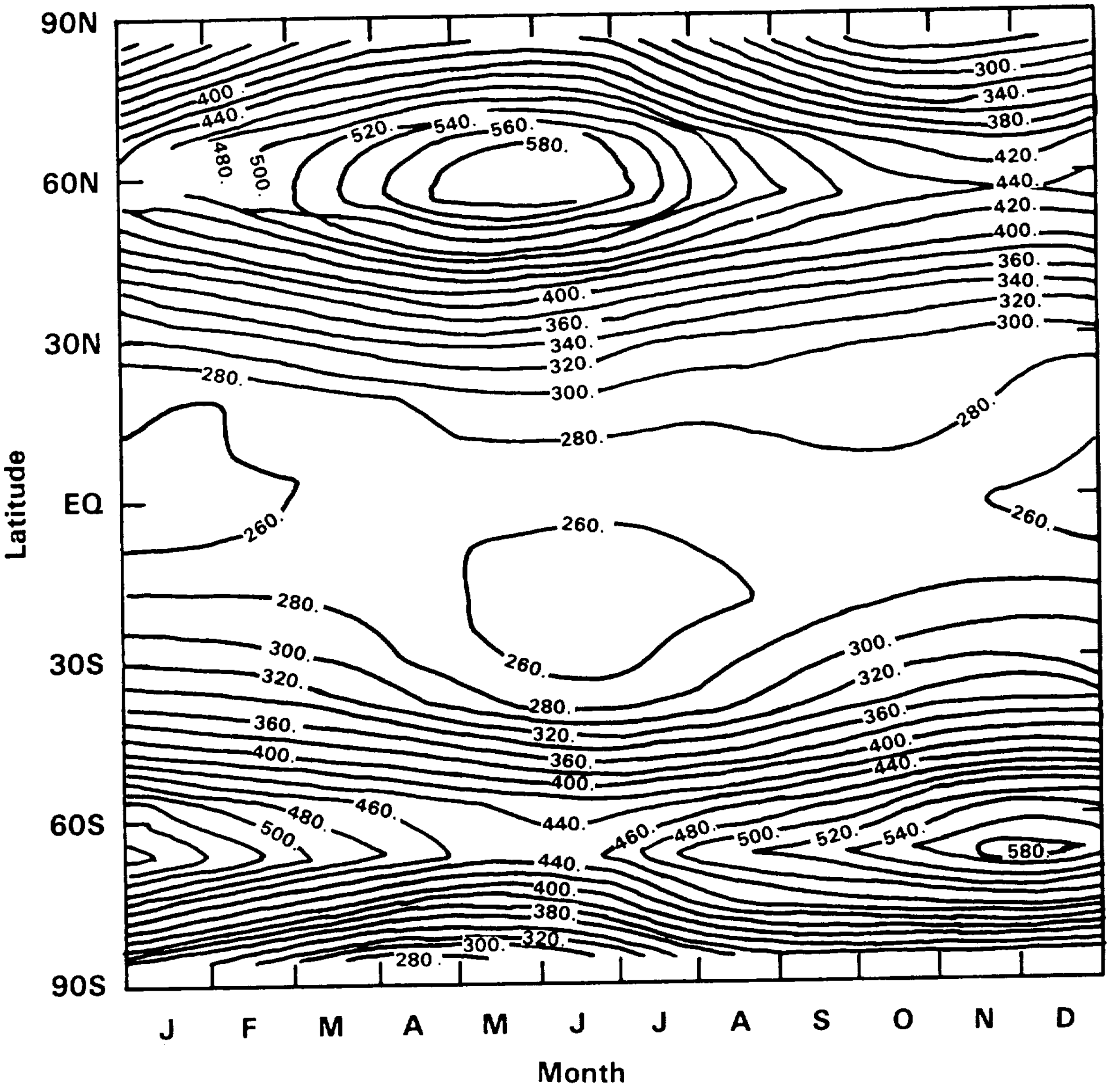


Figure 17B. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 2 of Transport Sensitivity Study) (AER-2D).

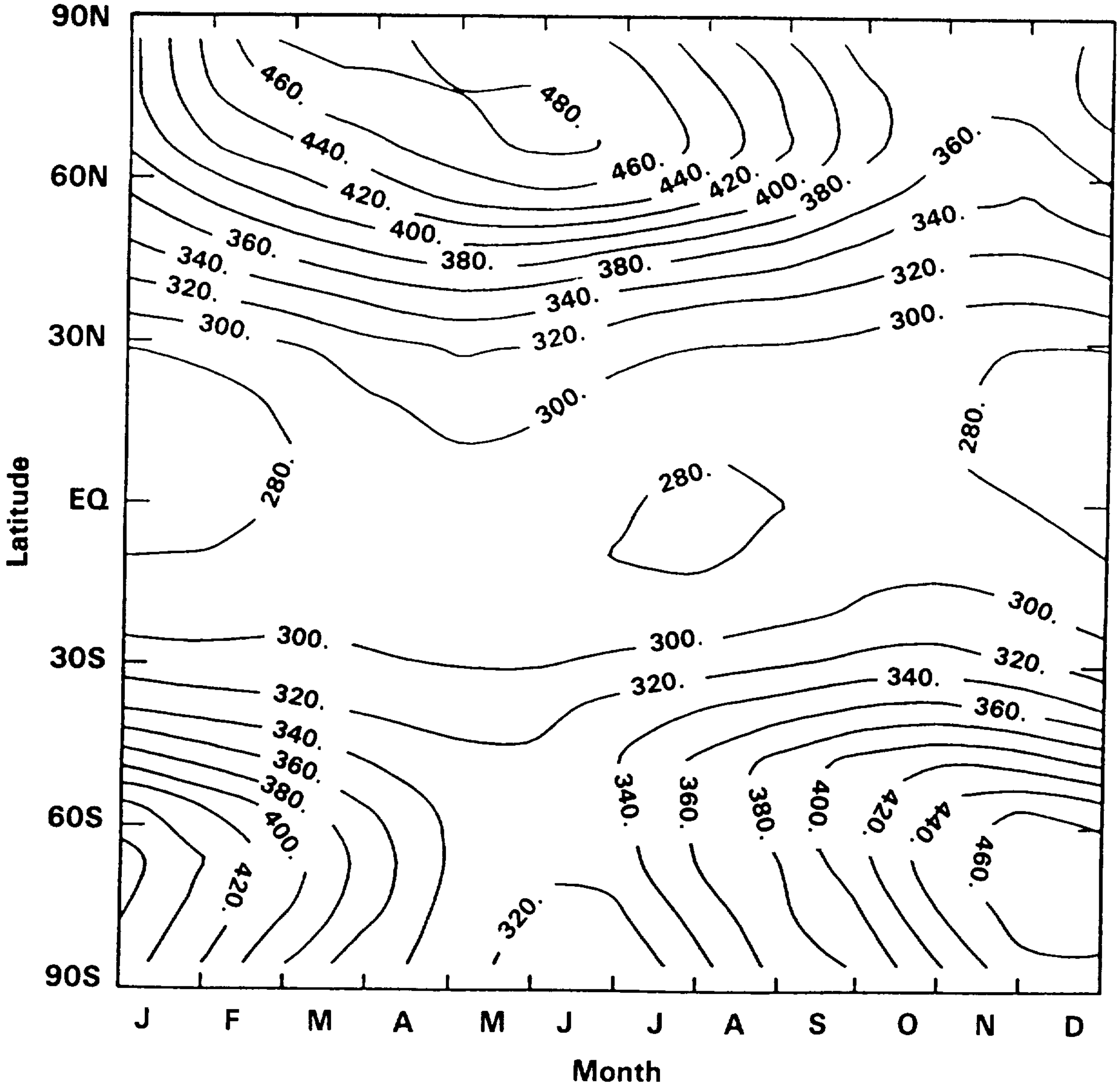


Figure 17C. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 3 of Transport Sensitivity Study] (AER-2D).

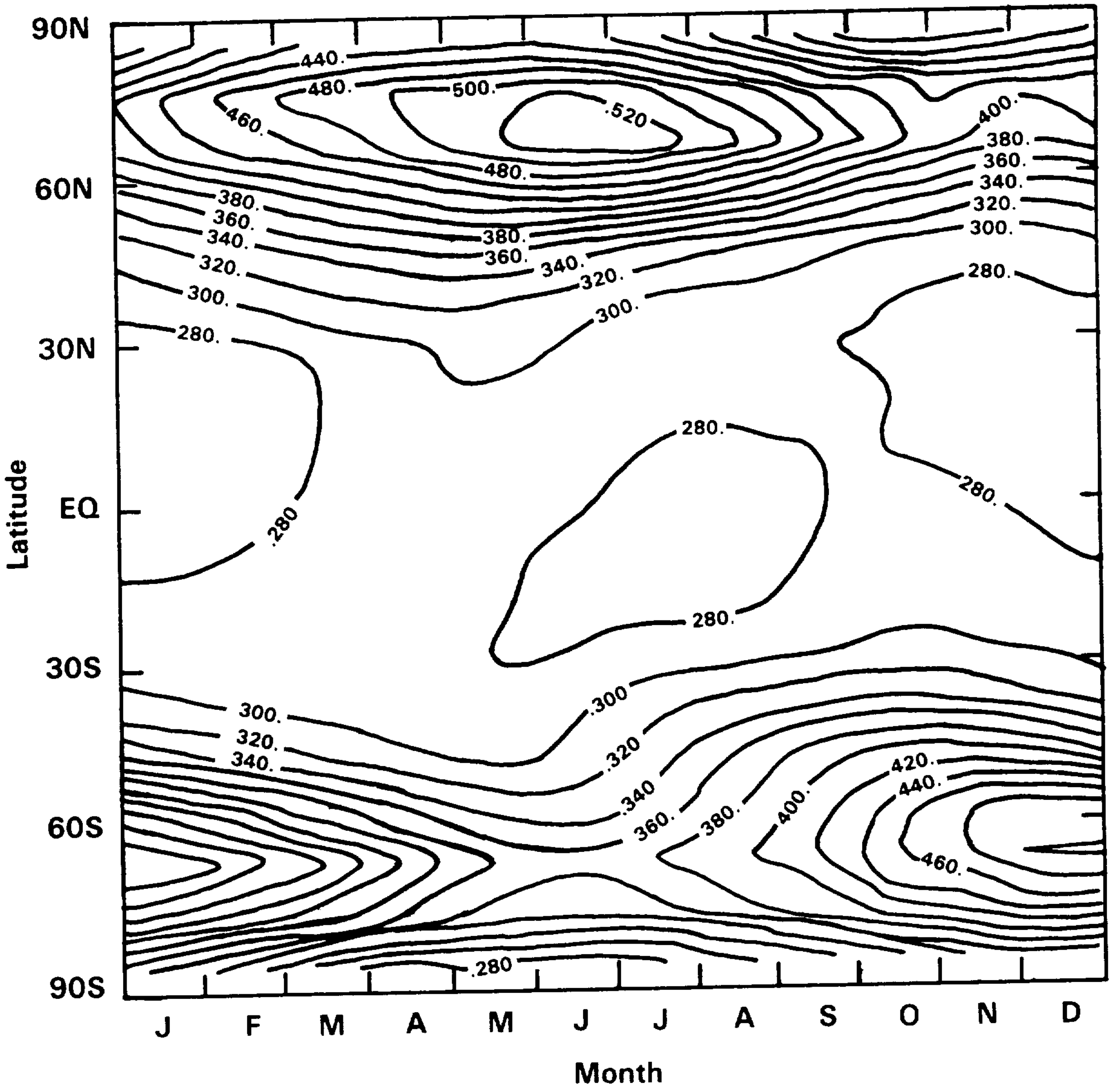


Figure 17D. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 4 of Transport Sensitivity Study] (AER-2D).

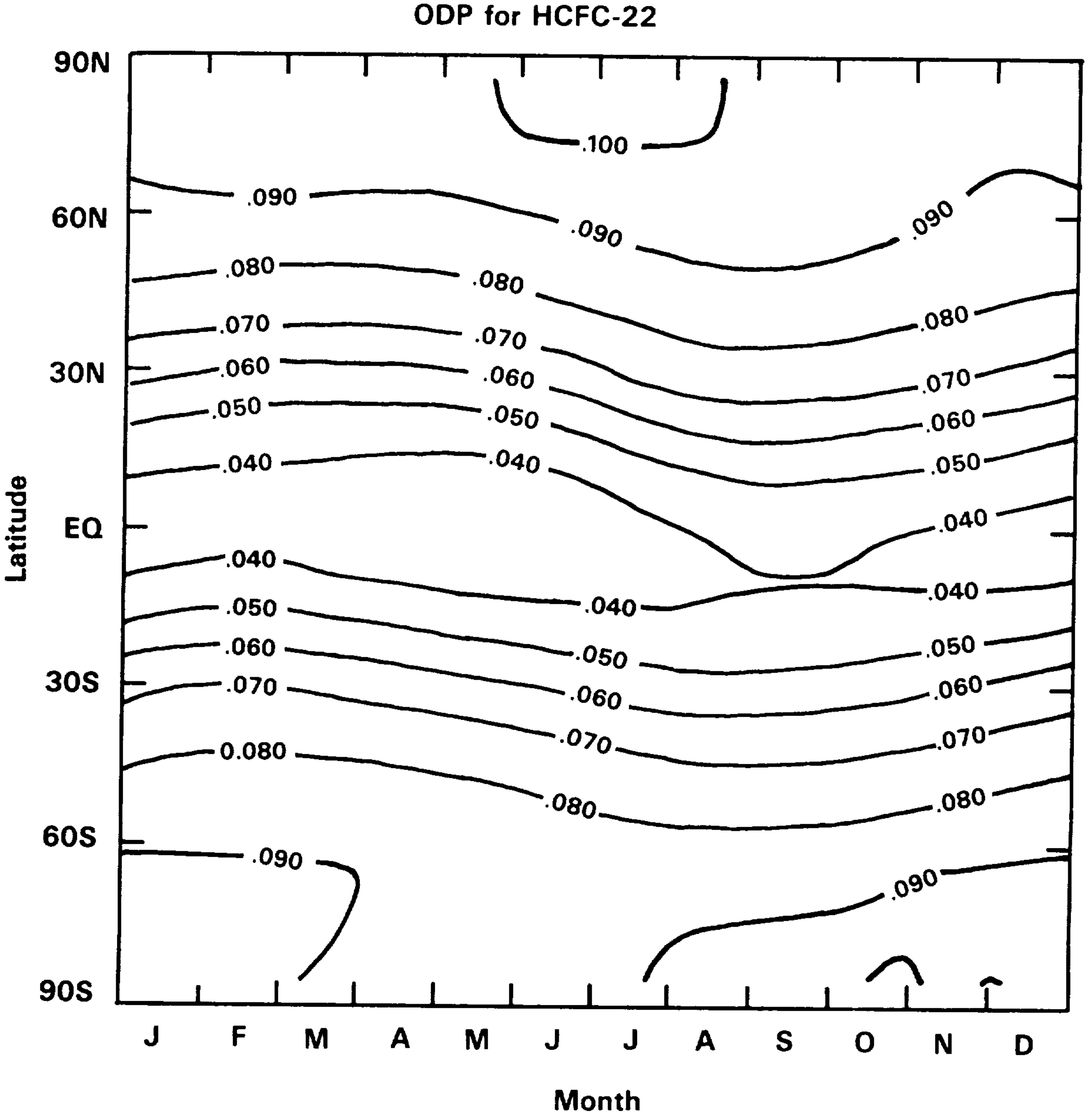


Figure 18A. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 1 of Transport Sensitivity] (AER 2-D).

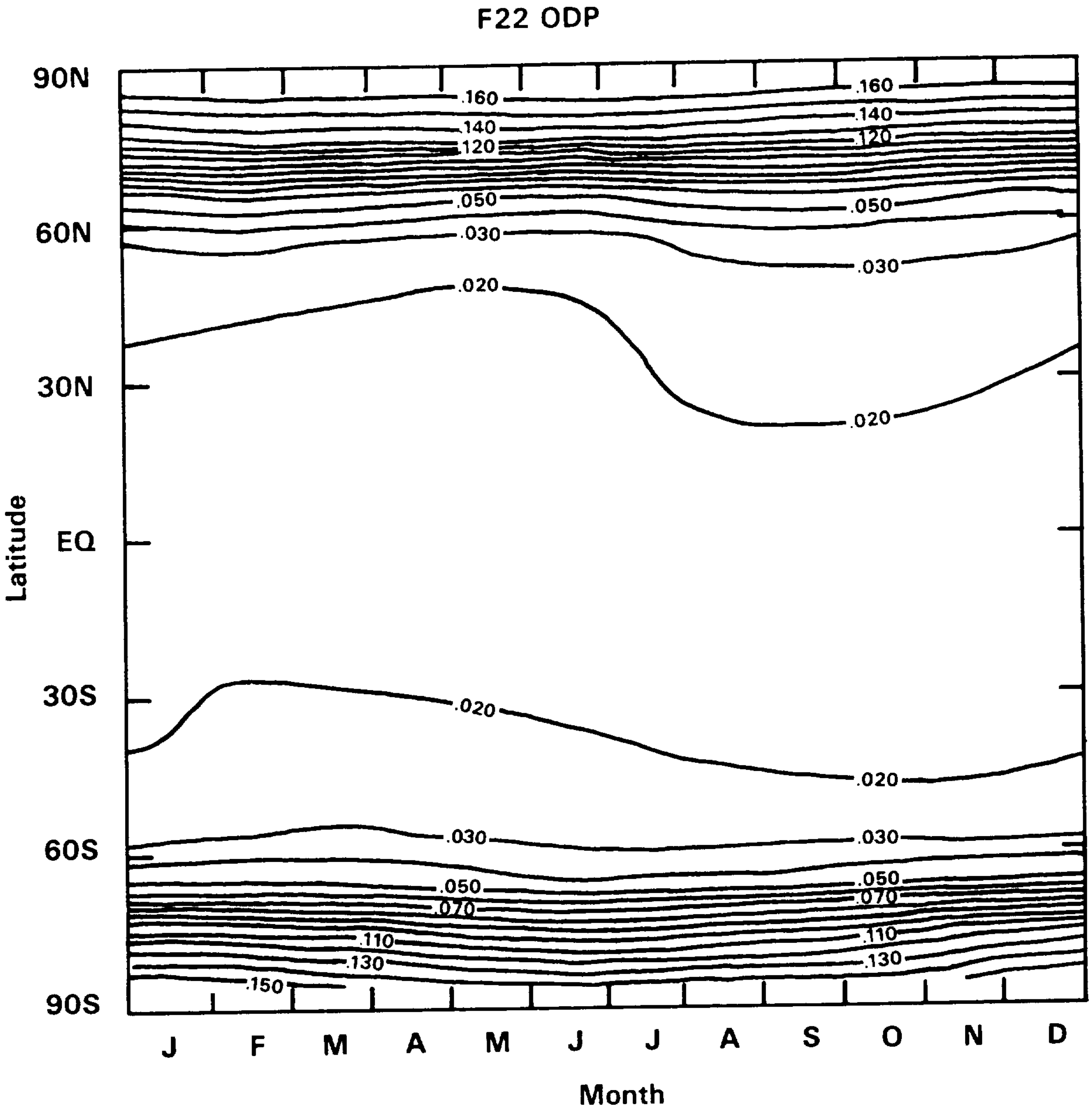
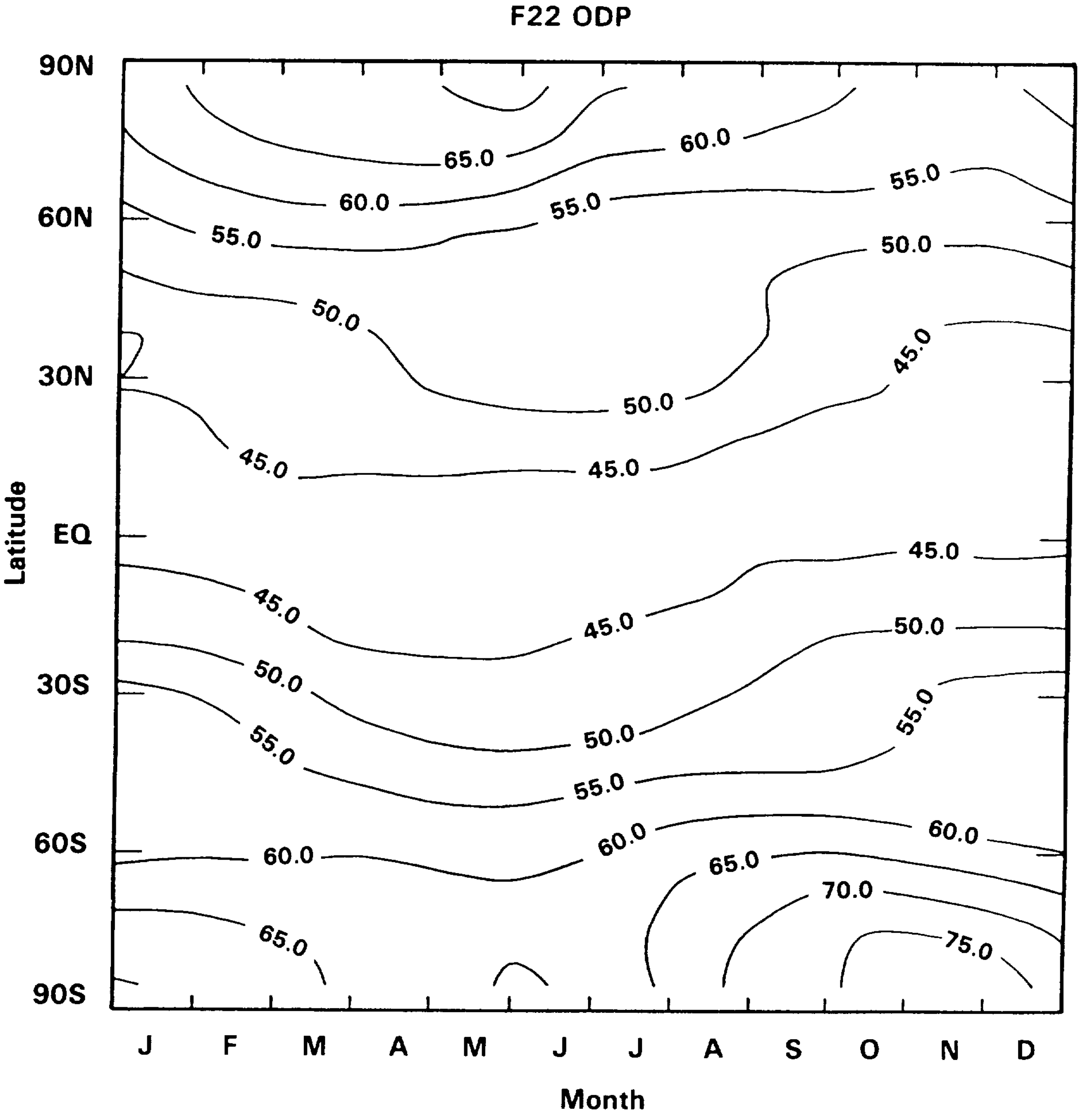
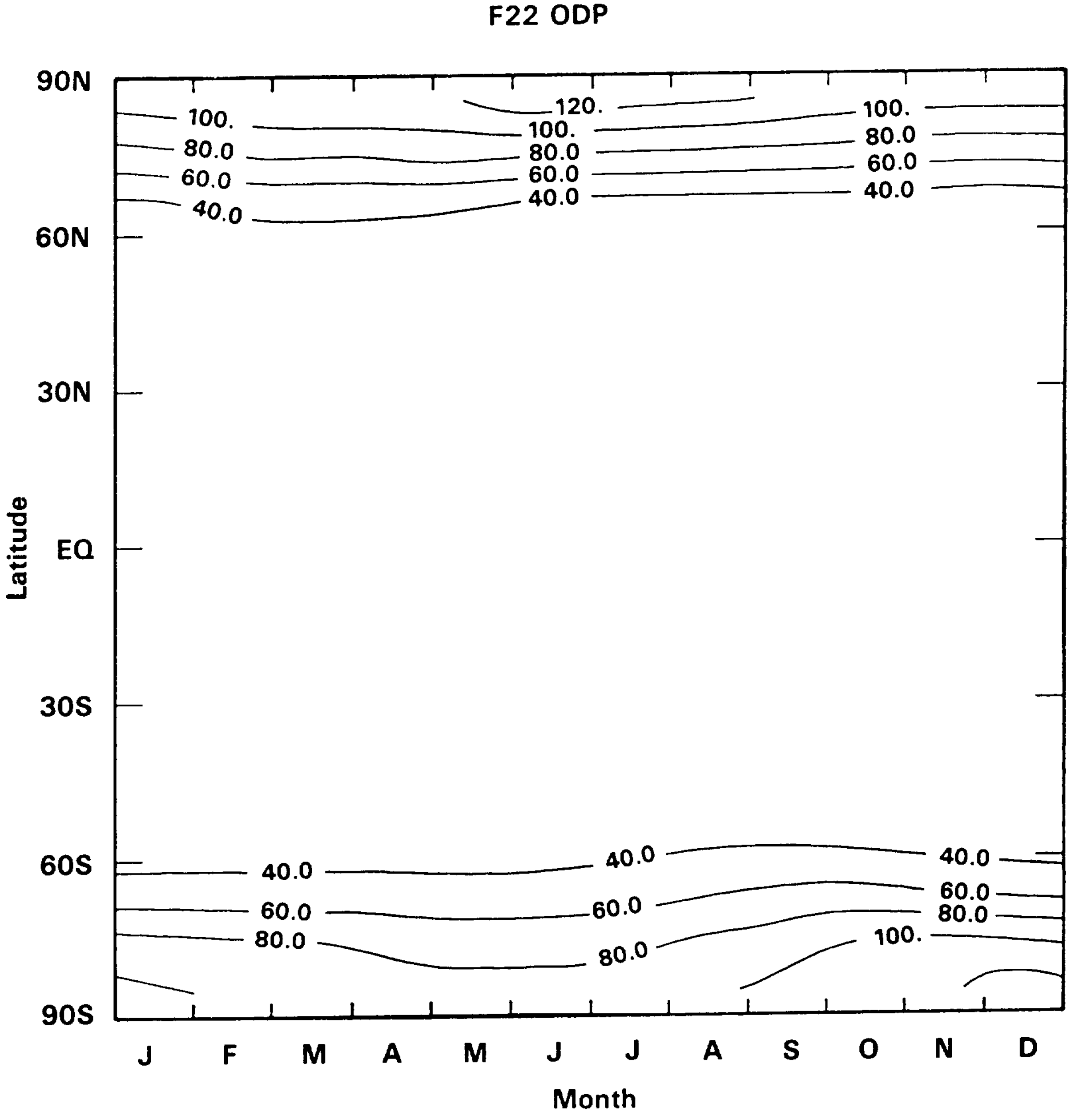


Figure 18B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 2 of Transport Sensitivity] (AER 2-D).



NOTE: Contours are ODP x 1000

Figure 18C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 3 of Transport Sensitivity Study] (AER 2-D).



NOTE: Contours are ODP x 1000

Figure 18D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 4 of Transport Sensitivity Study] (AER 2-D).

ture since modeling of heterogeneous chemistry in general, and the polar phenomena in particular are still in the early stages. Furthermore, increases in carbon dioxide and other greenhouse cases may impact on stratosopheric cooling resulting in wider spread occurrence of polar stratospheric clouds.

The Ozone Depletion Potential concept is based on the annual-averaged changes in global ozone. Since the polar region constitutes a small percentage of the global area and since ODP is a relative measure of the effect on ozone, the overall impact of these phenomenon on global ODP depends on, 1) the impact of polar processes on ozone at lower latitude either by dilution effects or by a ''chemical processor'' mechanism, and 2) the inter-species differences in the heterogeneous processes. The indirect impact on ozone at lower latitude is a subject of intense investigation yet to be resolved. Below, we focus on the species-to-species differences in the chlorine distribution that lead to differences in enhanced ozone depletion due heterogeneous processing important in the polar regions.

Chlorine Loading and ODP

In order to bracket the impact of this phenomena, we have estimated two limits for relative impact. First, a conservative estimate was determined based on chlorine transport to the stratosphere. and secondly, a less conservative estimate was made based on inorganic chlorine profiles from model output.

A conservative estimate for ODP can be derived based on the chlorine transported into the stratosphere. The relative effects on ozone and, therefore, on ODPs can be bracketed by the values indicated by the relative weighting of the total possible chlorine loading in the stratosphere.

Atmospheric models indicate that the steady state impact of an emitted CFC on ozone depends on both the distribution as well as the number of the chlorine atoms released by the CFC upon photodecomposition. At steady state, the expected chlorine loading (CL) from emission of a species is given by

$$\mathrm{CL} \propto \mathrm{E}^*\mathrm{T}^*\mathrm{N}/\mathrm{MW}$$

where E is the mass emitted per year, T is the lifetime, N is the number of chlorine atoms in the molecule, and MW is the molecular weight. The constant of proportionality depends on the properties of the atmosphere and is independent of species. The quantity CL represents the asymptotic concentration of inorganic chlorine in or above the upper stratosphere where all the chlorine atoms have been released. The expression for CL is valid for species with atmospheric lifetime longer than one year so that the species is vertically well-mixed in the troposphere. Similar to the definition of the ODP, a chlorine loading potential (CLP) can be defimed as the ratio of CL for the species to that of CFC-11 for the same emission, i.e.

$$\mathrm{CLP(x)} = \mathrm{CL(x)/CL(CFC\text{-}11)}$$

The ratio of ODP to CLP is representative of the effect of the chlorine distribution on ozone and can be represented by a Chlorine Effectiveness Factor (CEF) ratio defined by

$$\mathrm{CEF} = \mathrm{ODP/CLP}$$

Table 10 Chlorine Loading Potentials (CLP) and Chlorine Efficiency Factors (CEF) from 2-D Models (HCFCs and HFCs scaled by lifetime of CH_3CCl_3 = 63.)

	Oslo		LLNL		AER		DuPont	
Species	CLP	CEF	CLP	CEF	CLP	CEF	CLP	CEF
CFC11	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
CFC12	1.325	0.694	1.465	0.594	1.531	0.575	1.939	0.459
CFC113	1.234	0.697	1.110	0.685				
CFC114	2.108	0.389	2.022	0.277				
CFC115	2.579	0.155	2.232	0.121	2.517	0.147		
HCFC22	0.152	0.303	0.171	0.273	0.215	0.268	0.197	0.220
HCFC123	0.017	0.766	0.018	0.919	0.025	0.883	0.022	0.815
HCFC124	0.041	0.432	0.045	0.408	0.058	0.420	0.052	0.338
HFC125	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HFC134a	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HCFC141b	0.104	0.852	0.114	0.781	0.148	0.764	0.132	0.661
HCFC142b	0.159	0.353	0.180	0.277	0.219	0.284	0.202	0.235
HFC143a	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HFC 152A	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CCl_4	1.036	1.159	1.077	1.022	1.013	0.938	1.031	1.135
CH_3CCl_3	0.108	1.295	0.124	1.058	0.138	1.170	0.140	1.061

The values for CEF can be calculated once the model simulated ODP and lifetimes are given. Table 10 shows the ODP, CLP and CEF as calculated by three 2-D models.

Chlorine Distribution and ODP

The reader may wonder why the values of the chlorine loading potential CLP are often larger than the ODPs for the same species or alternatively why most CEF values are less than 1.0. If all sources of stratospheric chlorine were equivalent in the photochemical reactivity sense once they reached the stratosphere, ODP values would be identical to the CLP values. Two reasons account for the chlorine loading potential values being larger than the ODPs for many of the species. First, several of the CFCs and HCFCs, such as HCFC-22 and HCFC-142b, are incompletely dissociated within the stratosphere. Second, differences in the dissociation reactivity produce different chlorine distribution for the various gases.

Note that values of CEF are notably consistent among the models, to within 20% of each other for most species. In addition, the value for CEF can be larger than 1 as in the case of CH_3CCl_3 for which a larger portion of the chlorine atoms is deposited in the lower stratosphere compared to CFC-11. The value for CEF can be related to the calculated chlorine distribution as follows. We will use HCFC-22 as an example in the following discussion. One can calculate the two steady state Cly distributions resulting from emissions of CFC's that maintain a surface mixing ratio of 1 ppbv for CFC-11 and 3 ppbv for HCFC-22 respectively and defime the ratio of the concentrations as the Normalized Chlorine Distribution (NCD). Note that NCD is a function of latitude and height. One expects the Cly distributions for CFC-11 and HCFC-22 to be different since the local loss frequencies for the two species are quite different and the chlorine atoms will be released in different regions of the stratosphere. If the stratospheric loss frequencies for both species were the same, the resulting distributions would be identical, and the values for NCD would be identically 1 everywhere (the factor of three in surface mixing ratio takes care of the fact that CFC-11 has 3 chlorine atoms while HCFC-22 only has 1) and CEF = 1.

A better estimate for the potential impact of polar ozone loss processes is perhaps possible based on the NCD. The difficulty for estimation of polar chemistry impact on local and global ODP from the local NCD arises for two reasons. First, the repartition of the chlorine species depends on the absolute amount of Cly in the the atmosphere, a larger portion of the chlorine will be converted to ClO, the higher the concentration of Cly, Second, the O_3 removal rate is approximately proportional to the square of the C1O concentration.

The 2-D NCD for HCFC-22 is shown in Figure 19A for January as calculated by the AER 2D model. The quantity CEF can be interpreted as a weighted average of NCD with the weighting determined by the response of ozone to the local chlorine concentration. Comparison of the latitudinal variation of the 2-D ODP for January (Figure 18A) with NCD (Figure 19A) indicates that the 2-D ODP is approximately

local ODP $\sim$ CLP*NCD (in the lower stratosphere).

Thus, it is reasonble that if the NCD in the polar lower stratosphere (NCDpl) is less than 1, then

local ODP $\leq$ CLP * (NCDpl)

holds even in the presence of heterogeneous conversion. With more chlorine available in the CFC-11 case, the response of O_3 will be larger than that of the substitute compound with NCDpl $\leq$ 1.

In estimating the effect of polar chemistry on the calculated global ODP, one must include the dilution effect away from the local effect (ozone hole) as well as the direct contribution from local effect. A simple estimate can be provided as follows. Noting that the ratio CEF for most substitute compounds are approximately equal to NCDpl, an argument can be put forward that if CEF, NCDpl and NCD $\leq$ 1

then Global ODP $\leq$ CLP * (NCDpl).

in the presence of polar chemistry. The above conditions are satisfied for all HCFC's we have examined except for CH_3CC_3. Thus for HCFC-22, this reasoning leads to an estimate bound of

Global ODP(HCFC-22) $\leq$ .27*.500
$\leq$ .135

which is approximately double the global ODP value calculated by AER, but only <50% of the CLP limit posed as the conservative estimate above.

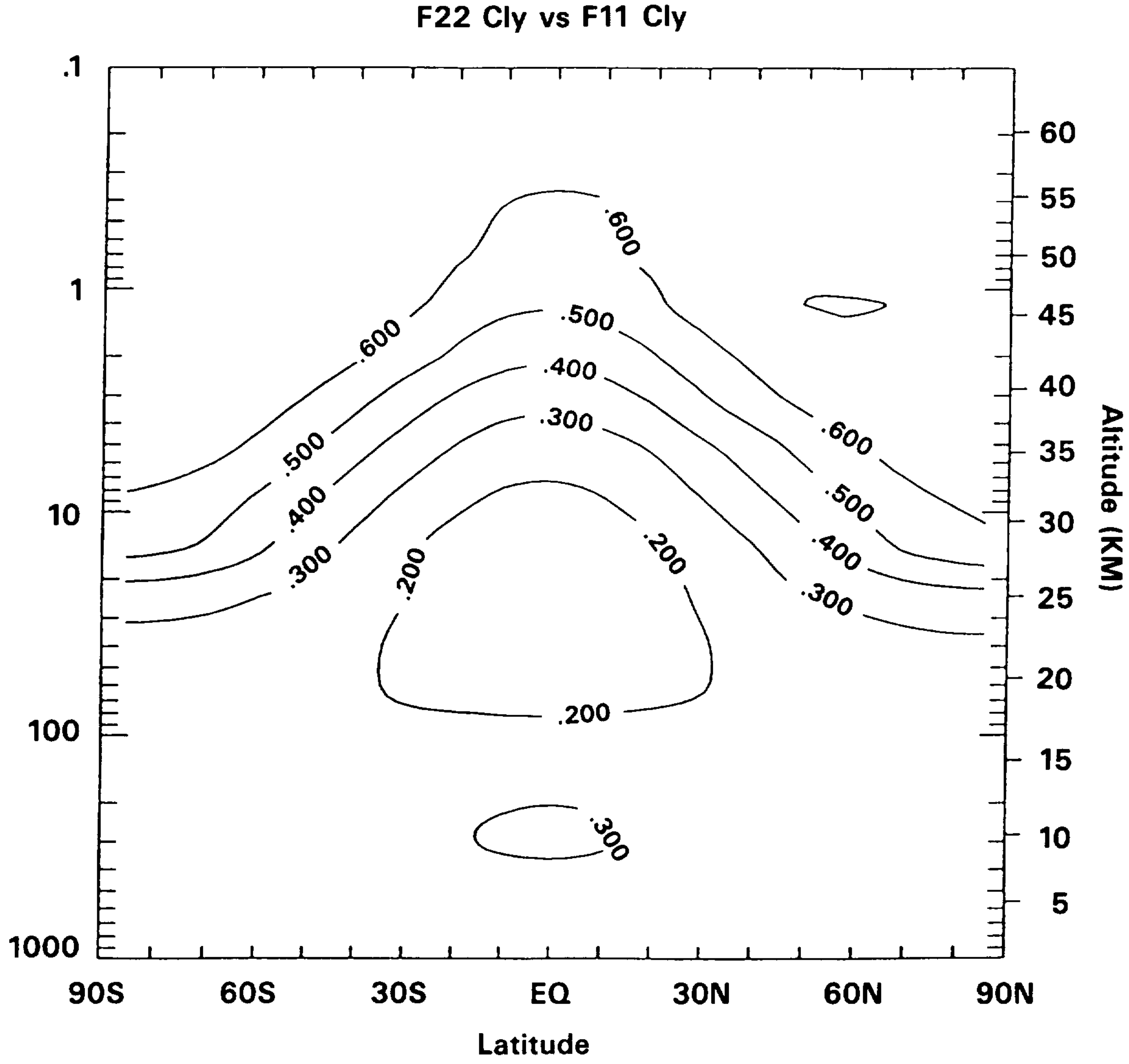


Figure 19A. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 1 of Transport Sensitivity Study] (AER-2D).

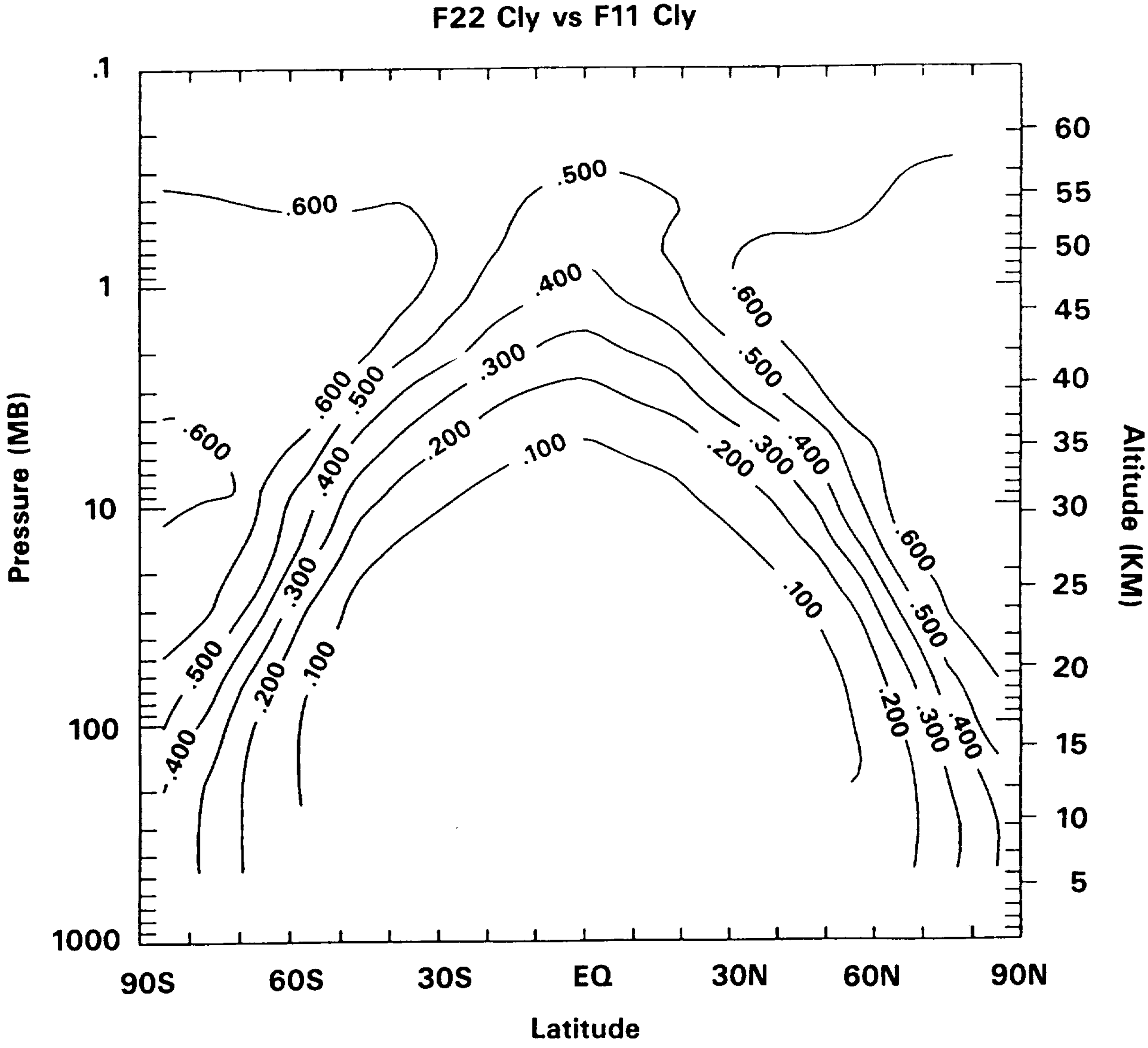


Figure 19B. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 2 of Transport Sensitivity Study] (AER-2D).

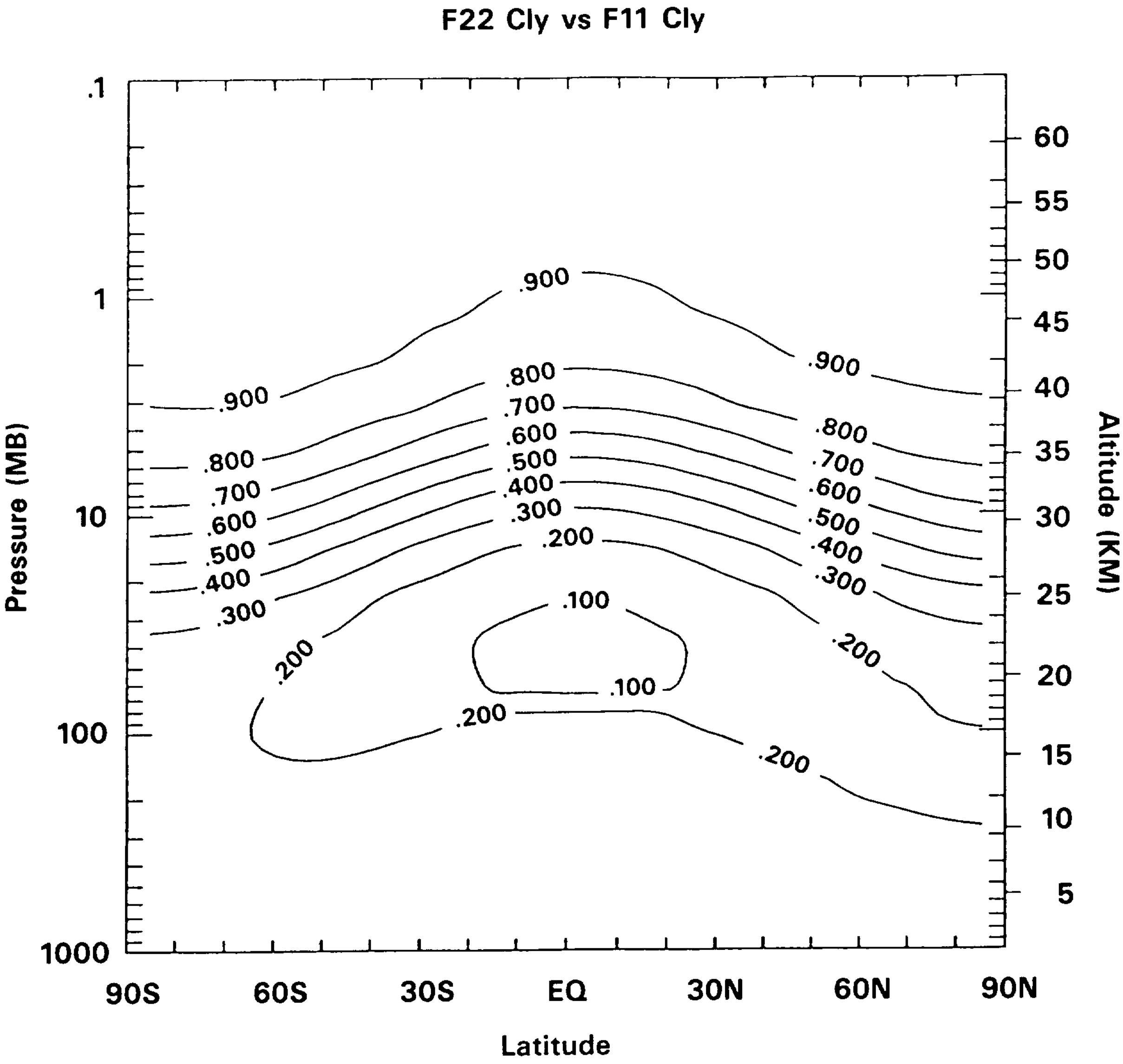


Figure 19C. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 3 of Transport Sensitivity Study] (AER-2D).

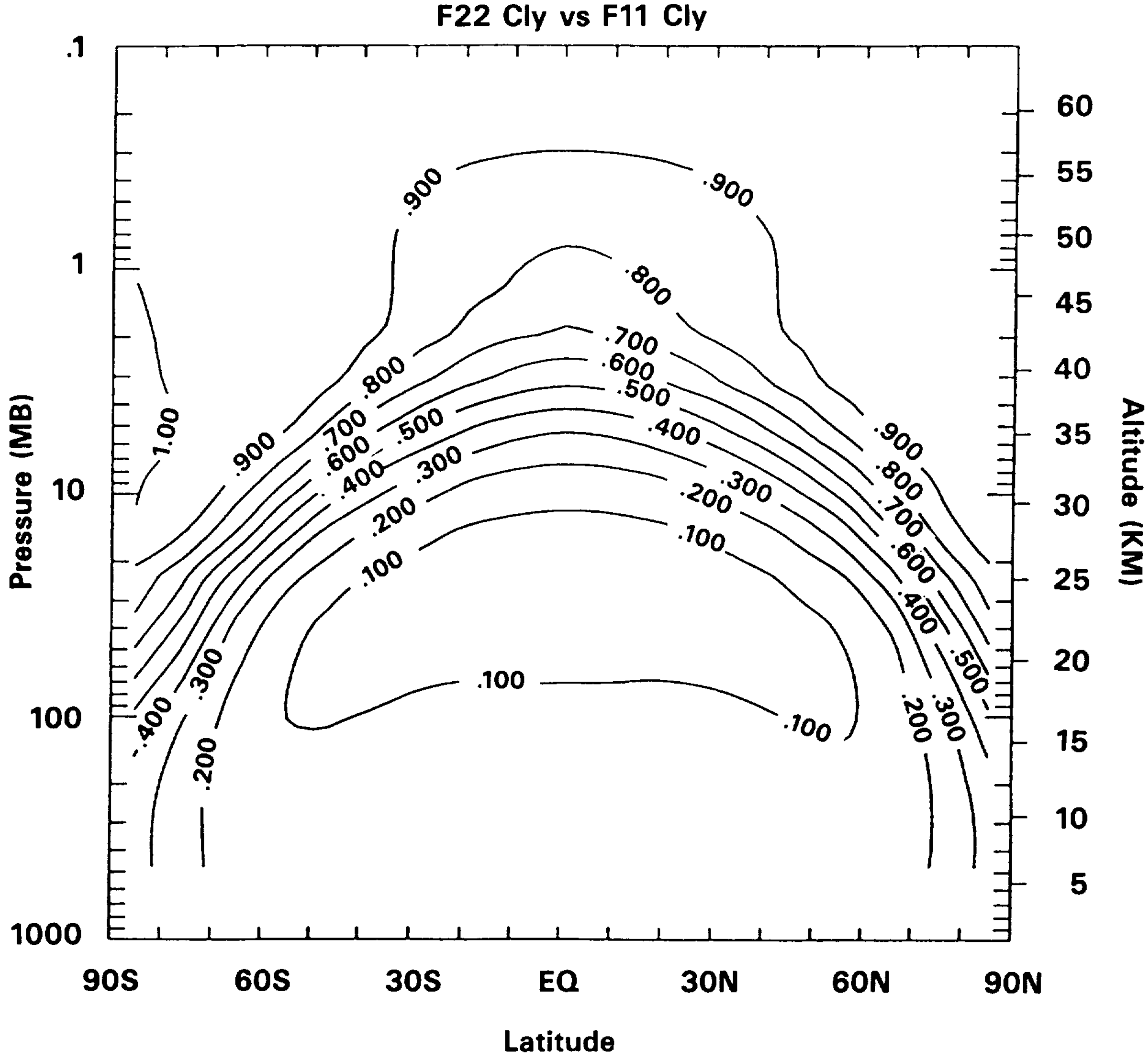


Figure 19D. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 4 of Transport Sensitivity Study] (AER-2D).

Because of apparent significant downward advection within the vortex (sufficient to explain tile observed low concentrations of N_2O, CH_4, and CFCs), it can be argued that active chlorine at all altitudes within the stratosphere and, perhaps, the mesosphere, may be available for affecting ozone within the polar vortex. The implication of this hypothesis on the derived ODPs is unknown.

At this time, until model studies of heterogeneous chemistry effects have been completed, we cannot conclude that using the ODP values in Table 4 is more definitive than using the chlorine loading potential values in Table 10. The answer to this open question depends on the maximum extent of the influence that polar springtime ozone destruction will have on global ozone, and on the extent of the downward transport within the Antarctic and Artic polar vortices.

In summary, the impact of the unique polar chemistry on the relative effects can only be estimated quite crudely. The most conservative estimate is that the effects are bounded by a Chlorine Loading Potential which is substantially greater than the Ozone Depletion Potential for most chemicals. A less conservative estimate can be derived from the calculated profiles of inorganic chlorine distributions indicating that the relative effect may be substantially below the CLP values.

7. TIME-DEPENDENT RELATIVE OZONE DEPLETION

One of the limitations associated with the ODP parameter is that it is based on steady state perturbations; it does not consider the relative time-dependent effects of different constituents on ozone. While we have shown that ODP is equivalently a measure of the cumulative chronic effects of unit emitted mass of a gas over its life cycle in the atmosphere, we are also interested in the transient response at a constant emission level.

As mentioned in the first section, ODP values determined at steady-state are not expected to be representative of the relative transient effects expected for shorter-lived compounds during the early years of emission. During these early years, before one to two equivalent species lifetimes have passed, the ozone depletion per unit mass relative to CFC-11 can be much larger than the steady state ODP value for some of the short-lived constituents. We note from Figure 20, however, that the changes in ozone occurring, at these times are also relatively small compared to the steady-state ozone change.

The calculated time-dependent ozone depletions for several of the HCFCs following a step increase in emission level are shown in Figure 20. These results can be compared relative to CFC-11 to give relative ozone depletions. Results from the LLNL 1-D model are shown in Figure 21 and from the DuPont 1-D model in Figure 22 for a range of compounds. Results for the first few years are not shown because the derived changes in ozone were too small to be numerically accurate.

The transient values for relative ozone depletion and the time it takes to approach the steady state values depend on the time-dependent behavior of the calculated O_3 decrease for the species and the reference gas CFC-11 which depends on the stratospheric lifetimes as well as the atmospheric lifetimes. Since the

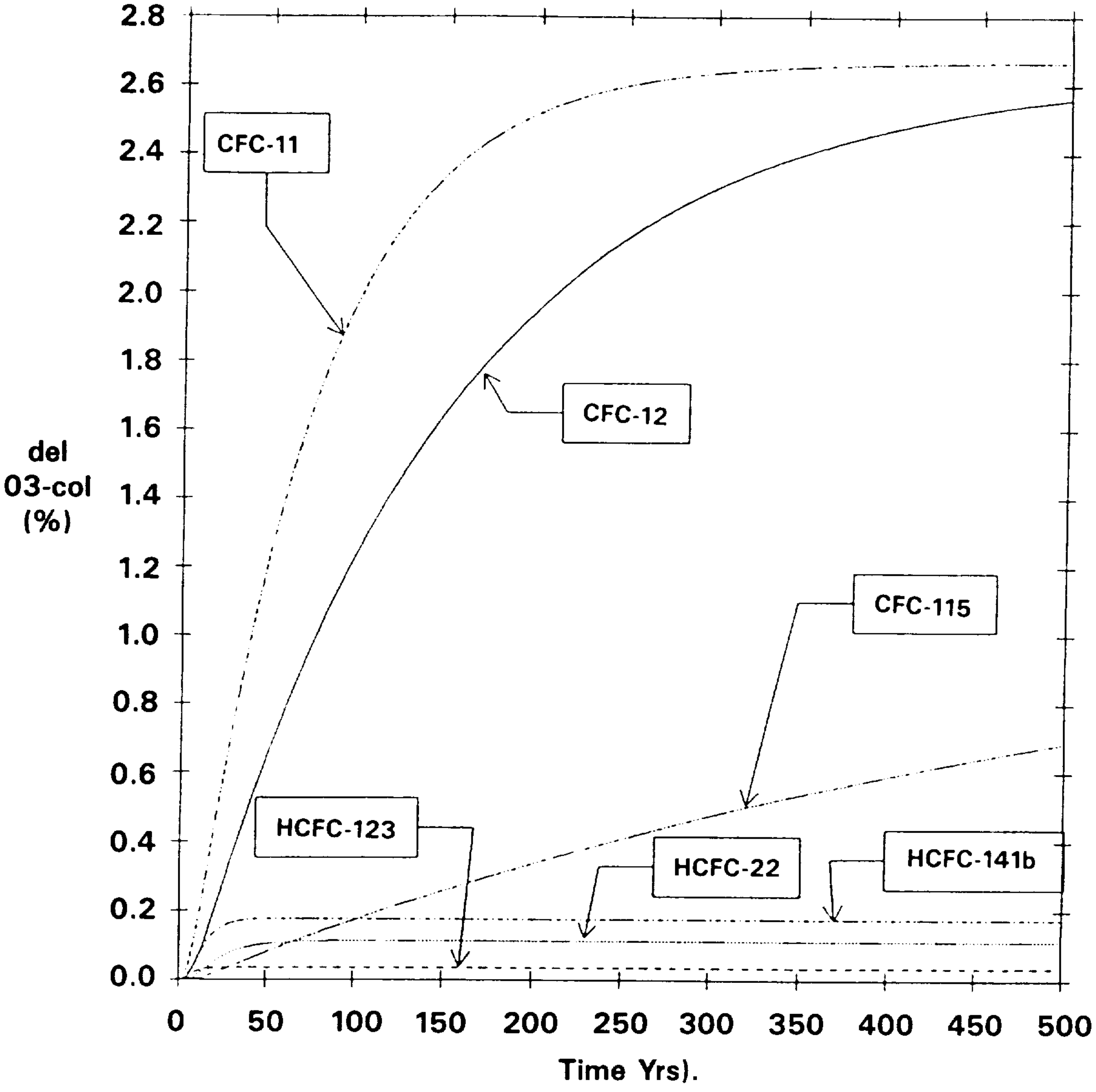


Figure 20. Time Response of Column Ozone Following Step Change in Release of Specified Gas at 5.0 x 10^8 kg/yr. (DuPont 1-D Model)

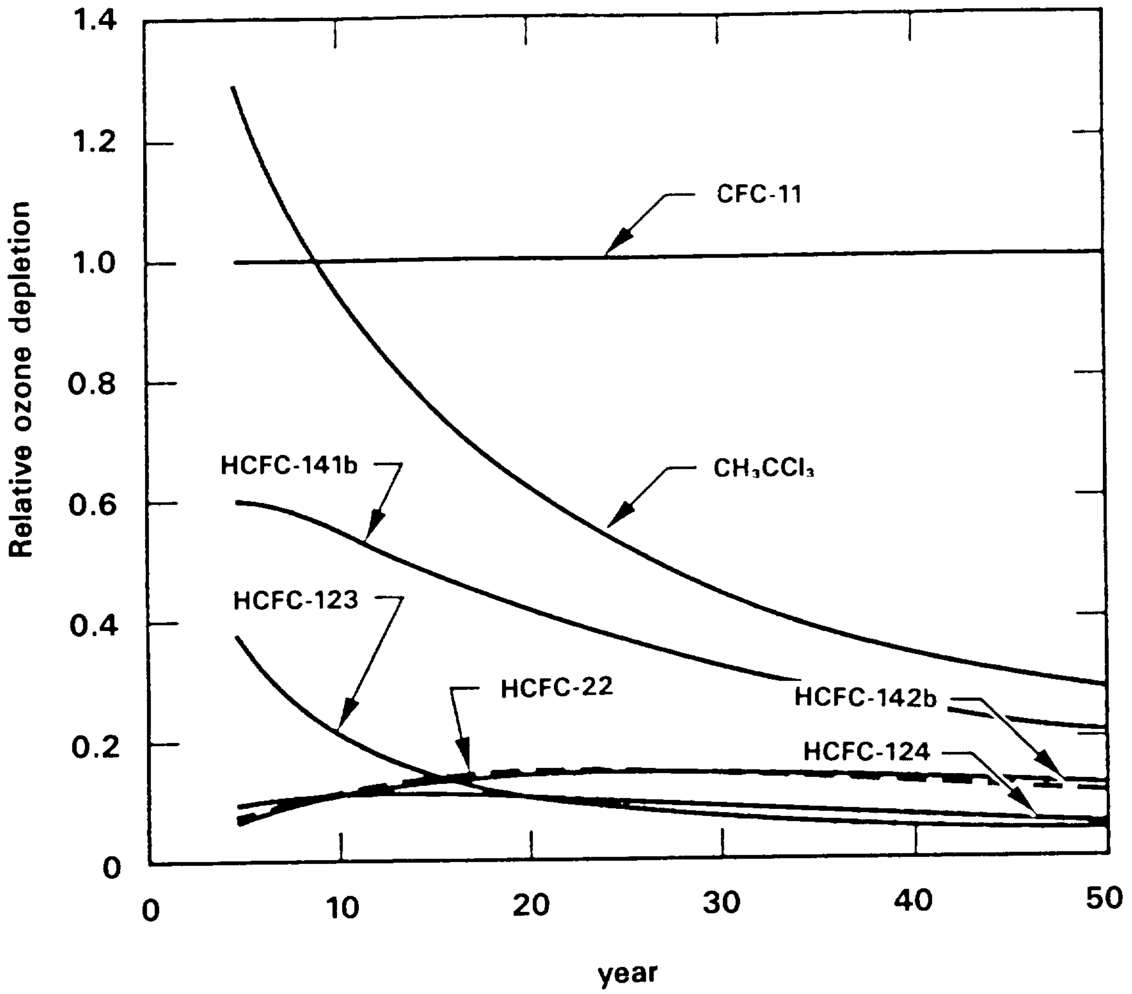


Figure 21. Calculated time-dependent change in relative ozone column depletion. (LLNL 1-D Model)

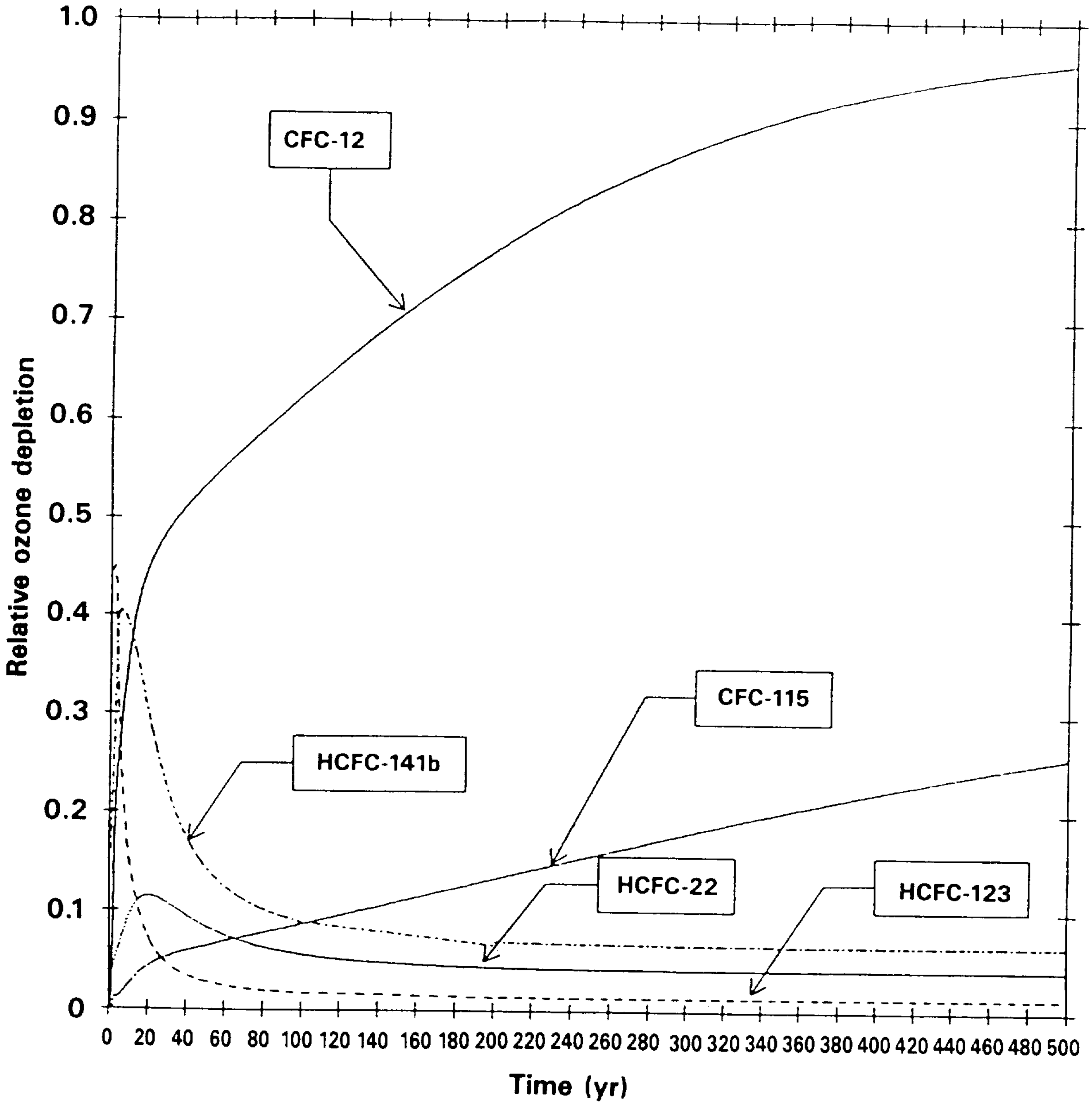


Figure 22. Calculated time-dependent change in relative ozone column depletion following a step change in emission of Halocarbons. (DuPont 1-D).

atmospheric lifetimes of the HCFC's examined in this study are shorter than that of CFC-11, the time constant for exponential decay to the ODP asymptote is determined by the CFC-11 lifetime. The magnitude of the transient relative ozone depletion depends on the stratospheric lifetimes and how fast the chlorine atoms are released after transport into the stratosphere.

Several of the HCFCs, namely HCFC-123, HCFC-141b, and CH3CC3, have much larger relative ozone depletions at early times compared to the Ozone Depletion Potential values. Each of these cases have relatively short reaction time constants within the stratosphere - compared to CFC-11. As a result, chlorine atoms are quickly released by these gases and the full effect on ozone is reached much sooner than CFC-11. At longer times the relative ozone depletions asymptotically approach the ODP value.

Other species, such as HCFC-22, HCFC-124, and HCFC-142b, have long reactive time constants in the stratosphere. The time-dependent relative ozone depletions have much different behavior for these species. The relative ozone depletion builds gradually to a maximum value for these species, reflective of their long stratospheric time constants and the amount of time needed to build-up stratospheric concentrations. After the first 2040 years, the relative ozone depletion for these species gradually decays to the ODP value.

For gases with longer lifetimes than the reference gas, no maximum in relative ozone depletion is noted. This can be seen by examining the results for CFC-12 and CFC-115 in Figure 22.

Of equal interest to many is the relative ozone depletions once emssions cease. Figure 23 shows the calculated change in ozone column when gases are emitted at a constant level of 5.0×10^8 kg/yr, for 50 years and at which point emissions stop (Du Pont 1-D model). Calculated effects for the HCFCs fall to near zero at the end of the 100 year period whereas a significant fraction of the calculated effects for CFCs remain at the end of this period. The relative (to CFC-11) effect for each of the species is shown in Figure 24. Response during the first 50 years is the same as shown in Figure 22. Once emissions are curtailed, all of the curves for HCFCs drop signficantly faster than during the emission period whereas the curves for CFC-12 and CFC-115 increase in slope. In other words, this reinforces the conclusion that it takes far less time for any residual effect from HCFCs to diminish than from CFCs once emissions are stopped.

Figures 25 and 26 show the relative time-dependent behavior of chlorine being transported through the tropopause for these same gases (taken relative to CFC-11). In all cases, the time-dependent stratospheric chlorine loading is much larger initially compared with their eventual steady-state relative Chlorine Loading Potential value (given previously in Table 10) if the lifetime of the species is less than the reference gas.

In summary, time dependent ozone depletion and chlorine loading values for species with lifetimes shorter than CFC-11 are generally larger than the ODP and CLP values defined at steady state. Time dependent relative ozone depletion and chlorine loading for CFCs with lifetimes longer than CFC-11 show a monotonic increase to the steady state ODP and CLP value.

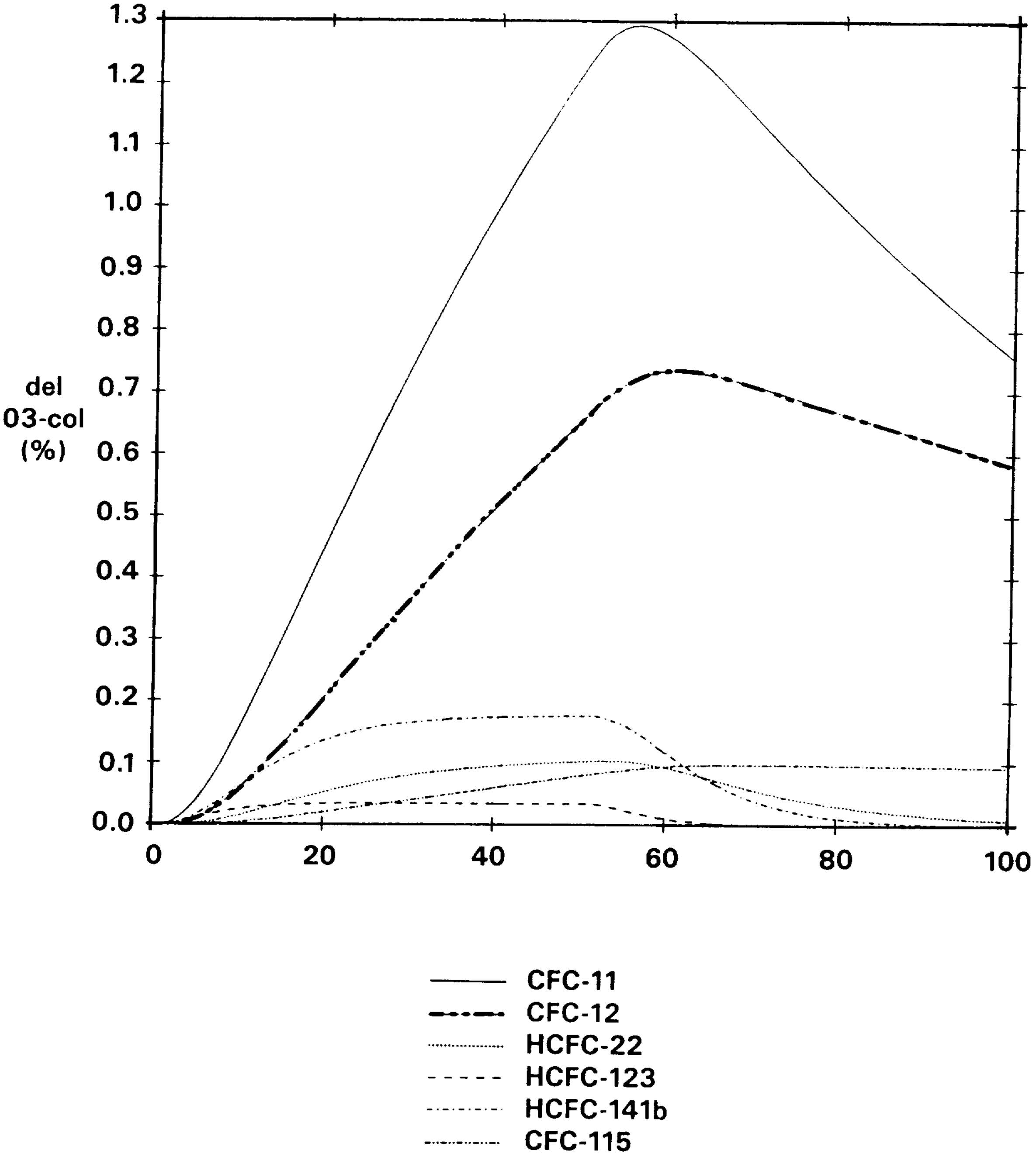


Figure 23. Column Ozone Change Following Step Emission Increase of Specified Gas of 5.0 x 10**8 kg/yr for 50 years, and then Cut to 0 Emissions for Next 50 Years. [DuPont 1-D Model]

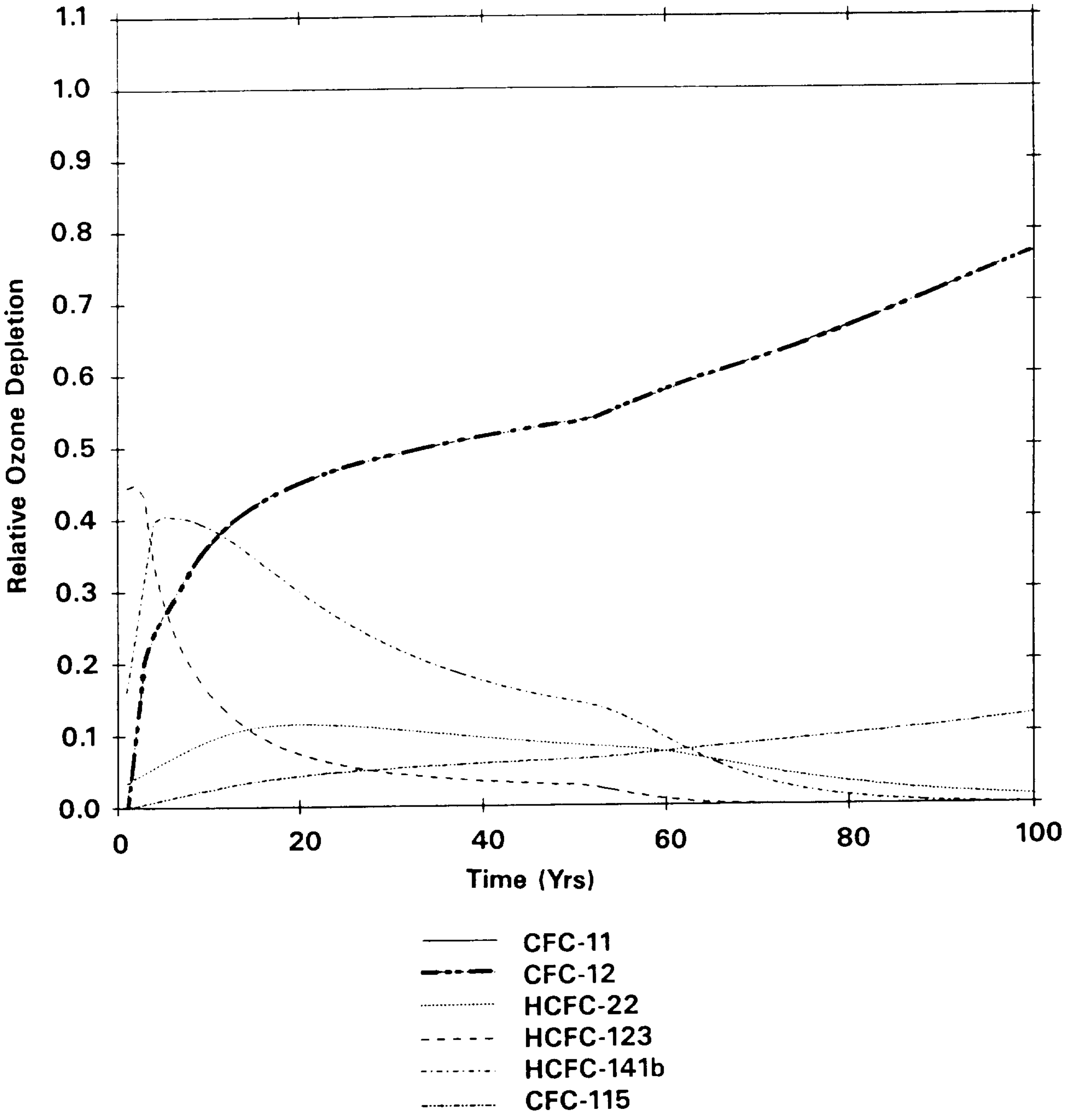


Figure 24. Relative Column Ozone Change Following Step Emission (of 5.0 x 10**8 kg/yr) Increase for Specified Gases for 50 Years, and then Cut to 0 Emissions for Next 50 Years. (Basis: CFC-11 = 1.0) [DuPont 1-D Model]

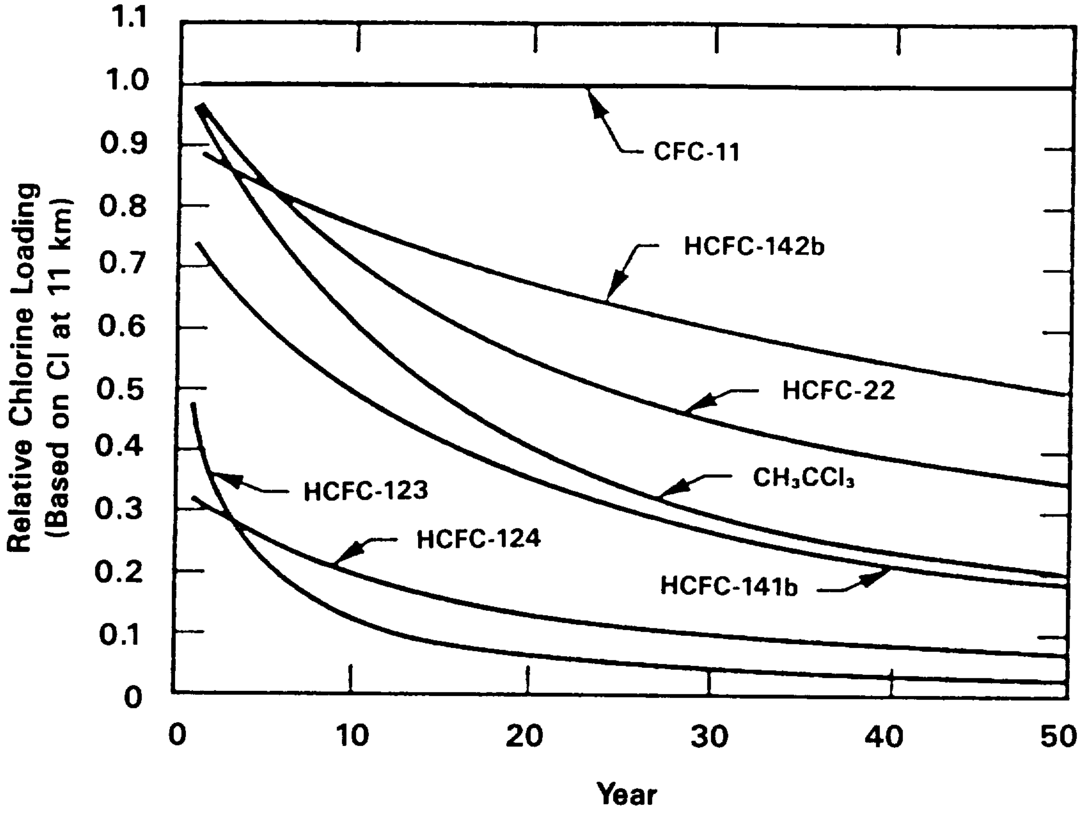


Figure 25. Calculated Time-Dependent Relative Chlorine Loading Following a Step Change in Emission of Halocarbons. (LLNL 1-D).

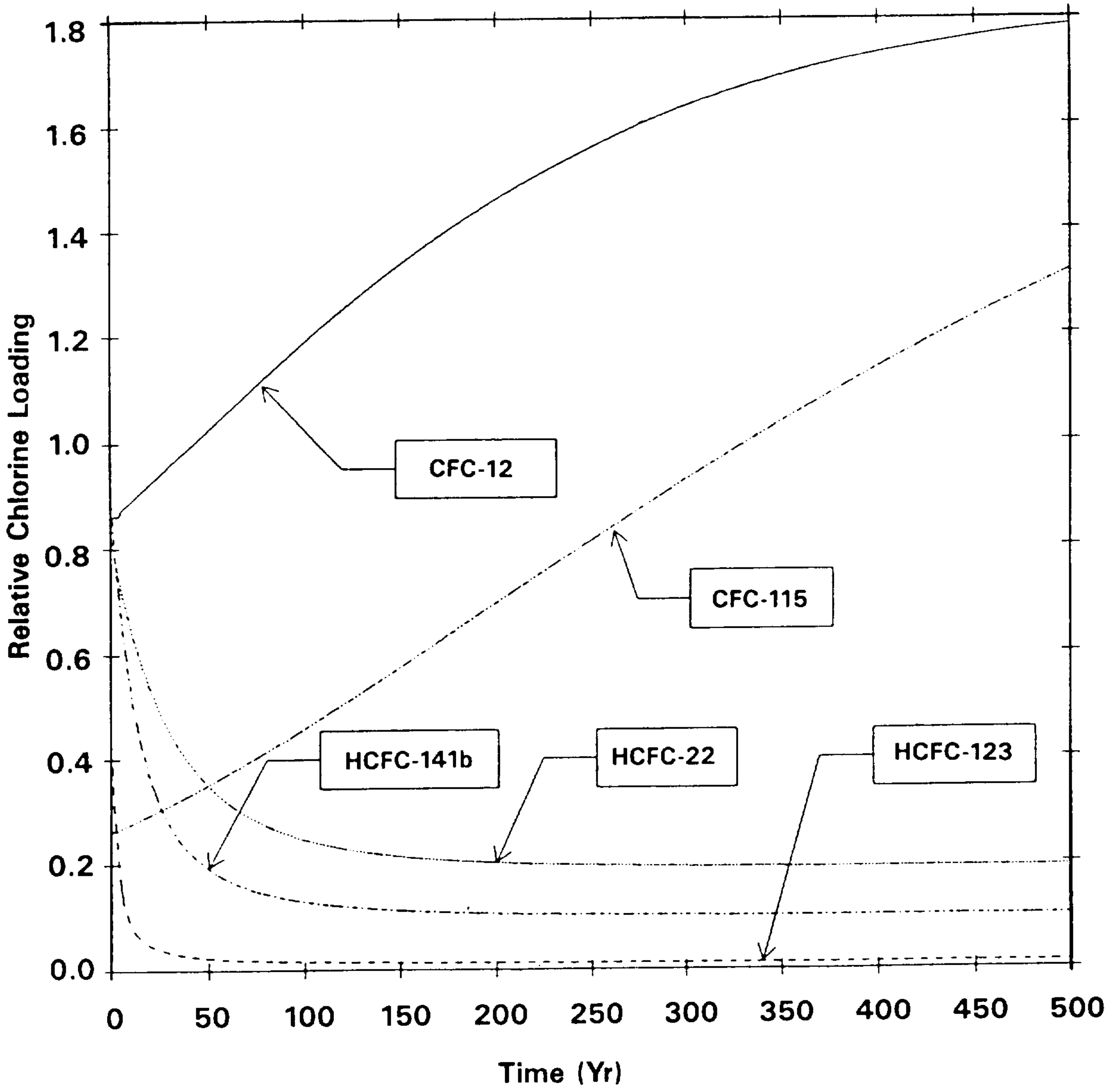


Figure 26. Calculated Time-Dependent Relative Chlorine Loading Following a Step Change in Emission of Halocarbons. (DuPont 1-D).

8. ACKNOWLEDGMENTS

The authors are grateful for the support received for this work from the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS). Additional funding was provided by the following companies: Allied-Signal Corporation, Atochem, E.I. du Pont de Nemours & Co., Hoechst Aktiengesellschaft, ICI Chemicals and Polymers Limited, and Montefluos SPA.

Work at AER, Inc. is also supported by the National Aeronautics and Space Administration, Upper Atmospheric Theory and Data Program (NASW-4080). Work at LLNL is also supported bv the National Aeronautics and Space Administration, as well as being under the auspices of the U.S. Department of Energy (W-7405-ENG-48).

APPENDIX A: RELATIONSHIP BETWEEN FORMS OF ODP

It is helpful to look at the various formulations for ODP and explore the background relationships between them. We have chosen our definition for ODP to be the column ozone change following a constant release of a given compound divided by the column ozone change resulting from the same mass release rate of CFC-11 at steady state. Subsequently, we showed, based on model exercises, that the ratio of cumulative effects following a one-time input of gases was virtually equivalent to ODP. The purpose of this section is to examine the background mathematical formulations in order to define the relationship(s) between the formulations.

Let G (t-to) be the response function [which in this example corresponds to the ozone column change] at time t = to a stimulus S(to) [which in this example corresponds to a release of a set mass of chlorine containing gas into the atmosphere] at time to. We furthermore make the assumption that the response is linear so that it can be normalized to the source strength to Dive:

$$g(t\text{-}to) = G(t\text{-}to)/S(to)$$

Properties of the function g(t) are that:

$$g(\infty) = 0$$ (i.e., the response decays to 0 at infinite time),

In terms of physical processes, the function g(t-to) contains the results from the transport and chemistry within the reacting system (atmosphere) and is specific to one set of reaction parameters, and therefore is species specific.

STEADY STATE

Let us first examine the case of a steady-state response. If a stimulus started at time = 0 and held constant at S = S_0 until steady state is realized, then the steady-state response is reached at time T and is the integrated response from all gas released over history and is of the form:

$$Gss = \int_{t_0 = 0}^{to = T} S_0 * g(T-t_0)\, dt_0$$

Since by definition of steady state, it is insensitive to starting time, so we could have started the release at time, t = - . Thus, Gss can be expressed, without loss of generality, as:

$$Gss = \int_{to = -\infty}^{to = T} S_0 * g(T-t_0)dt_0$$

Therefore if we use the notation that Gss-x is the steady state response for compound x, and Gss-11 is the corresponding response for CFC-11, then ODP(ss) can be expressed as:

STRATOSPHERIC OZONE

$$\mathrm{ODP(ss)} = \frac{\mathrm{Gss\text{-}x}/S_0\text{-x}}{\mathrm{Gss\text{-}11}/S_0\text{-}11}$$

or,

$$\mathrm{ODP(ss)} = \frac{\int_{-\infty}^{T} gx(T-t_0)dt_0}{\int_{-\infty}^{T} g11\ (T-t_0)dt_0} \qquad \text{(A)}$$

With a substitution of integration variables of t^5T-to. equation A becomes:

$$\mathrm{ODP(ss)} = \frac{-\int_{+\infty}^{0} gx(t)dt}{-\int_{+\infty}^{0} g11(t)dt}$$

or,

$$\mathrm{ODP(ss)} = \frac{-\int_{0}^{\infty} gx(t)dt}{-\int_{0}^{\infty} g11(t)dt} \qquad \text{(B)}$$

PULSED INPUT

Now, let us focus on the ratio of integrated responses to a pulsed input. For a pulsed input of value PS at time to, the integrated resulting effect, GP, on the system over the ensuing period is:

$$GP = \int_{t_o}^{\infty} PS *g(t-to)\ dt$$

Since PS is constant, GP becomes:

$$GP = PS * \int_{t_o}^{\infty} g(t-t_0)\ dt$$

We can again change the integration variable such that T = t-to and since the values for PS will be the same both in the numerator and the denominator, the ratios of integrated responses reduces to:

$$\frac{\text{GP-x}}{\text{GP-11}} = \frac{\int_0^{\infty} gx(T)\, dT}{\int_0^{\infty} g11(T)\, dT} \qquad \text{(C)}$$

Which is the same functional form as ODP expressed by equation B.

Therefore we have shown mathematical equivalence as long as we have linear relationships between release (stimuli) and ozone chance (response). Real world interpretations as well as model exercises indicate that the relationships are not exactly linear. Therefore, discrepancies between ODP and ratio of responses to pulsed releases do exist but are caused by the (minor) non-linearities of the phenomena and/or numerical round-off errors associated with the numerical models.

IX. HALOCARBON GLOBAL WARMING POTENTIALS

Relative Effects on Global Warming of Halogenated Methanes and Ethanes of Social and Industrial Interest

D. A. Fisher and Charles H. Hales
E. I. du Pont de Nemours & Company
Wilmington, DE

Wie-Chyung Wang, Malcolm K. W. Ko and N. Dak Sze
Atmospheric and Environmental Research, Inc.
Cambridge, MA

EXECUTIVE SUMMARY

Halocarbon Global Warming Potentials have been defined and calculated in order to allow estimates of the relative environmental effects of halocarbons to be made. The results presented here indicate that the HGWPs of the hydrohalocarbons depend primarily on the atmospheric lifetime of the compounds and to a lesser degree on the molecular IR absorption characteristics.

The reduction in HGWP that might be expected due to use replacement of a CFC by a hydrohalocarbon can be estimated by taking the ratio of the HGWP of the hydrohalocarbon to the HGWP of the CFC it would replace. For example, the reduction in HGWP in replacing uses of CFC-12 by HCFC-134a is (0.26 ± .010)/(3.05) = 0.085 ± 0.003. Of course, the relative quantities of the compound required in the use application must also be taken into account.

Although the HGWP values reported here agree between models reasonably well once accounting is made for the differences in lifetimes, uncertainties in the values still exist due to the uncertainties in modeled chemistry and dynamics and their direct effect on the chemical lifetimes of these compounds. We expect that these values will be updated once better data is available for the ultraviolet reactions and the hydroxyl radical reactions with the respective compounds.

The HGWP values appear to be reasonably robust parameters since their calculated values are nearly insensitive to assumed values of other radiative gases. The minor shifting of the HGWP values in primarily influenced by the changes in calculated lifetimes and therefore the abundance in the atmosphere.

Calculated time-dependent relative global warmings for halocarbons are initially on order unity but decrease or increase depending on whether their lifetimes are shorter or longer than that of the reference gas. At longer times, the Relative Global Warmings asymptotically approach the HGWP values.

N92-15447

RELATIVE EFFECTS ON GLOBAL WARMING OF HALOGENATED METHANES AND ETHANES OF SOCIAL AND INDUSTRIAL INTEREST

Donald A. Fisher and Charles H. Hales
E.I. du Pont de Nemours & Company

Wei-Chyung Wang, Malcolm K. W. Ko and N. Dak Sze
Atmospheric and Environmental Research, Inc.

ABSTRACT

The relative potential global warming effects for several halocarbons (CFCs -11, 12, 113, 114, and 115; HCFCs 22, 123, 124, 141b, and 142b; and HFCs 125, 134a, 143a, and 152a; carbon tetrachloride; and methyl chloroform) have been calculated by two atmospheric modeling groups. These calculations were based on atmospheric chemistry and radiative convective models to determine the chemical profiles and the radiative processes. The resulting relative greenhouse warming when normalized to the effect of CFC-11 agree reasonably well as long as we account for differences between modeled lifetimes. Differences among results are discussed. Sensitivity of relative warming values is determined with respect to trace gas levels assumed. Transient relative global warming effects are analyzed.

1. INTRODUCTION

A systematic environmental evaluation of replacements for fully halogenated chlorofluorocarbons (CFCs) includes the potential effects of each replacement chemical on global warming. While the major focus for rising environmental concerns centers on the potential effects of long-lived CFCs on stratospheric ozone, the role of these gases as contributors to an enhanced greenhouse or global warming also needs examination. This concern is based on the ability of these gases to absorb infrared radiation in the atmospheric 'window' between 8 and 12 μm.

First, a brief background to establish the role of these gases in the 'greenhouse warming' phenomena. The radiative and thermal balance of planet Earth is established primarily by balancing the incoming (UV and visible) solar energy to the Earth's surface and atmosphere with the outgoing (infrared) radiation from the Earth's surface and atmosphere eventually being lost to space. Infrared energy is partially blocked at many wavelengths by naturally occurring gases such as carbon dioxide, methane, and stratospheric water vapor. These gases absorb energy at fundamental frequencies characteristic of their structure. This energy contributes to local warming and is eventually re-radiated. Changing gas concentrations change the radiative balance of the infra-red cooling process. Hence, the concern that increasing CO_2 concentration will significantly impede infrared cooling of the Earth with a decrease in energy loss to space and a corresponding increase in the Earth's surface temperature.

The atmosphere 'window' between 8 and 12 μm is virtually transparent, i.e. since few gases are present that absorb energy at these wavelengths, outgoing infrared radiation passes through the atmosphere essentially unimpeded. However, both C-Cl and C-F bonds have natural vibrational, bending, and rotational excitation frequencies in this infrared frequency range such that CFCs absorb the infrared energy to become very effective greenhouse gases. Their effectiveness as greenhouse gases is accentuated by their long lifetimes. Since functional replacements may also absorb infrared energy in the window region, it is important to estimate their potential impact on global climate as part of this evaluation. As will be demonstrated below, the effectiveness of these gases is determined in large part by their lifetimes. Longer lived gases build up higher tropospheric concentrations. Of fundamental importance in determining the effectiveness as greenhouse gases are the infra-red band strengths, i.e. the wave length intervals and the amount of energy absorbed within these intervals by each molecule.

Besides the influence on the infrared radiative fluxes at the top of the atmosphere and at the surface, there is yet another aspect of the radiative perturbations from halogenated compounds — namely the additional heating induced in the tropical upper troposphere and lower stratosphere which has the potential to increase temperatures in this region. Any change in the temperatures near the tropopause region is of considerable significance for the tropospheric-stratospheric exchange water vapor.

Candidate alternatives are composed of either carbon, hydrogen and fluorine (hydrofluorocarbons or HFCs) or carbon, hydrogen, chlorine and fluorine (hydrochlorofluorocarbons or HCFCs). For simplicity, both classes of compounds are referred to as hydrohalocarbons. Because they contain hydrogen, the hydrohalocarbons are subject to destruction in the atmosphere through reaction with hydroxyl radicals. This destruction mechanism leads to much shorter atmospheric lifetimes for the hydrohalocarbon compounds (see [Fisher et al. (1989a)] for a discussion of the chemistry affecting the atmospheric lifetimes of these gases). By contrast, the only known destruction process of CFCs is through photolysis in the upper stratosphere. As will be shown below, the shorter atmospheric lifetime of HCFCs and HFCs is a primary factor in reducing their potential to affect global warming.

This paper examines the calculated greenhouse effects of several one and two carbon halocarbons. Estimates of these effects will be quantified in terms of a relative potential to enhance global warming (halocarbons global warming potential or HGWP). Sensitivity to assumed levels of trace gases will be examined. Transient relative warming effects will be analyzed.

Table 1 Compounds Examined in this Study

HALOCARBON	FORMULA	IUPAC NAME
CFC-11	CCl_3F	METHANE, TRICHLOROFLUORO-
CFC-12	CCl_2F_2	METHANE, DICHLORODIFLUORO-
CFC-113	CCl_2FCClF_2	ETHANE, 1,1,2-TRICHLORO-1,2,2-TRIFLUORO-
CFC-114	$CCClF_2CClF_2$	ETHANE, 1,2-DICHLORO-1,1,2,2-TETRAFLUORO-
CFC-115	$CClF_2CF_3$	ETHANE, CHLOROPENTAFLUORO-
HCFC-22	$CHClF_2$	METHANE, CHLORODIFLUORO-
HCFC-123	CF_3CHCl_2	ETHANE, 2,2-DICHLORO-1,1,1-TRIFLUORO-
HCFC-124	CF_3CHClF	ETHANE, 2-CHLORO-1,1,1,2-TETRAFLUORO-
HFC-125	CF_3CHF_2	ETHANE, PENTAFLUORO-
HFC-134a	CF_3CH_2F	ETHANE, 1,1,1,2-TETRAFLUORO-
HCFC-141b	CCl_2FCH_3	ETHANE, 1,1-DICHLORO-1-FLUORO-
HCFC-142b	$CClF_2CH_3$	ETHANE, 1-CHLORO-1,1-DIFLUORO-
HFC-143a	CF_3CH_3	ETHANE, 1,1,1-TRIFLUORO-
HFC-152a	CHF_2CH_3	ETHANE, 1,1-DIFLUORO-
CARBON-TETRACHLORIDE	CCl_4	METHANE, TETRACHLORO-
METHYL CHLOROFORM	CCl_3CH_3	ETHANE, 1,1,1-TRICHLORO-

Halocarbon Global Warming Potential is based on a concept similar to Ozone Depletion Potential and is used to describe the relative potential of each halocarbon as a greenhouse gas. No attempt is made to calculate HGWPs for non-halocarbon gases such as carbon dioxide and methane. Because of the current atmospheric concentrations and spectral locations of the infrared absorption bands of these other gases, calculated global warming is not a linear function with increases in their atmospheric concentrations. In contrast, a calculated warming is linearly proportional to concentrations of halocarbons. Thus, Greenhouse Warming Potentials for carbon dioxide and methane would not be meaningful.

Two atmospheric modeling groups, Atmospheric and Environmental Research, Inc. (AER), and Du Pont Central Research (Du Pont), have calculated HGWP values for sixteen gases. These groups used Radiative Convective models that are described in the literature (Wang and Molnar 1985, Owens et al. 1985). The halocarbons considered in this study are listed in Table 1 along with their chemical formula and IUPAC names and are the same as evaluated for effect on stratospheric ozone (Fisher, et al., 1989a).

This paper will discuss the definition of HGWP, as well as examine the basis for selecting its definition. The results calculated by the two models and an examination of the differences and uncertainties in model results is also presented.

2. DEFINITION BASIS

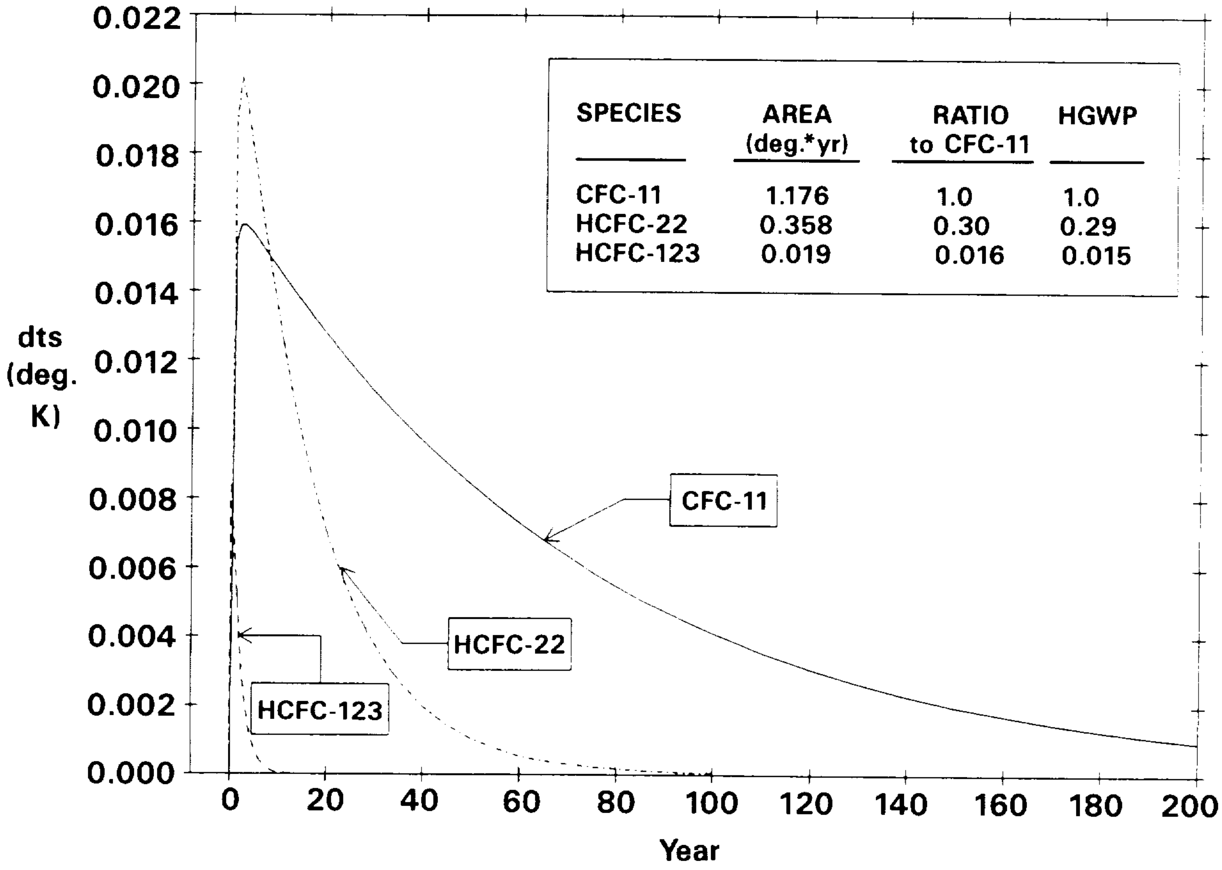
Halocarbon Global Warming Potential (HGWP) is defined in a manner parallel to the definition of Ozone Depletion Potential. It is defined as the ratio of calculated warming for each unit mass of a gas emitted into the atmosphere relative to the calculated warming for a mass unit of reference gas CFC-11. This definition was chosen as a representative measure of the potential of a compound to effect global warming for several reasons:

(1) It provides a measure of the cumulative effect on the radiastive balance over its chemical lifetime for each unit released into the atmosphere (see below).

(2) The HGWP yields a single value for each compound rather than a time varying multitude of values.

(3) It provides a measure of the maximum calculated effect of a compound compared to the maximum calculated effect of CFC-11 on an equal mass basis.

The first of these reasons is perhaps the most important in that it estimates the cumulative chronic effect on global warming of each unit released. An illustrative test was performed which quantified the chronic effect from a single pulsed release of test gas into the atmosphere, analogous to a test on effect on stratospheric ozone (Fisher et al., 1989a). The test used the Du Pont model to calculate cumulative global warmings over a 500 year time period following impulse releases of HCFCs -123, -22, and CFC-11.



SPECIES	AREA (deg.*yr)	RATIO to CFC-11	HGWP
CFC-11	1.176	1.0	1.0
HCFC-22	0.358	0.30	0.29
HCFC-123	0.019	0.016	0.015

Figure 1. Calculated Change in Surface Temperature Following a Pulsed Emission of 5.0x10**9 kg of Specified Gas

The calculated cumulative warmings are shown in Figure 1. For each case, the effect peaks very rapidly following the release and tails off with an exponential decay function having a time constant equal to the atmospheric lifetime of the species. As seen in the insert table, the time-integrated warming following such an event echo the relative values of the HGWP calculated from steady state figures. Referring to Appendix A of Fisher et al. (1989a), this is not surprising if the response function, g(t), is to represent greenhouse warming.

3. DEFINITIONS

In order to make the definition of HGWP consistent between models as well as a conservative estimate of relative effects, the following criteria have been selected:

1) Trace gas levels -- Changing the concentration of other trace gases will affect the calculated future equilibrium temperature rise from gases under evaluation here for two reasons. First if there is overlap of absorption spectra, certain bands have less effect. Secondly, chemistry and therefore lifetime can be

affected by perturbation of these chemicals. Current levels of CO_2, CH_4, N_2O, O_3 and stratospheric H_2O were used in model calculations. Sensitivity of this assumption will be tested in a following section.

2) Gas perturbation levels -- Atmospheric concentrations of the test gases were chosen to yield model responses large enough to avoid the ''noise levels'' of the numerical models and still be in a linear response region.

3) Reference gas -- CFC-11 has been chosen as the reference compound for HGWP calculations in order to have a reference material consistent for both HGWP and ODP.

4) Specific Surface Temperature Change -- We define the calculated surface temperature increase for a one part per billion surface increase of any gas to be specific surface temperature change, or symbolically dT_S.

The HGWP definition resembles the ODP definition. Thus for any gas, the general definition is:

$$\text{HGWP} = \frac{\text{Calculated IR forcing due to Compound X/ Emission rate (steady state) of Compound X}}{\text{Calculated IR forcing due to CFC-11/ Emission rate (steady state) of CFC-11}}$$

Note: IR forcing is the net change in IR flux at the tropopause.

Since radiative convective models calculate a surface temperature change approximately proportional to the IR forcing level (to be examined below) and since lifetimes are proportional to the ratio of atmospheric abundance to (moleculear weight * emission rate), an equivalent form of this definition is:

$$\text{HGWP} = \frac{[\text{dTs(x)} * \text{Lifetime(x)/Molecular weight(x)}]}{[\text{dTs(CFC11)} * \text{Lifetime(CFC11)/Molecular weight(CFC11)}]}$$

Note also, many of the gases have the potential of affecting heating rates indirectly as well since they can chemically influence the distribution of ozone which would affect both the solar and the long wave heating rates. An examination of model results indicates that this is a second order effect, at least two orders of magnitude below the IR effect and well below the sensitivity of these calculations (Wang et al. private communication, 1989).

4. MODEL CALCULATIONS

The primary input to these radiative calculations are the altitudinal steady-state concentration profiles using appropriate chemistry models.

Once the concentration profile is determined, the effect of each gas is calculated using a Radiative Convective model. These models utilize infrared absorption spectra to quantify a gas's ability to absorb IR

Table 2 Total Band Strengths of Halocarbons

Species	Rogers & Stephens (1988)	Varanasi & Chudamani (1988)	Kagann et al. (1983)	Gehring (1987)	Magid + (1988)
CFC-11		2389	2566		2389*
CFC-12		3267	3364	3310	3240*
CFC-113	4822	3507		3126	3401*
CFC-114	5935	3937			4141*
CFC-115					4678*
HCFC-22				2399	2554*
HCFC-123				2552	2859*
HCFC-124				4043*	
HFC-125				3908*	
HFC-134a				3169	3272*
HCFC-141b				1732	1912*
HCFC-142b				2474	2577*
HFC-143a				3401*	
HFC-152a					1648*
CCl_4				1195*	
CH_3CCl_3				1184	1209*

* Infrared data used in model calculations

\+ The IR data from Magid (1988) were given with spectral resolutions of 0.5 to 0.25 cm^{-1}. The integrated band strengths are given here so that they can be compared to other data.

energy and thereby impact the earth's heat balance. Equilibrium temperature profiles are calculated such that the solar heating is balanced by the infrared cooling at all altitudes through the atmosphere. The calculation accounts for the amount of energy absorbed by each IR gas (the band strength) at specified wavelengths (the band location) including spectral overlap with other IR gases. Quantitative infrared data for this input are available from literature sources for the CFCs (Kagann et al. 1983; Varanasi and Chudamani, 1988; and Rogers and Stephens, 1988) and measurements for the HCFCs and the HFCs were obtained from industry laboratories (Magid 1988, and Gehring 1987).

Total band strengths available for these calculations as shown in Table 2 are within about 10% with the exception of Rogers and Stephens (1988). The band strengths used for the model calculations are marked with an asterisk. Since there appear to be systematic differences between laboratories for band strength measurements, the values from a common data base [Magid (1988)] were used since it covered most of the compounds of interest in this study. For compounds not available from this source, data from Gehring (1987) was used.

Table 3 Absorbance Bands Used in Study
(1/atm*cm*cm) @STP

BIN MIN	BIN MAX	CFC-11	CFC-12	CFC-113	CFC-114	CFC-115	HCFC-22	HCFC-123	HCFC-124	HFC-125	HFC-134a	HCFC-141b	HCFC-142b	HCFC-143a	HFC-152a	CC14	CH3-CC13
0.000	220.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
220.00	440.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
440.00	500.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500.000	555.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	49.6	30.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
555.000	616.256	0.0	0.0	0.0	23.9	0.0	0.0	0.0	21.3	61.0	0.0	82.2	0.0	65.1	0.0	0.0	0.0
616.256	618.030	0.0	0.0	0.0	3.8	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	3.4	0.0	0.8	0.0
618.030	647.085	0.0	0.0	14.7	17.1	20.9	0.0	0.0	0.0	6.2	10.8	0.0	0.0	18.6	0.0	9.3	0.0
647.085	648.825	0.0	0.0	1.2	0.0	8.1	0.0	0.0	0.0	0.3	2.0	0.0	0.0	0.0	0.0	0.3	0.0
648.825	667.370	0.0	19.8	19.1	0.0	21.8	0.0	27.6	11.2	2.5	64.9	0.0	17.2	0.0	0.0	0.0	0.0
667.370	669.250	0.0	3.0	0.0	3.0	1.3	0.0	6.9	0.6	0.0	9.2	0.0	6.6	0.0	0.0	0.0	0.0
669.250	718.550	0.0	23.3	0.0	14.2	0.0	0.0	77.5	137.4	24.5	52.2	0.0	160.6	0.0	0.0	0.0	172.1
718.550	720.800	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.4	0.0	0.0	0.0	0.0	0.0	0.0	73.2
720.800	775.000	0.0	0.0	0.0	0.0	107.4	0.0	43.8	0.0	79.0	0.0	542.1	0.0	0.0	0.0	260.0	488.5
775.000	862.000	1675.0	21.8	722.4	578.6	0.0	566.3	449.6	200.5	46.8	69.6	33.3	0.0	16.5	17.1	910.0	24.8
862.000	924.000	32.0	962.0	706.1	394.0	0.0	0.0	83.8	294.9	120.3	14.4	97.7	406.2	13.2	65.6	11.5	0.0
924.000	928.000	7.4	144.5	32.3	66.7	0.0	0.0	0.0	0.0	0.7	0.0	45.2	2.9	1.4	16.0	1.1	0.0
928.000	934.000	15.0	228.0	30.7	64.2	0.0	0.0	0.0	0.0	1.1	0.0	54.3	0.0	2.4	28.2	1.7	0.0
934.000	1004.000	34.6	67.2	36.9	57.4	923.3	0.0	0.0	0.0	0.0	220.8	70.3	203.0	423.4	178.7	0.0	0.0
1004.000	1036.000	0.0	0.0	71.2	19.3	51.7	0.0	0.0	0.0	0.0	11.8	9.0	5.7	10.4	7.6	0.0	9.4
1036.000	1042.000	1.9	0.0	90.7	53.2	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	1.2	0.0	2.9
1042.000	1048.000	2.8	0.0	105.6	129.9	0.0	0.0	0.0	0.0	0.0	3.8	0.0	0.0	0.0	1.3	0.0	0.0
1048.000	1060.000	17.3	0.0	156.9	352.1	0.0	0.0	0.0	0.0	0.0	14.4	3.3	0.0	0.0	3.6	0.0	6.6
1060.000	1065.000	27.5	2.3	21.0	57.2	0.0	0.0	0.0	1.5	0.0	9.2	2.1	0.0	0.0	0.0	0.0	9.1
1065.000	1071.000	71.1	5.3	8.5	11.4	0.0	1.4	0.0	2.2	1.9	13.7	3.6	0.0	0.0	0.0	0.0	18.8
1071.000	1190.000	504.6	1763.00	1023.0	1539.0	1178.0	1661.0	926.1	1393.0	1106.0	1118.0	890.3	916.8	96.3	1026.0	0.0	371.3
1190.000	1225.000	0.0	0.0	329.0	551.5	202.5	11.3	514.0	791.5	1653.0	533.9	6.2	636.0	473.9	6.6	0.0	0.0
1225.000	1250.000	0.0	0.0	13.3	13.5	1702.0	0.0	101.4	257.0	370.2	30.0	0.0	128.6	1317.0	5.7	0.0	0.0
1250.000	1301.000	0.0	0.0	0.0	172.4	204.6	45.9	619.8	423.6	236.3	693.8	0.0	0.0	551.6	12.3	0.0	0.0
1301.000	1307.000	0.0	0.0	0.0	0.0	5.6	32.8	9.7	126.8	155.8	170.9	0.0	0.0	14.9	0.0	0.0	0.0
1307.000	1397.000	0.0	0.0	19.1	18.7	251.0	236.6	0.0	283.2	0.0	194.7	60.2	94.1	68.6	148.6	0.0	32.0
1397.000	1420.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.6	0.0	32.4	12.9	0.0	154.9	128.9	0.0	0.0
1420.000	1535.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	169.9	0.0	0.0	0.0
1535.000	1590.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1590.000	1640.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1640.000	1717.500	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1717.500	1845.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1845.000	1972.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1972.500	2100.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2100.000	2450.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Both these data sets were measured at room temperature. Since temperature dependent data sets are not yet available, band strengths used in the study were assumed constant through the atmosphere. This assumption will need to be checked once temperature dependent measurements become available.

Individual band strengths and band locations are important in these calculations. Table 3 details the locations and strengths for the absorption spectra used in this work broken down into the bin structure of the Du Pont radiative-convective model. The greatest amount of absorption for many species occurs at wave lengths between 1070 and 1400 cm^{-1}. Absorption by methane and N_2O in the background atmosphere occurs in this region of the spectrum. Some species (e.g. CFC-113 and CFC-114) show significant absorption in the 934 to 1070 cm^{-1} region and therefore overlaps the IR absorption bands of ozone.

Tables 4 and 5 detail preliminary steps of the calculations for HGWP. Table 4 shows the net IR radiative flux at the tropopause (@12 km) for tropospheric concentrations of 1ppbv as calculated by each model. Note that each of the model's calculations were based on different cloud assumptions (Du Pont used fixed 50% grey (albedo = 0.5) cloud cover while AER was based on a non-grey cloud with 48.5% cover). Table 5 shows the resulting values for Specific Surface Temperature Increases for each of the compounds. Each group's results correlate to each chemical's total band strengths, with compensation made by the

Table 4 Net IR Radiative Flux at the Tropopause
(at 12 km and 1 ppbv tropospheric mixing ratio)

Species	AER	Du Pont
CFC-11	0.175	0.133
CFC-12	0.248	0.158
CFC-113	0.223	0.163
CFC-114	0.258	0.181
CFC-115	0.204	0.164
HCFC-22	0.151	0.107
HCFC-123	0.140	0.092
HCFC-124	0.153	0.108
HFC-125	0.189	0.119
HFC-134a	0.135	0.095
HCFC-141b	0.109	0.076
HCFC-142b	0.144	0.101
HFC-143a	0.111	0.087
HFC-152a	0.092	0.059
CCl_4	0.080	0.063
CH_3CCl_3	0.038	0.033
[2 x CO_2]	4.41	3.87

Table 5 Specific Surface Temperature Increases
(warming resulting from 1 ppbv of each gas)

Species	Modeled Warming ($^oK/ppbv$)		Normalized Warming # ($^oK/ppbv$)		Lambda value, λ ($^oK/ppbv/Wm\text{-}2$)	
	AER	Du Pont	AER	Du Pont	AER	Du Pont
CFC-11	0.135	0.084	0.088	0.102	0.771	0.632
CFC-12	0.202	0.102	0.131	0.124	0.815	0.647
CFC-113	0.174	0.103	0.113	0.125	0.780	0.632
CFC-114	0.208	0.115	0.135	0.139	0.806	0.635
CFC-115	0.170	0.107	0.110	0.130	0.833	0.652
HCFC-22	0.124	0.070	0.081	0.084	0.821	0.650
HCFC-123	0.111	0.059	0.071	0.072	0.793	0.644
HCFC-124	0.126	0.070	0.082	0.084	0.824	0.645
HFC-125	0.160	0.078	0.104	0.094	0.847	0.654
HFC-134a	0.114	0.061	0.074	0.074	0.844	0.647
HCFC-141b	0.086	0.048	0.056	0.059	0.789	0.637
HCFC-142b	0.120	0.066	0.078	0.080	0.833	0.651
HFC-143a	0.092	0.054	0.060	0.066	0.829	0.625
HFC-152a	0.076	0.038	0.049	0.046	0.826	0.649
CCl_4	0.062	0.040	0.040	0.048	0.775	0.628
CH_3CCl_3	0.027	0.020	0.018	0.025	0.710	0.618

\# Normalized by : $dTs *2\ ^oK/(dT_S$ for 2X $CO_2)$
where dT_S for 2X CO_2 is 3.08 ^oK using AER model
1.651 ^oK using Du Pont model

radiative convective models for overlapping absorption by other IR active gases and for profile differences due to chemical reactivity. The inter-model differences are consistent with previously reported pattern (Owens et al., 1985) due primarily to different treatments of tropospheric feedbacks.

One can account for effects of the various feedback assumptions by normalizing the surface warming by the calculated surface warming from a doubling of carbon dioxide and a common warming of 2°C. The normalized results, shown in the middle two columns of Table 5, indicate good agreement between the two model results. All results are credible to 2 significant figures at best.

Also included on Table 5 are tabulations of the climate feedback factor, l, which is the ratio of the model calculated surface temperature change to the perturbation in the net radiative forcing. As seen from the table, these values are consistent for each of the models thereby validating the assumptions made for equivalency of the two forms of the HGWP definition.

One generalization at this point is drawn from this set of data. Whereas the total infrared band strengths

Table 6 Halocarbon Global Warming Potentials Based on Modeled Lifetimes

Species	HGWP rel. to CFC11	
	AER	Du Pont
CFC-11	1.0	1.0
CFC-12	3.5	2.9
CFC-113	1.5	1.4
CFC-114	5.4	4.5
CFC-115	13.	8.2
HCFC-22	0.49	0.29
HCFC-123	0.026	0.015
HCFC-124	0.14	0.080
HFC-125	0.84	0.42
HFC-134a	0.39	0.22
HCFC-141b	0.12	0.073
HCFC-142b	0.51	0.29
HFC-143a	0.97	0.63
HFC-152a	0.045	0.024
CCl_4	0.36	0.36
CH_3CCl_3	0.026	0.022

are on the average comparable among the species, both the net IR flux and the specific surface warming values for HCFCs and HFCs on average are lower than values for CFCs by 40%. This lower value results from the fact that most hydrogenated halocarbons have bands that overlap the bands of both CH_4 and N_2O as well as water vapor unlike CFC-11 and CFC-12.

Because the total infrared band strengths for halocarbons are of the same order of magnitude (within a factor of 3x) and generally share the same amount of overlap with other radiatively active gases, the dT_S values have a similar range. However, once atmospheric lifetime factors are utilized to calculate HGWP values, the spread among chemicals is much more pronounced. Table 6 shows each modeling group's HGWP results with a range among chemicals of about 400X. Between modeling groups, the tropospheric sensitivity factor is removed since we are normalizing results to CFC11, yet substantial differences persist. Most of these differences are due to differences in modeled lifetimes. As previously reported in Fisher et al. (1989a), calculated lifetimes are only in fair agreement between models.

Since lifetime has a dominant factor on calculated HGWP, basing the HGWP values on a common reference set of lifetimes seems appropriate. Table 7 shows the results of such a rescaling. The reference lifetimes for CFCs are based on the estimates used in model calculations done for the WMO 1989 report. Reference lifetimes for HCFCs and HFCs are from the analysis of Prather (1989). As seen in this table, normaliza-

Table 7 Halocarbon Global Warming Potentials Based on a Common Set of Reference Lifetimes

Species	Reference* Lifetimes (Yrs)	AER	DuPont
CFC-11	60.	1.0	1.0
CFC-12	120.	3.4	2.8
CFC-113	90.	1.4	1.4
CFC-114	200.	4.1	3.7
CFC-115	400.	7.5	7.6
HCFC-22	15.3	0.37	0.34
HCFC-123	1.6	0.020	0.017
HCFC-124	6.6	0.10	0.092
HFC-125	28.1	0.65	0.51
HFC-134a	15.5	0.29	0.25
HCFC-141b	7.8	0.097	0.087
HCFC-142b	19.1	0.39	0.34
HFC-143a	41.0	0.76	0.72
HFC-152a	1.7	0.033	0.026
CCl_4	50.	0.34	0.35
CH_3CCl_3	6.3	0.022	0.026

* Lifetimes for CFCs are based on estimated lifetimes used in scenario development in WMO, 1989. Lifetimes for HCFCs and HFCs are based on Prather, 1989.

tion in this fashion diminishes differences between the two model's results. Furthermore, the HGWP values for fully halogenated CFCs range from 1.0 to 7.5 whereas the HCFC and HFC values range from 0.02 to 0.7.

5. SENSITIVITY TO TRACE GAS LEVELS

Calculated HGWP vlaues have all been based on present day levels of trace gases of CO_2, CH_4, CO, and N_2O. Because the HGWP values are for consideration in future atmospheres as well as today's, we have examined the sensitivity of these parameters to changes in CO_2 and CH_4 to levels that might be achieved if current trends continue.

The trace gas changes and the resulting calculated changes in lifetimes, surface temperature rises, and HGWP values (from the AER model) are shown in Table 8. Calculated changes in surface temperature for tested CFCs and HCFCs were compared to a reference atmosphere including the assumed gas perturbation.

Table 8 Sensitivity Study
Variation in Trace Gase Levels and Impact on HGWP values (AER 1-D model)

	Atmosphere	CFC-11	CFC-12	HCFC-22	HCFC-123
Lifetime (yrs)	Present Day	60	125	20	2.1
	CH_4 (1.6 → 3.2 ppb)	60	126	23	2.5
	CO_2 (340 → 680 ppm)	61	128	20	2.1
dT_S (°C/ppb)	Present Day	0.14	0.20	0.12	0.11
	CH_4 (1.6 → 3.2 ppb)	0.14	0.20	0.12	0.11
	CO_2 (340 → 680 ppm)	0.12	0.17	0.12	0.11
HGWP	Present Day	1.0	3.5	0.49	0.026
	CH_4 (1.6 → 3.2 ppb)	1.0	3.5	0.56	0.031
	CO_2 (340 → 680 ppm)	1.0	3.4	0.49	0.027

(Species: CFC-11, CFC-12, HCFC-22, HCFC-123)

As seen in Table 8, trace gas changes have little effect on HGWP values. CO_2 has the greatest effect on CFC radiative forcing because the albedo feedback is weaker in the warmer atmosphere. As a result, the radiative forcing for CFCs -11 and -12 is weakened somewhat. Methane affects the chemical lifetimes of the HCFCs, resulting in slightly greater HGWP values for these compounds.

6. TIME DEPENDENCE OF RELATIVE GLOBAL WARMING

Since the HGWP parameter is based on steady state effects, it does not describe the relative time-dependent effects of constituents on warming. Even though the HGWP is an equivalent measure of the cumulative warming during its lifetime for each unit mass emitted, the transient response to a constant emission level is also of interest.

The calculated warmings for a number of halocarbons are shown in Figure 2. As seen, the calculated warming reaches an asymptote rapidly for the HCFCs, but requires longer periods to approach steady state for CFCs. These response patterns echo the respective patterns for increases in atmospheric abundances for each species, as seen in Figure 3.

Relative warmings are shown in Figure 4. For HCFCs, the relative effects are at a maximum at very short times. One can easily show (using L'Hospital's rule), that the initial relative value is the ratio of the value of the Specific Surface Temperature Increase (°C /ppb) / moleculear weight -- relative to the corresponding ratio for CFC-11. Thus the relative effects are on the order unity at times when the individual effects are small. However, as atmospheric concentrations build and chemistry differences affect

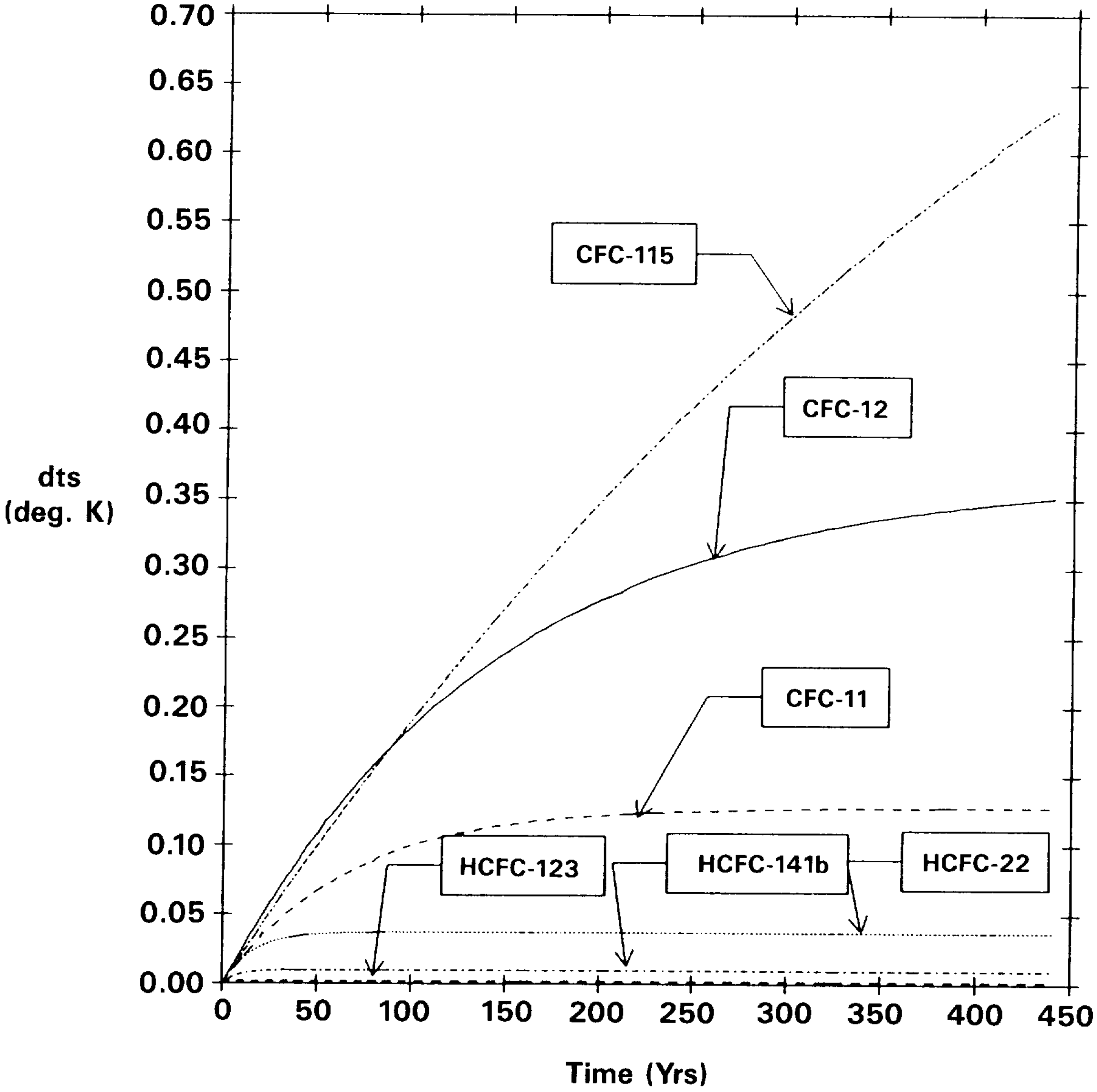


Figure 2. Change of Calculated Warming Following a Step Change of Emission of Specified Gas at 5 x10**8 kg/yr [Du Pont 1-D Model]

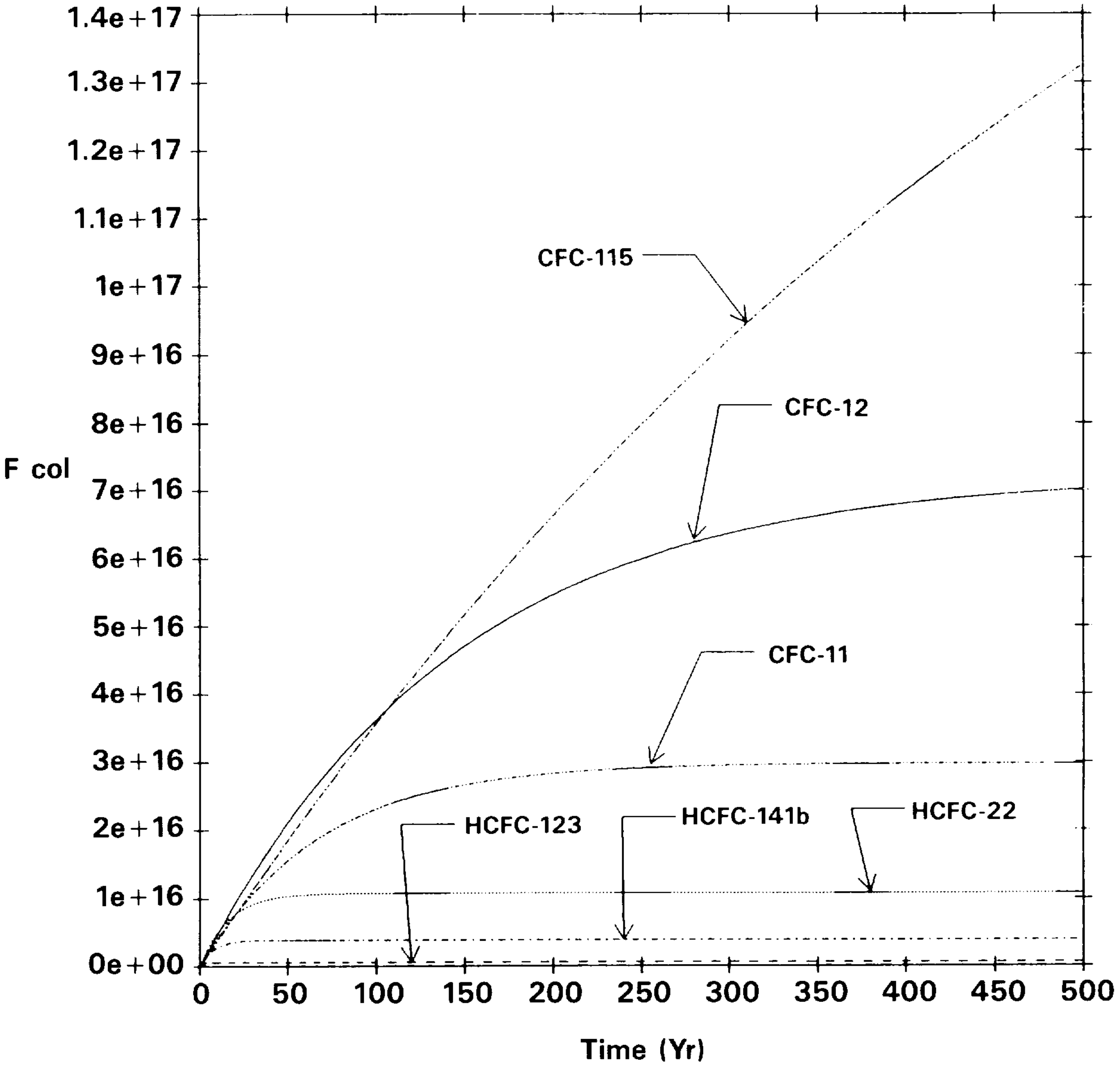


Figure 3. Column of (hydro) Chlorofluorocarbons Following Step Change of Emission of Specified Gas at 5.0 x 10**8 kg/yr. [Du Pont 1-D Model]

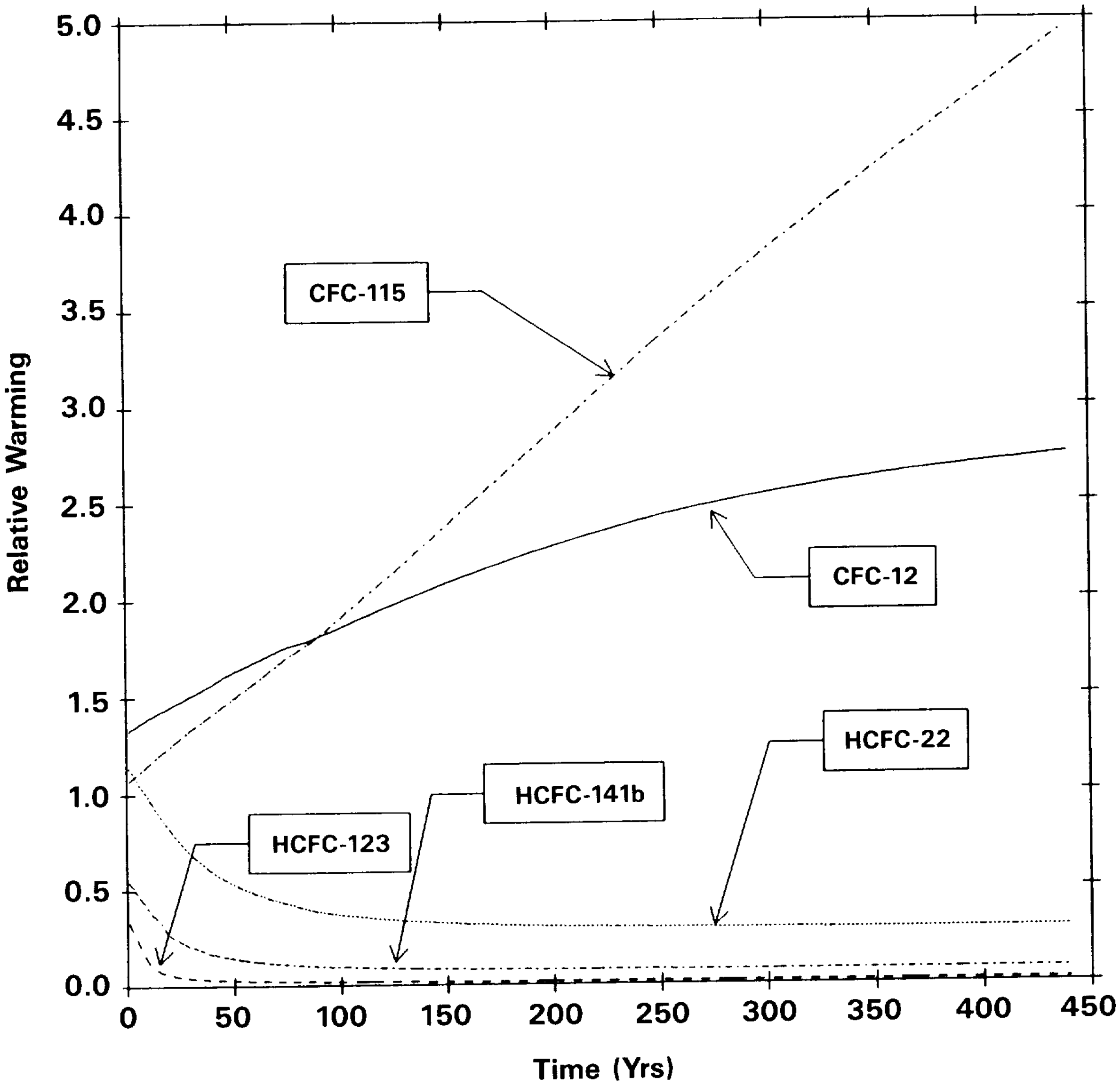


Figure 4. Calculated Relative Warming Following a Step Change of Emission of Specified Gas (CFC-11 Reference) [Du Pont 1-D Model]

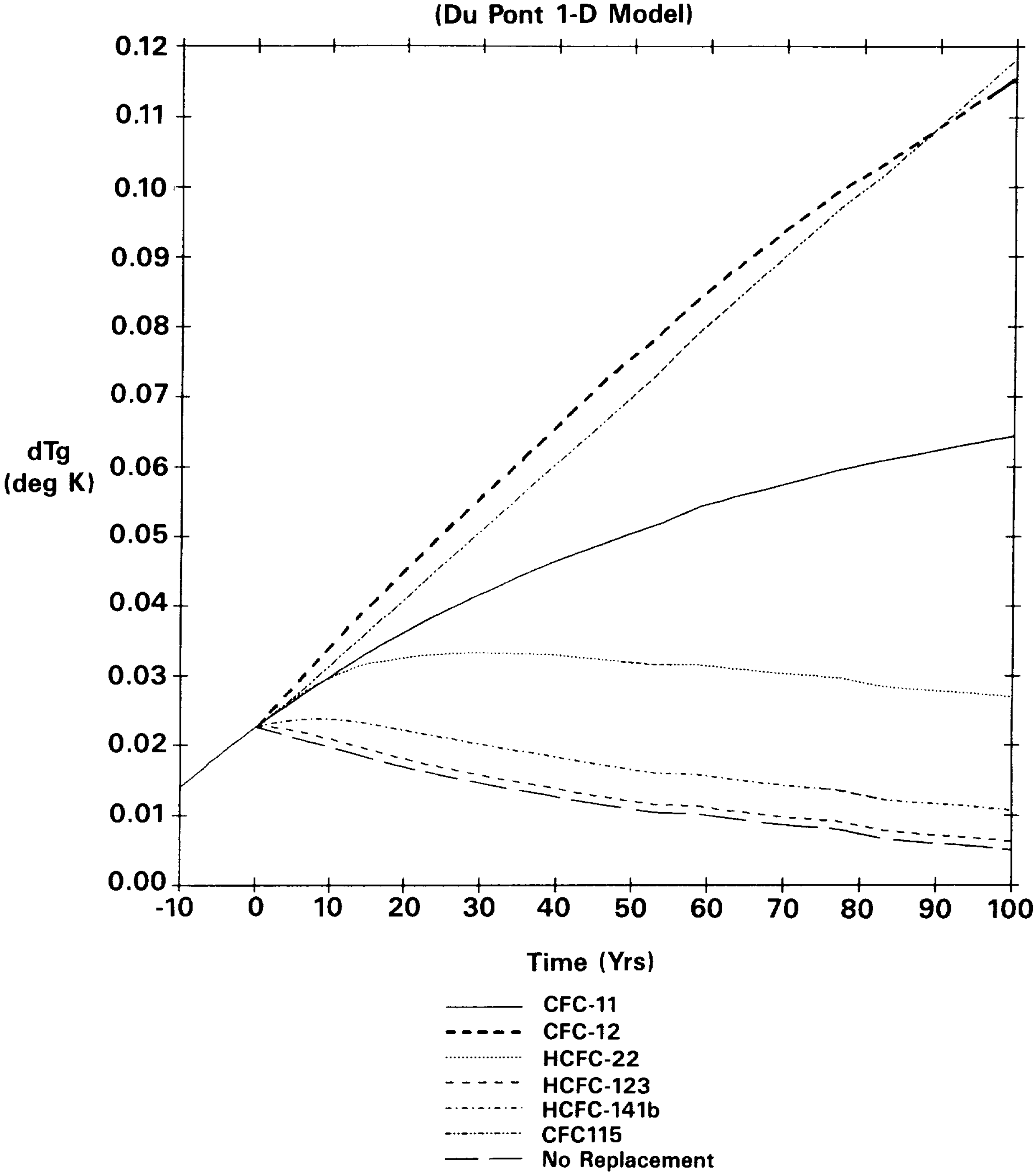


Figure 5. Transient Calculated Global Warming; lb/for/lb replacement of CFC-11 with various species at t = 0 and constant emission.

the relative amount in the atmosphere, the relative effects either grow or decrease depending on whether the lifetimes are longer or shorter than that of CFC-11. As seen in Figure 4, the HCFCs have lifetimes shorter than the lifetime of the reference gas and have relative effects that asymptotically approach the HGWP value with a time constant equal to the lifetime of CFC-11. Longer lived species have relative effects that grow with time asymtotically approaching their HGWP value with time constant of THEIR OWN lifetime.

Another perspective on the transient response is to consider the replacement of compounds and the resulting transitions in calculated warming. Figure 5 shows the results of a simple set of substitution scenarios performed using the Du Pont model. These calculations were meant to estimate the warming changes resulting from substitution of various gases for CFC-11 at time, t = 0. Current level and growth (in atmospheric concentrations) for CFC-11 were used, namely 260 pptv and 4.0%/yr. Emission levels were assumed constant. Compounds are substituted on an equal mass basis. Results for all HCFCs fall within the envelope bounded by the no replacement results and the results for continued emission of CFC-11 and show a negative trend in warming within a few years of substitution. Results for CFC-12 and CFC-115 on the other hand show continued positive slope exceeding the CFC-11 no-substitution case for all times.

UNCERTAINTIES

Uncertainties in the the effectiveness of gases to produce global warming fall into two general classes -- those that are generalized to the total greenhouse effect and those that are specific to the individual species considered here.

There are a number of problems that need to be resolved in the modeling of greenhouse warming. The radiative properties of the earth's surface such as changes in the surface and ice cover albedos, and changes in cloud cover and composition need to be quantified as a function of surface warming. Changes in the temperature structure of the atmosphere will affect the convective patterns and chemistry of the stratosphere. The coupling of oceans (as heat reservoirs) and ocean currents to surface temperature changes will also affect the timing and location of the warming. Research is being carried out worldwide to understand these questions which apply to ALL trace gases that affect the future radiative balance of the earth.

Uncertainties also exist regarding the CFCs, HCFCs, and HFCs and their influence on the radiative balance. The temperature dependence of the absorptances of individual species need to be resolved and parameterized for use in climate models. The chemical processes affecting both lifetimes and atmospheric profiles are also the subject of continuing research.

Resolution of questions related to the general greenhouse warming will directly affect the modeled timing and magnitude of global warming, whereas resolution of the radiative and chemical parameterizations for halocarbons will have a direct effect on the HGWP values for these species.

7. ACKNOWLEDGMENTS

The authors are grateful for the support received for this work from AFEAS , (Alternative Fluorocarbon Environmental Acceptability Study).

X. IMPACT ON PHOTOCHEMICAL OXIDANTS INCLUDING TROPOSPHERIC OZONE

An Assessment of Potential Impact of Alternative Fluorocarbons on Tropospheric Ozone

Hiromi Niki

Centre for Atmospheric Chemistry
Department of Chemistry
York University
4700 Keele Street, North York
Ontario, Canada M3J 1P3

EXECUTIVE SUMMARY

One type of tropospheric impact of the alternative halocarbons may arise from their possible contribution as precursors to the formation of O_3 and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants are addressed:

1. Is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release?
2. On a global basis, how would emissions of HCFCs and HFCs compare to natural sources of O_3 precursors?

Since almost all CFCs are emitted in urban environments, the first question deals primarily with urban "smog" formation. Salient features of chemical relationships between oxidants and their precursors as well as the relevant terminologies are described briefly in order to provide a framework for the discussion of these two issues.

Based on an analysis of the atmospheric concentrations of various O_3 precursors, and their atmospheric reactivity and O_3 forming potential, the maximum projected contributions of the alternative fluorocarbons to O_3 production in both urban and global atmospheres have been derived as follows:

1: Urban Atmosphere (values in parenthesis in units of $10^{-3}\%$ of the total contribution of all O_3 precursors):

HFCs: CH_3CHF_2-152a (59), CH_2FCF_3-134a (8), CHF_2CF_3-125 (4)

HCFCs: $CHClF_2$-22 (8), CH_3CClF_2-142b (6), CH_3CHClF-124 (16),

CH_3CCl_2F-141b (13), $CHClCF_3$-123 (59)

2: Global Atmosphere (values in parenthesis in units of $10^{-3}\%$ of the total contribution of all O_3 precursors):

HFCs: CH_3CHF_2-152a (92), CH_2FCF_3-134a (11), CHF_2CF_3-125 (7)

HCFCs: $CHClF_2$-22 (11), CH_3CClF_2-142b (10), CH_3CHClF-124 (25),

CH_3CCl_2F-141b (20), $CHClCF_3$-123 (92)

N92-15448

ASSESSMENT OF POTENTIAL IMPACT OF ALTERNATIVE FLUOROCARBONS ON TROPOSPHERIC OZONE

Hiromi Niki

Centre for Atmospheric Chemistry
Department of Chemistry
York University
4700 Keele St., North York
Ontario, Canada M3J 1P3

C-5

1. INTRODUCTION

While the chlorofluorocarbons (CFCs) such as CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) are chemically inert in the troposphere, the hydrogen-containing halocarbons being considered as their replacements can, to a large extent, be removed in the troposphere by the HO radical. These alternative halocarbons include the hydrochlorofluorocarbons (HCFCs) 123 (CF_3CHCl_2), 141b ($CFCl_2CH_3$), 142b (CF_2ClCH_3), 22 (CHF_2Cl) and 124 (CF_3CHFCl) and the hydrofluorocarbons (HCFs) 134a (CF_3CH_2F), 152a (CHF_2CH_3) and 125 (CF_3CHF_2). Listed in Table 1 are the rate constants (k) for the HO radical reaction of these compounds [Hampson, Kurylo and Sander, 1989] and their estimated chemical lifetimes in the troposphere [Prather, 1989; Derwent and Volz-Thomas, 1989]. In this table, values of the lifetimes of these selected HCFCs and HCFs are seen to vary by more than a factor of more than ten ranging from 1.6 years for HFC 152a and HCFC 125 to as long as 28 years for HFC 125. Clearly, from the standpoint of avoiding or minimizing impact on stratospheric O_3, those halocarbons with short tropospheric lifetimes are the desirable alternates. However, potential environmental consequences of their degradation in the troposphere should be assessed and taken into account in the selection process.

One type of tropospheric impact of the alternative halocarbons may arise from their possible contribution as precursors to the formation of O_3 and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants will addressed:

1. Is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release?
2. On a global basis, how would emissions of HCFCs and HFCs compare to natural sources of O_3 precursors?

Since almost all CFCs are emitted in urban environments, the first question deals primarily with urban "smog" formation. In the following section, salient features of chemical relationships between oxidants and their precursors as well as the relevant terminologies will be described briefly first in order to provide a framework for the subsequent discussion of these two issues. It should be mentioned that the present report deals only with possible direct chemical effects and not with indirect climate-chemical interactions [cf. Wang 1986; Ramanathan et al. 1987; Wuebbles et al. 1989]. Namely, the alternative halocarbons and/or their degradation products may act as "green-house" gases and alter the global tropospheric O_3 distribution via changes in climate and emission rates of natural precursors of O_3. The latter topic is discussed elsewhere in the AFEAS report.

2. BACKGROUND

2.1. Photochemical Oxidants

The present assessment deals specifically with issues concerning O_3 rather than "oxidants" in general. The term "oxidant" is often used loosely and deserves clarification. Very often, it refers implicitly to O_3, the most abundant oxidant in the troposphere. However, there are many other trace atmospheric gases which are also known as "oxidants," e.g. hydrogen peroxide (H_2O_2), peroxyacetyl nitrate (PAN), and formic acid (HCOOH). As already discussed elsewhere in the AFEAS report [cf. "Degradation Products

PRECEDING PAGE BLANK NOT FILMED

Table 1 Rate Constants for the HO Reaction of Alternative Fluorocarbons

Compound		A-Factor x 10^{-12}	E/R	k(298 K)[(a)] x 10^{-15}	Lifetime[(d)] (yr)
HFCs[(b)]					
CH_3CHF_2	152a	1.20	1100 ± 200	37.0	1.7
CH_2FCF_3	134a	1.70	1750 ± 300	4.8	13.2
CHF_2CF_3	125	0.38	1500 ± 500	2.5	25.4
HCFCs[(b)]					
$CHClF_2$	22	1.20	1650 ± 150	4.7	3.5
CH_3CClF_3	142b	0.96	1600 ± 150	3.8	16.7
CH_3CHClF	124	0.66	1205 ± 300	10.0	6.3
CH_3CCl_2F	141b	0.27	1050 ± 300	8.0	7.9
$CHCl_2CF_3$	123	0.64	850 ± 150	34.0	1.7
Other[(c)]					
CO		0.15 $(1 + 0.6\ P_{atm})$	0 ± 300	150.0 $(1 + 0.6\ P_{atm})$	0.3
CH_4		2.30	1700 ± 200	7.7	8.2
C_2H_6		11.00	1100 ± 200	280.0	0.2
CH_3CCl_3		5.00	1800 ± 200	12.0	5.3

(a) k in cm^3 $molecule^{-1}$ s^{-1}

(b) Taken from Hampson, Kurylo and Sander (AFEAS Report, 1989)

(c) Taken from NASA Kinetic Data (1987)

(d) Lifetime = 1/k[HO]; k at 298 K; [HO] taken to be 5×10^5 molecule cm^{-3} (Crutzen and Gidel, 1983; Volz et al., 1981) of Alternative Fluorocarbons in the Troposphere''], the alternative halocarbons can lead to the formation of a variety of products which can be considered as ''oxidants.'' Some of the halogen/carbon-containing oxidants derived from the alternative halocarbons may play important roles in atmospheric environments and their potential tropospheric impact must be assessed.

Broadly speaking, the term ''oxidant'' simply refers to the oxidizing ability of a reagent, i.e. to remove electrons from, or to share electrons with, other molecules or ions [Finlayson-Pitts and Pitts, 1986]. The ability of a chemical species to oxidize or reduce other chemical species is termed its ''redox potential'' and is expressed in volts. For example, O_3 has a standard potential of +2.07 volts in the redox pair of O_3/H_2O, and hydrogen peroxide +1.776 volts in the redox pair, H_2O_2/H_2O [Weast, 1977]. Historically, the term ''oxidant'' has been defined by a wet chemical technique; that is, an oxidant is any species giving a positive response in the KI method. The basis of this method is the oxidation of the colorless iodide ion in solution to form brown I_2:

$$2H^+ + 2I^- + O_3 \rightarrow I_2 + O_2 + H_2O$$

This technique of measuring and reporting total oxidants was used almost exclusively until the mid-1970s. In addition, the U.S. Federal Air Quality Standard was written in terms of ''total oxidant'' (0.08 ppm oxidant for 1 h) rather than O_3 specifically. A variety of air pollutants give a positive response, but some interfere negatively. Namely, ''total oxidants'' will include a weighted combination of various pollutants such as O_3, NO_2, and PAN, but SO_2 gives a 100% negative response and must therefore be removed with the use of a scrubber, e.g. Cr_2O_3, from the gas stream prior to analysis.

The recognition of the problems with the wet chemical KI technique and the simultaneous development of physical techniques for monitoring the major oxidant O_3 specifically, led to a change in the Federal Air Quality Standard from oxidant to O_3; simultaneously the standard was relaxed to higher concentrations, 0.12 ppm O_3 for 1 hr. Today, the UV method is most commonly used to monitor O_3 in ambient air, and is accepted as an ''equivalent method'' by the EPA [Finlayson-Pitts and Pitts 1986]. In any case, the term ''photochemical oxidant'' must be defined in a species-specific manner depending upon the particular context.

2.2 Ozone Precursors

Within the context of the present assessment, the term ''ozone precursor'' can be equated with carbon monoxide and various volatile organic compounds, particularly hydrocarbons, for reasons stated briefly below. Namely, it is now well-established that significant in-situ photochemical production and destruction of O_3 takes place on urban, regional and global scales [WMO 1985; Logan 1985; Finlayson-Pitts and Pitts 1986; Crutzen 1988]. Tropospheric O_3 production occurs via carbon monoxide and hydrocarbon oxidation, with NO_x (= NO + NO_2) acting as a catalyst. A large number of molecular and free radical species participate interactively in these chemical processes. The overall reaction mechanism can be represented as:

$$HC + NO_x + h\nu \rightarrow O_3 + \text{other products} \qquad (1)$$

where HC denotes various reactive carbon-containing compounds, particularly hydrocarbons, and $h\nu$ is solar radiation reaching the earth's surface in the wavelength region from 280 to 430 nm. Tropospheric production of O_3 is due entirely to the photodissociation of NO_2 at these wavelengths into NO and O followed by the recombination of O with O_2:

$$NO_2 + h\nu(\leq 430\text{ nm}) \rightarrow NO + O \qquad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (3)$$

where M is any third body, such as O_2 and N_2, that removes the energy of the reaction and stabilizes O_3. Thus, strictly speaking, O atoms are the primary precursor of O_3. NO_2 can act as both the source and sink for O_3, since NO produced in reaction 2 removes O_3 and regenerates NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4)$$

Reactions 2-4 alone do not provide a net production of O_3 but are largely responsible for controlling the formation and destruction of O_3, thus establishing a steady O_3 concentration governed by the so-called photostationary state relation,

$$[O_3] = J[NO_2]/k[NO] \qquad (5)$$

where k is the rate constant for reaction 4 and $J[NO_2]$ is the NO_2 photodissociation rate.

According to the above relationship among O_3, NO and NO_2, photochemical production of O_3 can be attributed to the occurrence of reactions which reduce NO by oxidizing it to NO_2 without removing O_3. Such oxidation paths are provided by peroxy radicals (RO_2; R = H atom or organic group) which are, in turn, produced primarily in the HO-radical initiated oxidation of various hydrocarbons and their degradation products (e.g. CO and organic carbonyl compounds derived from RO radicals).

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6)$$

One of the principal sources of HO radicals is the photolysis of O_3 in the presence of H_2O:

$$O_3 + h\nu(\leq 310\text{ nm}) \rightarrow O(^1D) + O_2 \qquad (7)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (8)$$

Namely, O_3 can serve as its own precursor in the HO-radical initiated oxidation of hydrocarbons via reaction 6. Note also that reaction 6 can regenerate HO radicals via reaction 6 for R = H atom, thereby providing a chain reaction. To illustrate this in its simplest form, the conversion of NO to NO_2 and the formation of O_3 can take place in the HO radical initiated chain oxidation of CO:

$$HO + CO \rightarrow CO_2 + H \qquad (9)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (10)$$

$$HO_2 + NO \rightarrow HO + NO_2 \qquad (11)$$

$$NO_2 + h\nu(\leq 430\text{ nm}) \rightarrow NO + O \qquad (2)$$

$$\underline{O + O_2 + M \rightarrow O_3 + M} \qquad (3)$$

$$\text{Net: } CO + 2O_2 \rightarrow CO_2 + O_3 \qquad (12)$$

In these reactions, NO_x and odd hydrogen ($HO + HO_2$) are not consumed directly and thus act as catalysts in the production of O_3. The overall reaction (1) for the formation of O_3 involves a much larger number of mutually interactive free radicals and molecular species than those encountered in CO oxidation. In the present assessment of the potential impact of the alternative halocarbons on tropospheric O_3, "O_3 precursors" can be appropriately defined as reactive HCs and CO, since the atmospheric role of the alternative halocarbons in O_3 production is chemically analogous to that of HCs and CO in that their HO radical initiated oxidation produces RO_2 radicals capable of converting NO to NO_2.

2.3. Ozone Forming Potential

A prerequisite to the assessment of the contribution of the alternative halocarbons to tropospheric O_3 is a quantitative knowledge of the relationship between photochemical O_3 production and the concentrations of its precursors, i.e. HCs and NO_x. This issue has been addressed extensively using detailed model calculations, and its key features will be described briefly below. Notably, the O_3 forming potential defined in terms of O_3 production for each HC molecule consumed is known to be nonlinearly dependent on the absolute and relative concentrations of NO_x and HCs, and on the HC composition. In certain circumstances O_3 production even decreases with increasing concentrations of the precursors.

This nonlinear phenomenon can be readily discerned in the O_3 isopleths calculated for urban atmospheres using so-called the EKMA technique (Empirical Kinetic Modeling Approach) which is used in formulating control strategies [Dodge 1977a,b; Dimitriades and Dodge 1983] (cf. Fig.1a). The series of O_3 isopleths shown in this figure correspond to daily maximum hourly average O_3 concentrations produced in mixtures with various initial HC and NO_x concentrations. Among various assumptions made in deriving the results shown in Fig. 1a, the total non-methane hydrocarbons (NMHC) are taken to be a lumped parameter mixture [Hogo and Gery, 1988]. Although a single plot such as that in figure 1a is an oversimplification of urban chemistry and meteorological conditions, it clearly illustrates the highly nonlinear dependence of O_3 on the initial NMHC and NO_x concentrations and their ratio. Model calculations of O_3 isopleths corresponding to rural and regional atmospheres are shown in Fig. 1b for comparison [Liu et al. 1987; Lin, Trainer and Liu 1988].

In the global atmosphere, the oxidation of CO and hydrocarbons leads to the production of O_3 when sufficient NO is present [Crutzen, 1988]. In fact, at very low NO_x concentrations, these carbon-containing compounds can serve as a sink for O_3. For instance, CO oxidation can proceed via

$$CO + HO \rightarrow CO_2 + H \tag{9}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{10}$$

$$\underline{HO_2 + O_3 \rightarrow HO + 2O_2} \tag{13}$$

$$\text{Net: } CO + O_3 \rightarrow CO_2 + O_2 \tag{14}$$

rather than via the O_3 forming channel for CO oxidation in the presence of NO, i.e. reactions 9, 10, 11, 2, and 3, as discussed earlier. Namely, HO_2 radicals can react with either NO or O_3 leading to either O_3 production or destruction, respectively, depending on the concentration ratio $[NO]/[O_3]$. Since the rate

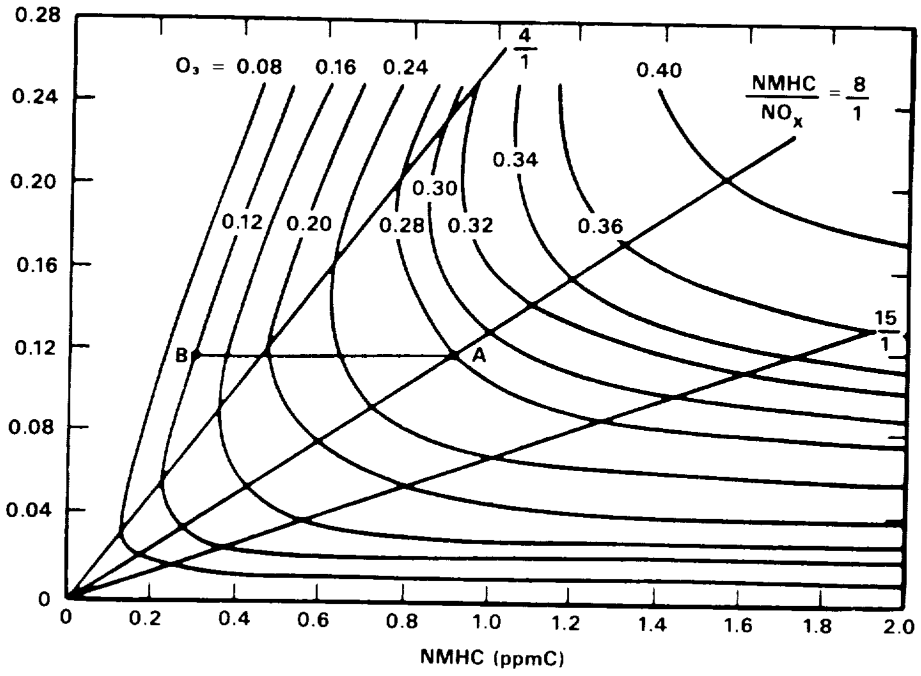


Figure 1a: Ozone Isopletes used in EKMA Approach (from Dodge, 1977a)

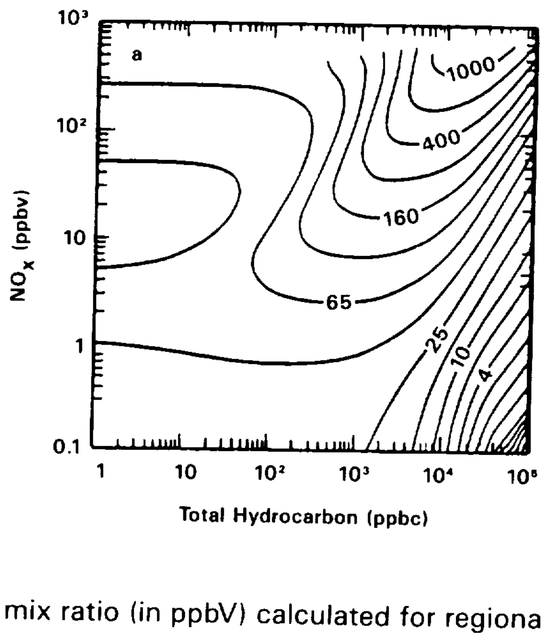


Figure 1b: Isoplete of O_3 mix ratio (in ppbV) calculated for regional atmospheres by Lin et al., (1988).

constant ratio $k_6/k_{13} \simeq$) 4000, the transition from O_3 destruction to production occurs at $[NO]/[O_3]$ = 1/4000, typically corresponding to [NO] $\simeq$ 5-10 ppt. Values of [NO] at this level or even below are known to occur in the lower atmosphere in remote marine environment [McFarland et al., 1979; Davis et al., 1987; Ridley et al., 1987]. Model calculations suggest that in NO-rich environments two O_3 molecules can be produced for each carbon atom in any NMHC [Liu et al., 1987]. According to the tropospheric O_3 budget analysis by Crutzen [1988], at most only 10% of the O_3 forming potential of HCs is actually realized at the present time, due to insufficient NO_x in the background troposphere.

3. CONTRIBUTION OF THE HFCs AND HCFCs TO THE PRODUCTION OF PHOTOCHEMICAL OXIDANTS IN THE VICINITY OF RELEASE

3.1. Approach

The major technological uses of the alternative halocarbons mean that almost all of their release will occur in urban surroundings [WMO 1985]. Thus, the O_3 forming potential of the alternative fluorocarbons in urban atmospheres will be assessed specifically in this section. In order to address this issue properly, the crucial observational data that will be required are:

1. How much HFCs or HCFCs will be present in a typical urban atmosphere?
2. How much HCs are currently present in a typical urban atmosphere, and what is the representative composition of urban HCs?
3. What is the O_3 forming potential of the alternative fluorocarbons as compared with that of urban HCs?

Each question is dealt with separately in the following sub-sections. Note that a plausible approach to answering Question #1 is to use the available data on urban concentrations of CFC-11 and CFC-12, since calculation of the actual absolute emission strength and the resulting ambient concentration for a particular source region is a difficult task for any atmospheric species.

3.2. Urban Chlorofluorocarbons

There are a number of recent measurements of urban concentrations of CFC-11 and CFC-12 together with those of other atmospherically important trace gases. For instance, summarized in Table 2a are the measured concentrations of CH_4 and CFC-11 reported by Blake et al. [1984] for 22 urban samples collected over a four year period from many different geographical locations. Approximate background concentrations are given for contemporary samples collected away from these urban locations. Table 2b shows a more detailed analysis of the London data given in Table 2a, for CH_4, CFC-11, CFC-12 and CH_3CCl_3. It can be noted from the ambient air data in these two tables that urban tropospheric concentrations of CFC-11 and CFC-12 are typically less than 1 ppbV and are up to three times higher than the corresponding background concentrations.

Extensive measurements of halocarbons and other trace gases in several U.S. cities have been made over the past decade by Singh et al. [1977,1986]. Table 3 shows a set of data from Los Angeles obtained by these authors in 1976. Concentrations of various trace gases indicated in this table are in the highest range reported from all cities. For the purpose of deriving a realistic upper limit of the contribution of

Table 2a Urban Tropospheric Concentrations of CH_4 and CCl_3F (Blake et al., 1984)

Location	Date	Concentrations $[CH_4]^{(a)}$		$[CCl_3F]^{(a)}$			Urban Excesses Fractional			
		U*	R**	U*	R**	(b)	CH_4	CCl_3F	(c)	(d)
Santiago, Chile	1/20/80	1.59	1.51	204	165	2100	0.053	0.24	0.22	0.15
Rio de Jan., Brazil	1/26/80	1.72	1.51	236	165	3000	0.14	0.43	0.32	0.22
Paramaribo, Surinam	2/01/80	2.44	1.61	474	165	2700	0.52	1.87	0.28	0.18
Cracow, Poland	5/08/80	3.42	1.65	599	180	4200	1.07	2.33	0.46	0.31
Warsaw, Poland	5/09/80	1.96	1.65	422	180	1300	0.19	1.34	0.14	0.09
London, England	7/25/80	2.03	1.62	564	184	1200	0.25	2.07	0.12	0.08
London, England	7/25/80	2.03	1.62	509	184	1300	0.25	1.77	0.14	0.09
Copenhagen, Denmark	8/01/80	1.68	1.60	455	182	300	0.05	1.50	0.03	0.02
Copenhagen, Denmark	8/01/80	1.69	1.60	570	182	200	0.06	2.13	0.03	0.02
Sao Paulo, Brazil	8/13/80	1.66	1.52	226	175	2700	0.09	0.29	0.32	0.22
Santiago, Chile	8/21/80	1.69	1.52	251	175	2200	0.11	0.43	0.26	0.17
Beijing, China	9/16/80	1.65	1.62	197	182	2000	0.02	0.08	0.25	0.16
Dalian, China	9/22/80	1.67	1.62	209	182	1900	0.03	0.15	0.02	0.13
Ketchikan, Alaska	11/22/80	1.92	1.63	329	189	2100	0.17	0.68	0.25	0.17
New York City	2/20/81	1.91	1.64	590	193	700	0.17	2.06	0.08	0.03
Rio de Jan., Brazil	6/14/81	1.62	1.53	192	175	5000	0.06	0.10	0.60	0.04
Hamburg, Germany	8/22/83	1.83	1.67	353	210	1100	0.10	0.68	0.14	0.10
Hamburg, Germany	8/24/83	1.82	1.67	317	210	1400	0.09	0.51	0.18	0.12
London, England	9/09/83	1.75	1.67	318	210	700	0.05	0.51	0.09	0.06
Brussels, Belgium	9/16/83	1.70	1.67	378	210	200	0.03	0.80	0.04	0.03
Rome, Italy	11/09/83	2.16	1.67	894	210	700	0.29	3.26	0.09	0.06
Rome, Italy	11/10/83	1.93	1.67	837	210	400	0.16	2.99	0.05	0.03

(a) Concentrations of CH_4 in ppmv (10^{-6}) and of CCl_3F in pptv (10^{-12}).
(b) Ratio of absolute increase in CH_4 to absolute increase in CCl_3F.
(c) Ratio of fractional increase in CH_4 to fractional increase in CCL_3F.
(d) Ratio of (a) corrected by 10/15, the years required to emit the observed atmospheric burden for CH_4 divided by the years required for CCl_3F.
* U = urban **R = remote

Table 2b Urban Excesses of CH_4 versus CCl_3F, CCl_2F_2, and CH_3CCl_3 (Blake et al., 1984)

Concentrations in pptv (10⁻*12)	CH_4	CCl_3F	CCl_2F_2	CH_3CCl_3
London, England (7/25/80)	2.02×10^6	509	817	638
Remote Location Background	1.62×10^6	184	330	120
Absolute Concentration Excess	0.41×10^6	325	487	518
Molar Excess Ratio CH_4/Halocarbon)		1260	840	790
Estimated 1980 Release (kilotons)		265	393	504
Estimated 1980 CH_4 Emissions (megatons)		39	44	48
Excess Ratio (Urban/Remote-1.00)	0.25	1.77	1.48	4.32
Ratio of Excess Ratios (CH_4/X)		1.77	1.48	4.32
Corrected Ratio of Excess Ratios		0.10^3	0.11	0.12

(a) Corrected for total atmospheric burden divided by yearly release in 1980: CH_4, 10; CCl_3F, 15: CCl_2F_2, 16; CH_3CCl_3, 4.8.

Table 3 Urban Halocarbons and Other Trace Gases[(a)]: Los Angeles

Compounds	Concentrations Maximum	Minimum	Average	Std. Dev.
	(ppt)			
CCl_2F_2	2,476.6	225.5	860.4	599.4
CCl_3F	6,953.3	98.4	617.1	636.6
$CHC1_2F$	90.0	21.0	38.1	16.4
CCl_2FCClF_2	398.0	29.0	119.1	77.5
$CClF_2CClF_2$	150.0	7.5	39.8	32.2
$CHCl_3$	877.8	23.1	103.1	103.4
CH_3Cl	943.9	707.9	833.8	80.2
CH_3CCl_3	7,663.2	100.4	1,539.3	1,574.7
CCl_2CCl_2	2,267.3	60.8	674.4	498.4
$CHClCCl_2$	1,772.3	25.5	312.6	302.3
$COCl_2$	61.1	21.1	31.8	8.3
	(ppb)			
NO	259.1	0.5	49.0	60.9
NO_2	302.4	16.9	82.7	68.8
CH_4	5,202.0	1,402.3	2,299.2	1,188.6
TNMHC	4,491.3	570.1	1,706.5	1,106.1
CO	5,740.0	76.7	1,530.2	1,354.1
O_3	213.4	0.0	38.0	53.1

(a) Measured during 4/29-5/4/76 (Singh et al., 1977)

the alternative fluorocarbons to urban O_3 formation, the most appropriate concentration to be used is a sum of the maximum concentrations of CFC-11 and CFC-12 shown in Table 3, i.e. (6,953.3 pptV + 2,476.6 pptV) $\simeq$ 9.5 ppbV. Thus, in the calculations that follow, the maximum concentration of total alternative fluorocarbons anticipated in a given urban atmosphere will be assumed to be 9.5 ppbV.

3.3 Urban Hydrocarbons

The feature that distinguishes the chemistry of urban atmospheres from that of the natural troposphere is the greater variety, and higher concentrations of HCs due to anthropogenic sources. In order to assess the O_3 forming potential of urban hydrocarbons, the concentrations of individual hydrocarbons must be known so that the vast difference in their atmospheric reactivity can be properly taken into account. Table 4 gives a summary of urban hydrocarbon composition measured by Seila and Lonneman [1988] in 39

Table 4 Ambient Air Hydrocarbons in 39 U.S. Cities[(a)]

Compound	Formula	Concentration (ppbC) Median	Concentration (ppbC) Maximum
Isopentane	C_5H_{12}	45.3	3,393
n-Butane	C_4H_{10}	40.3	5,448
Toluene	C_7H_8	33.8	1,299
Propane	C_3H_8	23.5	393
Ethane	C_2H_6	23.3	475
n-Pentane	C_5H_{12}	22.0	1,450
Ethylene	C_2H_4	21.4	1,001
m-, p-Xylene	C_8H_{10}	18.1	338
2-Methylpentane	C_6H_{14}	14.9	647
Isobutane	C_6H_{10}	14.8	1,433
Acetylene	C_2H_2	12.9	114
Benzene	C_6H_6	12.6	273
n-Hexane, 2-Ethyl-1-butene	C_6H_{14},C_6H_{12}	11.0	601
3-Methylpentane	C_6H_{14}	10.7	351
1.2,4-Trimethylbenzene	C_9H_{12}	10.6	81
Propylene	C_3H_6	7.7	455
2-Methylhexane	C_7H_{16}	7.3	173
o-Xylene	C_8H_{10}	7.2	79
2,2,4-Trimethylpentane	C_8H_{18}	6.8	106
Methylcyclopentane	C_7H_{12}	6.4	293
3-Methylhexane	C_7H_{16}	5.9	168
2-Methylpropene,1-butene	C_7H_8	5.9	365
Ethylbenzene	C_8H_{10}	5.9	159
m-ethyltoluene	C_9H_{12}	5.3	83
n-Heptane	C_7H_{16}	4.7	233
		378.3	19,411

(a) Ambient air hydrocarbons in 39 U.S. cities - the 25 most abundant based on median concentration (Seila and Lonneman, 1988; quoted by Seinfeld, 1989)

U.S. cities which was quoted recently by Seinfeld [1989]. Listed in this table are the 25 most abundant compounds based on median concentration in terms of ppbC. Methane is normally the most abundant and least reactive among the urban HCs, and is seldom reported in air quality data such as those in Table 4. The median concentrations, rather than the maximum, for individual compounds will be used in the following calculations.

3.4 Contribution of Hydrocarbons vs. Alternative Fluorocarbons to Urban Ozone Production

To a good first-order approximation, relative contributions of individual hydrocarbons to overall O_3 production in a given urban air mass can be evaluated based on their removal rates by HO radicals, i.e. $-d[HC]/dt = k_i[HO][HC]_i$ where k_i is the rate constant for the HO radical reaction of the i-th hydrocarbon [Winer et al., 1979; Finlayson-Pitts and Pitts, 1986]. Namely, as stated in Sections 2.2 and 2.3, attack by HO is primarily responsible for the consumption of most hydrocarbons, and this process leads to the free radicals, e.g. HO_2 and RO_2, that oxidize NO to NO_2, which then forms O_3. While this approach is useful for some hydrocarbons, it has significant disadvantages as well [Finlayson-Pitts and Pitts, 1986]. This arises because the HC removal rates by HO do not necessarily reflect important mechanistic aspects of atmospheric reactions of HC-NO_x mixtures leading to the formation of O_3. For instance, the long chained alkanes and some aromatics produce nitrates which do not contribute significantly to the O_3 production. However, despite the potential deficiencies, the O_3 forming potential of organic mixtures in ambient air assessed using the HO reaction rates, has been shown to give results which are generally consistent with those based on experimentally observed O_3 formation in irradiation of urban air samples [Uno et al., 1985]. Presented below are the results of calculations based on the HO reaction rates.

Table 5 shows relative removal rates, i.e. $k_i[HC]_i$, computed from the HC composition (median) given in Table 4, in combination with the respective HO rate constants. Concentrations of HCs in Table 5 are given in units of molecules cm^{-3} and relative rates in $seconds^{-1}$. Since CH_4 is not included among the HCs listed in Table 4, its concentration is taken from the average value given in Table 3. The contribution of CO is not included in Table 5 because of its large variability in ambient urban air. However, it should be noted that with an average value of CO = 1.53 ppm (cf. Table 2), the relative removal rate of CO can be as much as 40% of those of the total HCs. Thus, the exclusion of CO in the above calculations leads to a conservative estimate for the O_3 forming potential of urban atmospheres.

Similarly, relative removal rates of the alternative fluorocarbons were calculated from their HO-reactivity and the assumed concentrations of individual fluorocarbons present at 9.5 ppbV each together with the HC composition given in Table 5. Results of these calculations are summarized in Table 5. According to the percentage rates shown in the last column of this table, all the fluorocarbons listed contribute less than 0.1% each to the O_2 forming potential of the total HCs, and less than 2% of that of CH_4. It is also to be noted in this table that other urban halocarbons reported in Table 3 such as $CCl_2=CCl_2$ and $CHCl=CCl_2$ surpass the alternative fluorocarbons in their O_3 forming potential.

Additionally, an upper limit for the fractional conversion of the alternative fluorocarbons can be calculated to be 7% in two successive "smoggy" days with daily average concentration of HO radicals assumed to be as high as 1×10^7 molecule cm^{-3}. Thus, if an oxidant is formed which contains all the carbon atoms in the parent fluorocarbon, its concentration can reach at most 0.7 ppbV in urban air.

Table 5 Relative Removal Rates of Urban Hydrocarbons by HO Radicals[(a)]

Compound	k (x10^{-12}) at 25 C cm^3/molec s	Concentration (x 10^{10}) molec/cm^3	Rate (x10^{-2}) Second^{-1}	% Rate
Methane	0.0077	5,748.0	44.3	3.0
Isopentane	3.9	22.7	88.8	5.9
n-Butane	2.7	25.2	68.0	4.5
Toluene	6.4	12.1	77.3	5.2
Propane	1.1	19.6	21.5	1.4
Ethane	0.3	29.1	8.7	0.6
n-Pentane	4.1	11.0	45.1	3.0
Ethylene	8.8	26.8	235.4	15.7
m-Xylene	(20.6)			
p-Xylene	(13.0)AV 16.8	5.7	95.0	6.4
2-Methylpentane	5.5	6.2	34.1	2.3
Isobutane	2.2	9.3	20.4	1.4
Acetylene	0.9	16.1	14.5	1.0
Benzene	1.0	5.3	0543	
n-Hexane,	(5.3)			
2-Ethyl-1-butene	(60.1)AV 32.7	4.6	149.9	10.0
3-Methylpentane	5.5	4.5	24.5	1.6
1.2,4-Trimethylbenzene	40.0	2.9	117.8	7.9
Propylene	24.6	6.4	157.9	10.5
2-Methylhexane	5.5	2.6	14.3	1.0
o-Xylene	14.2	2.3	32.0	2.1
2,2,4-Trimethylpentane	3.6	2.1	7.7	0.5
Methylcyclopentane	5.2	2.3	11.9	0.8
3-Methylhexane	7.1	2.1	15.0	1.0
2-Methylpropene,	(52.3)			
1-butene	(31.9)AV 42.1	3.7	155.2	10.4
Ethylbenzene	8.0	1.8	14.8	1.0
m-ethyltoluene	17.1	1.5	25.2	1.7
n-Heptane	7.4	1.7	12.4	0.8
		Total	1,496.3	100.0

(a.) The 25 most abundant compounds based on median concentration (cf. Table 4)

4. EMISSIONS OF HFCs AND HCFCs VS. NATURAL SOURCES OF OZONE PRECURSORS IN GLOBAL TROPOSPHERE

4.1 Approach

As stated in Section 2, the photochemical oxidation of CO and HCs in the presence of NO leads to the production of O_3. However, most CO and HCs emitted into the atmosphere from natural sources are oxidized in NO poor atmospheric environments, and thus do not contribute to effective O_3 production. Nevertheless, the global O_3 forming potential, (i.e. the maximum possible global O_3 production), of the alternative fluorocarbons relative to those of CO and various HCs can be assessed based on knowledge of (1) the relative reactivity of these compounds toward HO radicals, (2) the mean global distributions of these compounds, and (3) the NO-to-NO_2 conversion efficiency per molecule of these compounds consumed. Alternatively, global emission rates of these compounds can be used to derive an upper limit for the contribution of the alternative fluorocarbons to the overall budget of tropospheric O_3. Both approaches will be used in the present analysis.

Table 6 Relative Removal Rates of HFCs and HCFCs by HO Radicals in Urban Air

Compound		**k(298 K)(a) x 10^{-15}**	**Relative Rate ($x10^{-4}$) s^{-1}**	**Percentage Rate(e) %**
HFCs(b,d)				
CH_3CHF_2	152a	37.0	87.9	0.059
CH_2FCF_3	134a	4.8	11.4	0.008
CHF_2CF_3	125	2.5	5.9	0.004
HCFCs(b)				
$CHClF_2$	22	4.7	11.2	0.008
CH_3CClF_2	142b	3.8	9.0	0.006
CH_3CHClF	124	10.0	23.8	0.016
CH_3CCl_2F	141b	8.0	19.0	0.013
$CHCl_2CF_3$	123	37.0	87.9	0.089
Other(c)				
CH_4		7.7	4,430.0	2.961
CH_3CCl_3		12.0	23.0	0.015
CCl_2CCl_2(f)		170.0	97.7	0.065
$CHClCCl_2$		2,460.0	1,107.0	0.740

(a) k in cm^3 molecule^{-1} s^{-1}

(b) Taken from Hampson, Kurylo and Sander (AFEAS Report, 1989)

(c) Taken from Atkinson (1985) and NASA Kinetic Data (1987)

(d) Ambient concentrations of HFCs and HCFCs taken to be 9.5 ppbV.

(e) Fractional rate of the total rates of all HCs (15.0 s^{-1}) given in Table 5.

(f) Taken from the maximum concentration of CH_3CCl_3 in Table 3.

TROPOSPHERIC OZONE

The pertinent data on sources, distribution and trends of tropospheric trace gases are taken largely from the WMO report [1985], and will be described here only briefly. Also, the projected contribution of the alternative fluorocarbons will be estimated relative to natural CO and HCs only, although the oxidation of anthropogenic HCs from polluted industrial areas is an important contribution to the global O_3 budget [Crutzen 1988].

4.2 Halocarbons

Summarized in Table 7 are the measured concentrations, estimated yearly production rates, and estimated atmospheric lifetimes of representative atmospheric halocarbons [WMO 1985]. Among these halocarbons, CFC-11, CFC-12 and CH_3CCl_3 serve as reference compounds for estimating the projected global emission rates (R) and ambient concentrations (C) of the alternative fluorocarbons. Namely, in the present analysis the value of R_{AF} for a given alternative fluorocarbon (AF) is taken to be the sum of $R_{CFC\text{-}11}$ and $R_{CFC\text{-}12}$ on a molar rather than weight basis. In Table 7, $R_{CFC\text{-}11}$ and $R_{CFC\text{-}12}$ in 1982 are shown to be 310×10^6 and 444×10^6 kg/yr (or 2.3×10^9 and 3.7×10^9 mole/yr), and hence, $R_{AF} = 6.0 \times 10^9$ mole/yr.

The projected ambient concentration of a given alternative fluorocarbon (AF) is expected to be equal to or less than the combined value of $C_{CFC\text{-}11}$ and $C_{CFC\text{-}12}$ shown in Table 7, i.e. $C_{AF} \leq 0.6$ ppbV. This value of C_{AF} will be used in the present assessment. It should be noted in Table 7 that values of both R and C for CFC-11, CFC-12 and CH_3CCl_3 are all comparable despite great differences in their atmospheric lifetimes (τ), i.e. $\tau_{CFC\text{-}11} = 65$ yr, $\tau_{CFC\text{-}12} = 120$ yr, and $TCH_3CCl_3 = 6.5$ yr. These estimates for τ are based on the inventory technique [Prinn et al. 1983], and not on calculated tropospheric chemical lifetimes such as those given in Table 1. In the case of CH_3CCl_3 reaction with tropospheric HO radicals as the major removal mechanism, and current models for tropospheric photochemistry appear to give a removal rate very close to the τCH_3CCl_3 given in Table 7 [Logan et al. 1981; Prather, 1989].

4.3 Methane

Methane dominates among global atmospheric hydrocarbons. The WMO report gives an estimate for the global emission rate of $R_{CH_4} = (500 \pm 145) \times 10^9$ kg/yr or $(33 \pm 9) \times 10^{12}$ mole/yr. The detailed global distribution and seasonal variation of CH_4, (C_{CH_4}), is now available. The latitudinal distribution of annual mean C_{CH_4} in 1985 ranges from 1.6 ppm in the Southern Hemisphere to 1.7 ppm in the Northern Hemisphere. Thus, $C_{CH_4} = 1.6$ ppm will be adopted for the present analysis.

An updated version of the photochemical model by Logan et al. [1981] gives a tropospheric chemical lifetime of 11 yrs for CH_4. The approximate value of $\tau_{CH_4} = 8.2$ yr given in Table 1 is close to this value. This value of τ_{CH_4} is judged to be one of the better known quantities in the global CH_4 budget, as it is tied to the empirical determination of the lifetime for CH_3CCl_3. An accurate value of τ_{CH_4} is needed to estimate the oxidation rate of CH_4 and the production rate of the ensuing product CO, as discussed below.

4.4 Carbon Monoxide

The major global sources of CO have been identified as the oxidation of CH_4 and other natural HCs, and direct emissions from fossil fuel combustion, with an estimated total production R_{CO} of 1060×10^9 kg as carbon/yr (or 88×10^{12} mole/yr). CO reacts rather rapidly with HO radicals ($\tau_{CO} \cong 0.4$ yr). The short atmospheric lifetime allows concentrations of CO to vary considerably in both space and time, mak-

Table 7 Atmospheric Halocarbons (WMO Report, 1985)

Substance	Measured concentration (pptv)	Time (year)	Est. global industrial production x 10^6 kg	Year	Reference	Est. atmospheric lifetime $^{(a)}$ years (NAS 1984)
CFC 11 (CCl_3F	200	1983	310	1982	1,8	65
CFC 12 (CCl_2F_2)	320	1983	444	1982	1,8	120
CFC 13 (CF_3Cl)	~ 3.4	1980	—	—	10	400
CFC 22 ($CHCl_2F$)	~ 52	1980	206	1984	2,7	20
CFC 113	~ 32	1/85	138-141	1984	2,5	90
CFC 114	—	—	13-14	1984	2	180
CFC 115	4	1980	—	—	10	380
CH_3CCl_3	~ 120	1983	545	1983	3,11	6.5
CFC 116	~ 4	1980	—	—	10	>500
CCl_4	~ 140	1979	~830	1983	3,12	50
CH_3Cl	630	1980	~830	1984	3,6	~ 1.5
CH_3I	~ 1	1981	—	—	9	0.02
$CBrClF_2$	~ 1.2	1984	(~5?)‡	—	4	25
$CBrF_3$	~ 1	1984	7-8	1984	2,4	110
CH_3Br	9.0	1984	—	—	4	2.3
CH_2BrCl	3.2	1984	—	—	4	—
$CHBr_2Cl$	0.9	1984	—	—	4	—
$C_2H_4Br_2$	~ 1	1984	—	—	4	~ 1
$CHBr_3$	~ 2	1984	—	—	4	

‡ Estimated release from atmospheric increase, uncertain delay between industrial production and release to the atmosphere.

1. CMA, 1984.
2. DuPont, private communication, 1985.
3. ICI, private communication, 1985.
4. Khalil and Rasmussen, 1985a [mean of arctic and antarctic values, fall, 1984].
5. Khalil and Rasmussen, 1985d.
6. Rasmussen et al., 1980.
7. Khalil and Rasmussen, 1981.
8. Cunnold et al., 1982.
9. Rasmussen et al., 1982.
10. Penkett et al., 1981.
11. Prinn et al., 1983b; Khalil and Rasmussen, 1984a.
12. Simmons et al., 1983; Rasmussen and Khalil, 1981.

(a) More updated information is available in the AFEAS Report: papers by Prather; Derwent and Volz-Thomas ing it difficult to assign a representative concentration on a global scale. Hurst and Rowland have recently reported the results of measurements of CO in remote tropospheric air samples collected quarterly in the Pacific region over a wide latitudinal range (71 °N-47 °S) since March 1986. Carbon monoxide mixing ratios in northern hemisphere samples were found to be consistently higher than those found in southern hemisphere samples. In northern temperate and arctic samples (>30 °N), CO ranged from 80 to 170 ppbV, and exhibited a large seasonal dependence. Southern hemisphere (> 10 °S) CO ranged from 30 to 70 ppbV, and exhibited a smaller seasonal and latitudinal dependence. In the present analysis, the global average concentration of CO will be arbitrarily taken to be 100 ppb.

4.5 Nonmethane Hydrocarbons

Tropospheric photochemistry and HO-O_3-CO global distributions are also strongly influenced by natural non-methane hydrocarbons (NMHC), particularly isoprene, terpenes, and the C_2-C_5 alkenes. The most recent estimate for an annual global NMHC emission flux gives 3.7 x 10^{11} kg C/yr (or 3.1 x 10^{13} moleC/yr) [Lamb et al. 1985], and this value will be used in the present assessment. While the global distributions of various non-methane hydrocarbons have not yet been well characterized, very large temporal and spatial variations are expected because of their short chemical lifetimes and source distributions. Measured concentrations of light HCs (C_2-C_5) in the free troposphere away from source regions are typically less than 1 ppbV [Rudolph and Ehhalt 1981; Singh and Salas 1982; Sexton and Westberg 1984; Greenberg and Zimmerman 1984; Bonsang and Lambert 1985].

4.6 Contribution of Alternative Fluorocarbons vs. Natural Sources

Table 8a gives a summary of the estimated global production of HCFs and HCFCs, and background O_3 precursors, i.e. CH_4, CO and non-methane hydrocarbons in units of mole/yr. The projected figure indicated for all HFCs and HCFCs combined is based on an estimate for the current production rates of both CFC-11 and CFC-12. The percentage contributions of various O_3 precursors shown in the last column have been derived from the corresponding production rates multiplied by their relative O_3 forming potentials. The O_3 forming potential for CO is assumed to be one half of those for all the other compounds listed [Crutzen, 1988]. The percentage contribution of all the HFCs and HCFCs is shown in this table

Table 8a Estimated Production of HCFs and HCFCs vs. Natural Ozone Precursors(a)

Compound		Production ($x10^{12}$)	% Contribution
HCFs & HCFCs		0.006	0.0056
CH_4		33	30.6
CO		88	40.7
NMHC		31	28.7
	Total	152	100.0

(a) Ozone forming potential of CO is assumed to be one half of other compounds.

Table 8b Relative Contributions of HCFs and HCFCs vs. Natural Ozone Precursors (NOP) to Global Ozone Production: Based on HO Radical Reaction Rates

Compound		Global Mean Concentration (ppbV)	k_{HO}(298 K)[(a)] x 10^{-15}	Relative Rate (s^{-1}) ($x10^{-4}$)	Percentage Contribution
HFCs					
CH_3CHF_2	152a	0.6[(b)]	37.0	5.6	0.092
CH_2FCF_3	134a	0.6	4.8	0.7	0.011
CHF_2CF_3	125	0.6	2.5	0.4	0.007
HCFCs					
$CHClF_2$	22	0.6	4.7	0.7	0.011
CH_3CClF_3	142b	0.6	3.8	0.6	0.010
CH_3CHClF	124	0.6	10.0	1.5	0.025
CH_3CCl_2F	141b	0.6	8.0	1.2	0.020
$CHCl_2CF_3$	123	0.6	37.0	5.6	0.092
NOPs					
CH_4		1,600	7.7	3,080.0	50.522
CO		100	240.0	3,000.0	49.210

(a) k_{HO} in cm^3 $molecule^{-1}$ s^{-1}

(b) Upper limit value assumed for all HFCs and HCFCs.

to be 0.0056% of total natural O_3 precursors. Estimation of the relative contribution of the alternative fluorocarbons (AFs) based on their projected emission rates, such as that given in Table 8a, seems reasonable, particularly in view of the comparable atmospheric reactivity of the AFs and CH_4 (cf. Table 8b).

The results of an analysis of the relative oxidation rates of individual AF vs. natural O_3 precursors are summarized in Table 8b. The global mean concentration of each AF is assumed to be 0.6 ppbV (or 1.5 x 10^{10} molecule/cm^3 at 298 K). The relative rates given in this table have been derived from these concentrations multiplied by the rate constants for the corresponding HO radical reactions at 298 K. Percentage contributions of various AFs and major natural O_3 precursors, i.e. CH_4 and CO, have been calculated, in turn, from these relative rates corrected for their O_3 forming efficiencies. As before, the O_3 production potential of CO is taken to be one half of all the other compounds listed. The contributions of NMHCs are not included in this analysis because their global concentrations are highly uncertain. Such an omission of NMHCs should result in a slight overestimation of the percentage contributions of various AFs. In fact, the fractional contributions of the AFs given in the last column of this table are seen to be generally greater than that calculated from their estimated emission rates (cf. Table 8a). However, both methods can be considered to yield mutually consistent results on the potential contribution of the AFs to the global O_3 production. It can also be noted from a comparison of Tables 6 and 8b that the percentage contributions of individual AFs are, coincidentally, identical in both urban and global atmospheres.

5. ACKNOWLEDGEMENTS

The author wishes to thank G. Yarwood and C. Francis for their assistance in the preparation of this manuscript.

XI. NATURAL SOURCES

Natural Chlorine and Fluorine in the Atmosphere, Water and Precipitation

James P. Friend
Drexel University
Department of Chemistry
Philadelphia, PA

EXECUTIVE SUMMARY

The geochemical cycles of chlorine and fluorine are surveyed and summarized as framework for the understanding of the global natural abundances of these species in the atmosphere, water and precipitation. In the cycles the fluxes into and out of the atmosphere can be balanced within the limits of our knowledge of the natural sources and sinks. Sea salt from the ocean surfaces represent the predominant portion of the source of chlorine. It is also an important source of atmospheric fluorine, but volcanos are likely to be more important fluorine sources. Dry deposition or sea salt returns about 85% of the salt released there. Precipitation removes the remainder. Most of the sea salt material is considered to be cyclic, moving through sea spray over the oceans and either directly back to the oceans (about 90%) or deposited dry and in precipitation on land (about 10%), whence it runs off into rivers and streams and returns to the oceans. Most of the natural chlorine in the atmosphere is in the form of particulate chloride ion with lesser amounts as gaseous inorganic chloride (most likely HlC) and methyl chloride vapor. Fluorine is emitted from volcanos primarily as HF. It is possible that HF may be released directly from the ocean surface but this has not been confirmed by observation. HCl and mostly likely HF gases are released into the atmosphere by sea salt aerosols. The mechanism for the release is likely to be the provision of protons from the so-called excess sulfate (that which results from the oxidation of SO_2) and HNO_3. Sea salt aerosol contains fluorine as F^-, MgF^+, CaF^+ and NaF. The concentrations of the various species of chlorine and fluorine that characterize primarily natural, unpolluted atmospheres are summarized in tables and are discussed in relation to their fluxes through the geochemical cycle.

N92-15449

NATURAL CHLORINE AND FLUORINE IN THE ATMOSPHERE, WATER AND PRECIPITATION

James P. Friend
Department of Chemistry
Drexel University
Philadelphia, PA

1. GEOCHEMICAL CONSIDERATIONS

The Origins of Chlorine and Fluorine

A summary of the principal features of the geochemical cycles of chlorine and fluorine is given here and is based on National Research Council (1971) for fluorine and on Siever (1974), MacIntyre (1970) and Sillen (1967) for chlorine. Chlorine and fluorine are volatile elements that are considered to have been extensively outgassed from the interior of the earth and now are concentrated in the crust. The principal reservoir for the storage of chlorine is the oceans where it is dissolved as Cl^- ions while that for fluorine is in the lithospheric rocks mainly as the minerals fluorapatite, fluorspar, and cryolite. Soils may contain fluoride in these and several other mineral forms. The upper layers of soil tend to have somewhat lower concentrations of fluorine than the underlying layers.

Volcanoes are the vents through which recycled sediments containing fluorine and chlorine reach the earth's surface and the atmosphere. Volcanoes are important natural sources of gaseous atmospheric fluorine, primarily as HF as indicated by Symonds et al. (1988), but other gases as well as solid compounds have been variously reported in fumeroles. Because of the uncertainties in estimating volcanic emissions, it is impossible to know whether or not volcanic sources are responsible for most of the natural atmospheric contents of fluorine. Though chlorine concentrations in volcanic emissions are higher than those of fluorine, volcanoes are relatively lesser sources of atmospheric chlorine. They are, however, of some importance since the injection of HCl into the stratosphere by large explosive volcanic eruptions can have consequences for ozone chemistry.

The most important source of atmospheric chlorine is the ocean surface which, through the actions of wind, waves and bubbles, injects sea salt particles. Much of this particulate matter is redeposited in the ocean by sedimentation, diffusion and impaction. However, important amounts of chloride ions in this maritime aerosol find their way into precipitation over both continents and oceans. Furthermore, a highly uncertain amount (ranging from 2 to 20%) of the chlorine in sea salt aerosol is released as gas. Although the identity of the species released has not been definitely established, recent investigators have been inclined to the view that it is HCl. Also, as discussed below, they indicate that the interaction with acidic sulfate residing in submicrometer particles is responsible for the release. Sea salt also contains fluorine as F^-, and like Cl^-, a portion is transported over land and deposited in precipitation and in dry fallout. As in the case of chlorine, the release of gaseous fluorine, as HF or other species, from fresh sea salt aerosol could be an important process as in the case of chlorine. However there exists very little direct observational data to reveal the extent and nature of such a process.

The problem of assessing the rates and amounts of gaseous release of Cl and F from marine aerosol particles is complicated by the fact that the soluble gases (presumably HCl and HF) are readily reincorporated with unreleased sea salt components by absorption into cloud droplets and precipitation. This phenomenon makes it difficult, if not impossible, to use the results of chemical analyses of precipitation to determine the amounts of gaseous and aerosol Cl and/or F that might have been present in the atmosphere. Another complicating factor is that the admixture of soil dust with marine aerosols presents a challenge to the scientist/analyst to determine the amounts of soil mineral components which may be present in aerosol samples in order to correct for additions of the relevant elements (such as Na and F) to the marine components. The challenge here (aside from representative sampling) is to provide such precise analyses of the necesessary components that the propagated errors still permit a reasonable determination of the sea salt contributions. Size segregation of aerosol samples has proved to be very useful in this regard.

When the possibilities for anthropogenic contributions to airborne mineral fluoride and gaseous chlorine and fluorine compounds (organic as well as inorganic) are taken into account, the difficulties in deciphering the natural cycles of F and Cl are further enhanced. Analyses of aerosols and precipitation that have been affected by pollution sources have to meet at least the same challenge as those described above for separating the soil and marine components. The situation is most complex in coastal areas where all three classes of materials may blend together in varying proportions. The realization of the many difficulties and the amounts of time and effort necessary have probably discouraged scientists and their sponsors from attempting to define more accurately the global cycles of chlorine and fluorine.

From a global geochemical perspective, precipitation and river waters, especially in the tropics where rainfall dominates the river flow, derive much of their composition from sea salt. This gives rise to the notion of "cyclic salts" which are placed in the atmosphere as sea salt aerosol, blown over the land, deposited by wet and dry processes, run off to rivers, and returned to the oceans. A remarkable comparison discussed by Raiswell et al (1979) based on the work of Gibbs (1970) (see Figure 1) illustrates the similarity of relative proportions of Na, K, Mg, Ca, Cl, HCO_3 and Si in average precipitation and water from Rio Tefe (a tributary of the Amazon River) with average sea water. The river water contained relatively larger proportions of K and Si because of dissolved minerals from weathering of igneous rocks. The bicarbonate ion, HCO_3^-, is also quite different relative to the others in the various waters due to different geochemically important interactions with terrestrial sedimentary rocks, atmospheric CO_2, and marine sediments.

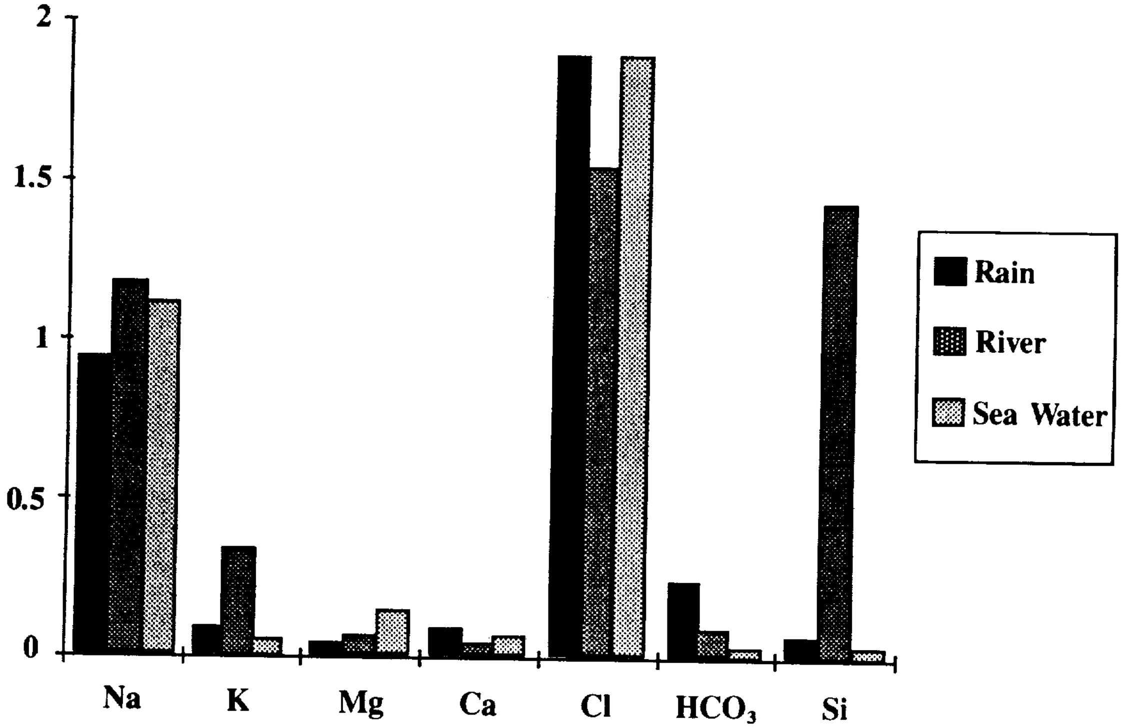


Figure 1. The Composition of Rio Tefé Water (mg/1), Rainwater in the Rio Tefé Basin (mg/1) and Sea Water ((g/1)/(10)) (from Gibbs, 1970).

The Chlorine Cycle

> *"All of the chlorine that has appeared at the surface of the earth through geologic time, ultimately derived from outgassed hydrogen chloride, has either accumulated in the oceans or has been deposited in sedimentary rocks as salt beds or briny pore waters."*
>
> *Siever, R. (1974).*

Figure 2 shows the chlorine cycle corresponding to Siever's statement. The transformation of HCl to Cl^- occurs when HCl is absorbed in cloud droplets, raindrops, and moist surfaces. These and other processes important in the atmospheric behavior of natural chlorine are schematically depicted in Figure 3.

a. The sea salt source

The largest source of atmospheric chlorine is the injection of sea-salt aerosol through the air-sea interface where wind and waves interact to produce droplets, foam and bubbles. The mass of the aerosol has essentially the same composition as the dissolved sea salt and resides in large and giant particles having radii $> 0.5\ \mu m$. These large particles originate from the mechanical injection of droplets by the various air-sea interactions. The small particle fraction, which comprises about 10% of the mass of the sea-salt aerosol, derives from the breakup of surface film by bursting bubbles. Estimation of the annual fluxes of sea-salt into and out of the atmosphere is a challenging task which has been undertaken by very few investigators. The most recent assessment is by Erickson and Duce (1988). This thorough and systematic study provides a global sea-salt flux through a plane of 15 m elevation of $(1 - 3) \times 10^{16}\ g\ yr^{-1}$. Further it finds that about 85% of the injected sea salt that crosses returns by dry deposition while the remainder

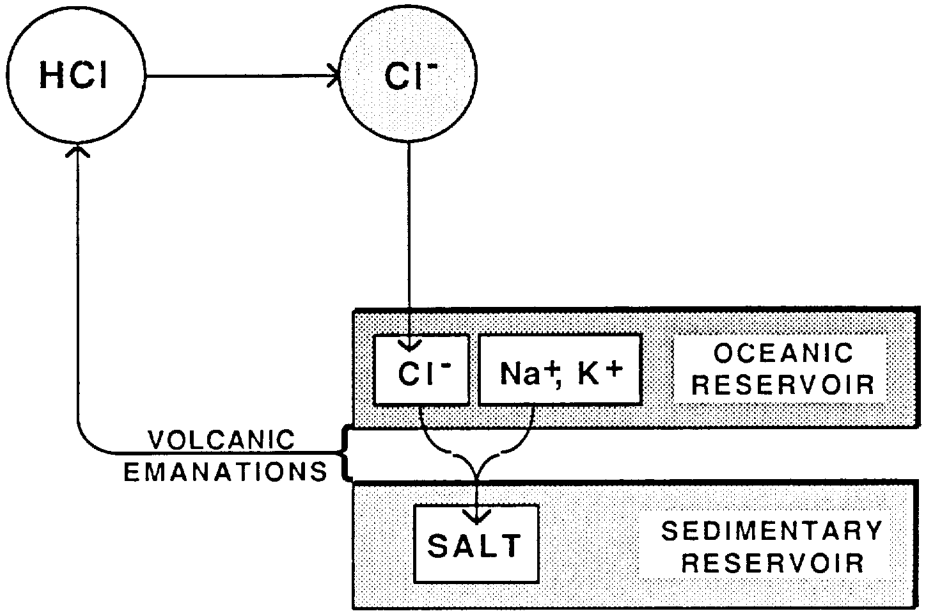
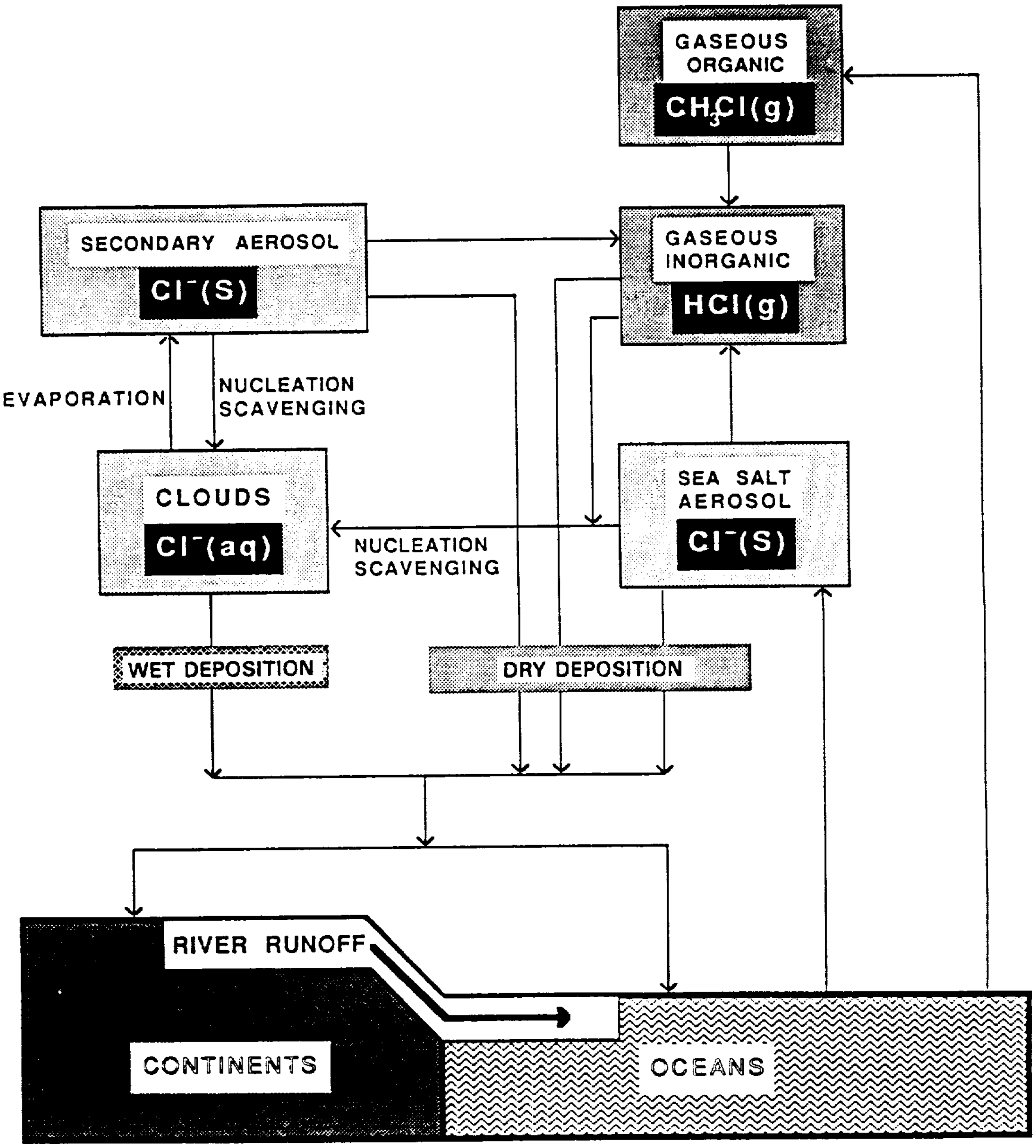


Figure 2. The Global Cycle of Chlorine.



THE GLOBAL CYCLE OF ATMOSPHERIC CHLORINE

Figure 3. The Wet and Dry Depositions onto the Respective Continental and Ocean Surfaces are not Explicitly Depicted.

is deposited in precipitation. Erickson and Duce (1988) accept the estimate made by others (cf. Eriksson, 1959) that about 10% of the sea-salt aerosol is deposited on continents. Chloride fluxes derived from these estimates using a factor of 0.55 (the fraction of Cl in the dissolved matter in sea water) as the fraction of the chlorine mass in sea salt are shown schematically in Figure 2 and listed in Table 1.

MacIntyre (1970), following Eriksson (1959), indicates that about 90% of the chloride in rivers derives from the cycling of the sea-salt aerosol to the continents and subsequent deposition and runoff from soil. This is the general view of geochemists concerned about global cycles as exemplified by Sillen (1967). In accord with this cyclic salt view, he suggested that the Cl^--contents of river water derives mainly from sea salt blown inland over the continents, deposited and then washed back. The average concentration of Cl^- in the world's rivers is about 220 μM (Livingstone, 1963). Table 1 lists the annual flux of Cl^- carried to the oceans by rivers based on Livingstone's (1963) estimates. While it appears that the river water flux is too small to balance the land deposition, it must be born in mind that the sea salt deposition falls off approximately exponentially with distance inland (as noted by Hutton, 1976 and shown quite definitively by Junge and Werby, 1958) and that water deposited on coastal plains mostly drain to the oceans in small streams rather than major rivers. Thus the amount of 260 tg yr^{-1} of river runoff is not incommensurate with the range given for land deposition in Table 1. Further comment on the balance of the cycle is given below.

b. Forests as sources

Recent studies of aerosols in Amazonia [Artaxo et al. (1988) and Talbot et al. (1988)] found that forested areas of the world can emit particulate material derived from plant components. Their results raise the possibility that there may be another independent cycling mechanism involving a considerable amount of global atmospheric chlorine and other materials, especially particulate organic carbon. The chlorine contents of the aerosol over Amazonia were of the order of 1/5 to 1/10 those of aerosols over the mid-oceans, but were equivalent to those measured in continental air over Europe. See below for further discussion.

c. The volcanic source

Symonds, Rose and Reed (1988) provide an estimate of the average annual volcanic flux of HCl to the atmosphere of 0.4 -11 Tg. They estimate that > 90% of the emissions are to the troposphere. The remainder is injected into the stratosphere in large explosive eruptions. Eventually those emissions enter the troposphere where they join with the gases there. These flux estimates reflect a considerable uncertainty, due in part to the great variability of volcanic activity in time and location and due in part to the great difficulties in sampling plumes under various conditions of eruptive activity. In view of the uncertainties, the earlier estimate made by Eriksson (1960) of 9 Tg yr^{-1} is essentially in agreement with the present estimates of Symonds et al.(1988).

Table 1. Global Atmospheric Fluxes of Chlorine

Cl - Carrier and Transfer	Fluxes of Cl (Tg/yr)	Ref
Cl(sea-salt) to atmosphere	5200 - 15000	a
Cl(sea-salt) land deposition (10% of above)	520 - 1500	a,b
Cl(aq) precipitation (global deposition)	830 - 2500	a
Cl(sea-salt) dry deposition (global)	4400 - 12000	a
Cl(river water) to oceans	260	b,c
Cl(g) sea-salt aerosol to atmosphere (3 - 20%)	160 - 3000	d
CH_3Cl ocean to atmosphere	3.5	e
Cl(g) volcanos to atmosphere	0.4 - 11	f
Cl (g) anthropogenic input to atmosphere	3	f

References: a. Erickson and Duce (1988); b.Eriksson (1959); c. Livingstone (1963); d. Cicerone (1981); e. Logan et al. (1981); f. Symonds et al. (1988)

d. The gaseous inorganic chlorine source

Among the most perplexing and uncertain aspects of the atmospheric chemistry of chlorine are (i.) the chemistry underlying the release of gaseous chlorine from sea-salt particles and (ii.) the amounts of chlorine involved. There have been several studies of limited scope in terms both of the regions of the oceans studied and the duration of the observations (Duce et al.,1965, Chesselet et al., 1972, Martens et al., 1973 and Kritz and Rancher, 1980). Martens et al.(1973) studied aerosols at coastal and inland sites in Puerto Rico using size separation techniques and found that the Cl/Na ratio decreased with decreasing size as shown in Figure 4 which is a composite of four samples. Martens et al.(1973) attributed this decrease of Cl enrichment ($EF_{Na} = [(Cl/Na)_{sample}/(Cl/Na)_{sea\ salt}] -1$) to the release of gaseous Cl from the aerosol. Upon correction for Na contributions for weathered crustal material, Martens et al.(1973) calculated Cl depletions in their samples of 7 - 25% relative to sea water. Wilkniss and Bressan (1972) found that the lower stages of cascade impactor samples of marine aerosols were more depleted in Cl than the upper stages which contained the larger particles. This reinforces the findings of Martens et al. (1973).

Duce and Hoffman (1976) systematically reviewed chemical fractionation processes at the air/sea interface including those of concern here. They point out that the observations support the idea that chlorine is released from the aerosol particles once they are in the atmosphere and not during the process of generation from the ocean surface. They also underscore the need to take into account contributions from and interactions with non-sea salt atmospheric components, even over the oceans. Cicerone (1981), in the most recent review of atmospheric halogens, summarized by noting that the amounts of chlorine released were variously found to be in the range 3 - 20%. The recent paper by Vong et al.(1988) indicates that during April and May of 1984 maritime air in the Pacific Northwest contained aerosol derived predominantly from sea-salt and that only the submicrometer fraction was, on the average, depleted in Cl relative to sea water. The overall average depletion, though unstated, would thus have amounted to something of the order of a few percent because about 90% of the mass of sea salt aerosol is in particles with $r > 1\ \mu m$. Table 2 surveys numerous investigations of the depletion of Cl from marine aerosols. Only those samples that were clearly dominated by marine aerosols are included in this compilation.

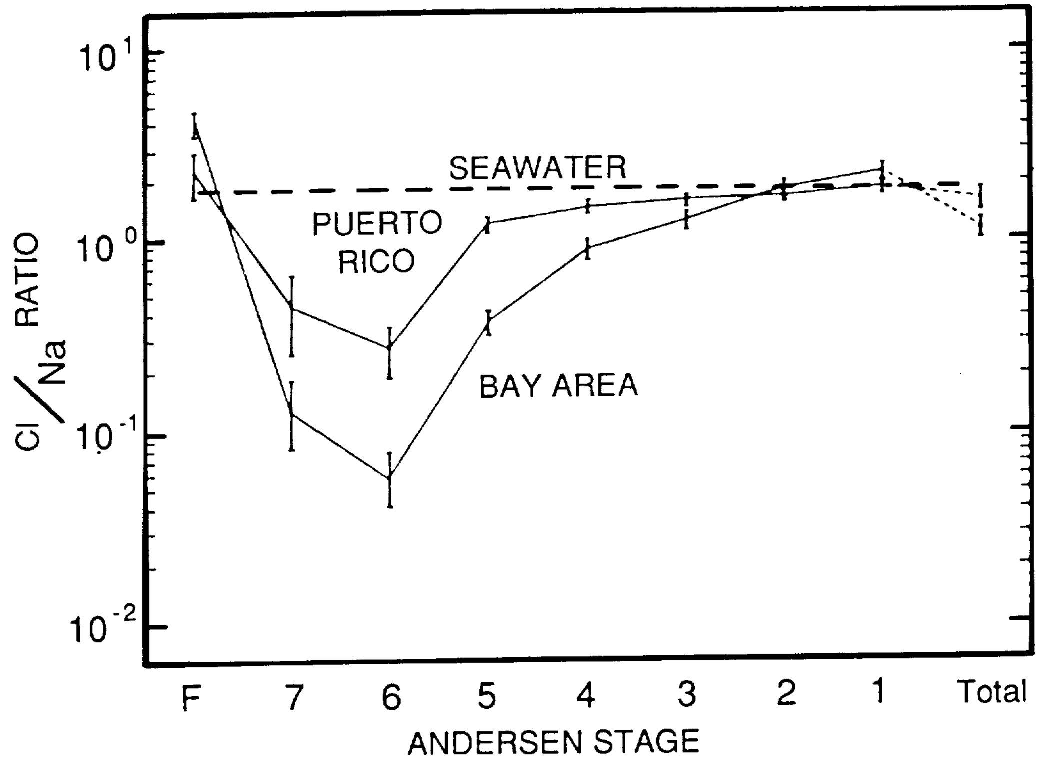


Figure 4. Average Cl/Na Ratios Versus Anderson Impactor Stage for Puerto Rican and Bay Area Marine Aerosols.

Warneck (1988), in a summary of marine aerosol constituents, uses the data of Buat-Menard et al. (1974) to suggest an average depletion of 12%. In reviewing the information of Table 2 and recalling that the submicrometer particle fraction bears most of the depletion, it is seen that, except for the results of Kritz and Rancher (1980), all results are consistent with average overall depletions of considerably less than 20%, probably less than 10%. In calculating the annual fluxes of gaseous chlorine released from sea-salt aerosol in Table 1, the uncertainties (as reflected by the ranges) in the flux of sea-salt aerosol and those in the fraction of gas released combine to give the range of a factor of 20.

Table 2. Chlorine depletions from marine aerosols.

Location	EF(range)	EF(ave)	Comment	Reference
U.S. East Coast	-0.99 to -0.31	—	Continental Na present.	Wilkniss and Bressan (1972)
Mid-Ocean	-0.39 to +0.22	-0.07		Wilkniss and Bressan (1972)
Mid-Ocean		-0.04		Chesselet et al. (1972)
Shetland Is.		-0.09		Peirson et al. (1974)
Mid-Pacific		-0.03		Wada and Kakubu (1973)
North Atlantic		-0.12		Buat-Menard et al. (1974)
Puerto Rico	-0.25 to -0.07	-0.12	Corrections for soil Na	Martens et al. (1973)
Gulf of Guinea	-0.51 to -0.11	-0.28	Maritime winds	Kritz and Rancher (1980)
Mid Pacific	-0.34 to +0.39	-0.08	20°N to 55°S	Parungo et al. (1986)
Pacific N.W.		-0.23	Particles with r> μm.	Vong et al. (1988)

Robbins et al. (1959) suggested that aerosol chloride could react according to

$$NaCl + 2NO_2 \rightarrow NaNO_3 + NOCl. \qquad (R1)$$

Thus nitrosyl chloride (NOCl) would be the form in which the chlorine is released from aerosol. Robbins et al (1969) noted that NOCl would rapidly hydrolyze in the atmosphere to form HCl. This mechanism is deemed unlikely now (cf. NRC, 1975). Eriksson (1959), and Duce et al. (1973) assumed that the gaseous inorganic chlorine is most likely to be HCl which is released via

$$\underset{\text{(sea-salt)}}{H_2SO_4 + 2NaCl} \rightarrow Na_2SO_4 + 2\ HCl. \qquad (R2)$$

Hitchcock et al. (1980) found high correlations between Cl-depletion and excess (non-sea salt) SO_4^{2-} in filter samples of aerosols collected on the coast of North Carolina and interpreted their findings as strong confirmation of Eriksson's hypothesis of R2.

Clegg and Brimblecombe (1986) have shown that Henry's law considerations involving equilibrium between gaseous HCl and the aqueous ions indicate that reaction R2 or any similar reaction involving a mineral acid that is less volatile than HCl goes essentially to completion for relative humidities below 98%. In respect to the atmosphere, this means that HNO_3 can release HCl as well as H_2SO_4. Thus to explain the release of gaseous HCl to the atmosphere when the primary sea salt particles dehydrate, R2 can be rewritten as

$$\underset{\text{(sea-salt)}}{H^+ + NaCl} \rightarrow Na^+ + HCl. \qquad (R3)$$

In this equation, it must be understood that the hydrogen ion is supplied by acids of lower volatility than HCl and that for the atmosphere H_2SO_4 and HNO_3 are the most abundant species available for the task. Given the observations that the degree of chlorine depletion of sea salt aerosols is generally less than 20%, it is clear that the gaseous and aerosol forms of HCl are not in equilibrium, even over the oceans.

The mechanism represented by R3 has received considerable support from the recent work of Legrand and Delmas (1988) who examined the results of several ice core (Delmas et al. 1982, Legrand and Delmas, 1984, 1985) and air sampling programs (Duce et al., 1973 and Maenhaut et al., 1979) in Antarctica concerning chlorine. They used ion balances and calculated acidity for two circumstances as indicated below.

1. When Cl^- is in excess of Na^+ relative to bulk sea water:
$$[H^+] = [xsSO_4^=] + [NO_3^-] + [xsCl^-].$$
2. When Cl^- is depleted relative to Na^+ :
$[H^+] = [xsSO_4^=]_a + [NO_3^-]$, where $[xsSO_4^=]_a$ is the portion of excess sulfate that has not been neutralized by the above reaction.

This system thus assumes that when Cl^- is in excess the reaction has not proceeded to an important extent, whereas when Cl^- is depleted the reaction has proceeded toward completion leaving some unneutralized $xsSO_4^=$ behind to contribute its acidity (thus the subscript a). All quantities in brackets are chemical equivalent concentrations, which is the reason there is no factor of 2 preceding the sulfate terms. Excess sulfate is that which cannot be ascribed to sea-salt based on the assumption that all of the sodium comes from sea-salt. The original sea-salt contents are assumed to have the same relative composition as bulk sea water. The excess sulfate is considered to be the result of the conversion of gaseous SO_2 to particulate $SO_4^=$. The difference between the total excess sulfate and $xsSO_4{}^={}_a$ represents the amount by which the Cl^- is depleted.

Legrand and Delmas (1988) used the above model and the observed concentrations of Na^+, $SO_4^=$, NO_3^- and Cl^- in the ice cores to calculate the acidity which they then compared to the observed H^+. The agreement was very good for the two-hundred year period (a 16m long ice core) studied in detail. All of the major features and most of the minor variations were very closely in agreement. The model was able to account for the acidity during prolonged periods when Cl^- was both in excess and in deficit relative to Na^+. The authors could not state with certainty that the HCl (i.e., the $xsCl^-$) was derived entirely from sea-salt since volcanoes and other sources, including human activities, are known. However, they suggest that the aerosol source is the most likely one to account for the Antarctic data. A glance at Table 1 shows that even at the lower limit, the flux of gaseous Cl derived from sea salt is estimated to be much larger than the sum of all of the known other sources. This then supports Legrand's and Delmas' conclusion and permits a useful view of the global chlorine cycle.

From a global perspective, the operation of reaction R3 represents an important link between the sulfur and nitrogen cycles on the one hand and the chlorine cycle on the other because, as shown in Table 1, it may be the main source of reactive chlorine in the troposphere. Over continents where much of the excess sulfate is from pollution sources, the amounts of HCl released must be considered to be affected by human activities.

e. The organic chlorine source

The most abundant natural chlorine containing molecule in the atmosphere is methyl chloride, CH_3Cl which has its origin in the oceans. The details of its source in the oceans are not known. Zafiriou (1975) has shown that CH_3I readily exchanges its iodine atom for a chlorine atom in the laboratory at temperatures approximating that of the surface oceans. CH_3I also has been found in low concentrations in ocean water and in the air over the oceans. Lovelock et al. (1973) suggested that biomethylation of I in the oceans is the source of CH_3I. So it is possible through the exchange reaction that CH_3Cl is a secondary product of biological processes in the oceans. Despite the uncertainty of the origin of CH_3Cl it is relatively straightforward to estimate its flux into the atmosphere based on measured concentrations in surface ocean waters and tropospheric air and on its tropospheric lifetime. Other organic chlorine molecules have been found in marine organisms (cf Burreson et al., 1975) but their concentrations are so small as to be entirely negligible as sources of atmospheric chlorine. Finally it is noteworthy that CH_3Cl represents the major natural source of active chlorine in the stratosphere which in turn represents a natural regulator of stratospheric ozone concentrations.

f. The cycle and its balance

From the above discussion of chlorine sources it is clear that the oceans are the overwhelming source of atmospheric chlorine and that the bulk of atmospheric chlorine exists over the oceans in the forms of aerosol derived from sea salt and gas, probably HCl, released from the aerosol. The continents receive both forms of chlorine by transport from the marine atmosphere. About 90% of the sea-salt derived chlorine is deposited back into the oceans. Thus it is seen that most of the atmospheric chlorine cycle operates over the oceans. The 10% of chlorine transported to the continents is deposited on the surface from which it finds its way to rivers and streams and back to the oceans. Recent studies indicate that there may be significant aerosol chlorine contributions by forested areas. The possible release of gaseous chlorine from the plant derived aerosol has not been investigated. Chlorine found in continental air, particularly in industrial regions, in excess of that which can be ascribed to sea salt (relative to sodium) has generally been presumed to be of anthropogenic origin.

The amounts of chlorine injected into the atmosphere in sea salt and the amounts deposited as given in Table 1 represent a forced balance. The magnitude of the uncertainty of sea salt source strength makes it is possible that a secondary source, such as forests might make a significant contribution to natural chlorine in continental air. This is a subject for further investigation. We can judge the consistency of the cycle by using the estimates of Cl-deposition in precipitation on continents and the known total precipitation over continents to estimate the average Cl concentrations in precipitation and compare them to observed concentrations. Table 3 provides the necessary information. The precipitation data of Junge and Werby (1958) for the United States (mid 1955 - mid 1966) were selected because they are continental in extent and are less affected by pollution than subsequent surveys. The relatively close agreement between the calculated and observed quantities listed in Table 3b reflect consistency in the quantitative aspects of the cycle. That is to say that there appear to be no unknown sources or sinks of chlorine that could significantly alter the balance as represented by the rather generous ranges in Table 1. However, it is clear that there is much more insight to be gained by narrowing the ranges of uncertainty in the various components of the chlorine cycle. Obviously lacking are reliable global average values of concentrations in air and precipitation.

Table 3a. Fluxes of water and chlorine (Tg yr^{-1})

Precipitation over continents	9×10^7
Cl deposition	520 - 1500

Table 3b. Cl concentration (ppm)

	Calculated from above	Observed
Precipitation	6 - 17	0.1 - 8[a]

Reference: a. Junge and Werby (1958)

The Fluorine Cycle

Most of the fluorine in the earth's crust is in solid mineral form where it constitutes between 0.06% and 0.09% by weight of the upper layers of the lithosphere (National Research Council, 1971). Windborne soil dust can and does contribute to the atmospheric burden of fluorine in the form of soil minerals. The abundance of fluorine in the oceans is 1.3 ppm by weight and is controlled by equilibrium relationships among the dissolved species F^-, MgF^+, CaF^+, and NaF and the solids MgF_2 and CaF_2. The mass ratio of F/Cl in seawater is 6.7×10^{-5}. The marine aerosol is therefore a source of atmospheric fluorine as it is for chlorine. The question arises as to what extent, if any, gaseous fluorine is released to the atmosphere from the sea salt aerosol.

Cicerone (1981) noted in his review that there is virtually no quantitative information about natural fluorine in the atmosphere. Barnard and Nordstrom (1982) have reviewed most of the prior work, which is mainly concerned with fluoride in precipitation. The work of Symonds, Rose and Reed (1988) provides a new perspective for the role of volcanoes, albeit the flux estimates range over an order of magnitude. In contrast to the case of chlorine, volcanic activity could be the most important natural source of gaseous fluorine, most likely in the form of HF. Symonds, Rose and Reed (1988) give estimates of various emission rates for natural and anthropogenic sources of fluorine. These estimates along with information from Erickson and Duce's (1988) study of sea-salt flux are incorporated in Table 4.

Table 4. Global Atmospheric Fluxes of Fluorine

Natural	
F(sea-salt) to atmosphere:	0.4 - 1 Tg yr^{-1}
HF(g) sea salt to atmosphere:	0 - 1 Tg yr^{-1}
HF (g) volcanos to atmosphere:	0.06 - 6 Tg yr^{-1}
Soil dust to atmosphere:	<0.5 Tg yr^{-1}
Other	
HF (g) coal burning:	0.18 Tg yr^{-1}
F (g) as halocarbons:	0.27 Tg yr^{-1}

The recent work by Brimblecombe and Clegg (1988) and prior work by both authors cited therein on equilibrium (Henry's law) of acid gases in the marine atmosphere indicates that the low solubility of aqueous undissociated HF favors the gas phase and suggests rather strongly that HF should be totally depleted from the aerosol. If that is the case, the marine aerosol could be a major source of tropospheric HF(g), as can be seen from the figures in Table 4. However, as in the case of chlorine generated in the marine atmosphere, most of the cycling of fluorine, as both aerosol and gas, is confined to air over the oceans. The studies of Wilkniss and Bressan (1971, 1972) were aimed at trying to understand apparently complex fractionation behavior of F and Cl in marine aerosols. They found average F^- depletions of 62%, which now appears to be consistent with the idea of Brimblecombe and Clegg that much of the fluoride is released as HF(g).

As indicated above, soil dust contributes to the atmospheric burden of fluorine. Bewers and Haysom (1974) estimated that atmospheric dust could contribute a maximum of 1 ppb fluoride to precipitation which globally, amounts to a flux of about 0.5 Tg. yr^{-1}(This calculation uses a global annual rainfall amount of 4.8×10^8 Tg yr^{-1} as per Barnard and Nordstrom (1982).) This estimate is very close to an upper limit for total soil fluorine emissions that can be calculated using the annual flux of soil particles (radius < 20 μm) of 200 - 3000 Tg yr^{-1} (Ryaboshapko, 1983) in conjunction with an average surface soil F-content of 200 ppm.

Bewers and Haystrom (1974) also examined the global fluorine cycle and concluded that terrigenous dust, sea salt, volcanos and known industrial emissions could not supply enough fluorine to account for the observed concentrations of F$^-$ in precipitation. That is, they could not balance the cycle. The minimum amount of F missing was 10 Tg yr^{-1}. The quantities used by Bewers and Haysom (1974) that differ from those in Table 4 are: maximum fluoride from sea salt (0.06 Tg yr^{-1}) and maximum volcanic emissions (1 Tg yr^{-1}). Assuming F$^-$ derived from sea salt is unfractionated in precipitation, Bewers and Haysom (1974) calculated a cyclic salt component in precipitation of 0.062 Tg yr^{-1}. Bewers and Yeats (1975), citing a calculation using the thin film transfer model of Liss and Slater (1974), suggested that direct outgassing of HF from the ocean water to the atmosphere is sufficient to account for the entire F-contents of global precipitation. To the knowledge of this author, no computations to support this suggestion have been published. Table 4 and Table 5, which do not contain estimates of HF outgassing from the oceans, show that our present precipitation of the fluorine cycle is quite different from that of Bewers and his coworkers, primarily because of larger estimated sea salt-to-atmosphere and β volcanic fluxes. Now there is a sufficiency of fluorine sources to be able to account for the amounts observed in the hydrologic cycle. Whether or not the direct outgassing of HF from the oceans is a significant contributor remains to be seen.

As we did with the chlorine cycle, we can use flux estimates for fluorine and precipitation to provide an estimate of average F-concentration in precipitation and compare it to observed values. This is done in Table 5. Here we need however, to estimate wet and dry deposition on a global basis. The assumptions used for these estimates are indicated in Table 5. The maximum precipitation flux of 5.6 Tg yr^{-1} corresponds an average maximum concentration of 11.7 ppb which is in reasonable agreement with the observations reported by Barnard and Nordstorm (1981) and those of Mahadevan et al. (1986). Barnard and Nordstrom (1981) found an average of 8.1 ppb (range of 1-24 ppb) in rainwater samples obtained in eastern U.S. Mahadevan et al. (1986) found averages for marine, coastal, inland and deep inland regions of India and the Bay of Bengal unaffected by pollution of 6.5 ppb, 16.0 ppb, 16.0 ppb and 3.3 ppb respectively. These will be further discussed below.

Table 5a. Maximum fluorine emission fluxes (Tg yr^{-1})

Sea salt to atmosphere	1
Volcanos to atmosphere	6
Soil	0.5
Anthropogenic	0.5
Total	8

Table 5b. Dry deposition fluxes (Tg yr^{-1})

Sea salt (80%)	0.8
Soil dust (50%)	0.25
Volcanic and anthropogenic (20%)	1.3
Total	2.35
Precipitation F needed to balance	$\leq$ 5.6

To summarize the natural fluorine cycle, the total flux is in the range 0.5 - 7.5 Tg yr^{-1} with volcanoes able to account for as much as 6, but as little as 0.06 Tg yr^{-1}. This leaves sea salt F^{-} as a likely second in importance, with as much as 1 Tg yr^{-1} and as little as 0.4 Tg yr^{-1}. However, over the continents, blowing soil dust can be a major contributor to aerosol fluoride. The cycle is in reasonable balance with known sources and sinks. The estimates of fluxes are, however, based on very limited sampling and analyses of flourine in the atmosphere and in precipitation which may or may not be representative of global abundances.

2. DISTRIBUTIONS

Chlorine

a. Abundances in reservoirs

1. *Gaseous organic chlorine.* The average tropospheric concentrations of CH_3Cl were found by Singh et al.(1983) to be 633 ppt (volumetric mixing ratio). They also found that the surface oceans averaged 11.5 ng L^{-1} which represents 275% saturation. By using a thin film model (cf Liss and Slater, 1974) they estimate a global flux of 4.9 Tg yr^{-1}. Logan et al. (1981) used a tropospheric chemistry model which simulated the OH radical concentrations and accounted for the reaction of CH_3Cl with OH. They computed a global loss rate of CH_3Cl of 5.2 Tg yr^{-1} which is in excellent agreement with the estimate of Singh et al.(1983). Both computations of flux involve the assumption that CH_3Cl is in steady state balance between emission to and loss from the atmosphere. The good agreement of the two results lends credibility to the concept of a global steady state of CH_3Cl abundance as a balance between emission from the ocean and destruction by reaction with OH. Singh et al.(1983) found that the Eastern Pacific Ocean is the dominant source region and estimated that it could conceivably account for the entire atmospheric burden of CH_3Cl.

2. *Gaseous inorganic chlorine.* From the reviews of Cicerone (1981), the NRC (1976), and the discussion in Warneck (1988), the various findings of several investigators form a somewhat consistent picture as seen in the items below.

i. Total aerosol samples in marine atmospheres and precipitation collected in maritime air show depletions of Cl relative to Na of about 2 - 20%.
ii. The submicrometer (diameter) particles display depletions of up to 90% and the larger particle fractions have depletions of less than 10%.
iii. Cl/Na ratios in precipitation are relatively close to that in sea water near the coasts of continents and tend to decrease toward the interiors. Some urban areas of the U.S. were found even in the early 1960's to have notably higher ratios.
iv. The only gaseous inorganic Cl-species identified in the troposphere is HCl (Farmer et al., 1976). His results yielded estimated concentrations in the lower tropospheric that are in general agreement with measurements of total inorganic Cl gas made by others in maritime air.

Farmer et al.'s measurements showed column abundances of HCl that were substantially the same for inland desert and for a coastal region with overall variability of about a factor of 2. As Cicerone (1980) points out, these results raise the question about whether sea salt is the dominant source of HCl and if it is, why was there no gradient with distance from the coast? The answer that can be inferred is that over the continents (at least North America and Europe) pollution sources of HCl contribute significantly to its concentrations. This is supported by the item iii above which notes the higher Cl/Na ratios in urban regions.

Comparison of the inorganic chlorine gas contents with the aerosol chlorine contents of maritime air indicates they are of the same magnitude, viz. about 1-2 $\mu g\ m^{-3}$ and 5 $\mu g\ m^{-3}$ respectively. It would appear that more than 15% of the inorganic chlorine in maritime air is in gaseous form. This finding is consistent with the larger values of observed chlorine depletions of marine aerosols which have an upper limit of 20%. However, if the lifetime of gaseous HCl is longer than that of aerosol Cl^- as may be possible, then lower values of chlorine depletions would be favored. The specification of a reliable average value of chlorine depletion awaits more intensive and extensive measurements of the global distributions in space and time of the Cl-species than are now available.

3. *Aerosol inorganic chlorine.* Raemdonck et al (1986) found sea salt concentrations over the Eastern Tropical and Equatorial Pacific to range from 2.6 to 8.2 $\mu g\ m^{-3}$ and that the average enrichment factor of Cl referred to Na was -0.08 on one type of sample and was -0.06 on another type. This corresponds to Cl^- concentrations of 1.3 to 4.2 $\mu g\ m^{-3}$. These recent results can be compared to earlier chemical measurements of Cl^- in aerosols over the central Atlantic Ocean as summarized by Warneck (1988) which average to 4.6 $\mu g\ m^{-3}$.

Talbot et al (1988) sampled and analyzed aerosols over Amazonia by aircraft and found that both in the mixed layer and the free troposphere virtually all of the Cl^- resided in the coarse particle mode (d $> 1\mu m$). They found average aerosol Cl^- atmospheric concentrations of 43 ng m^{-3} in the mixed layer and 29 ng m^{-3} in the free troposphere. These results are commensurate with those of Artaxo et al. (1988) who studied natural aerosols at two sites in Amazonia which were found to contain concentrations of Cl of 60 ± 45 ng m^{-3} and 90 ± 30 ng m^{-3}. Most of the Cl was found in the coarse particle mode (d $\geq$ 2 μm) but was not of marine origin since the sites are more than 1000 km from the coast. Principal factor analysis led the authors to conclude that the Cl and other elements included in the group (mostly S, K and Ca) originated from plant material such as waxes, abraded leaves, etc. The authors conclude that over forested areas of the world which are large, the aerosols have a predominantly biogenic component compared to soil dust and sea salt. Aside from the potential importance of this aerosol to global mass loadings, it is evident that the small Cl-contents, though small in the global balance which is dominated by sea salt, may be a significant natural continental source of aerosol chlorine.

Vong et al (1988) reported that the average mass ratio of Na/Cl of 41 rainwater samples taken at a single site (found to be suitable for Northern Hemisphere background precipitation measurements) on the coast of the Pacific Northwest was 1.96 ± 0.43 while that for 14 submicrometer aerosol samples was 1.39. This latter figure represents a 20% depletion of Cl relative to sea water. The variability of the ratio in rainwater is due predominantly to meteorological and/or emission source factors. The depletion of Cl in the small particle fraction is consistent with the original observations of Duce (1969) and many others since. Multivariate analyses ascribed all of the Cl in both rainwater and submicrometer aerosol to a sea salt aerosol source. Average rainwater Cl concentrations were 98 $\mu eq\ L^{-1}$ (3500 $\mu g\ L^{-1}$) and average aerosol Cl concentrations were 390 ng m^{-3}.

Fluorine

Fluorine in soil.

A survey of 30 U.S. soil types (National Research Council, 1971) showed fluoride concentrations of 20 - 500 ppm in samples taken from 0 - 3 inch depths yielding an average concentration of 190 ppm. Samples taken to 12-inch depths ranged to 1620 ppm with an average of 292 ppm.

Fluorine in water.

The fluoride concentrations in the oceans are probably governed by equilibrium relationships among the species F^- (48-50%), MgF^+(47-49%), CaF^+(2%), NaF(1%) and the solids MgF_2 and CaF_2. The percentages in parentheses are the relative amounts of dissolved fluorine in each species (Dahlem Conference, 1975). The mass ratio of F/Cl in seawater is 6.7×10^{-5}. The average fluoride concentration in sea water is 1.3 mg/kg and, as indicated above is governed by equilibrium with Ca and Mg species. Natural fresh waters have fluoride contents that depend on the soil or rocks with which they associated. African lakes of volcanic origin have F^- contents as high as 67 ppm while most fresh waters have been found to have contents in the range 0.1 - 2 ppm. The lower limit of detection is about 0.1 ppm which prevents understanding the lowest natural levels. (See Faust and Aly, 1981).

Fluorine in air.

Gregory et al. report a few measurements of fluoride in aerosols over the tropical forest of Guyana. They found a free tropospheric concentration of 0.74 ng/std m^3 at 3.5 km height and a forest boundary layer concentration of 5.1 ng/std m^3. They also report a coastal boundary layer concentration of 3.8 ng/std m^3.

Fluorine and Chlorine in precipitation.

Barnard and Nordstrom (1982) found F^- concentrations in precipitation in a coastal site in Delaware and an inland site in Virginia that varied over similar ranges from 0 - 18 ppb with a mean of 8.1 ppb. The difference in mean concentrations between the two sites was not statistically different from zero.

Mahadevan et al. (1986) have reported precipitation fluoride data from India and the Bay of Bengal that give perhaps the best insight to the natural background concentrations. These are summarized in Table 7 where it is to be noted that the values for the Indian data are geometric means and the quantities in parentheses are the geometric standard deviations, all reflecting the approximate log-normality of the distributions of concentration values. The sites chosen for sampling are remote from any known pollution sources including volcanos. The study found concentrations upwards of about 1 μM for polluted urban locations in Bombay.

The following tables are given for reference. Some of the entries and references come from review articles or books rather than the original work. The measurements by Gregory et al. (1986) were made in a single day aboard an aircraft over the tropical forest of Guyana. The measurements of Galloway et al. (1982) were on samples of precipitation collected in several locations around the world deemed to be remote from pollution sources. Both sets of results can be considered to be representative of natural abundances of the substances measured.

Table 6. Concentrations of Cl and F in Air ($\mu g\ m^{-3}$).

	Continental	Maritime	Reference
	Range	Average	
Cl(aerosol)	0.08 - 0.14	0.114.6	Warneck (1988)
Cl(gas)inorganic	1.6 - 3.3[a]	1 - 2[b]	a. Farmer et al. (1976)
			b. Cicerone (1981)
CH_3Cl(gas)		0.9 - 1.3	Singh et al. (1983)
F(aerosol)	(1 - 5) x 10^{-3}		Gregory et al. (1986)

Table 7. Concentrations of Cl and F in Precipitation (∼M). (1ppb F is equivalent to 0.053 μM)

		Continental	Maritime	Reference
Cl^-		0.0 - 22.9	12.6 - 1780	Galloway et al (1982)
F^-	U.S.A.[a]	0 - 0.56(0-0.95)	0.43(0 - 0.74)	Barnard and Nordstrom (1982)
	Indian[b]		0.27(2.0)	Mahadevan et al. (1986)
	Coastal		0.69(1.8)	
	120 km inland	0.26(1.0)		
	1200 km inland	0.14(.20)		

Notes: a. Entries are arithmetic means (90 percentile ranges); b. All data on and below this line pertain to the same reference. Entries are geometric means (geometric standard deviations).

XII. BIOLOGICAL AND HEALTH EFFECTS

Combined Summary and Conclusions

Toxicology of Atmospheric Degradation Products of Selected Hydrochlorofluorocarbons

Laurence S. Kaminsky
Department of Environmental Health & Toxicology
School of Public Health
State University of New York at Albany
Empire State Plaza
Albany, NY

Assessment of Effects on Vegetation of Degradation Products from Alternative Fluorocarbons

D. C. McCune and L. H. Weinstein
Boyce Thompson Institute for Plant Research
Ithaca, NY

COMBINED SUMMARY AND CONCLUSIONS

There is a need for more information on exposure, especially to organic breakdown products. This should include estimates of ground level concentrations, modes of deposition (wet & dry) and should extend to identification of half-lives in soil and water, and the products of microbial transformation.

Nothing is known of the toxicology to humans, animals or plants of any of the organic breakdown products other than trifluoroacetic acid. It was considered dubious to extrapolate from analogous compounds (e.g. trichloroacetic acid). The limited work on toxicology of TFA was with very high concentrations compared with those potentially arising from HCFC's and CFC's. Studies should aim to determine the long-term threshold level for toxicological effects.

One of the major uncertainties is the fate of -CF_3 as there is conflict of opinion about the stability of the C-F bond. The biological evidence (from toxicology and pesticide biochemistry) indicates that- CF_3 is recalcitrant and may persist in the environment but an opinion was expressed that there may be significant chemical defluorination at room temperature. Because of the mammalian toxicity of monofluoracetate, the possibility of defluorination of trifluoro- to monofluoro- needs to be firmly clarified.

In contrast with position regards organic products, and notwithstanding uncertainties about rates of deposition, it can be stated with a high degree of confidence that inorganic fluoride (HF) does not present a significant risk to human, animals, plants, or soil.

Likewise HCl is of no direct risk to humans, animals or plants. Acidity from inorganic acids or as a result of mineralization of organic products does not add any significant burden to the environment in the form of acide deposition.

N92-15450

TOXICOLOGY OF ATMOSPHERIC DEGRADATION PRODUCTS OF SELECTED HYDROCHLOROFLUOROCARBONS

Laurence S. Kaminsky

Department of Environmental Health & Toxicology
School of Public Health
State University of New York at Albany
Empire State Plaza
Albany, NY 12201

EXECUTIVE SUMMARY

The potential environmental degradation products of the hydrochlorofluorocarbons are trifluoroacetic acid (TFA), mixed fluorochloroacetic acids, and hydrofluoric acid. There is no available toxicologic data on mixed fluorochloroacetic acids. The additional fluoride burden, arising from environmental degradation of hydrochlorofluorocarbons, (1 to 3 ppb) in rainwater is trivial compared to levels in fluoridated drinking water (1 ppm), and would provide an insignificant risk to humans.

Overall there is sparse available toxicologic data on TFA. The acute lethality of TFA in mice suggests that it is only slightly toxic, and that its lethal effects at high doses are not dependent on its metabolism.

While a no adverse effect level has not been determined, 240 mg TFA/kg in rats produced no bone marrow or small intestinal effects, 25 mg TFA/kg produced no body weight gains, relative testis weight gains, or testicular histologic changes in rats, and 2000 mg/kg every second day for 14 days in mice produced no hepatic necrosis, or heart and kidney histological changes.

TFA at 2000 mg/kg in mice significantly decreased hepatic NADPH and reduced glutathione levels, but after 24-hr both levels returned to normal. Administration of 150 mg TFA/kg/day for 5-6 days to rats decreased the hepatic glycogen content by 24%, the percent liver/body weight by 43%, hepatic pyruvate kinase activity by 42%, and increased hepatic glycerol 1-phosphate oxidase activity by 125%. Thus the lowest dose at which effects have been reported is 150 mg/day for 5-6 days.

TFA is not mutagenic, but no carcinogenicity data is available. However, trichloroacetic acid is hepatocarcinogenic in mice, although it is also not mutagenic in the Ames assay. While no chronic toxicity data on TFA is available it appears likely that on the basis of its resistance to metabolism, rapid clearance, lack of mutagenic potential, and low acute toxicity TFA is unlikely to exhibit significant chronic toxic effects. For a more complete assessment of TFA toxicity chronic studies are required, as well as acute studies in species other than the mouse. The potential for TFA to act as a peroxisome proliferator should be investigated, to gain insight into its hepatocarcinogenic potential.

A German Senate Commission for the Evaluation of Health Hazards in the Work Environment has recommended that a blood TFA level of 2.5 μg/ml is risk-free. However, the assessment has no experimental or epidemiologic basis.

1. INTRODUCTION

Trifluoroacetic acid (TFA) is a liquid bp 72.4°C, mp 15.4°C, with a sharp biting odor. It has been proposed as the product of environmental degradation of the hydrochlorofluorocarbons HCFC-123, HCFC-124, HFC-134a, and HFC-125. Compounds HCFC-141b and HCFC-142b could yield mixed fluorochloroacetic acids, for which there is no available toxicologic data. The release of hydrochlorofluorocarbons into the environment could also give rise to HF, but the additional fluoride burden (1 to 3 ppb) in rainwater is trivial compared to levels in fluoridated drinking water (1 ppm), and would provide an insignificant risk to humans (Murray, 1986; World Health Organization, 1984; US EPA, 1986). Thus, in this paper only the toxicologic data on TFA is reviewed to assess the potential risks of environmental exposure.

Pharmacokinetics

There is little or no available data on the absorption, disposition, and elimination of TFA. In healthy human volunteers the half-life for renal excretion of TFA administered intravenously is 16 hr (Holaday and Cummah, 1976). In patients receiving halothane anesthesia the resultant metabolically-formed TFA had a half-life in the blood of 52-60 hr (Dallmeier and Henschler, 1977).

For rats (200-260 g) administered 1.3 mmol TFA/kg/day (150 mg TFA/kg/day) for 5 days the plasma TFA levels (μmol/ml blood) were 0.7 and 0.75 after 1 day, 0.8 and 1.0 after 2 days, 1.1 and 1.25 after 3 days, 1.06 and 0.6 after 4 days, and 1.3 and 1.1 after 5 days. Each value represents a single estimation and results are for two different animals at each time point (Stier et al., 1972). The average TFA concentration in the livers of these animals was 1.1 μmol/g liver. These values represent approximately 10% of the administered dose of TFA in the liver and 10% in the plasma (Stier et al., 1972).

TFA is not metabolized to any significant extent by rats (Fraser and Kaminsky, 1988). In humans TFA is not metabolized and is quantitatively excreted in urine (D.A. Holaday and R. Cummah, personal communication reported in Fiserova-Bergerova, 1977). Fluoro substituents, when constituents of a trifluoromethyl group, are metabolically stable relative to monofluoro substituents. Thus TFA is not metabolically defluorinated, in contrast to fluoroacetic acid, which has been demonstrated to be defluorinated by the rat hepatic microsomal system (Smith et al., 1977; Kostyniak et al., 1978).

Acute Toxicity

The majority of studies on TFA toxicity involve acute administration. Several LD50 values have been reported. For male Swiss-Webster, albino mice administered sodium trifluoroacetate intraperitoneally, values of > 400 mg/kg (> 2.9 mmol/kg) (Rosenberg, 1971), > 2000 mg/kg (> 14.7 mmol/kg) (Airaksinen and Tammisto, 1968), > 5000 mg/kg (> 37 mmol/kg) (Blake et al., 1969), and > 2000 mg/kg (> 14.7 mmol/kg) (Airaksinen et al., 1970) were obtained. TFA itself produced death in two of five mice treated intraperitoneally at 150 mg/kg (1.1 mmol/kg), probably as a consequence of its acidity (Blake et al., 1969). The LD_{50} of sodium trifluoroacetate when administered intravenously to mice was 1,200 mg/kg (10.5 mmol/kg) (Airaksinen and Tammisto, 1968). Preadministration of phenobarbital (40 mg/kg/day) for three days, or L-cysteine, isoniazid, ethanol, 4-iodopyrazole, or allopurinol administration 10 min before and 3 hr after sodium trifluoroacetate administration did not affect its LD_{50}, suggesting that the acetate was not being metabolized to toxic products (Airaksinen et al., 1970). Acute lethalities of the order reported for TFA, categorize it as a ''slightly toxic'' substance (Klaasen et al., 1986). Other toxic endpoints, primarily involving effects on metabolic activity, have also been investigated. Sodium trifluoroacetate in saline was administered by a single injection intraperitoneally to Swiss, albino, male mice (17-20 g) (Rosenberg, 1971). By 12-hr after administration of 2000 mg/kg (14.7 mmol/kg) the concentration of the coenzyme NADPH in the liver was statistically significantly decreased from 0.44 to 0.25 μmol/g. The decreased levels returned to normal by 24-hr after administration (Rosenberg, 1971). Reduced glutathione levels in the livers were also statistically significantly decreased from 4.33 to 3.94 μmol/100 mg at 12-hr after administration and by 24-hr these levels had also returned to normal (Rosenberg, 1971).

Male Wistar rats (200-260 g) were administered TFA in the drinking water for 5-6 days, equivalent to a dose of 150 mg TFA/kg body weight/day (1.3 mmol TFA/kg body weight/day) (Stier et al., 1972). In TFA-treated rat liver relative to untreated rat liver, the soluble protein increased by 6%, the glycogen content decreased by 24%, the neutral fat increased by 10% and the percent liver weight to body weight by 43%. None of these effects were evaluated for statistical significance. A number of enzyme activities in liver of TFA-treated animals was altered relative to control rat livers: pyruvate kinase decreased by 42%, phosphoglycerate kinase decreased by 10%, glycerol 1-phosphate oxidase increased by 125%, glycerolphosphate dehydrogenase decreased by 4%, malic enzyme increased by 4%, glucose 6-phosphate dehydrogenase decreased by 17%, glyceraldehyde 3-phosphate dehydrogenase decreased by 4%, enolase decreased by 7%, malate dehydrogenase decreased by 10%, isocitrate dehydrogenase decreased by 10% and NADPH-oxidase increased by 7%. Again differences were not evaluated for statistical significance and it is doubtful whether any of the activities, with the possible exception of pyruvate kinase and glycerol 1-phosphate oxidase, were significantly affected.

In several studies TFA has been administered to animals, but without producing the certain specific effects which were sought. However, there has been no systematic attempt made to determine a no adverse effect level for TFA. TFA was neutralized in water and administered orally in a single dose to ten-week-old male Alpk/AP strain rats (Lloyd et al., 1988; Lloyd et al., 1986). At doses of 10 or 25 mg/kg (0.09 or 0.22 mmol/kg) body weight gains and relative testis weight were not affected, and no histological changes were noted in the testes relative to untreated controls (Lloyd et al., 1988; Lloyd et al., 1986). Equivalent doses of 2,2,2-trifluoroacetaldehyde and 2,2,2-trifluoroethanol significantly reduced body weight gain and relative testis weight, and produced histologically-detectable testicular damage.

When TFA (240 mg/kg, 2.1 mmol/kg) was administered intravenously to male Wistar rats no bone marrow or small intestinal toxicity was detected (Fraser and Kaminsky, 1988). The metabolic precursors of TFA, 2,2,2-trifluoroethanol and 2,2,2-trifluoroacetaldehyde, at equimolar doses produced significant decreases in intestinal dry weight and leukocyte counts (Fraser and Kaminsky, 1988).

Swiss male mice (17-20 g) were injected intraperitoneally with sodium trifluoroacetate at 1000 mg/kg (7.4 mmol/kg) and killed 24 hr later, at 2000 mg/kg (14.7 mmol/kg) and killed at 12 or 24 hr later, at 2000 mg/kg (14.7 mmol/kg) every second day for 14 days and killed on the 14th day (Rosenberg and Wahlstrom, 1971). There were no TFA-induced histological changes in hearts or kidneys of any of the treated mice. At the lowest dose of sodium trifluoroacetate (1000 mg/kg) histological changes in the liver were noted including a cloudy swelling of the hepatocytes with a slight fat accumulation. At the higher dose (2000 mg/kg) vacuolization of the hepatocytes was detected at all time periods (Rosenberg and Wahlstrom, 1971). However, even after multiple doses no hepatic necrosis was detected.

Mutagenicity

TFA has been tested for mutagenicity in the Ames bacterial assay using two histidine-dependent strains of Salmonella typhimurium, TA98 and TA100 (Baden et al., 1976). TFA (150 mg/plate, 1.32 mmol/plate) was incubated in an agar-overlay assay at 37°C for 2 days without a microsomal activating system. No indication of mutagenicity was obtained under conditions where a positive control (N-methyl-N'-nitro-N-nitrosoguanidine) was highly mutagenic. This lack of mutagenicity of TFA was confirmed under similar conditions (Waskell, 1978). In a third study sodium trifluoroacetate was not mutagenic with Salmonella typhimurium TA98, TA100, and TA1535 at all concentrations used up to 35.7 mg/ml (0.26 mmol/ml), in the presence or absence of polychlorinated biphenyl (Aroclor 1254)-induced rat liver or testes post mitochondrial supernatants (Blake et al., 1981). The concentration of TFA in these assays was the maximum non-toxic concentration for the bacteria.

It is important to note that while trichloroacetic acid has also been found to be nonmutagenic in the Ames assay (Rapson et al., 1980; Waskell, 1978), it is a hepatocarcinogen in mice (Herren-Freund, 1987). Trichloroacetic acid has been demonstrated to produce peroxisome proliferation in mice (DeAngelo et al., 1986), which has been proposed as one of the mechanisms of hepatocarcinogenesis (Reddy et al., 1980), although it is questionable whether this mechanism applies in humans (Elcombe et al., 1985). Based on these reports the potential of TFA to act as a peroxisome proliferator should be investigated to gain insight into its potential as a hepatocarcinogen.

In Vitro Toxicology

TFA at 4 mM (450 mg/l) reduced the binding of the drugs warfarin and phenytoin to human serum albumin to 56% and 85% of controls, respectively. TFA at 10 mM (1140 mg/l) correspondingly reduced the binding to 44% and 77% (Dale, 1986). The results suggest that TFA generally affects the conformation of the albumin. The potential of TFA to produce metabolic disturbances was tested in vitro in cultured Morris rat hepatoma 7288C cells (Ishii and Corbascio, 1971). TFA (2.0 mM, 230 mg/l) did not affect uridine or thymidine uptake, while at 10 mM (1140 mg/l) leucine and acetate uptake by the cells was not affected. Thus at these concentrations DNA, RNA, protein and lipid synthesis by the cells was not affected.

When TFA was infused at 200 μmol/hr into 100 ml of perfusion medium for an isolated perfused rat liver the levels of lactate and pyruvate decreased after 10 min (Stier et al., 1972). TFA produced a higher uptake and turnover of lactate and pyruvate. This result is unusual in that fluorinated compounds usually inhibit rather than accelerate metabolic processes.

Antigenicity

Aqueous solutions of chicken serum globin (10-15 mg/ml) and TFA (1.2 M) were mixed in a ratio of 1 to 1.5 at 4°C for 15 min. The mixture was dialyzed against water and lyophilized to produce a complex of TFA and chicken serum globin, which was used to immunize rabbits (Rosenberg and Wahlstrom, 1973). Under these conditions TFA acted as a hapten and elicited antibodies. The clinical significance of this observation is unknown.

Analysis

Several methods are available for the analysis of TFA in biological material. In urine or serum TFA is quantitated by neutralizing with sodium hydroxide, esterifying with 2,2,2-trichloroethanol, and gas chromatographic analysis with a nickel-63 electron-capture detector (Witte et al., 1977). The detection limit is 1 μg TFA/ml body fluid. Another method uses isotachophoresis to quantitate urinary or blood TFA (Mario et al., 1980). In serum TFA has been methylated and the head space vapor phase analyzed by gas chromatography on Poropak Q (Fraser and Kaminsky, 1987).

2. CONCLUSIONS

Overall there is sparse available toxicologic data on TFA. The acute lethality of TFA in mice suggests that it is only slightly toxic, and that its lethal effects at high doses are not dependent on its metabolism.

While a no adverse effect level has not been determined, 240 mg TFA/kg in rats produced no bone marrow or small intestinal effects, 25 mg TFA/kg produced no body weight gains, relative testis weight gains, or testicular histologic changes in rats, and 2000 mg/kg every second day for 14 days in mice produced no hepatic necrosis, or heart and kidney histological changes.

TFA at 2000 mg/kg in mice significantly decreased hepatic NADPH and reduced glutathione levels, but after 24-hr both levels returned to normal. Administration of 150 mg TFA/kg/day for 5-6 days to rats decreased the hepatic glycogen content by 24%, the percent liver/body weight by 43%, hepatic pyruvate kinase activity by 42%, and increased hepatic glycerol 1-phosphate oxidase activity by 125%. Thus the lowest dose at which effects have been reported is 150 mg/day for 5-6 days.

TFA is not mutagenic, but no carcinogenicity data is available. However, trichloroacetic acid is hepatocarcinogenic in mice, although it is also not mutagenic in the Ames assay. While no chronic toxicity data on TFA is available it appears likely that on the basis of its resistance to metabolism, rapid clearance, lack of mutagenic potential, and low acute toxicity TFA is unlikely to exhibit significant chronic toxic effects. For a more complete assessment of TFA toxicity chronic studies are required, as well as acute studies in species other than the mouse. The potential for TFA to act as a peroxisome proliferator should be investigated, to gain insight into its hepatocarcinogenic potential.

A German Senate Commission for the Evaluation of Health Hazards in the Work Environment has recommended that a blood TFA level of 2.5 μg/ml is risk-free (Dallmeier and Henschler, 1981). However, the assessment has no experimental or epidemiologic basis.

N92-15451

ASSESSMENT OF EFFECTS ON VEGETATION OF DEGRADATION PRODUCTS FROM ALTERNATIVE FLUOROCARBONS

D.C. McCune and L.H. Weinstein
Boyce Thompson Institute for Plant Research
Ithaca, New York

EXECUTIVE SUMMARY

If one assumes that the mass of fluorine (F) deposited under steady-state conditions will have an upper limit of 1.5×10^9 per year and all F returns as hydrogen fluoride (HF) that is uniformly dispersed into global rainfall and is deposited by wet deposition, an upper limit for the concentration of F in precipitation would be about 3 μg per liter (3 ppb).

This quantity of F, with reference to concentration or rate of deposition, is well below that heretofore considered to be of significance with respect to the direct effects on plants of air-borne F from industrial operations. It also represents a 30 to 100% increase in what would be estimated to be natural background (3 to 10 ppb). Moreover, F at this concentration would be passively transported as a complex with essentially no capacity to modify the chemical speciation of elements in rain. The activity of F in rain is principally determined by Ca or Al, and pH and concentration of sulfate ions in precipitation could affect the potential of these elements to alter the activity of F. Nevertheless, Al concentrations in rain at the lower range of pH should be sufficient to complex F derived from the degradation of fluorocarbons.

The wet deposition of 3 ppb HF in rain and a total precipitation of 1000 mm per year would constitute a negligible enrichment of the soil in terms of its normal contents or in comparison to that from perhaps the lowest detectable atmospheric concentration of gaseous F. Nor would this deposition of HF affect the chemistry of acidic soils, and rain with a concentration of HF at least 10^3 greater would be needed to affect the chemistry of alkaline soils.

If one assumes that any or all F returns as a fluorinated acetic acid, the effects cannot be estimated because no data are presently available on the effects or degradation of trifluoroacetic acid in plants. Nevertheless, some species of plants can synthesize monofluoroacetate and omega-fluorooleate and -fluoropalmitate. Despite the great chemical stability of the methylene carbon-fluorine bond, plants can metabolize monofluoroacetate and enzymes capable of degrading it occur in soil microorganisms. This leads to the question of the ultimate fate of trifluoroacetic acid with reference to the possible mechanisms for biological dehalogenation and what end products could occur.

It is recommended that research be directed to: (1) metabolism of trifluoro- and other halidoacetates by plants and microorganisms; (2) phytotoxicity of perchloroacetate and alkylhydroperoxides; (3) bioaccumulation and toxicology of these compounds in components of terrestrial and aquatic ecosystems; (4) further quantitative knowledge of the biogeochemistry of F in natural systems.

1. ASSUMPTIONS

The interaction of the degradation products of fluorocarbons with vegetation could occur in several modes: by direct effects on the plant; by changes mediated by the plant; or indirectly, by an affect on the immediate environment of the plant. For an assessment of any of these, certain assumptions are necessary as to the nature of the environmental exposures that could be expected. Ours will be based upon an envelope with the following boundaries.

Firstly, we shall assume that the mass of fluorine deposited globally per annum under steady-state conditions will have upper and lower limits of 1.5×10^9 and 0.5×10^9 kg, respectively. These values are based on another assumption that upper and lower annual rates for global emissions of fluorocarbons are, respectively, 3×10^9 and 1×10^9 kg with fluorine constituting an average of 50% of the mass of the fluorocarbons.

Secondly, we shall assume that all fluorine (F) returns either as hydrogen fluoride (HF) or as a fluorinated acetic acid. A subsidiary assumption is that the latter occurs as the trifluoro-form although the occurrence of difluoromonochloro- and monofluorodichloro-forms are possibilities and the partitioning of fluorine among them could be considered.

Thirdly, we shall assume that fluorine is deposited by the mode of wet deposition, i.e., by rainout in precipitation. Concomitant assumptions are that this is uniformly dispersed into an average global rainfall of 4.9×10^{17} liters per year (Erchel, 1975). Consequently, upper and lower limits for the concentration of fluorine in precipitation would be, respectively, 3 and 1 μg per liter (3 and 1 ppb).

2. INORGANIC FLUORINE

Concern with the effects of fluorides on plants has been devoted to that resulting from dry deposition (mainly with reference to gaseous HF and secondarily with particulate forms). The occurrence of precipitation as rain or mist and the presence of dew or free water on the foliage has mainly been considered with respect to their effects on the accumulation of air-borne fluoride and not with fluoride in wet deposition. That is, precipitation has been viewed primarily with respect to its facilitation of the solution and subsequent absorption of deposits by the foliar tissues or its elution of deposited fluoride from foliage. (For example: the effects of mist on toxicity of HF and cryolite, McCune et al, 1977; models for the accumulation of fluoride by forage, Craggs and Davison, 1985).

Accordingly, our evaluation of inorganic fluoride from fluorocarbon degradation rests upon a comparison with what is known about the effects of industrial emissions and what could be considered the natural condition.

2.1. HF in precipitation

One problem is to what extent the concentration of fluoride in rain can be partitioned into natural and anthropogenic sources, and then to what extent the products from the atmospheric degradation of fluorocarbons represent an increased burden over that contributed by the other sources. In general, one can come to the conclusion that the assumed quantities of fluoride in rain due to the degradation of fluorocarbons may represent close to the detectable increment of present levels, be deposited as complexes, and have no effect on the chemistry of rain water or on the plant.

2.1.1. Quantity

In a metropolitan area (Yonkers, New York), fluoride concentrations never exceeded 100 ppb and infrequently were greater than 50 ppb in rainfall (Jacobson et al., 1976). In Newfoundland, rain and snow considered free of anthropogenic influence had fluoride averaging less than 10 ppb whereas precipitation enriched by a source (probably by washout) had average concentration of 280 ppb in rain (range of 110 to 580 ppb) and an average of 360 ppb in snow water (range of 110 to 1040 ppb) (Sidhu, 1982). Barnard and Nordstrom (1982) found a difference between coastal and inland sites in the distribution of values. Coastal values ranged from 2 to 24 ppb with a median of 4.2 ppb and were uncorrelated with sodium concentrations; inland values ranged up to 34 ppb with a median of 9.4 ppb. They further concluded, from mass balance considerations, that most of the fluoride in precipitation was anthropogenic in origin rather than from maritime aerosols, volcanic activity (2 to 3 ppb), or soil particles (ca 1 ppb).

2.1.2. Chemistry

Ares (unpublished) has concluded that at the concentrations present in rainfall, fluoride is passively transported as a complex with essentially no capacity to modify the chemical speciation of elements in rain water. Basically, the composition and form of minerals in dust determine, in addition to quantity, the activity of fluoride in rain.

Ares also concluded that the major ions determining the activity of fluoride in solution would be Ca or Al, depending upon the pH. Above pH 5.0, the solubility of Ca and other salts of fluoride limit its activity to a level no greater than 10^{-4} M. Below pH 4.5, hydrates of Al(III) regulate nearly all fluoride at molar ratios of Al:F of greater than 4 by the formation of Al-F complexes.

The solution of sulfate ions in precipitation will secondarily affect Ca and Al and thereby their potential to alter the activity of fluoride. Nevertheless, at the concentrations of fluoride assumed, HF derived from the degradation of fluorocarbons would not alter the acidity or composition of rain.

That Al concentrations in rain should be sufficient to complex fluoride at the lower pH range is deduced from limited data. In the vicinity of Göttingen, levels of Al ranged from 48 to 174 ppb with a mean of 89 ppb (Ruppert, 1975). In the vicinity of Solling, Ares (unpublished) found concentrations of Al in rain ranging from 10 to 1720 with a median of 100 ppb.

2.2. Effects on soil

The fluoride content of normal soils ranges from 20 to 1000 ppm depending upon minerals present, depth in the soil, and content of organic matter, with an average of about 200 ppm (see review by Davison, 1983). Assuming a concentration of 3 ppb in rain and a total precipitation of 1000 mm per year, about 30 gF ha^{-1} would be deposited per year, which is equivalent to an enrichment of about 0.04 ppm (using Davison's bulk density factor for soil). By comparison and using Davison's estimate of deposition velocity, exposure to air averaging 0.05 μgF m^{-3} would result in the deposition of about 380 gF ha^{-1} per year. Consequently, this wet deposition would constitute a negligible contribution to the soil in terms of normal contents or in comparison to that from perhaps the lowest detectable atmospheric concentration of gaseous fluoride.

The data of Ares (1986) would also indicate that wet deposition of HF in the assumed range of concentrations would not affect the soil solution in acidic forest soils. In these, it was estimated that 99.9% of fluoride was complexed with Al, and one could conclude that 3 ppb in rain would not affect the chemistry of the soil. Ares postulated that the solubility of fluoride in alkaline soils (pH 7.2 to 8.2) is controlled by ralstonite ($NaMgAlF_6$) at high Na levels or fluorite (CaF_2) at low Na levels and that rain with a concentration at least 10^3 greater than that assumed in this assessment would be needed to affect the soil chemistry.

In areas subject to airborne fluoride from industrial emissions, enrichment of fluoride and changes in soil chemistry have been observed (Ares, 1978; Fluhler et al., 1982; Polomski et al., 1982; Sidhu, 1982). Nevertheless, it has been concluded that the increased levels of fluoride found in foliage in these areas represents more the result of increased deposition directly to the plant than of uptake from an increased level of fluoride in soil (Braen and Weinstein, 1985; McClenahen, 1976).

2.3. Gaseous HF

By way of comparison, the effects of gaseous fluoride are relatively well known although knowledge is not as plentiful as would be desired for practical applications to environmental quality. Table 1 lists some values for different averaging times of what could be considered protective for three classes of vegetation. Some standards for fluoride are also based on the concentration present in foliar tissue, and Table 2 presents a example of this kind of standard.

The short-term (24-hour) value for highly sensitive plants is based upon the effects of HF on gladiolus or young foliage of conifers, such as spruce, fir, and pine (see reviews by McCune, 1969; Weinstein, 1977). The 1-month value for highly sensitive plants represents what could be protective for grapevines

Table 1. Possible acceptable limits for atmospheric concentrations of gaseous fluoride with reference to effects on vegetation.

Plant Sensitivity class	Concentration (μgF m^{-3}) Averaging time 24 hours	1 month	7 months
High	1.6	0.4	0.25
Moderate	3.6	1.5	0.6
Low	10.0	2.5	1.2

Table 2. Standards of the State of Maryland for the concentration of fluoride in vegetation.

Class of vegetation	Concentration of fluoride (μgF per g dry mass)		
Forage for cattle[a]	80	60[b]	35[c]
Field crops	35[d]		
Ornamental plants	40[d]		
Conifers & evergreens (current)	50[d]		
" " (older)	75[d]		
Deciduous trees & shrubs	100[d]		
Grasses & herbs (not grazed)	150[d]		

a) Unwashed samples
b) Mean for two months
c) Mean for 12 months
d) Foliage washed before analysis

based on the work of Doley (1986) with the Chardonnay cultivar of *Vitis vinifera*. The 7-month concentration for highly sensitive plants is based in part on the results of MacLean et al. (1984) as related to the occurrence of suture red spot (SRS) on fruit of peach. This is one of the most sensitive responses of plants to HF and also an economically significant effect. If protection against the occurrence of SRS is not of concern, a higher value such as 0.4 μgF m^{-3} based upon Doley (1986) could be used.

The averaging periods above were chosen mainly because they represent the exposure regimes used to furnish the experimental data. However, they should also recognize what characteristics of exposure could be operationally significant in the vicinities of the sources and receptors. Given the variability observed in the concentrations of HF in quotidian or weekly cycles and the temporal variations in the susceptibility of plants under ambient conditions, one could propose periods shorter than 24 hours or greater than 24 hours and less than 30 days. With respect to a seven-month value, there is some question as to whether a mean value is appropriate when the median of the population of samples from which it is derived could be zero.

In general one could conclude that atmospheric levels of gaseous fluoride below those considered protective for vegetation would result in greater accumulations of fluoride in foliage and soil than would the wet deposition of HF from fluorocarbon degradation.

3. HYDROGEN CHLORIDE

Although hydrogen chloride could also result from degradation of some compounds proposed as alternatives, it is much less toxic to plants than fluoride. For example, Guderian (1977) recommends a concentrations no greater than 50 μg m^{-3} as being protective of the most sensitive vegetation. In addition, concentrations of chloride in foliage associated with thresholds for foliar injury are in the range of 0.2 to 2% by dry weight.

4. FLUORO-ORGANIC COMPOUNDS

No data are presently available of the effect of trifluoroacetic acid on plants. Nevertheless, some plants do synthesize monofluoroacetate and some data is available on the degradation of this compound by plants and microbes.

The distribution of fluorine-containing organic molecules in nature appears to be limited to its occurrence as monofluoroacetate (Marais, 1944) and in omega-fluorine homologues, fluorooleate and fluoropalmitate (Peters et al. 1960; Ward et al., 1964). For more details on their distribution see Weinstein et al. (1972). The carbon-fluorine bond in these compounds has extraordinary stability and its slow release is accomplished by refluxing in 20 percent sodium hydroxide or heating at 100C in concentrated sulfuric acid. Complete release occurs only after refluxing in 30 percent sodium hydroxide or by sodium fusion at 400C.

Monofluoroacetate is a naturally-occurring compound in plants, and has been implicated in "lethal synthesis" in many mammals (Peters, 1952), i.e., the biosynthesis of monofluorocitrate from fluoroacetate, which blocks aconitic hydratase and can result in death. It seemed likely that, despite the great chemical stability of the methylene carbon-fluorine bond, there might be enzymes capable of degrading it. The cleavage of the carbon-fluorine bond of monofluoroacetate was first reported by Horiuchi (1962) using extracts from a pseudomonad isolated from soil. Although defluorination occurred, significant defluorination was not reported until Goldman (1965) isolated a pseudomonad from soil that grew on a medium containing monofluoroacetate as the sole carbon source. The results were quickly verified for other soil organisms (Tonomura et al., 1965; Kelly, 1965). The enzyme capable of cleaving the carbon-fluorine bond was a haloacetate halidohydrolase (Goldman and Milne, 1966; Goldman et al., 1968; Goldman, 1969) that catalyzes the reaction

$$XCH_2COO^- + OH^- \rightarrow X^- + HOCH_2COO^-$$

where X = F, Cl, or I.

Preuss et al. (1968, 1969) first reported that higher plants can cleave the methylene carbon-fluorine bond. This was shown by the liberation of $^{14}CO_2$ following incubation with 2-^{14}C-fluoroacetate in germinating seeds of peanut, castor bean, and *Acacia georginae.* Pinto bean seeds were not able to liberate $^{14}CO_2$. In peanut, inorganic fluoride was one product of the reaction. The other was postulated to be glycolic acid. The enzyme that accomplishes defluorination in plants has not been characterized.

The facility by which the carbon-fluorine bond can be cleaved by enzymes found in soil microorganisms and higher plants, leads to the question of the ultimate fate of trifluoroacetic acid (Pattison, 1959), one of the major products of photochemical oxidation of several of the alternative fluorocarbons. It is probable that plant and/or microbial enzymes can remove fluorine atoms from the molecule. Whether dehalogenation will occur as it does with dichloroacetate (Goldman et al., 1968), i.e., removal of both halogen atoms together, or whether it might be a stepwise dehalogenation, with monohalidoacetate as the end product, is not known.

5. RECOMMENDATIONS

It is apparent that the quantities of inorganic fluoride assumed in this discussion are well below those heretofore considered to be of interest with respect to the environmental consequences of industrial operations. They could represent a doubling of what would be estimated to be natural background. Accordingly, research on their possible biogeochemical effects should be directed to the identification of natural systems presently uninfluenced by anthropogenic fluoride and a better understanding of pathways of transport and transformation for fluoride in them.

With reference to the effects of fluoro-organic compounds, it is recommended that research be directed to: (1) metabolism of trifluoro- and other halidoacetates by plants and microorganisms; (2) bioaccumulation and toxicology of these compounds in components of terrestrial and aquatic ecosystems; (3) phytotoxicity of perchloroacetate and alkylhydroperoxides.

Annex A Experts and Reviewers

PRECEDING PAGE BLANK NOT FILMED

ANNEX A

EXPERTS AND REVIEWERS INVOLVED IN AFEAS

EXPERTS

R. Atkinson	University of California, Riverside
W.L. Chameides	Georgia Institute of Technology
P.S. Connell	Lawrence Livermore National Laboratory
R.A. Cox	Harwell Laboratory
R.G. Derwent	Harwell Laboratory
D.L. Filkin	E. I. du Pont de Nemours & Co., Inc,
D.A. Fisher	E. I. du Pont de Nemours & Co., Inc.
J.P. Friend	Drexel University
C.H. Hales	E. I. du Pont de Nemours & Co., Inc.
R.F. Hampson	National Institute of Standards and Technology, Gaithersburg
I.S.A. Isaksen	Oslo University
L.S. Kaminsky	State University of New York at Albany
M.K.W. Ko	Atmospheric and Environmental Research, Inc
M.J. Kurylo	National Institute of Standards and Technology, Gaithersburg
R. Lesclaux	University of Bordeaux
D.C. McCune	Boyce Thompson Institute for Plant Research, Ithaca
M.O. McLinden	National Institute of Standards and Technology, Boulder
M.J. Molina	Jet Propulsion Laboratory
H. Niki	York University, Ontario
M.J. Prather	NASA Goddard Institute for Space Studies
V. Ramaswamy	Princeton University
S.P. Sander	Jet Propulsion Laboratory
F. Stordal	Oslo University
N.D. Sze	Atmospheric and Environmental Research, Inc.
A. Volz-Thomas	Kfa Julich
W-C Wang	Atmospheric and Environmental Research, Inc,
L.H. Weinstein	Boyce Thompson Institute for Plant Research, Ithaca
P.H. Wine	Georgia Institute of Technology
D.J. Wuebbles	Lawrence Livermore National Laboratory
R. Zellner	University of Hannover

REVIEWERS

D.L. Albritton	National Oceanic and Atmospheric Administration
J.G. Anderson	Harvard University
R.E. Banks	University of Manchester Institute of Science and Technology
J.J. Bufalini	US Environmental Protection Agency
A.W. Davison	Newcastle University
W.B. DeMore	Jet Propulsion Laboratory
D.D. Des Marteau	Clemson University
R.A. Duce	University of Rhode Island
A. Goldman	University of Denver

EXPERTS AND REVIEWERS INVOLVED IN AFEAS (Continued)

M.R. Hoffman	California Institute of Technology
C.J. Howard	National Oceanic and Atmospheric Administration
N. Ishikawa	F&F Research Centre, Tokyo
J.L. Moyers	National Science Foundation
V. Ramanathan	University of Chicago
A.R. Ravishankara	National Oceanic and Atmospheric Administration
F.S. Rowland	University of California, Irvine
P. Simon	Institut d'Aeronomie Spatiale de Belgique
H.O. Spauschus	Georgia Institute of Technology
S. Solomon	National Oceanic and Atmospheric Administration
A. Tuck	National Oceanic and Atmospheric Administration
R.T. Watson	National Aeronautics and Space Administration
S. Wofsy	Harvard University

Annex B Companies Sponsoring AFEAS

ANNEX B
COMPANIES SPONSORING AFEAS

Akzo Chemicals	Netherlands
Allied-Signal Corporation	USA
Asahi Glass Co., Ltd.	Japan
Atochem	France
Chemical Industries of Northern Greece, S.A.	Greece
Daikin Industries, Ltd,	Japan
E. I. du Pont de Nemours & Co., Inc.	USA
Hoechst AG	Germany
ICI Chemicals and Polymers Ltd.	UK
ISC Chemicals	UK
Kali-Chemie AG	Germany
LaRoche Chemicals	USA
Montefluos SpA	Italy
Pennwalt Corporation	USA
Racon (Atochem)	USA

Annex C Statement of Work

ANNEX C

STATEMENT OF WORK

Each reviewer should prepare a one page written review of each paper specified with their name in the following. The reviews should be sent to the chairman of the AFEAS science committee as early as possible and fifty copies of the reviews should be brought to the AFEAS conference.

The reviews should address the following questions:

1. Is there significant information relevant to the subject that is not included in the review paper?

2. Are the conclusions supported by the information presented in the review paper?

3. Are the findings reported in the executive summary supported by the information in the body of the paper? Are all of the important points covered in the executive summary? Does the summary provide the correct level of detail or is information included that should be removed?

I. Physical and Chemical Properties:

Since model calculations and evaluations of potential biological and health effects will require the information developed in these reviews as input, Experts answering these questions will be required to submit their review papers by not later than 28 February, 1989.

A. Solubility in Water, Vapor Pressure, Hydrolysis Rates

Based on information in the literature, supplied by AFEAS member companies and available from other sources, what are the recommended temperature dependent values of the solubility in pure water, solubility in sea water, vapor pressure, and hydrolysis rates for each of the HCFCs and HFCs? Expert - Mark McLinden

Reviewer - H.O. Spauschus

B. Reaction Rate Constants

Based on available information, what is the recommended temperature dependent rate constant for reaction of each of the HCFCs and HFCs with hydroxyl and $O(^1D)$? What are the error limits on these rate constants? Experts - Bob Hampson, Mike Kurylo and Stan Sander working together.

Reviewers - W. B. DeMore and A. R. Ravishankara

C. Absorption Cross-Sections

Based on available information, what are the recommended ultraviolet (190-400 nm) and infra-red (primarily in the 8 - 13 m range) cross-sections for each of the HCFCs and HFCs? What are the error limits on these cross-sections? Expert - Mario Molina

Reviewers - P. Simon and A. Goldman

D. Degradation Mechanisms

Based on available information, how will the HCFCs and HFCs degrade in the troposphere after the initial hydrogen atom abstraction by hydroxyl, what are the intermediate and final products and what is the most likely atmospheric lifetime of each of these products? Is it likely that relatively stable fluorine-containing intermediates would be formed? How would the products be removed from the atmosphere? As this is one of the more important set of questions, four experts, or teams of experts, are being asked to address these questions. Experts - Tony Cox and R. Lesclaux working together; Roger Atkinson; Hiromi Niki; and Reinhardt Zellner.

Reviewers - All reviewers should compare the papers to identify inconsistencies and determine if they are due to uncertainties that cannot be resolved without further research or if they are due to errors in one or more of the papers. Specific responsibilities for more extensive reviews are:

J. G. Anderson - papers prepared by R. A. Cox and R. Lesclaux and R. Zellner

J. Bufalini - papers prepared by R. Atkinson and H. Niki

W. B .DeMore - papers prepared by H. Niki and R. Zellner

A.R. Ravishankara - papers prepared by R. Atkinson and R. A. Cox and R. Lesclaux

Each of the following reviewers should prepare a single review of the group of four papers. The group should be reviewed for completeness and consistency. Causes of any inconsistencies should be discussed. Each of these reviewers should suggest a single executive summary based on the four executive summaries.

F. S. Rowland

R. E. Banks

N. Ishikawa

II. Uncertainties in Atmospheric Lifetimes

Experts answering these questions will be required to submit their review papers by not later than 1 April, 1989.

A. Tropospheric Hydroxyl Concentrations

Based on measurements of the isotopic ratio of carbon in atmospheric carbon monoxide, what is the average tropospheric hydroxyl radical concentration and what are the uncertainties in the derived concentration? Given that the rate constant of the reactions of HCFCs and HFCs with hydroxyl are temperature dependent, what is your best estimate of lifetime (with uncertainty limits) of each of the HCFCs and HFCs? Experts - Andreas Volz-Thomas and R. G. Derwent working together.

Given the available data base on methyl chloroform and HCFC-22 (measured atmospheric concentrations and estimated global emissions), what are the calculated atmospheric lifetimes of these compounds and how sensitive are the lifetime to variations in these data, e.g. latitudinal, seasonal, vertical profile? Calculate the effect of a reasonable variation in each of these parameters in turn. Assuming that reaction with OH is the only sink for methyl chloroform and HCFC-22, how do uncertainties in the data base for these compounds extrapolate to influence the derived OH concentration? Extend the sensitivity calculation from effect on lifetime to effect on *OH* and hence on the lifetimes of alternative fluorocarbons. Based on this analysis, what is your best estimate of lifetime (with uncertainty limits) of each of the HCFCs and HFCs.

Are the inferred lifetimes for methyl chloroform and HCFC-22 consistent with the assumption that reaction with OH is the only sink? Is it possible that there is another sink for one or other compound, e.g. hydrolysis of methyl chloroform? Expert - Michael Prather

Reviewer - S. Wofsy
Individual reviews should be prepared for each paper and the conclusions of the papers should be compared. If there are inconsistencies the reviewer should determine if they are due to uncertainties that cannot be resolved without further research or if one or both of the papers contain errors.

B. Hydrolysis

Based on available information on hydrolysis rates, what are the most likely atmospheric lifetimes of methyl chloroform, HCFC-22 and the other HCFCs and HFCs against hydrolysis? (Estimates of average hydroxyl concentrations derived using measurements of methyl chloroform are based on the assumption that there are no other significant atmospheric sinks of methyl chloroform. This question is being asked to determine if that is a valid assumption.) Experts - Paul Wine and Bill Chameides working together.

What are the atmospheric lifetimes of the compounds identified in I.D. against hydrolysis? What are the ultimate products that would be formed in solution? Experts - Paul Wine and Bill Chameides working together.

Reviewers - M. R. Hoffmann and D. D. Des Marteau
In addition to preparing reviews of the papers the reviewers should prepare brief summaries of other potentially important liquid phase reactions involving compounds identified in I.D. and not addressed by AFEAS.

III. Natural Sources

Experts answering these questions will be required to submit their review paper by not later than 1 May, 1989.

What are the source strengths and atmospheric concentrations of compounds containing chlorine and/or fluorine due to natural sources? What are natural concentrations of fluoride in ground water? What are the concentrations of fluoride from natural sources in rain water and surface waters (oceans, rivers, lakes)? What concentrations are found in metropolitan water supplies before and after fluoridation? What are the source strengths of other inorganic compounds that would be converted to acidic compounds in the atmosphere? Expert - J. Friend

Reviewers - J. L. Moyers and R. A. Duce

IV. Model Calculations

Experts answering these questions will be required to submit their review papers by not later than 1 May, 1989.

A. Stratospheric Ozone

Given the information supplied by the experts answering I.B., I.C. and II., what are the calculated ozone depletion potentials (including uncertainties) of the HCFCs? Based on available information, could HFCs contribute to ozone depletion? Experts - Don Fisher, Ivar Isaksen, Dak Sze and Don Wuebbles working together.

Reviewers - S. Solomon and A. F. Tuck

B. Tropospheric Ozone

Given the information supplied by the experts answering I.B., is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release? on a global basis, how would emissions of HCFCs and HFCs (currently, emissions of CFCs are about one billion kilograms per year) compare to natural sources of ozone precursors? Expert - Hiromi Niki.

Reviewer - J. Bufalini

C. Global Warming

Given the information supplied by the experts answering I.B., I.C. and II., what are the halocarbon global warming potentials (including uncertainty limits) of the HCFCs and HFCs? Experts - Don Fisher, Dak Sze, and one other climate modeler, working together.

Reviewer - V. Ramanathan

V. Biological and Health Effects

Experts answering these questions will be required to submit their review papers by not later than I May, 1989.

Based on the answers to these questions in sections I. and II., is it likely that the decomposition products from annual emissions of one billion kg. (an amount that is approximately equal to current emissions of CFCs) could contribute to biological or health effects? The organisms to be considered should range from humans all the way down to microorganisms. The review should address the following topics for each of the classes of degradation compounds on the list:

1. Known acute and chronic affects to all concentrations, but with emphasis on the lowest concentrations for which data are available.
2. Existence of a dose-response threshold.
3. Availability of data on quantitative dose-response relationships.
4. Biochemists reaction mechanisms, if known.

5. Repair mechanisms and/or ability of the organism to adapt.

6. Potential effects at projected concentrations corresponding to hypothetical emissions for a given parent compound of 1 billion kg/year at steady state.

7. Most important research needed to resolve uncertainties relevant to the above items.

Experts - L. S. Kaminsky; and L. H. Weinstein and D. C McCune working together.

Reviewer - A. Davison
Individual reviews should be prepared for each paper and the conclusion of the papers should be compared. If there are inconsistencies the reviewer should determine if they are due to uncertainties that cannot be resolved without further research or if one or both of the papers contain errors.

REFERENCES

AFEAS REFERENCE LIST

Adachi, H., and N. Basco, Kinetic spectroscopy study of the reaction of $C_2H_5O_2$ with NO, *Chem. Phys. Lett.*, *64*, 431-434, 1979a.

Adachi, H., and N. Basco, The reaction of ethylperoxy radicals with NO_2, *Chem. Phys. Lett.*, *67*, 324-328, 1979b.

Adachi, H., and N. Basco, Reactions of isopropylperoxy radicals with NO and NO_2, *Int. J. Chem. Kinet.*, *14*, 1243-1251, 1982.

Addison, M. C., R. J. Donovan, and J. Garraway, Reactions of $O(^1D)$ and $O(^3P)$ with halogenomethanes, *Faraday Disc. Chem. Soc.*, *67*, 286-296, 1979.

Afanassiev, A. M., K. Okazaki, and G. R. Freeman, Effect of solvation energy on electron reaction rates in hydroxylic solvents, *J. Phys. Chem.*, *83*, 1244-1249, 1979.

Airaksinen, M. M., and T. Tammisto, Toxic actions of the metabolites of halothane: LD50 and some metabolic effects of trifluorethanol and trifluoroacetate acid in mice and guinea pigs, *Ann. Med. Exp. Fenniae*, *46*, 242-248, 1968.

Airaksinen, M. M., P. H. Rosenberg, and T. Tammisto, A possible mechanism of toxicity of trifluoroethanol and other halothane metabolites, *Acta Pharmacol. Toxicol.*, *28*, 299-304, 1970.

Alfassi, Z. B., S. Mosseri, and P. Neta, Halogenated alkyl peroxyl radicals as oxidants: Effects of solvents and of substituents on rates of electron transfer, *J. Phys. Chem.*, *91*, 3383-3385, 1987.

Allied-Signal Corporation, unpublished data, private communication with S. R. Orfeo and R. G. Richard, Buffalo, NY, 1989.

Ambrose, D., D. H. S. Sprake, and R. Townsend, Thermodynamic properties of aliphatic halogen compounds, part 1 -- vapour pressure and critical properties of 1,1,1-trichloroethane, *J. Chem. Soc., Faraday Trans. 1*, *69*, 839-841, 1973.

Anastasi, C., D. J. Waddington, and A. Woolley, Reactions of oxygenated radicals in the gas phase. Part 10 - Self reactions of ethylperoxy radicals, *J. Chem. Soc., Faraday Trans. 1*, *79*, 505-506, 1983.

Anastasi, C., I. W. M. Smith, and D. A. Parkes, Flash photolysis study of the spectra of CH_3O_2 and $C(CH_3)_3O_2$ radicals and the kinetics of their mutual reactions and with NO, *J. Chem. Soc., Faraday Trans. 1*, *74*, 1693-1701, 1978.

Anbar, M., and E. J. Hart, The reaction of haloaliphatic compounds with hydrated electrons, *J. Phys. Chem.*, *69*, 271-274, 1965.

Andon, R. J. L., J. F. Counsell, D. A. Lee, and J. F. Martin, Thermodynamic properties of aliphatic halogen compounds, part 2 -- Heat capacity of 1,1,1-trichloroethane, *J. Chem. Soc., Faraday Trans. 1*, *69*, 1721-1726, 1973.

REFERENCES

Ares, J. O., Fluoride cycling near a coastal emission source, *J. Air Pollut. Control Assoc.*, *28*, 344-349, 1978.

Ares, J. O., Identification of aluminum species in acid forest soil solution on the basis of Al:F reaction kinetics: 2. An example at the Solling area, *Soil Sci.*, *142*, 13-19, 1986.

Artaxo, P., H. Storms, F. Bruynseels, R. Van Grieken, and W. Maenhaut, Composition and sources of aerosols from the Amazon Basin, *J. Geophys, Res.*, *93*, 1605-1615, 1988.

ASHRAE, *ASHRAE Handbook of Fundamentals*, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, 1985.

ASHRAE, *ASHRAE Thermodynamic Properties of Refrigerants*, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, 1987.

Atkinson, R., Kinetics and mechanisms of the gas-phase reaction of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.*, *86*, 69-201, 1986.

Atkinson, R., A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds, *Int. J. Chem. Kinet.*, *19*, 799-828, 1987.

Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: A review, *Atmos. Environ.*, in press, 1989a.

Atkinson, R., Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, *J. Phys. Chem. Ref. Data*, in press, 1989b.

Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data*, *13*, 315-444, 1984.

Atkinson, R., and S. M. Aschmann, Kinetics of the gas phase reactions of Cl atoms with a series of organics at 296± 2 K and atmospheric pressure, *Int. J. Chem. Kinet.*, *17*, 33-41, 1985.

Atkinson, R., and W. P. L. Carter, Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions, *Chem. Rev.*, *84*, 437-470, 1984.

Atkinson, R., D. A. Hansen, and J. N. Pitts, Jr., Rate constants for the reaction of OH radicals with CHF_2Cl, CF_2Cl_2, $CFCl_3$, and H_2 over the temperature range 297-434 K, *J. Chem. Phys.*, *63*, 1703-1706, 1975.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement III, *Int. J. Chem. Kinet.*, *21*, 115, 1989.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement III, *J. Phys. Chem Ref. Data*, *18*, 881-1097, 1989.

Atkinson, R., G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, Tropospheric and stratospheric sinks for halocarbons: Photooxidation, O(^{1}D) atom, and OH radical reactions, *J. Geophys. Res.*, *81*, 5765-5770, 1976.

Atkinson, R., S. M. Aschmann, and A. M. Winer, Alkyl nitrate formation from the reaction of a series of branched RO_2 radicals with NO as a function of temperature and pressure, *J. Atmos. Chem.*, *5*, 91-102, 1987.

Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., Alkyl nitrate formation from the NO_x-air photo-oxidations of C_2-C_8 n-alkanes, *J. Phys. Chem.*, *86*, 4563-4569, 1982.

Auerbach, I., F. H. Verhoek, and A. L. Henne, Kinetics studies on the decarboxylation of sodium trifluoroacetate in ethylene glycol, *J. Am. Chem. Soc.*, *72*, 299-300, 1950.

Baden, J. M., M. Brinkenhoff, R. S. Wharton, B. A. Hitt, V. F. Simmon, and R. I. Mazze, Mutagenicity of volatile anesthetics: Halothane, *Anesthesiology*, *45*, 311-318, 1976.

Bahnemann, D. W., C. Kormann, and M. R. Hoffman, Preparation and characterization of quantum size zinc oxide: A detailed spectroscopic study, *J. Phys. Chem.*, *91*, 3789-3798, 1987.

Baker, J. W., and D. M. Easty, Hydrolytic decomposition of esters of nitric acid. Part I. General experimental techniques. Alkaline hydrolysis and neutral solvolysis of methyl, ethyl, isopropyl, and tert-butylnitrates in aqueous alcohol, *J. Chem. Soc.*, 1193-1207, 1952.

Balkas, T. I., The radiolysis of aqueous solutions of methylene chloride, *Int. J. Radiat. Phys. Chem*, *4*, 199-208, 1972.

Balkas, T. I., J. H. Fendler, and R. H. Schuler, Radiolysis of solutions of methyl chloride. The concentration dependence of scavenging electrons within spurs, *J. Phys. Chem*, *74*, 4497-4505, 1970.

Balkas, T. I., J. H. Fendler, and R. H. Schuler, The radiation chemistry of aqueous solutions of $CFCl_3$, CF_2Cl_2, and CF_3Cl, *J. Phys. Chem*, *75*, 455-466, 1971.

Balla, R. J., H. H. Nelson, and J. R. McDonald, Kinetics of the reactions of isopropoxy radicals with NO, NO_2, and O_2, *Chem. Phys.*, *99*, 323-335, 1985.

Ballinger, P., and F. A. Long, Acid ionization constants of alcohols. II. Acidities of some substituted methanols and related compounds, *J. Am. Chem. Soc.*, *82*, 795-798, 1960.

Barnard, W. R., and D. K. Nordstrom, Fluoride in precipitation. II. Implications for the geochemical cycling of fluorine, *Atmos. Environ.*, *16*, 105-111, 1982.

Batt, L., The gas phase decomposition of alkoxy radicals, *Int. J. Chem. Kin.*, *11*, 977, 1977.

Batt, L., Reactions of alkoxy and alkyl peroxy radicals, *Int. Rev. Phys. Chem.*, *6*, 53-90, 1987.

REFERENCES

Batt, L., and R. Walsh, A reexamination of the pyrolysis of bis trifluoromethyl peroxide. Addendum: Concerning D(CF_3O_2-CF_3) and D(CF_3-O_2), *Int. J. Chem. Kinet., 15*, 605-607, 1983.

Batt, L., M. MacKay, I. A. B. Reid, and P. Stewart, The pressure dependent decomposition of the trifluoromethoxy radical, *9th International Symp. Gas Kinetics*, University of Bordeaux, Bordeaux, France, July 20-25, 1986.

Baulch, D. L., R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement I, *J. Phys. Chem. Ref. Data, 11*, 327-496, 1982.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, CODATA Task Group on Chemical Kinetics, Evaluated kinetic and photochemical data for atmospheric chemistry, *J. Phys. Chem. Ref. Data, 11*, 327-496, 1982; 13, 1259-1380, 1984.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry, *J. Phys. Chem. Ref. Data, 9*, 295-471, 1980.

Beilsteins Handbuch der Organischen Chemie, Vierte Auflage, Springer, 1960.

Benson, S. W., *Thermochemical Kinetics, 2nd ed.*, Wiley, New York, NY, 1976.

Berdnikov, V. M., and N. M. Bazhin, Oxidation-reduction potentials of certain inorganic radicals in aqueous solutions, *Russ. J. Phys. Chem. Engl. Trans., 44*, 395-398, 1970.

Bernstein, P. A., F. A. Hohorst, and D. D. DesMarteau, Trifluoromethyl hydroperoxide. Properties and reactions with some acid fluorides, *J. Am. Chem. Soc., 93*, 3883-3886, 1971.

Bertrand, L., J. A. Franklin, P. Goldfinger, and G. Huybrechts, The point of attack of a chlorine atom of trichloroethylene, *J. Phys. Chem., 72*, 3926, 1968.

Betrand, L., L. Exsteen-Meyers, J. A. Franklin, G. Heubrecht, and J. Olbregts, Chlorine photosensitized oxidations of chloroethanes and chloroethylenes in the gas phase, *Int. J. Chem. Kin., 3*, 89, 1971.

Betterton, E. A., and M. R. Hoffman, Henry's law constants for some environmentally important aldehydes, *Environ. Sci. Technol., 22*, 1415-1418, 1988.

Bewers, J. M., and H. H. Haysom, The terrigenous dust contribution to fluoride and iodide in atmospheric precipitation, *J. Rech. Atmos., 13*, 689-697, 1974.

Bewers, J. M., and P. A. Yeats, Fluoride in global circulation, *Limnology and Oceanography, 20,* 149-150, 1975.

Bielski, B. H. J., Reevaluation of the spectral and kinetic properties of HO_2 and O_2-free radicals, *Photochem. Photobiol., 28*, 645-649, 1978.

Blake, D. A., H. F. Cascorbi, R. S. Rozman, and F. J. Meyer, Animal Toxicity of 2,2,2-trifluoroethanol, *Toxicol. Appl. Pharmacol., 15*, 83-91, 1969.

Blake, D. A., M. C. DiBlasi, and G. B. Gordon, Absence of mutagenic activity of trifluoroethanol and its metabolites in salmonella typhimurium, *Fund. Appl. Toxicol.*, *1*, 414-418, 1981.

Blake, D. A., V. H. Woo, S. C. Tyler, and F. S. Rowland, Methane concentrations and source strengths in urban locations, *Geophys. Res. Lett.*, *11*, 1211-1214, 1984.

Bonsang, B., and G. Lambert, Nonmethane HC in an oceanic atmosphere, *J. Atmos. Chem.*, *2*, 257-271, 1985.

Braen, S. N., and L. H. Weinstein, Uptake of fluoride and aluminum by plants grown in contaminated soils, *Water Air Soil Pollut.*, *24*, 215-223, 1985.

Brimblecombe, P., and S. L. Clegg, The solubility and behavior of acid gases in the marine aerosol, *J. Atmos. Chem.*, *7*, 1-18, 1988.

Buat-Menard, P., J. Morelli, and R. Chesselet, Water-soluble elements in atmospheric particulate matter over tropical and equatorial Atlantic, *J. Res. Atmos.*, *8*, 661-673, 1974.

Bullock, G. and R. Cooper, Reactions of aqueous trifluoromethyl radicals, *Trans. Far. Soc.*, *66*, 2055-2064, 1970.

Bunton, C. A., and J. H. Fendler, The hydrolysis of acetyl fluoride, *J. Org. Chem.*, *31*, 2307-2312, 1966.

Burreson, B. J., R. E. Moore, and P. Roller, Haloforms in the essential oil of alga Asparagopsis taxiformis (rhodophyta), *Tetrahedron Lett.*, *7*, 473-476, 1975.

Calvert, J. G., and J. N. Pitts, Jr., *J. Photochemistry*, Wiley, New York, 1967.

Caralp, F., A. M. Dognon, and R. Lesclaux, *8th International Symposium on Gas Kinetics, University of Nottingham*, Nottingham, U.K., July 15-20, 1984.

Caralp, F., and R. Lesclaux, Rate constant for the reaction of the $CFCl_2$ radical with oxygen in the pressure range 0.2-12 torr at 298 K, *Chem. Phys. Lett.*, *102*, 54-58, 1983.

Caralp, F., R. Lesclaux, and A. M. Dognon, Kinetics of the reaction of CF_3 with O_2 over the temperature range 233-373 K, *Chem. Phys. Lett.*, *129*, 433, 1986.

Caralp, F., R. Lesclaux, M.-T. Rayez, J.-C. Rayez, and W. Forst, Kinetics of the combination reactions of chlorofluoromethylperoxy radicals with NO_2 in the temperature range 233-373 K, *J. Chem. Soc., Faraday Trans. 2*, *84*, 569-585, 1988a.

Caralp, F., R. Lesclaux, M.-T. Rayez, J.-C. Rayez, and W. Forst, *J. Chem. Soc., Faraday Trans. 2*, *84*, 429, 1988b.

Carr, R. W., Jr., D. G. Peterson, and F. K. Smith, Flash photolysis of 1,3-dichlorotetrafluoroacetone in the presence of oxygen. Kinetics and mechanisms of the oxidation of the chlorodifluoromethyl radicals, *J. Phys. Chem.*, *90*, 607-614, 1986.

REFERENCES

Carter, W. P. L., and R. Atkinson, Atmospheric chemistry of alkanes, *J. Atmos. Chem.*, *3*, 337-405, 1985.

Carter, W. P. L., and R. Atkinson, Alkyl nitrate formation from the atmospheric photooxidation of alkanes: A revised estimation method, *J. Atmos. Chem.*, *8*, 165-173, 1989.

Cattell, F. C., J. Cavanagh, R. A. Cox, and M. E. Jenkin, A kinetics study of reactions of HO_2 and $C_2H_5O_2$ using diode laser absorption spectroscopy, *J. Chem. Soc., Faraday Trans. 2*, *82*, 1999-2018, 1986.

Chameides, W. L., The photochemistry of a remote marine stratiform cloud, *J. Geophys. Res.*, *89*, 4739-4755, 1984.

Chameides, W. L., and D. D. Davis, Chemistry in the troposphere, *Special Report in Chem. and Eng. News*, *60*, 38-52, 1982.

Chameides, W. L., S. C. Liu, and R. C. Cicerone, Possible variations in atmospheric methane, *J. Geophys. Res.*, *82*, 1795, 1977.

Chang, J. S., and F. Kaufman, Kinetics of the reactions of hydroxyl radicals with some halocarbons: $CHFCl_2$, CHF_2Cl, CH_3CCl_3, C_2HCl_3, and C_2Cl_4, *J. Phys. Chem.*, *66*, 4989-4994, 1977.

Chemical Manufacturers Association, CMA, *Production, sales and calculated release of CFC 11 and CFC 12 through 1982*, 1983.

Chemical Manufacturers Association, CMA, *Production, sales and calculated release of CFC 11 and CFC 12 through 1983*, October, 1984.

Chemical Manufacturers Association, CMA, *Production, sales and calculated release of CFC 11 and CFC 12 through 1987*, 1988.

Chen, S. S., A. S. Rodgers, J. Chao, R. C. Wilheit, and B. J. Zwolinski, Ideal gas thermodynamic properties of six fluoroethanes, *J. Phys. Chem. Ref. Data*, *4*, 441, 1975.

Cherneeva, L. I., Experimental investigation of the thermodynamic properties of Freon 142, *Teploenergetika 1958(7)*, 38-43, 1958.

Chesselet, R., J. Morelli, and P. Buat-Menard, Some aspects of the geochemistry of marine aerosols, *The Changing Chemistry of the Oceans*, D. Dryssen and D. Jagner, eds., 94-120, John Wiley, New York, 1972.

Cicerone, R. J., Halogens in the atmosphere, *Rev. Geophys. Space Phys.*, *19*, 123-139, 1981.

Clegg, S. L., and P. Brimblecombe, The dissociation constant and Henry's Law constant of HCl in aqueous solution, *Atmos. Environ.*, *20*, 2483-2485, 1986.

Clemitshaw, K. C., and J. R. Sodeau, Atmospheric chemistry at 4.2 K: A matrix isolation study of the reaction between CF_3O_2 radicals and NO, *J. Phys. Chem.*, *91*, 3650-3653, 1987.

Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground $X^2\Pi$ and excited $A^2\Sigma$ hydroxyl radicals. Part 1. Quenching kinetics of OH $A^2\Sigma$ and rate constants for reactions of OH $X^2\Pi$ wth CH_3CCl_3 and CO, *J. Chem. Soc. Faraday Trans. 2*, *75*, 569-581, 1979a.

Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground $X^2\Pi$ and excited $A^2\Sigma$ hydroxyl radicals. Part 2. Rate constants for reactions of OH $X^2\Pi$ wth halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans. 2*, *75*, 582-591, 1979b.

Cohen, N., and K. R. Westberg, Chemical kinetic data sheets for high-temperature chemical reactions, vol. II, *Aerospace Report No. ATR-88(7073)-3*, Nov. 14, 1988.

Cohen, N., and S. W. Benson, Transition-state-theory calculations for reactions of OH with haloalkanes. I. Halomethanes, *Aerospace Report No. ATR-85(7072)-1, I*, The Aerospace Corporation, El Segundo, CA, 1985.

Cohen, N., and S. W. Benson, Transition-state-theory calculations for reactions of OH with haloalkanes. I. Haloethanes, *Aerospace Report No. ATR-85(7072)-1, II*, The Aerospace Corporation, El Segundo, CA, 1985.

Cooper, R., J. B. Cumming, S. Gordon, and W. A. Mulac, The reactions of the halomethyl radicals CCl_3 and CF_3 with oxygen, *Radiat. Phys. Chem.*, *16*, 169, 1980.

Cox, R. A., *Tropospheric Ozone - Regional & Global Scale Interactions, NATO ASI Series C, vol. 227*, ed. I. S. Isaksen, D. Reidel, Dordrecht, 1988.

Cox, R. A., and G. S. Tyndall, Rate constants for reactions of CH_3O_2 in the gas phase, *Chem. Phys. Lett*, *65*, 357-360, 1979.

Cox, R. A., and G. S. Tyndall, Rate constants for the reactions of CH_3O_2 with HO_2, NO, and NO_2 using molecular modulation spectrometry, *J. Chem. Soc., Faraday Trans. 2*, *76*, 153-163, 1980.

Cox, R. A., and M. J. Roffey, *Environ. Sci. Technol*, *11*, 900, 1977.

Cox, R. A., R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Photochemical oxidation of halocarbons, *Atmos. Environ.*, *10*, 305-308, 1976.

Craggs, C., and A. W. Davison, The effect of simulated rainfall on grass fluoride concentrations, *Environ. Pollut. (Series B)*, *9*, 309-318, 1985.

Crutzen, P. J., Tropospheric ozone: An overview, *Tropospheric Ozone*, I. S. A. Isaksen, ed., Reidel, Dordrecht, Holland, 3-32, 1988.

Crutzen, P. J., The global distribution of hydroxyl, *Atmos. Chem.*, E. D. Goldberg, ed., Springer-Verlag, Berlin, 313-328, 1982.

Crutzen, P. J., Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air, *Tellus*, *26*, 47-57, 1974.

Crutzen, P. J., The possible importance of CSO for the sulphate layer of the stratosphere, *Geophys. Res. Lett.*, *3*, 73-76, 1976.

REFERENCES

Crutzen, P. J., The role of NO and NO_2 in the chemistry of the stratosphere and troposphere, *Annual Rev. Earth Planet Sci.*, *7*, 443-472, 1979.

Crutzen, P. J., and L. T. Gidel, A two dimensional model of the atmosphere, 2. The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3Cl, and the effect of various NO_x sources on tropospheric ozone, *J. Geophys. Res.*, *88*, 1983.

Crutzen, P. J., and J. Fishman, Average concentrations of OH in the troposphere, and the budgets of CH_4, CO, H_2, and CH_3CCl_3, *Geophys. Res. Lett.*, *4*, 321-324, 1977.

Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, A. J. Crawford, P. J. Fraser, and R. D. Rosen, The atmospheric lifetime experiment, 3: Lifetime methodology and application to 3 years of $CFCl_3$ data, *J. Geophys. Res.*, *88*, 8379-8400, 1983.

Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, A. J. Crawford, P. J. Fraser, and R. D. Rosen, The atmospheric lifetime experiment, 4: Results for CF_2Cl_2 based on 3 years of data, *J. Geophys. Res.*, *88*, 8401-8414, 1983.

Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, A. J. Crawford, P. J. Fraser, and R. D. Rosen, Atmospheric lifetime and annual release estimates for $CFCl_3$ and CF_2Cl_2 from 5 years of ALE data, *J. Geophys. Res.*, *91*, 10,797-10,817, 1986.

Curtis, A. R., and P. W. Sweetenham, *FACSIMILE/CHECKMAT User's Manual, AERE Report R12805*, Harwell Laboratory, Oxfordshire, England, 1987.

Dagaut, P., T. J. Wallington, and M. J. Kurylo, Temperature dependence of the rate constant for the HO_2 + CH_3O_2 gas-phase reaction, *J. Phys. Chem.*, *92*, 3833-3836, 1988a.

Dagaut, P., T. J. Wallington, and M. J. Kurylo, Flash photolysis kinetic absorption spectroscopy study of the gas-phase reaction HO_2 + $C_2H_5O_2$ over the temperature range 228-380 K, *J. Phys. Chem.*, *92*, 3836-3839, 1988b.

Dagaut, P., T. J. Wallington, and M. J. Kurylo, A flash photolysis investigation of the UV absorption spectrum and self-reaction kinetics of $CH_2ClCH_2O_2$ radicals in the gas phase, *Chem. Phys. Lett.*, *146*, 589-595, 1988c.

Dagaut, P., T. J. Wallington, and M. J. Kurylo, The UV absorption spectra and kinetics of the self reactions of CH_2ClO_2 and CH_2FO_2 radicals in the gas phase, *Int. J. Chem. Kinet.*, *20*, 815-826, 1988d.

Dahlem Conference, *Report of the Dahlem Workshop on the nature of seawater, March 10-15, 1975,* E. D. Goldberg, ed., Dahlem Conferenzen, Publisher, Berlin, 1976.

Daikin, DaiflonGas technical information, Osaka, Japan, 1989.

Dale, O., The interaction of enflurane, halothane, and the halothane metabolite trifluoroacetic acid with the binding of acidic drugs to human serum albumin, *Biochem. Pharmacol.*, *35*, 557-561, 1986.

Dallmeier, E., and D. Henschler, Determination and pharmacokinetics of trifluoroacetic acid after inhalation of low concentrations of halothane, *Naunyn-Schmiedebergs Arch. Pharmacol.*, *297*, R20, 1977.

Dallmeier, E., and D. Henschler, Halothan-Belastung am arbeitsplatz im operationssaal, *Deutsche Medizinische Wochenschrift*, *106*, 324-328, 1981.

Danckwerts, P. V., *Gas-Liquid Reactions*, *276 pp.*, McGraw-Hill, 1970.

Davidson, J. A., H. I. Schiff, T. J. Brown, and C. J. Howard, Temperature dependence of the rate constants for reactions of $O(^1D)$ atoms with a number of halocarbons, *J. Chem. Phys.*, *69*, 4277-4279, 1978.

Davis, D. D., G. Machado, B. Conaway, Y. Oh, and R. T. Watson, A temperature dependent kinetics study of the reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br, *J. Chem. Phys.*, *65*, 1268-1274, 1976.

Davis, D. D., J. D. Bradshaw, M. O. Rogers, S. T. Sandholm, and S. Kesheng, Free tropospheric and boundary layer measurements of NO over the central and eastern north pacific ocean, *J. Geophys. Res*, *92*, D2, 2049-2070, 1987.

Davison, A. W., Uptake, transport and accumulation of soil and airborne fluorides by vegetation, *Fluorides: Effects on Vegetation, Animals, and Humans*, Ed. by Shupe, J. L., Peterson, H. B., and Leone, N. C., Paragon Press, Salt Lake City, UT, 61-82, 1983.

DeAngelo, A. B., S. Herren-Freund, M. A. Pereira, N. E. Shults, and J. E. Klaunig, Species sensitivity to the induction of peroxisome proliferation by trichloroethylene and its metabolites, *The Toxicologist*, *6*, 113, 1986.

Dean, J. A., ed., *Lang's Handbook of Chemistry, 12th Edition*, McGraw-Hill, 1979.

Delmas, R. J., M. Briat, and M. Legrand, Chemistry of south polar snow, *J. Geophys. Res.*, *87*, 4314-4318, 1982.

DeMore, W. B., M. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publication 87-41*, *Evaluation No. 8*, Jet Propulsion Laboratory, Pasadena, CA, 196, 1987.

Derwent, R. G., Two-dimensional model studies of the impact of aircraft exhaust emissions on tropospheric ozone, *Atmos. Environ.*, *16*, 1997-2007, 1982.

Derwent, R. G., and A. E. J. Eggleton, Halocarbon lifetimes and concentration distributions calculated with a two-dimensional model, *Atmos. Environ.*, *12*, 1261-1270, 1978.

Derwent, R. G., and A. R. Curtis, Two-dimensional model studies of some trace gases and free radicals in the troposphere, *AERE Report R8853*, H. M. Stationery Office, London, 1977.

Derwent, R. G., and A. Volz-Thomas, The tropospheric lifetimes of halocarbons and their reactions with OH radicals, *AFEAS Report*, Section V, this report, 1989.

REFERENCES

Dewar, M. J. S., and H. S. Rzepa, Ground state of molecules. 53. MNDO calculations for molecules containing chlorine, *J. Comput. Chem.*, *4*, 158-169, 1983.

Dilling, W. L., Interphase transfer processes. II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions, *Env. Sci. Technol.*, *11*, 405-409, 1977.

Dimitriates, B., and M. Dodge, ed., *Proceedings of the empirical kinetic modeling approach (EKMA) validation workshop*, EPA-600/9-83-014, U.S. Environ. Prot. Agency, Research Triangle Park, N.C., August, 1983.

Dobé S., T. Berces, and F. Marta, Gas phase decomposition and isomerization of 2-pentoxy radicals, *Int. J. Chem. Kin.*, *18*, 329, 1986.

Dodge M., Combines use of modeling techniques and smog chamber data to derive ozone-precursor relationships, *Proceedings of the International Conf. of Photochemical Oxidant Pollution and its Control, II*, EPA-600/3-77.001b, 881-889, U.S. Environ. Prot. Agency, Research Triangle Park, N.C., 1977a.

Dodge, M., Effect of selected parameters on predictions of a photochemical model, *EPT-600/3-77-048, U.S. Environ. Prot. Agency*, Research Triangle Park, N.C., June 1977b.

Dognon, A. M., F. Caralp, and R. Lesclaux, Reactions des radicaux chlorofluoromethyl peroxyles avec NO: Etude cinetique dans le domaine de temperature comris entre 230 et 430 L, *J. Chim. Phys.*, *82*, 349-352, 1985.

Doley, D., Experimental analysis of fluoride susceptibility of grape vine (Vitis vinefera L.): Foliar fluoride accumulation in relation to ambient concentration and windspeed, *New Phytol*, *96*, 337-351, 1984.

Donahue, T. M., R. J. Cicerone, S. C. Liu, and W. L. Chameides, Effect of odd hydrogen on ozone depletion on chlorine reactions, *Geophys. Res. Lett.*, *3*, 105-108, 1976.

Donovan, R. J., K. Kaufmann, and J. Wolfrum, Reactions of O(^{1}D) with chlorofluoromethanes and CCl_4, *Nature*, *262*, 204-205, 1976.

Downing, R. C., *Fluorocarbon Refrigerants Handbook*, Prentice Hall, Englewood Cliffs, NJ, 1988.

Duce, R. A., On the source of gaseous chlorine in the marine atmosphere, *J. Geophys. Res.*, *74*, 4597-4599, 1969.

Duce, R. A., and E. J. Hoffman, Chemical fractionation at the air/sea interface, *Ann. Rev. Earth and Planet. Sci.*, *4*, 187-228, 1976.

Duce, R. A., J. W. Winchester, and T. Van Nahl, Iodine, bromine and chlorine in the Hawaiian marine atmosphere, *J. Geophys. Res.*, *70*, 1775-1799, 1965.

Duce, R. A., W. H. Zoller, and J. L. Moyers, Particulate and gaseous halogens in the Antarctic atmosphere, *J. Geophys. Res.*, *78*, 7802-7811, 1973.

Dunnold, D., M., Fluorocarbon lifetime and releases from 5 years of ALE data, paper presented at CSIRO symposium, *The Scientific Application of Baseline Observations of Atmospheric Composition*, Aspendale, Australia, Nov. 7-9, 1984.

DuPont, "Freon technical information" data sheets and unpublished data, *private communication with C. A. McCain and T. C. Berger*, Wilmington, DE, 1989.

Eberson, L., Studies on the Kolbe electrolytic synthesis IV. A theoretical investigation of the mechanism by standard potential calculations, *Acta. Chem. Scand.*, *17*, 2004-2018, 1963.

Eberson, L., Electron-transfer reactions in organic chemistry, *Advances in Physical Organic Chemistry*, *18*, V. Gold and D. Bethell, eds., Academic Press, New York, 79-185, 1982.

Edney, E. O., J. W. Spence, and P. L. Hanst, Peroxy nitrate air pollutants: Synthesis and thermal stability, *Nitrogenous Air Pollutants*, D. Grosjean, ed., 111-135, Ann Arbor Science, Mich., 1979.

Edney, E. O., J. W. Spence, and P. L. Hanst, Synthesis and thermal stability of peroxy alkyl nitrates, *J. Air Pollut. Control Assoc.*, *29*, 741-763, 1979.

Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, *26*, 58-70, 1974.

Ehhalt, D. H., How has the atmospheric concentration of CH_4 changed?, *The Changing Atmosphere, Physical, Chemical, and Earth Science Research Report* 7, Wiley-Interscience, Chichester, England, 25-32, 1988.

Elcombe, C. R., M. S. Rose, and I. S. Pratt, Biochemical, histological, and ultrastructural changes in rat and mouse liver following the administration of trichloroethylene, *Toxicol. Appl. Pharmacol.*, *79*, 365-376, 1985.

Ellenrieder, W., and M. Reinhard, ATHIAS -- an information system for abiotic transformations of halogenated hydrocarbons in aqueous solutions, *Chemosphere*, *17*, 331-344, 1988.

Erchel, E., World Water Balance, Elsevier, 1975.

Erickson, III, D. J., and R. A. Duce, On the global flux of atmospheric sea salt, *J. Geophys. Res.*, *93*, 14,079-14,088, 1988.

Eriksson, E., The yearly circulation of chloride and sulfur in nature: meteorological, geochemical and pedological implications, 1, *Tellus*, *11*, 373-403, 1959.

Eriksson, E., The yearly circulation of chloride and sulfur in nature: meteorological, geochemical and pedological implications, 2, *Tellus*, *12*, 63-109, 1960.

Ernst, J., H. Gg. Wagner, and R. Zellner, A combined flash photolysis/shock-tube study of the absolute rate constants for reactions of the hydroxyl radical with CH_4 and CF_3H around 1300 K, *Ber. Bunsenges. Phys. Chem.*, *82*, 409-414, 1978.

REFERENCES

Farmer, C. B., O. F. Raper, and R. H. Norton, Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere, *Geophys. Res. Lett.*, *3*, 13-16, 1976.

Faust, S. D., and O. M. Aly, *Chemistry of Natural Waters*, Ann Arbor Science, Ann Arbor, 1981.

Finlayson-Pitts, B. J., and J. N. Pitts, Jr., *Atmospheric Chemistry: Fundamentals and experimental techniques*, Wiley, New York, 1986.

Fiserova-Bergerova, V., Metabolism and toxicity of 2,2,2-trifluoroethyl vinyl ether, *Environ, Health Perspect.*, *21*, 225-230, 1977.

Fisher, D. A., C. H. Hales, D. L. Filkin, M. K. W. Ko, N. D. Sze, P. S. Connell, D. J. Wuebbles, I. S. A. Isaksen, and F. Strodal, Relative effects on stratospheric ozone of halogenated methanes and ethanes of social and industrial interest, *AFEAS Report*, Section VIII, this report, 1989a.

Fisher, D. A., C. H. Hales, W.-C. Wang, M. K. W. Ko, and N. D. Sze, Relative effects on global warming of halogenated methanes and ethanes of social and industrial interest, *AFEAS Report*, Section IX, this report, 1989b.

Fletcher, I. S. and D. Husain, Absolute reaction rates of oxygen (^1D) with halogenated parafins by atomic absorption spectroscopy in the vaccuum ultraviolet, *J. Phys. Chem.*, *80*, 1837-1840, 1976.

Flühler, H., Polomski, J., and P. Blaser, Retention and movement of fluoride in soils, *J. Environ Qual.*, *11*, 461-468, 1982.

Force, A. P., and J. R. Wiesenfeld, Collisional deactivation of $O(^1D)$ by the halomethanes. Direct determination of reaction efficiency, *J. Phys. Chem.*, *85*, 782-785, 1981.

Fraser, J., and L. S. Kaminsky, Metabolism of 2,2,2-trifluoroethanol and its relationship to toxicity, *Toxicol. Appl. Pharmacol.*, *89*, 202-210, 1987.

Fraser, J., and L. S. Kaminsky, 2,2,2-Trifluoroethanol intestinal and bone marrow toxicity: the role of its metabolism to 2,2,2-Trifluoroacetaldehyde and trifluoroacetic acid, *Toxicol. Appl. Pharmacol.*, *94*, 84-92, 1988.

Galloway, J. N., G. E. Likens, W. C. Keene, and J. M. Miller, The composition of precipitation in remote areas of the world, *J. Geophys. Res.*, *87*, 8771-8786, 1982.

Gehring, D. G., Private communication, E. I. DuPont de Nemours, Inc., 1987.

Gerkens, R., and J. A. Franklin, Hydrolysis of 1,1,1-trichloroethane, manuscript in preparation, 1989.

Gibbs, R. J., Mechanisms controlling world water chemistry, *Science*, *170*, 1088-1090, 1970.

Gillespie, H. M., and R. J. Donovan, Reaction of $O(^1D)$ atoms with chlorofluoromethanes: Formation of ClO, *Chem. Phys. Lett.*, *37*, 468-470, 1976.

Gillespie, H. M., J. Garraway, and R. J. Donovan, Reaction of O(2^1D_2) with halomethanes, *J. Photochem.*, *7*, 29-40, 1977.

Gillotay, D., P. C. Simon, and G. Brasseur, *Planet. Space Sci.*, in press, 1989.

Giorgi, F. and W. L. Chameides, The rainout parameterization in a photochemical model, *J. Geophys. Res.*, *90*, 7872-7880, 1985.

Goldman, P., The carbon-fluorine bond in compounds of biological interest, *Science*, *164*, 1123-1130, 1969.

Goldman, P., The enzymatic cleavage of the carbon-fluorine bondin fluoroacetate, *J. Biol. Chem.*, *240*, 3434-3438, 1965.

Goldman, P., and G. W. A. Milne, Carbon-fluorine bond cleavage. II. Studies on the mechanism of the defluorination of fluoroacetate, *J. Biol. Chem.*, *241*, 5557-5559, 1966.

Goldman, P., G. W. A. Milne, and D. B. Keister, Carbon-halogen bond cleavage. III. Studies on bacterial halidohydrolases, *J. Biol. Chem.*, *243*, 428-434, 1968.

Goldstein, E., B. L. Hammond, B. Sadri, and Y.-P. Hsia, Theoretical study of the reactions of O(^3P) atoms with a series of fluoroolefins, *J. Molecul. Struct., THEOCHEM*, *105*, 315-324, 1983.

Goodwin, R. D., and W. M. Haynes, Thermophysical properties of isobutane from 114 to 700 K at pressures to 70 MPa, *National Bureau of Standards, Technical Note 1051*, U. S. Government Printing Office, Washington, DC, 1982.

Gossett, J. M., Measurement of Henry's law constants for C_1 and C_2 chlorinated hydrocarbons, *Env. Sci. Technol.*, *21*, 202-208, 1987.

Green, R. G., and R. P. Wayne, Relative rate constants for the reactions of O(^1D) atoms with fluorocarbons and N_2O, *J. Photochem.*, *6*, 371-374, 1976/77a.

Green, R. G., and R. P. Wayne, Vaccuum ultra-violet absorption spectra of halogenated methanes and ethanes, *J. Photochem.*, *6*, 375-377, 1976/77b.

Greenberg, J. P., and P. R. Zimmerman, Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres, *J. Geophys. Res.*, *89*, 4767-4778, 1984.

Gregory, G. L., et al., Air chemistry over the tropical forest of Guyana, *J. Geophys. Res. 91*, 8603-8612, 1986.

Guderian, R., Air Pollution: Phytotoxicity of acidic gases and its significance in air pollution control, Springer Verlag, Berlin, 127 pp., 1977.

Gutman, D., N. Sanders, and J. E. Butler, Kinetics of the reactions of methoxy and ethoxy radicals with oxygen, *J. Phys. Chem.*, *86*, 66-70, 1982.

Hacket, P. A., and D. Phillips, *J. Chem. Soc. Farad. I*, *68*, 329, 1962.

REFERENCES

Hammitt, J. K., F. Camm, P. S. Connell, W. E. Mooz, K. A. Wolf, D. J. Wuebbles, and A. Bemazai, Future emission scenarios for chemicals that may deplete stratospheric ozone, *Nature*, *330*, 711-716, 1987.

Hampson, R. F., M. J. Kurylo, and S. P. Sander, Evaluated rate constants for selected HCFCs and HCFs with OH and O(^{1}D), *AFEAS Report*, Section III, this report, 1989.

Handwerk, V., and R. Zellner, Kinetics of the reactions of OH radicals with some halocarbons ($CHClF_2$, CH_2ClF, CH_2ClCF_3, CH_3CClF_2, CH_3CHF_2) in the termperature range 260-370 K, *Ber. Bunsenges. Phys. Chem.*, *82*, 1161-1166, 1978.

Hansen, J., G. Russell, D. Rind, P. Stone, A. Lacis, S. Lebedeff, R. Ruedy, and L. Travis, Efficient 3-D global models for climate studies: Models I and II, *Mon. Weather Rev.*, *111*, 609-662, 1983.

Harris, S. J., and J. A. Kerr, A kinetic and mechanistic study of the formation of alkyl nitrates in the photooxidation of n-heptane studied under atmospheric conditions, *Int. J. Chem. Kinet.*, *21*, 207-218, 1989.

Hart, E. J., S. Gordon, and J. K. Thomas, Rate constants for hydrated electron reactions with organic compounds, *J. Phys. Chem.*, *68*, 1271-1274, 1964.

Hartmann, J. Karthäuser, and R. Zellner, Kinetics of the reactions $CH_3O_2 + HO_2$ studied by laser photofragment emission, *submitted to J. Phys. Chem*, 1989.

Hartmann, J. Karthäuser, J. P. Sawersyn, and R. Zellner, Kinetics and HO_2 product yield of the reaction $C_2H_5O + O_2$ between 298 and 411 K, *submitted to J. Phys. Chem*, 1989.

Hautecloque. S., On the photooxidation of gaseous $CHCl_3$, *J. Photochem.*, *14*, 157, 1980.

Hendry, D. G., and R. A. Kenley, Atmospheric reaction products of organic compounds, *EPA-560/12-79-001*, June, 1979.

Herren-Freund, S., M. Pereira, M. Khoury, and G. Olson, Biochemical, histological, and ultrastructural changes in rat and mouse liver following the administration of trichloroethylene, *Toxicol. Appl. Pharmacol.*, *90*, 183-189, 1987.

Herron, J. T., Private communication, 1989.

Higashi, Y., M. Ashizawa, Y. Kabata, T. Majima, M. Uematsu, and K. Watanabe, Measurements of vapor pressure, vapor-liquid coexistence curve and critical parameters of refrigerant 152a, *JSME Int. J.*, *30*, 1106-1112, 1987.

Hine, J., and D. C. Duffey, Methylene derivatives as intermediates in polar reactions. XV. The decomposition of dichlorofluoroacetic acid, *J. Am. Chem. Soc.*, *81*, 1129-1131, 1959a.

Hine, J., and D. C. Duffey, Methylene derivatives as intermediates in polar reactions. XVI. The decomposition of chlorodifluoroacetic acid, *J. Am. Chem. Soc.*, *81*, 1131-1136, 1959b.

Hine, J., R. Wiesboeck, and R. G. Ghirardelli, The kinetics of the base-catalyzed deuterium exchange of 2,2-dihalo-1,1,1-trifluoroethanes, *J. Am. Chem. Soc.*, *83*, 1219-1222, 1961.

Hitchcock, D. R., L. L. Spiller, and W. E. Wilson, Sulfuric acid aerosols and HCl release in coastal atmospheres: Evidence of rapid formation of sulfuric acid particulates, *Atmos. Environ.*, *14*, 165-182, 1980.

HMSO, Chlorofluorocarbons and their effect on stratospheric ozone, *Pollution Paper 5, Department of the Environment*, H.M. Stationery Office, London, 1976.

Hogo, H., and M. W. Gery, User's guide for executing OZIPM-4 with CPM-IV or optional mechanisms, Volume I, *EPA Report No. 600/8-88/073*, Research Triangle Park, N.C., 1988.

Hohorst, F. A., and D. D. DesMarteau, Some reactions of CF_3OO derivatives with inorganic compounds. Synthesis and vibrational spectrum of trifluoromethyl peroxynitrate, *Inorg. Chem.*, *13*, 715-719, 1974.

Holaday, D. A., and R. Cummah, Personal communication, reported in *Fiserova-Bergerova,* 1977.

Holaday, D. A., and R. Cummah, Annual Meeting, American Society of Anesthesiologists, San Francisco, 1976.

Holdren, M. W., C. W. Spicer, and J. M. Hales, Peroxyacetyl nitrate solubility and decomposition rate in acidic water, *Atmos. Environ.*, *18*, 1171-1173, 1984.

Hong, H., and D. R. Kester, Redox state of iron in the offshore waters of Peru, *Limnol. Oceanogr.*, *31*, 512-524, 1986.

Horiuchi, N., C-F bond rupture of monofluoroacetate by soil microbes. Properties of the bacteria and the enzyme, *Seikagaku*, *34*, 92-98, 1962.

Howard, C. J., and K. M. Evenson, Rate constants for the reactions of OH with CH_4 and fluorine, chlorine, and bromine substituted methanes at 296 K, *J. Chem. Phys.*, *64*, 197-202, 1976a.

Howard, C. J., and K. M. Evenson, Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296 K, *J. Chem. Phys.*, *64*, 4303-4306, 1976b.

Hubrich, C., and F. Stuhl, The ultraviolet absorption of some halogenated methanes and ethanes of atmospheric interest, *J. Photochem.*, *12*, 93-107, 1980.

Hudson, R. F., and G. E. Moss, The mechanism of hydrolysis of acid chlorides. Part IX. Acetyl chloride, *J. Chem. Soc.*, 5157-5163, 1962.

Huie, R. E., and P. Neta, Chemical behavior of SO_3^- and SO_5^- radicals in aqueous solutions, *J. Phys. Chem.*, *88*, 5665-5669, 1984.

REFERENCES

Huie, R. E., D. Brault, and P. Neta, Rate constants for one-electron oxidation by the $CF_3O_2\bullet$, $CCl_3O_2\bullet$, and $CBr_3O_2\bullet$ radicals in aqueous solutions, *Chem. Biol. Interactions*, *62*, 227-235, 1987.

Hurst, D. F., and F. S. Rowland, Seasonal variations in the latitudinal distribution of tropospheric carbon monoxide: 1986-1988, *EOS*, *70*, 288, 1989.

Hutton, J. T., Chloride in rainwater in relation to distance from the ocean, *Search*, *7*, 207-208, 1976.

Huybrechts, G., and L. Meyers, Gas-phase chlorine-photosensitized oxidation of trichloroethylene, *Trans. Faraday Soc.*, *62*, 2191-2204, 1966.

Huybrechts, G., G. Martens, L. Meyers, J. Olbregts, and K. Thomas,*Trans. Faraday Soc.*, *61*, 1921, 1965.

Huybrechts, G., J. Olbregts, and K. Thomas, Gas-phase chlorine-photosensitized oxidation and oxygen-inhibited photochlorination of tetrachloroethylene and pentachloroethylene, *Trans. Faraday Soc.*, *63*, 1647-1655, 1967.

Irmann, R. B., A simple correlation between water solubility and structure of hydrocarbons and halohydrocarbons, *Chem. Ing. Tech.*, *37*, 789-798, 1965.

Ishii, D. N., and A. N. Corbascio, Some metabolic effects of halothane on mammalian tissue culture cells in vitro, *Anesthesiology*, 427-438, 1971.

Jacob, D. J., Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *J. Geophys. Res.*, *91*, 9807-9826, 1986.

Jacob, D. J., and S. C. Wofsy, Photochemical production of carboxylic acids in a remote continental atmosphere, *Acid Deposition Processes at High Elevation Sites*, , M. H. Unsworth and D. Fowler, eds., D. Reidel, Hingham, MA, in press, 1989.

Jacobsen, J. S., L. I. Heller, and P. van Leuken, Acidic precipitation at a site within the northeaster conurbation, *Water Air Soil Pollut.*, *6*, 339-349, 1976.

JANAF Thermochemical Tables, 2nd Ed., Stull, R., and H. Prophet, eds., 1979.

Japanese Association of Refrigeration, Thermophysical properties of refrigerants, chlorodifluoromethane R22, *JAR*, , Tokyo, 1975.

Jayanty, R. K. M., R. Simonaitis, and J. Heicklen, The phytolysis of chlorofluoromethanes in the presence of O_2 or O_3 at 213.9 nm and their reactions with $O(^1D)$, *J. Photochem.*, *4*, 382-398, 1975.

Jenkin, M. E., R. A. Cox, G. D. Hayman, and L. J. Whyte, Kinetic study of the reactions $CH_3O_2 + CH_3O_2$ and $CH_3O_2 + HO_2$ using molecular modulation spectrometry, *J. Chem Soc., Faraday Trans. 2*, *84*, 913-930, 1988.

Jeong, K.-M., and F. Kaufman, Rates of the reactions of 1,1,1-trichloroethane (methyl chloroform) and 1,1,2-trichloroethane with OH, *Geophys. Res. Lett*, *6*, 757-759, 1979.

Jeong, K.-M., and F. Kaufman, Kinetics of the reaction of hydroxyl radical with methane and with nine Cl- and F-substituted methanes. I. Experimental results, comparisons, and applications, *J. Phys. Chem.*, *86*, 1808-1815, 1982a.

Jeong, K.-M., and F. Kaufman, Kinetics of the reaction of hydroxyl radical with methane and with nine Cl- and F-substituted methanes. 2. Calculation of rate parameters as a test of transition-state-theory, *J. Phys. Chem.*, *86*, 1816-1821, 1982b.

Jeong, K.-M., K.-J. Hsu, J. B. Jeffries, and F. Kaufman, Kinetics of the reactions of OH with C_2H_5, CH_3CCl_3, $CH_2ClCHCl_2$, $CH_2ClCClF_2$, and CH_2FCF_3, *J. Phys. Chem.*, *88*, 1222-1226, 1984.

Johnson, J. E., The lifetime of carbonyl sulfide in the troposphere, *Geophys. Res. Lett*, *8*, 938-940, 1981.

Junge, C. E., Air chemistry and radioactivity, 282pp., Academic Press, 1963.

Junge, C. E., and R. T. Werby, The concentration of Cl^-, Na^+, K_+, Ca^+ and $SO_4{}^=$ in rain water over the U.S., *J. Meteorol.*, *15*, 417-425, 1958.

Kabata, Y., S. Tanikawa, M. Uematsu, and K. Watanabe, Preprint, tenth symposium on thermophysical properties, Gaithersburg, MD, *Int. J. Thermophysics*, *10*, to be published, 1989.

Kagann, R. H., J. W. Elkins, and R. L. Sams, Absolute band strengths of halocarbons F-11 and F-12 in the 8- to 16-µm region, *J. Geophys. Res.*, *88*, 1427-1432, 1983.

Kanome, Y., and I. Fujita, B.S. Thesis, Department of Mechanical Engineering, Keio University, Yokahama, Japan, 1986.

Kelly, M., Isolation of bacteria able to metabolize fluoroacetate of fluoroacetamide, *Nature*, *208*, 809-810, 1965.

Kerr, J. A., and J. G. Calvert, Chemical transformation modules for eulerian acid deposition models, vol. I: The gas-phase chemistry, *NCAR Report DW 930237*, Dec., 1984.

Khalil, M. A. K., and R. A. Rasmussen, The atmospheric lifetime of methylchloroform (CH_3CCl_3), *Tellus*, *36B*, 317-332, 1984.

Khalil, M. A. K., and R. A. Rasmussen, Causes of increasing atmospheric methane: Depletion of hydroxyl radicals and the rise of emissions, *Atmos. Environ.*, *19*, 397-407, 1985.

Khalil, M. A. K., and R. A. Rasmussen, Increase of $CHClF_2$ in the earth's atmosphere, *Nature*, *292*, 823-824, 1981.

Khalil, M. A. K., and R. A. Rasmussen, Trichlorotrifluoroethane (F-113) trends at Pt. Barrow, Alaska, *Geophysical Monitoring for Climate Change, No. 13, Summary Report 1984*, U.S. Department of Commerce, ERL/NOAA, Boulder, CO, 1985.

Kinnison, D., H. Johnston, and D. J. Wuebbles, Ozone calculations with large nitrous oxide and chlorine changes, *J. Geophys. Res.*, *93*, 14,165-14,175, 1988.

Kirsch, L. J. and D. A. Parkes, Recombination of tertiary butyl peroxy radicals. Part 1. Product yields between 298 and 373 K, *J. Chem. Soc., Faraday Trans. 1*, *77*, 293-307, 1981.

Kirsch, L. J. D. A. Parkes, T. J. Wallington, and A. Woolley, Self-reactions of isopropylperoxy radicals in the gas phase, *J. Chem. Soc., Faraday Trans. 1*, *74*, 2293-2300, 1978.

Klaasen, C., M. Amdur, and J. Doull (eds), *Casarett and Doull's Toxicology*, MacMillan Publishing Company, 13, 1986.

Kletskii, A. V., *Inz.-Fiz. Zh.,* (in Russian only), *7(4)*, 40-43, 1964.

Ko, M. K. W., K. K. Tung, D. K. Weisenstein, and N. D. Sze, A zonal-mean model of stratospheric tracer transport in isentropic coordinates: numerical simulations for nitrous oxide and nitric acid, *J. Geophys. Res.*, *90*, 2313-2329, 1985.

Ko, M. K. W., N. D. Sze, M. Livshits, M. B. McElroy, and J. A. Pyle, The seasonal and latitudinal behavior of trace gases and O_3 as simulated by a two-dimensional model of the atmosphere, *J. Atmos. Sci.*, *41*, 2381-2408, 1984.

Kohlen, R., H. Kratzke, and S. Mueller, Thermodynamic properties of saturated and compressed liquid difluorochloromethane, *J. Chem. Thermodynamics*, *17*, 1141-1151, 1985.

Kormann, C., D. W. Bahnemann, and M. R. Hoffman, Environmental photochemistry: is iron oxide an active photocatalyst? A comparative study of Fe_2O_3, ZnO, and TiO_2, *J. Photochem. Photobiol. A: Chem.*, in press, 1989.

Kostyniak, P., H. B. Bosmann, and F. A. Smith, Defluorination of fluoroacetate in vitro by rat liver subcellular fractions, *Toxicol. Appl. Pharmacol.*, *44*, 89-97, 1978.

Koubek, E., M. L. Haggett, C. J. Battaghlia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, Kinetics and mechanism of the spontaneous decompositions of some peroxoacids, hydrogen peroxide, and t-butyl hydroperoxide, *J. Am. Chem. Soc.*, *85*, 2263-2268, 1963.

Kritz, M. A,. and J. Rancher, Circulation of Na, Cl and Br in the tropical marine atmosphere, *J. Geophys. Res.*, *85*, 1633-1639, 1980.

Kubota, H., Y. Tanaka, T. Makita, H. Kashiwagi, and M. Noguchi, Thermodynamic properties of 1-chloro-1,2,2,2-tetrafluoroethane (R124), *Int. J. Thermophsyics*, *9*, 85-101, 1988.

Kurylo, M. J., P. C. Anderson, and O. Klais, A flash photolysis resonance fluorescence investigation of the reaction $OH + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$, *Geophys. Res. Lett.*, *6*, 760-762, 1979.

Kurylo, M. J., P. Dagaut, T. J. Wallington, and D. M. Neuman, Kinetic measurements of the gas-phase $HO_2 + CH_3O_2$ cross-disproportionation reaction at 298 K, *Chem. Phys. Lett.*, *139*, 513-518, 1987.

Lacis, A., J. Hansen, P. Lee, T. Mitchell, and S. Lebedeff, Greenhouse effect of trace gases, 1970-1980, *Geophys. Res. Lett.*, *8*, 1035-1038, 1981.

Lal, M., C. Schoneich, J. Monig, and K. D. Asmus, Rate constants for the reactions of halogenated organic radicals, *Int. J. Radiat. Biol.*, *54*, 773-785, 1988.

Lamb, B., A. Guenther, D. Gay, and H. Westberg, A national inventory of biogenic hydrocarbon emissions, *Atmos. Environ.*, *21*, 1695-1705, 1987.

Landing, W. M., and S. Westerlund, The solution chemistry of iron (II) in Framvaren Fjord, *Mar. Chem.*, *23*, 329-343, 1988.

Latimer, W. M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., pp. 45 & 128, Prentice-Hall, New York, 1952.

Lee, Y. N., Kinetics of some aqueous-phase reactions of peroxyacetylnitrate, *Conference of Gas-Liquid Chemistry of Natural Waters*, Brookhaven National Laboratory, Upton, NY, 1984.

Lee,Y. N., G. I. Senum, and J. S. Gaffney, Peroxyacetylnitrate stability, solubility, and reactivity: implications for tropospheric nitrogen cycles and precipitation chemistry, *Fifth International Conference of the Commission on Atmospheric Chemistry and Global Pollution*, Oxford, England, 1983.

Legrand, M., and R. J. Delmas, The ionic balance of Antarctic snow: A 10-year detailed record, *Atmos. Envrion.*, *18*, 1867-1874, 1984.

Legrand, M., and R. J. Delmas, Spatial variations of snow chemistry in Adelie Land, *Ann. Glaciol.*, *7*, 20-25, 1985.

Legrand, M., and R. J. Delmas, Formation of HCl in the Antarctic atmosphere, *J. Geophys. Res.*, *93*, 7153-7168, 1988.

Leighton, P. A., *Photochemistry of Air Pollution*, Academic Press, New York, 1961.

Lenhardt, T. M., C. E. McDade, and K. D. Bayes, Rates of reaction of butyl radicals with molecular oxygen, *J. Chem. Phys.*, *72*, 304-310, 1980.

Lesclaux, R., A. M. Dognon, and F. Caralp, Photo-oxidation of halomethanes at low temperature: The decomposition rate of CCl_3O and $CFCl_2O$ radicals, *J. Photochem. Photobiol., A: Chemistry*, *41*, 1-11, 1987.

Lesclaux, R., and F. Caralp, Determination of the rate constants for the reactions of $CFCl_2O_2$ radical with NO and NO_2 by laser photolysis and time resolved mass spectrometry, *Int. J. Chem. Kinet.*, *16*, 1117-1128, 1984.

Lesclaux, R., F. Caralp, A. M. Dognon, and D. Cariolle, The rate of formation of halomethyl peroxy nitrates in the stratosphere and their possible role as temporary reservoirs for ClO_x and NO_x species, *Geophys. Res. Lett.*, *13*, 933-936, 1986.

Levy, H., Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, *173*, 141-143, 1971.

REFERENCES

Lewis, R. S., S. P. Sander, S. Wagner, and R. T. Watson, Temperature-dependent rate constants for the reaction of ground-state chlorine with simple alkanes, *J. Phys. Chem.*, *84*, 2009-2015, 1980.

Liebhafsky, H. A., and A. Mohammed, The kinetics of the reduction, in acid solution, of hydrogen peroxide by iodide ion, *J. Am. Chem. Soc.*, *55*, 3977-3986, 1933.

Liebl, K. H., and W. Seiler, CO and H_2 destruction at the soil surface, *Proc. Symp. "Microbial Production and Utilisation of Gases"*, Goltze Druck, Gottingen, Federal Republic of Germany, 1976.

Lightfoot, P. D., B. Veyret, and R. Lesclaux, A flash-photolysis study of the CH_3O_2 + HO_2 reaction between 248 and 573 K, *J. Phys. Chem.*, *93*, 1989.

Lin, X., M. Trainer, and S. C. Liu, On the linearity of the tropospheric ozone production, *J. Geophys. Res.*, *93*, D12, 15,879-15,888, 1988.

Lind, J. A., and G. L. Kok, Henry's law determinations for aqueous solutions of hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid, *J. Geophys. Res.*, *91*, 7889-7895, 1986.

Lingenfelter, R. E., Production of carbon 14 by cosmic ray neutrons, *Review in Geophysics*, *1*, 35-55, 1963.

Liss, P. S., Gas transfer: Experiments and geochemical implications, *Air-Sea Exchange of Gases and Particles*, NATO ASI Series, 559 pp., P. S. Liss and W. G. N. Slinn, eds., Reidel Publishing Company, 1983.

Liss, P. S., and P. G. Slater, Flux of gases across the air-sea interface, *Nature*, *247*, 181-194, 1974.

Liu, R., R. E. Huie, and M. J. Kurylo, Rate constants for the reactions of the OH radical with some hydrochlorofluorocarbons over the temperature range 270 to 400k, *submitted to J. Phys. Chem.*, 1989.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, *92*, 4191, 1987.

Livingstone, D. A., Chemical composition of rivers and lakes, *U.S. Geol. Surv. Profess. Paper 440-G*, 1963.

Lloyd, S. C., D. M. Blackburn, and P. M. D. Foster, Trifluoroethanol and its oxidative metabolites: Comparison of in vivo and in vitro effects in rat testis, *Fd. Chem. Toxic.*, *24*, 653-654, 1986.

Lloyd, S. C., D. M. Blackburn, and P. M. D. Foster, Trifluoroethanol and its oxidative metabolites: Comparison of in vivo and in vitro effects in rat testis, *Toxicol. Appl. Pharmacol.*, *92*, 390-401, 1988.

Logan, J. A., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, *J. Geophys. Res.*, *90*, 10,463-10,482, 1985.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86*, 7210-7254, 1981.

Lorenz, K., D. Räsa, R. Zellner, and B. Fritz, Laser photolysis-LIF kinetic studies of the reactions of CH_3O and CH_2CHO with O_2 between 300 and 500 K, *Ber. Bunsenges Phys. Chem.*, *89*, 341-342, 1985.

Louis, J. F., Mean meridional circulation. The natural stratosphere of 1974, *CIAP Monograph 1, Dept. of Trans., DOT-TST-75-51*, 6-23 to 6-49, 1975.

Lovelock, J. E., R. J. Maggs, and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, *Nature*, *241*, 194-196, 1973.

Lyman, W. J., Estimation of physical properties, *Environmental Exposure from Chemicals*, *I*, W. B. Neely and G. E. Blau, eds., CRC Press, Boca Raton, FL, 13-47, 1985.

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt, *Handbook of Chemical Property Estimation Methods*, McGraw-Hill Book Company, New York, 1982.

Mabey, W., and T. Mill, Critical review of hydrolysis of organic compounds under environmental conditions, *J. Phys. Chem. Ref. Data*, *7*, 383-483, 1978.

MacIntyre, F., Why the sea is salt, *Scientific American*, *233*, 104-115, 1970.

Mackay, D., and W. Y. Shiu, A critical review of Henry's law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data*, *10*, 1175-1199, 1981.

MacLean, D. C., L. H. Weistein, D. C. McCune, and R. E. Schneider, Fluoride-induced suture red spot in "Elberta' peach", *Environ. Exp. Bot.*, *24*, 353-367, 1984.

Madhavan, V., H. Levanon, and P. Neta, Decarboxylation by SO_4^-radicals, *Radiat. Res.*, *76*, 15-22, 1978.

Maenhaut, W., W. H. Zoller, R. A. Duce, and G. L. Hoffmann, Concentration and size distribution of particular trace elements in the South Polar atmosphere. *J. Geophys. Res.*, *84*, 2021-2031, 1979.

Magid, H., Allied Signal Corporation, Private communication, 1988.

Mahadevan, T. N., V. Meenakashy, and U. C. Mishra, Fluoride cycling in nature through precipitation, *Atmos. Environ.*, *20*, 1745-1749, 1986.

Makide, Y., and F. S. Rowland, Tropospheric concentrations of methyl chloroform, CH_3CCl_3, in January 1978 and estimates of atmospheric residence times for hydrohalocarbons, *Proc. Nat'l Acad. Sci.(USA)*, *78*, 5933-5937, 1981.

Marais, J. S. C., monofluoroacetic acid, the toxic principle of "Gifblaar" Dichapetalum cymosum (Hook), *Engl. Onderstepoort J. Vet Sci. Animal Ind*, *20*, 67-73, 1944.

Mario, M., K. Fiyu, R. Takiyama, F. Chikasue, H. Kikuchi, and L. Ribaric, Quantitative analysis of trifluoroacetate in the urine and blood by isotachophoresis, *Anesthesiology*, *53*, 56-59, 1980.

Martens, C. S., J. J. Wesolowski, R. C. Harriss, and R. Kaifer, Chlorine loss for Puerto Rican and San Francisco Bay area marine aerosols, *J. Geophys. Res*, *78*, 8778-8792, 1973.

Martens, G. J., M. Godfroid, J. Delvaux, and J. Verbeyst, Gas phase hydrogen abstraction from asymmetrically halogenated ethanes by chlorine atoms, *Int. J. Chem. Kin.*, *8*, 153, 1976.

Martin, J.-P., and G. Paraskevopoulos, A kinetic study of the reactions of OH radicals with fluoroethanes. Estimates of C-H bond strengths in fluoroalkanes, *Can. J. Chem.*, *61*, 861-865, 1983.

Mathias, E., E. Sanhueza, I. C. Hisatsune, and J. Heicklen, The chlorine atom sensitized oxidation and the ozonolysis of C_2Cl_4, *Can. J. Chem.*, *52*, 3852-3862, 1974.

McAdam, K., B. Veyret, and R. Lesclaux, UV absorption spectra of HO_2 and CH_3O_2 radicals and the kinetics of their mutual reactions at 298 K, *Chem. Phys. Lett*, *133*, 39-44, 1987.

McAdam, K. G., and R. W. Walker, Arrhenius parameters for the reaction $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$, *J. Chem. Soc., Faraday Trans. 2*, *83*, 1509-1517, 1987.

McCaulley, J. A., S. Anderson, J. B. Jeffries, and F. Kaufman, Kinetics of the reaction of CH_3O with NO_2, *Chem. Phys. Lett*, *115*, 180-186, 1985.

McClenahen, J. R., Distribution of soil fluorides near an airborne fluoride source, *J. Environ. Qual.*, *5*, 472-475, 1976.

McCune, D. C., On the establishment of air quality criteria, with reference to the effects of atmospheric fluorine on vegetation, *Air Quality Monograph 69-3* , American Petroleum Institute, New York, 33 pp., 1969.

McCune, D. C., D. H. Silberman, and L. H. Weinstein, Effects of relative humidity and free water on the phytotoxicity of hydrogen fluoride and cryolite, *Proc. Int. Clean Air Congr., 4th, Tokyo, 16-20 May 1977*, Japanese Union of Air Pollution Prevention Associations, Tokyo, 116-119, 1977.

McFarland, M., D. Kley, J. W. Drummond, A. L. Schmeltekopf, and R. H. Winkler, Nitric oxide measurements in the equatorial Pacific region, *Geophys. Res. Lett.*, *6*, 605-608, 1979.

McKay, C., M. Pandow, and R. Wolfgang, On the chemistry of natural radiocarbon, *J. Geophys. Res.*, *68*, 3829-3931, 1963.

McLinden, M. O., Physical properties of alternatives to the fully halogenated chlorofluorocarbons, *AFEAS Report,* Section II, this report, 1989.

McLinden, M. O., J. S. Gallagher, L. A. Weber, G. Morrison, D. Ward, A. R. H. Goodwin, M. R. Moldover, J. W. Schmidt, H. B. Chae, T. J. Bruno, J. F. Ely, and M. L. Huber, Measurement and formulation of thermodynamic properties of refrigerants 134 (1,1,1,2-tetrafluoroethane) and 123 (1,1-dichloro-2,2,2-trifluoroethane), *ASHRAE Trans. 95*, to be published, 1989.

McMillen, D. F., and D. M. Golden, Hydrocarbon bond dissociation energies, *Ann. Rev. Phys. Chem.*, *33*, 493-532, 1982.

Mears, W. H., R. F. Stahl, S. R. Orfeo, R. C. Shair, L. F. Kells, W. Thompson, and H. McCann, Thermodynamic properties of halogenated ethanes and ethylenes, *Ind. Eng. Chem.*, *47*, 1449-1454, 1955.

Midgley, P. M., The production and release to the atmosphere of 1,1,1-trichloroethane (methyl chloroform), *Atmos. Env.*, *23, No. 12*, 1989.

Miller, C., D. L. Filkin, A. J. Owens, J. M Steed, and J. P. Jesson, A two-dimensional model of stratospheric chemistry and transport, *J. Geophys. Res.*, *86*, 12,039, 1981.

Miller, C., J. M. Steed, D. L. Filkin, and J. P. Jesson, The fluorocarbon ozone theory, 7, one-dimensional modeling, an assessment of anthropogenic perturbations, *Atmos. Environ.*, *15*, 729, 1981a.

Moffett, J. W., and R. G. Zika, Reaction kinetics of hydrogen peroxide with copper and iron in seawater, *Env. Sci. Technol.*, *21*, 804-810, 1987a.

Moffett, J. W., and R. G. Zika, Photochemistry of copper complexes in seawater, *Photochemistry of Environmental Aquatic Systems*, ACS Symposium Series No. 327, R. G. Zika and W. J. Cooper, eds., Chapter 9, 116-330, 1987b.

Mohammed, A., and H. A. Liebhafsky, The kinetics of the reduction of hydrogen peroxide by the halides, *J. Am. Chem. Soc.*, *56*, 1680-1685, 1934.

Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluorocarbons. Chlorine atom-catalyzed destruction of ozone, *Nature*, *249*, 810-812, 1974.

Molina, M. J., and G. Arguello, Ultraviolet absorption spectrum of methylhydroperoxide vapor, *Geophys. Res. Lett.*, *6*, 953, 1979.

Molina, M. J., and L. T. Molina, Work in progress, 1990.

Monig, J., D. Bahnemann, and K. D. Asmus, One electron reduction of CCl_4 in oxygenated aqueous solutions: A CCl_3O_2-free radical mediated formation of Cl- and CO_2, *Chem. Biol. Interactions*, *45*, 15-27, 1983.

Moortgat, G., B. Veyret, and R. Lesclaux, Absorption spectrum and kinetics of reactions of the acetylperoxy radical, *J. Phys. Chem.*, *93*, 2362-2368, 1989.

Moortgat, G. K., B. Veyret, and R. Lesclaux, Rate constants for the reaction CH_3COO_2 + HO_2, *J. Phys. Chem.*, *93*, in press, 1989.

Moortgat, G. K., J. P. Burrows, W. Schneider, G. S. Tyndall, and R. A. Cox, A study of the HO_2 + CH_3CHO reaction in the photolysis of CH_3CHO, and its consequences for atmospheric chemistry, *Proc. 4th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*, D. Riedel Publ. Co., Dordrecht, 271-281, 1987.

Morel, O., R. Simonaitis, and J. Heicklen, Ultraviolet absorption spectra of HO_2NO_2, $CCl_3O_2NO_2$, $CCl_2FO_2NO_2$, and $CH_3O_2NO_2$, *Chem. Phys. Lett.*, *73*, 38-42, 1980.

Morrison, G., unpublished data, National Institute of Standards and Technology, Gaithersburg, MD, 1989.

Morrison, S. R., *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum, New York, 1980.

Müller, K. L., and H. J. Schumacher, *Z. Phys. Chem., B37*, 365, 1937a.

Müller, K. L., and H. J. Schumacher, *Z. Phys. Chem., B35*, 455, 1937b.

Murray, J.J. ed., *Appropriate use of fluorides for human health*, World Health Organization, 1-129, 1986.

NAS, *Halocarbons: Effects on stratospheric ozone*, National Academy of Science, Washington, DC, 1976.

NASA Panel for Data Evaluation, Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation Number 8, W. B. Demore, M. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, *JPL Publ. 87-41*, Sept. 15, 1987.

NASA/WMO, Atmospheric ozone 1985: assessment of our understanding of the processes controlling its present distribution and change, *WMO Report No. 16*, sponsored by WMO, NASA, NOAA, FAA, UNEP, CEC, and BMFT, Washington, DC, 1986.

National Research Council, *Biologic Effects of Atmospheric Pollutants: Flourides*, National Academy of Sciences, Washington, DC, 1971.

National Research Council, *Chlorine and Hydrogen Chloride*, National Academy of Sciences, Washington, DC, 1976.

Neely, W. B., Hydrolysis, *Environmental Exposure from Chemicals, I*, W. B. Neely and G. E. Blau, eds., CRC Press, Boca Raton, FL, 157-173, 1985.

Neely, W. B., and J. H. Plonka, Estimation of time-averaged hydroxyl radical concentrations in the troposphere, *Environ. Sci. Tech., 12*, 317-321, 1978.

Nelson, L., J. J. Treacy, and H. W. Sidebottom, Oxidation of methylchloroform, *Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, B. Versino and G. Angeletti, eds., D. Riedel Publ. Co., Dordrecht, 258-263, 1984.

Newell, R. E., J. W. Kidson, G. Vincent, and G. J. Boer, *The general circulation of the tropical atmosphere and interactions with extratropical latitudes, Vol. 1*, MIT Press, Cambridge, MA, 1972.

Nicksic, S. W., J. Harkins, and P. K. Mueller, Some analyses for PAN and studies of its structure, *Atmos. Environ., 1*, 11-18, 1967.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, FTIR spectroscopic study of haloalkyl peroxynitrates formed via $ROO + NO_2 \rightarrow ROONO_2$ ($R=CCl_3$, $CFCl_2$, and CF_2Cl), *Chem. Phys. Lett., 61*, 100-104, 1979.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, An FTIR study of the Cl-atom-initiated oxidation of CH_2Cl_2 and CH_3Cl, *Int. J. Chem. Kinet.*, *12*, 1001-1012, 1980a.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, FTIR studies of the kinetics and mechanism for the reaction of Cl atom with formyl chloride, *Int. J. Chem. Kinet.*, *12*, 915-920, 1980b.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, FTIR spectroscopic observation of peroxyalkyl nitrates formed via $ROO + NO_2 \rightarrow ROONO_2$, *Chem. Phys. Lett.*, *55*, 289-292, 1978.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, Fourier transform infrared studies of the self-reaction of CH_3O_2 radicals, *J. Phys. Chem.*, *85*, 877-881, 1981.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, Fourier transform infrared studies of the self-reaction of $C_2H_5O_2$ radicals, *J. Phys. Chem.*, *86*, 3825-3829, 1982.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, FTIR study of the kinetics and mechanism for Cl-atom-initiated reactions of acetaldehyde, *J. Phys. Chem.*, *89*, 588-591, 1985.

Nip, W. S., D. L. Singleton, R. Overand, and G. Paraskevopoulos, Rates of OH radical reactions. 5. Reactions with CH_3F, CH_2F_2, CHF_3, CH_3CH_2F and CH_3CHF_2 at 297 K, *J. Phys. Chem.*, *83*, 2440-2443, 1979.

Okabe, H., *Photochemistry of Small Molecules*, J.Wiley & Sons, 1978.

Orlando, J. J., J. B. Burkholder, and A. R. Ravishankara, Atmospheric chemistry of hydrofluoroethanes and hydrochlorofluoroethanes: II. UV absorption cross-sections, *to be submitted to J. Geophys. Res.*, 1990.

Owens, A. J., C. H. Hales, D. L. Filkin, C. Miller, J. M. Steed, and J. P. Jesson, A coupled one-dimensional radiative-convective, chemistry transport model of the atmosphere, *J. Geophys. Res.*, *90*, 2283-2311, 1985.

Packer, J. E., R. L. Willson, D. Bahnemann, and K. D. Asmus, Electron transfer reactions of halogenated aliphatic peroxyl radicals: Measurement of absolute rate constants by pulse radiolysis, *J. C. S. Perkin, Trans. II*, 296-299, 1980.

Paraskevopoulos, G., D. L. Singleton, and R. S. Irwin, Rates of OH radical reactions. 8. Reactions with CH_2FCl, CHF_2Cl, $CHFCl_2$, CH_3CF_2Cl, CH_3Cl, and C_2H_5Cl at 297 K, *J. Phys. Chem.*, *85*, 561-564, 1981.

Parkes, D. A., The roles of alkylperoxy and alkoxy radicals in alkyl radical oxidation at room temperature, *15th International Symp. Combustion, 1974*, The Combustion Institute, Pittsburgh, PA, 795-805, 1975.

Parmelee, H. M., Water solubility of Freon refrigerants, *Refrig. Eng.*, *61*, 1341-1345, 1953.

Parungo, F. P., C. T. Nagamoto, J. Rosinski, and P. L. Haagenson, A study of marine aerosols over the Pacific Ocean, *J. Atmos. Chem.*, *4*, 199-226, 1986.

REFERENCES

Pate, C. T., B. J. Finlayson, and J. N. Pitts, Jr., A longpath infrared spectroscopic study of the reaction of methylperoxy free radicals with nitric oxide, *J. Am. Chem. Soc.*, *96*, 6554-6558, 1974.

Pattison, F. L. M., Fluoroacetates, *Toxic Aliphatic Fluorine Compounds*, Elsevier Publishing Co., London, 12-81, 1959.

Peirson, D. H., P. A. Cawse, and R. S. Cambray, Chemical uniformity of airborne particulate material, and a maritime effect, *Nature, 251*, 675-679, 1974.

Penkett, S. A., N. J. D. Prosser, R. A. Rasmussen, and M. A. K. Khalil, Atmospheric measurements of CF_4 and other fluorocarbons containing the CF_3 grouping, *J. Geophys. Res.*, *86*, 5172-5178, 1981.

Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., Rate constants for the reaction of OH radicals with $CHFCl_2$ and CH_3Cl over the temperature range 298-423 K and with CH_2Cl_2 at 298 K, *J. Chem. Phys.*, *64*, 1618-1620, 1976.

Peters, L. K., Gases and their precipitation scavenging in the marine atmosphere, *Air-Sea Exhange of Gases and Particles, NATO ASI Series*, 559 pp., P. S. Liss and W. G. N. Slinn, eds., Reidel Publishing Company, 1983.

Peters, R. A., Lethal synthesis, *Proc. Royal Soc.*, *B139*, 143-170, 1952.

Peters, R. A., R. J. Hall, P. F. V. Ward, and N. Sheppard, The chemical nature of the toxic compounds containing fluorine in the seeds of Dichapetalum toxicarium, *Biochem J.*, *77*, 17-23, 1960.

Pickard, J. M., and A. S. Rodgers, Kinetics of the gas-phase reaction of $CH_3F + I_2 <-> CH_2FI + HI$: the C-H bond dissociation energy in methyl and methylene fluorides, *Int. J. Chem. Kinet.*, *15*, 569-577, 1983.

Pitts, J. N. Jr., H. L. Sandoval, and R. Atkinson, Relative rate constants for the reaction of $O(^1D)$ atoms with fluorocarbons and N_2O, *Chem. Phys. Lett.*, *29*, 31-34, 1974.

Plumb, I. C., and K. R. Ryan, Kinetics of the reaction of CF_3O_2 with NO, *Chem. Phys. Lett.*, *92*, 236-238, 1982.

Plumb, I. C., K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Kinetics of the reaction of $C_2H_5O_2$ with NO at 295 K, *Int. J. Chem. Kinet.*, *14*, 183-194, 1982.

Polomski, J., H. Fluhler, and P. Blaser, Fluoride-induced mobilization and leaching of organic matter, iron, and aluminum, *J. Environ. Qual.*, *11*, 452-456, 1982.

Prather, M. J., Tropospheric hydroxyl concentrations and the lifetimes of hydrochlorofluorocarbons (HCFCs), *AFEAS Report*, Section V, this report, 1989.

Prather, M .J., European sources of halocarbons and nitrous oxide: update 1986, *J. Atmos. Chem.*, *6*, 375-406, 1988.

Prather, M., M. McElroy, S. Wofsy, G. Russell, and D. Rind, Chemistry of the global troposphere: Fluorocarbons as tracers of air motion, *J. Geophys. Res.*, *92*, 6579-6613, 1987.

Preuss, P. W. A. G. Lemmens, and L. H. Weinstein, Studies on fluoro-organic compounds in plants. I. Metabolism of 2-^{14}C-fluoroacetate, *Contrib. Boyce Thompson Inst.*, *24*, 25-32, 1968.

Preuss, P. W., and L. H. Weinstein, Studies of fluoro-organic compounds in plants. II. Defluorination of fluoroacetate, *Contrib. Boyce Thompson Inst.*, *24*, 151-156, 1969.

Prinn, R. G., How have the atmospheric concentrations of the halocarbons changed?, *The Changing Atmosphere, Physical, Chemical, and Earth Science Research Report 7*, Wiley-Interscience, Chichester, England, 33-48, 1988.

Prinn, R.G., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric trends in methyl chloroform and the global average for the hydroxyl radical, *Science*, *238*, 946-950, 1987.

Prinn, R. G., P. G. Simmonds, R. A. Rasmussen, R. D. Rosen, F. N. Alyea, C. A. Cardelino, A. J. Crawford, D. M. Cunnold, P. J. Fraser, and J. E. Lovelock, The atmospheric lifetime experiment, 1. Introduction, instrumentation and overview, *J. Geophys. Res.*, *88*, 8353-8367, 1983.

Prinn, R. G., R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, D. M. Cunnold, B. C. Lane, C. A. Cardelino, and A. J. Crawford, The atmospheric lifetime experiments, 5, results for CH_3CCl_3 based on three years of data, *J. Geophys. Res.*, *88*, 8415-8426, 1983.

Pritchard, H. O., and H. A. Skinner, The heats of hydrolysis of the chloro-substituted acetyl chlorides, *J. Chem. Soc.*, *272*, 1950.

Raemdonck, H., W. Maenhaut, and M. O. Andreae, Chemistry of marine aerosol over the tropical and equatorial Pacific, *J. Geophys. Res.*, *91*, 8623-8636, 1986.

Raiswell, R. W., P. Brimblecombe, D. L. Dent, and P. S. Liss, *Environmental Chemistry*, John Wiley & Sons, New York, 1980.

Ramanathan, V., Greenhouse effect due to chlorofluorocarbons: Climate implications, *Science*, *190*, 50-52, 1975.

Ramanathan, V., L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lucas, F. Luther, J. Mahlman, R. Reck, and M. Schlesinger, Climate-chemical interactions and effects of changing atmospheric trace gases, *Rev. Geophys.*, *25*, 1441-1482, 1987.

Rapson, W., M. Nazar, and V. K. Bursky, Mutagenicity produced by aqueous chlorination of organic compounds, *Bull. Environ. Contam. Toxicol.*, *24*, 590-596, 1980.

Rasmussen, R. A., and M. A. K. Khalil, Atmospheric halocarbons: Measurements and analyses of selected trace gases, *Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone: Its Variation and Human Influences*, , Rep. FAA-EE-80-20, edited by A. C. Aikin, DOT, FAA, Washington, DC, 209-231, 1980.

Rasmussen, R. A., and M. A. K. Khalil, Latitudinal distributions of trace gases in and above the boundary layer, *Chemosphere*, *11*, 227-235, 1982.

REFERENCES

Rasmussen, R. A., M. A. K. Khalil, and R. W. Dalluge, Atmospheric trace gases in Antarctica, *Science*, *211*, 285-287, 1981.

Ravishankara, A. R., Kinetics of radical reactions in the atmospheric oxidation of CH_4, *Ann. Rev. Phys. Chem.*, *39*, 367-394, 1988.

Ravishankara, A. R., F. L. Eisele, and P. H. Wine, Pulsed laser photolysis-longpath laser abosrption kinetics study of the reaction of methylperoxy radicals with NO_2, *J. Chem. Phys.*, *73*, 3743-3749, 1980.

Ravishankara, A. R., F. L. Eisele, N. M. Kreutter, and P. H. Wine, Kinetics of the reaction of CH_3O_2 with NO, *J. Chem. Phys.*, *74*, 2267-2274, 1981.

Rayez, J.-C., M.-T. Rayez, P. Halvick, B. Duguay, R. Lesclaux, and J. T. Dannenberg, A theoretical study of the decomposition of halogenated alkoxy radicals. I. Hydrogen and chlorine extrusions, *Chem. Phys.*, *116*, 203-213, 1987.

Reddy, J. K., D. L. Azarnoff, and C. E. Hignite, Hypolipidaemic hepatic peroxisome proliferators form a novel class of chemical carcinogens, *Nature*, *283*, 397-398, 1980.

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids, fourth edition*, McGraw-Hill Book Company, New York, 1987.

Reimer, A., and F. Zabel, Thermal stability of peroxynitrates, *9th Int. Symposium on Gas Kinetics*, University of Bordeaux, Bordeaux, France, July 20-25, 1986.

Richardson, W.H., Acidity, hydrogen bonding and complex formation, *The Chemistry of Functional Groups*, S. Patai, ed., John Wiley & Sons, Chichester, Chapter 5, 129-160, 1983.

Ridley, B. A., M. A. Carroll, and G. L. Gregory, Measurements of nitric oxide in the boundary layer and free troposphere over the Pacific ocean, *J. Geophys. Res.*, *92*, D2, 2025-2048, 1987.

Robbins, R. C., R. D. Cadle, and D. L. Eckhardt, The conversion of sodium chloride to hydrogen chloride in the atmosphere, *J. Meteorol.*, *16*, 53-59, 1959.

Roberts, J. D., and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., New York, 1965.

Robertson, R. E., K. M. Kosky, A. Annessa, J. N. Ong, J. M. W. Scott, and M. S. Blandamer, Kinetics of solvolysis in water of four secondary alkyl nitrates, *Can. J. Chem.*, *60*, 1780-1785, 1982.

Robins, D. E., and R. S. Stolarski, Comparison of stratospheric ozone destruction by fluorocarbons 11, 12, 21, and 22, *Geosphys. Res. Lett.*, *3*, 603-606, 1976.

Rogers, J. D., and R. D. Stephens, Absolute infrared intensities for F-113 and F-114 and an assessment of their greenhouse warming potential relative to other chlorofluorocarbons, *J. Geophys. Res.*, *93*, 2423-2428, 1988.

Rognerud, B., I. S. A. Isaksen, and F. Stordal, Model studies of stratospheric ozone depletion, *Proc. Quadrennial Ozone Symposium*, Univ. of Gottingen, Rep. of Germany, 1988.

Rosenberg, P. H., and T. Wahlstrom, Hepatotoxicity of halothane metabolites in vivo and inhibition of fibroblast growth in vitro, *Acta Pharmacol. Toxicol.*, *29*, 9-19, 1971.

Rosenberg, P. H., and T. Wahlstrom, Trifluoroacetic acid and some possible intermediate metabolites of halothane as haptens, *Anesthesiology*, *38*, 224-227, 1973.

Rosenberg, P. H., Decrease in reduced glutathione and NADPH and inhibition of glucose-6-phosphate dehydrogenase activity caused by metabolites of fluroxene and halothane, *Ann. Med. Exp. Biol. Fenniae*, *49*, 84-88, 1971.

Rothenberger, G., J. Moser, M. Gratzel, N. Serpone, and D. K. Sharma, Charge carrier trapping and recombination dynamics in small semiconductor particles, *J. Am. Chem. Soc.*, *107*, 8054-8059, 1985.

Rowland, R. S., and I. S. A. Isaksen, Introduction, *The Changing Atmosphere, Physical, Chemical, and Earth Science Research Report 7*, Wiley-Interscience, Chichester, England, 1-4, 1988.

Rubin, T. R., B. H. Levendahl, and D. M. Yost, The heat capacity, heat of transition, vaporization, vapor pressure, and entropy of 1,1,1-trichloroethane, *J. Am. Chem. Soc.*, *66*, 279-282, 1944.

Rudolph, J., and D. H. Ehhalt, Measurements of C_2-C_5 hydrocarbons over the North Atlantic, *J. Geophys. Res.*, *86*, 11,959-11,964, 1981.

Ruppert, H., Geochemical investigations on atmospheric precipitation in a medium-sized city (Gottingen F.R.G.), *Water Air Soil Pollut.*, *4*, 447-460, 1975.

Ryaboshapko, A. G., The atmospheric sulfur cycle, *The Global Biogeochemical Sulfur Cycle*, M. V. Ivanov and B. R. Freney, eds., Wiley, New York, 203-296, 1983.

Ryan, K. R., and I. C. Plumb, Kinetics of the reactions of CF_3 with $O(^3P)$ and O_2 at 295 K, *J. Phys. Chem.*, *86*, 4678-4683, 1982.

Ryan, K. R., and I. C. Plumb, Kinetics of the reactions of CCl_3 with O and O_2 and of CCl_3O_2 with NO at 295 K, *Int. J. Chem. Kinet.*, *16*, 591-602, 1984.

Salih, I. M., T. Soeylemez, and T. I. Balkas, Radiolysis of aqueous solutions of difluorochloromethane, *Radiat. Res.*, *67*, 235-243, 1976.

Sander, S. P., and R. T. Watson, Kinetics studies of the reactions of CH_3O_2 with NO, NO_2, and CH_3O_2 at 298 K, *J. Phys. Chem.*, *84*, 1664-1674, 1980.

Sanders, N., J. E. Butler, L. R. Pasternack, and J. R. McDonald, $CH_3O(X^2E)$ production from 266 nm photolysis of methyl nitrite and reaction with NO, *Chem. Phys.*, *48*, 203-208, 1980.

Sandoval, H. L., R. Atkinson, and J. N. Pitts, Jr., Reactions of electronically excited $O(^1D)$ atoms with fluorocarbons, *J. Photochem.*, *3*, 325-327, 1974.

REFERENCES

Sanhueza, E., The chlorine atoms photosensitized oxidation of $CHCl_3$, $CHClF_2$, and CHF_3, *J. Photochem.*, *7*, 325, 1977.

Sanhueza, E., and J. Heicklen, Oxidation of chloroethylene, *J. Phys. Chem*, *79*, 677-681, 1975a.

Sanhueza, E., and J. Heicklen, The chlorine-atom initiated and $Hg(^3P_1)$-photosensitized oxidation of CH_2Cl_2, *J. Photochem.*, *4*, 17-26, 1975b.

Sanhueza, E., and J. Heicklen, The oxidation of CFClCFCl and CF_2CCl_2, *Int. J. Chem. Kinet*, *7*, 399-415, 1975c.

Sanhueza, E., and J. Heicklen, Chlorine atom senstized oxidation of dichloromethane and chloromethane, *J. Phys. Chem*, *79*, 7-11, 1975d.

Sanhueza, E., and J. Heicklen, *Int. J. Chem. Kinet*, *7*, 589, 1975e.

Sanhueza, E., I. C. Hisatsune, and J. Heicklen, Oxidation of haloethylenes, *Chem. Rev.*, *76*, 801-826, 1976.

Schmidt,. J. W., unpublished data, National Institute of Standards and Technology, Gaithersburg, MD, 1988.

Schumacher, H. J., and H. Thürauf, *Z. Phys. Chem.*, *A189*, 183, 1941.

Schwarz, H. A., and R. W. Dodson, Equilibrium between hydroxyl radicals and thallium(II) and the oxidation potential of OH(aq), *J. Phys. Chem.*, *88*, 3643-3647, 1984.

Seila, R. L. and W. A. Lonneman, *Paper 88-150.8, presented at the 81st Annual Meeting of Air Pollution Control Association*, Dallas, TX, June 20-24, 1988.

Seiler, W., The cycle of atmospheric CO, *Tellus*, *26*, 116-135, 1974.

Seiler, W., and R. Conrad, Contribution of tropical ecosystems to the global budget of trace gases, especially CH_4, H_2, CO, and N_2O, *The Geophysiology of Amazonia*, John Wiley and Sons, New York, 133-160, 1987.

Seiler, W., and U. Schmidt, New aspects of CO and H_2 cycles in the atmosphere, *Proc. Int. Conf. on the Structure, Composition, General Circulation in the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, IAMAP, Toronto, Canada,* 192-222, 1974.

Seinfeld, J. H., Urban air pollution: State of the science, *Science*, *243*, 745-752, 1989.

Seppelt, K., Trifluoromethanol, CF_3OH, *Agnew. Chem. Int. Ed. Engl.*, *16*, 322-323, 1977.

Sexton, K., and H. Westberg, Nonmethane HC composition of urban and rural atmospheres, *Atmos. Environ.*, *18*, 1125-1132, 1984.

C-6

Sidhu, S. S., Fluoride deposition through precipitation and leaf litter in a boreal forest in the vicinity of a phosphorus plant, *Sci. Total Environ.*, *23*, 205-214, 1982.

Siever, R., The steady state of the earth's crust, atmosphere and oceans, *Scientific American*, *230*, 72-79, 1974.

Siggia, S., and J. G. Hanna, *Quantitative Organic Analysis via Functional Groups*, John Wiley & Sons, New York, 325-372, 1979.

Sillen, L. G., The ocean as a chemical system, *Science*, *156*, 1189-1197, 1967.

Simmonds, P. G., F. N. Alyea, C. A. Cardelino, A. J. Crawford, D. M. Cunnold, B. C. Lane, J. E. Lovelock, R. G. Prinn, and R. A. Rassmussen, The atmospheric lifetime experiment, 6, results for carbon tetrachloride based on 3 years of data, *J. Geophys. Res.*, *88*, 8427-8441, 1983.

Simon, P. C., D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures, *J. Atmos. Chem.*, *7*, 107-135, 1988.

Simonaitis, R., and J. Heicklen, The reaction of CCl_3O_2 with NO and NO_2 and the thermal decomposition of $CCl_3O_2NO_2$, *Chem. Phys. Lett.*, *62*, 473-477, 1979.

Singh, H. B., Atmospheric halocarbons: evidence in favour of reduced averaged hydroxyl concentration in the troposphere, *Geophys. Res. Lett.*, *4*, 101-104, 1977.

Singh, H. B., and L. Salas, Measurement of selected light hydrocarbons over the Pacific Ocean: Latitudinal and seasonal variations, *Geophys. Res. Lett.*, *4*, 842-845, 1982.

Singh, H. B., L. J. Salas, and R. E. Stiles, Methyl halides in and over the Eastern Pacific (40°N-32°S), *J. Geophys. Res.*, *88*, 3684-3690, 1983.

Singh, H. B., L. Salas, H. Shigeishi, and A. Crawford, Non-urban relationships of halocarbons, SF_6, N_2O, and other atmospheric constituents, *Atmos. Environ.*, *11*, 819-823, 1977.

Singh, H. B., R. J. Ferek, L. J. Salas, and K. C. Nitz, Toxic chemicals in the environment: a program of filed measurements, *SRI International Report*, February, 1986.

Singleton, D. L., G. Paraskevopoulos, and R. S. Irwin, Reaction of OH with CH_3CH_2F: the extent of H abstraction from the *A* and ß positions, *J. Phys. Chem.*, *84*, 2339-2343, 1980.

Slagle, I. R., J.-Y. Park, and D. Gutman, Experimental investigation of the kinetics and mechanism of the reaction of n-propyl radicals with molecular oxygen from 297 to 635 K, *20th International Symp. Combustion, 1984*, The Combustion Institute, Pittsburgh, PA, 733-741, 1985.

Slagle, I. R., Q. Feng, and D. Gutman, Kinetics of the reaction of ethyl radicals with molecular oxygen from 294 to 1002 K, *J. Phys. Chem.*, *88*, 3648-3653, 1984.

Smith, F. A., D. E. Gardner, C. L. Yiule, O. H. deLopez, and L. L. Hall, Defluorination of fluoroacetate in the rat, *Life Sciences*, *20*, 1131-1138, 1977.

REFERENCES

Snider, J. R., and G. A. Dawson, Tropospheric light alcohols, carbonyls, and acetonitrile: concentrations in in the southwestern United States and Henry's law constants, *J. Geophys. Res.*, *90*, 3797-3805, 1985.

Solvay, Brussels, Belgium, private communication via J. von Schweinichen, Montefluos, Milan, Italy, 1989.

Spence, J. W., and P. L. Hanst, *J. Air Pollut. Control Assoc.*, *28*, 250, 1978.

Spivakovsky, C., et al., Tropospheric OH and seasonal variations of atmospheric halocarbons: Separating the influence of chemistry and transport, *submitted to J. Geophys. Res.*, 1989.

Stanbury, D. M., W. K. Wilmarth, S. Khalaf, H. N. Po, and J. E. Byrd, Oxidation of thiocyanate and iodide by iridium (IV), *Inorg. Chem.*, *19*, 2715-2722, 1980.

Stepakoff, G. L., and A. P. Modica, The hydrolysis of halocarbon refrigerants in freeze desalination processes: Pt. I. solubility and hydrolysis rates of Freon 114 ($CClF_2CClF_2$), *Desalination*, *12*, 85-105, 1973.

Stephens, E. R., The formation of molecular oxygen by alkaline hydrolysis of peroxyacetyl nitrate, *Atmos. Environ.*, *1*, 19-20, 1967.

Stewart, R. B., R. T. Jacobsen, J. H. Becker, and M. J. Zimmerman, A survey of the thermodynamic property data for the halocarbon refrigerants, *Center for Applied Thermodynamic Studies, Report no. 81-2*, University of Idaho, Moscow, ID, 1981.

Stier, A., H. W. Kunz, A. K. Walli, and H. Schimassek, Effect on growth and metabolism of rat liver by halothane and its metabolite trifluoroacetate, *Biochem. Pharmacol.*, *21*, 2181-2192, 1972.

Stordal, F., I. S. A. Isaksen, and K. Horntveth, A diabatic circulation two-dimensional model with photochemistry: Simulations of ozone and long-lived tracers with surface sources, *J. Geophys. Res.*, *90*, 5757-5776, 1985.

Stumm, W., and J. J. Morgan, *Aquatic Chemistry, an Introduction Emphasizing Chemical Equilibria in Natural Waters*, 583 pp., John Wiley & Sones, 1970.

Suong, J. Y., and R. W. Carr, Jr., The photo-oxidation of 1,3-dichlorotetrafluoroacetone: mechanism of the reaction of CF_2Cl with oxygen, *J. Photochem.*, *19*, 295-302, 1982.

Swain, C. G., and C. B. Scott, Rates of solvolysis of some alkyl fluorides and chlorides, *J. Am. Chem. Soc.*, *75*, 246-248, 1953.

Swallow, A. J., Hydrated electrons in seawater, *Nature*, *222*, 369-370, 1969.

Symonds, R. B., W. I. Rose, and M. H. Reed, Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, *Nature*, *344*, 415-418, 1988.

Sze, N. D., Anthropogenic CO emissions: Implications for the atmospheric CO-OH-CH_4 cycle, *Science*, *195*, 673, 1977.

Sze, N. D., and M. K. W. Ko, The effects of the rate of OH + HNO_3 and HO_2NO_2 photolysis on stratospheric chemistry, *Atmos. Environ.*, *7*, 1301-1367, 1981.

Talbot, R. W., M. O. Andreae, T. W. Andreae, and R. C. Harriss, Regional aerosol chemistry of the Amazon Basin during the dry season, *J. Geophys. Res.*, *93*, 1499-1508, 1988.

Taylor, W. D., T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. Takacs, Atmospheric photodissociation lifetimes for nitromethane, methyl nitrite, and methyl nitrate, *Int. J. Chem. Kinet.*, *12*, 231-240, 1980.

Thermodynamics Research Center, *TRC thermodynamic tables, non-hydrocarbons*, Texas A&M University, College Station, TX, 1986.

Tonomura, K., F. Futai, O. Tanabe, and T. Yamaoka, Defluorination of monofluoroacetate by bacteria. Part I. Isolation of bacteria and their activity of defluorination, *Agr. Biol. Chem.*, *29*, 124-128, 1965.

Troe, J., Predictive possibilities of unimolecular rate theory, *J. Phys. Chem.*, *83*, 114-126, 1979.

Tsalkani, N., A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, Rate constant measurements for the reactions of OH and Cl with peroxyacetyl nitrate at 298 K, *J. Atmos. Chem.*, *7*, 409, 1988.

Tschuikow-Roux, E., T. Yano, and J. Niedzielsky, Reactions of ground state chlorine atoms with fluorinated methanes and ethanes, *J. Chem. Phys.*, *82*, 65, 1985.

U.S. Environmental Protection Agency, Fed. Reg. 51, 11,396-11,414, 1986.

Ugi, I., and F. Beck, Reaktion von carbonsaurehalogeniden mit wasser und amiren, *Chem. Ber.*, *94*, 1839-1850, 1961.

Uno, I., S. Wakamatsu, R. A. Wadden, S. Konno, and H. Koshio, Evaluation of hydrocarbon reactivity in urban air, *Atmos. Environ.*, *19*, 1283-1293, 1985.

Vaghjiani, G. L., and A. R. Ravishankara, Kinetics and mechanism of OH reaction with CH_3OOH, *J. Phys. Chem*, *93*, 1948-1959, 1989.

Valtz, A., S. Laugier, and R. Richon, Bubble pressures and saturated liquid molar volumes of difluoromonochloromethane-fluorochloroethane binary mixtures, *Int. J. Refrigeration*, *9*, 282, 1986.

Varanasi, P., and S. Chudamani, Infrared intensities of some chlorofluorocarbons capable of perturbing the global climate, *J. Geophys. Res.*, *93*, 1666-1668, 1988.

Verhoek, F. H., The kinetics of the decomposition of the trichloroacetates in various solvents, *J. Am. Chem. Soc.*, *56*, 571-577, 1934.

Vogel, T. M., C. S. Criddle, and P. L. McCarty, Transformations of halogenated aliphatic compounds, *Env. Sci. Technol.*, *21*, 722-736, 1987.

REFERENCES

Volz, A., D. H. Ehhalt, and R. G. Derwent, Seasonal and latitudinal variation in ^{14}CO and the tropospheric concentration of OH radicals, *J. Geophys. Res.*, *86*, 5163-5171, 1981.

Volz, A., D. H. Ehhalt, R. G. Derwent, and A. Khedim, Messung von atmospharischenn ^{14}CO: eine methode zur bestimmung der tropospharischen OH radikalkonzentration, *KFA Julich Report Jul 1604*, Federal Republic of Germany, 1979.

Vong, R. J., H.-C. Hansson, H. B. Ross, D. S. Covert, and R. J. Charlson, Northeastern Pacific submicrometer aerosol and rainwater composition: A multivariate analysis, *J. Geophys. Res*, *93*, 1625-1637, 1988.

Wada, S. and N. Kokubu, Chemical composition of maritime aerosols, *Geochem. J., 6,* 131-139, 1973.

Wagman, D. G., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic subtances in SI units, *J. Phys. Chem. Ref. Data, 11*, Suppl. 2, 1-392, 1982.

Wallington, T. J., L. M. Skewes, and W. O. Siegl, Kinetics of the gas phase reaction of chlorine atoms with a series of alkenes, alkynes, and aromatic species at 295 K, *J. Photochem. Photobiol., A: Chemistry*, *45*, 167-175, 1988b.

Wallington, T. J., L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Gas phase reaction of Cl atoms with a series of oxygenated organic compounds at 295 K, *Int. J. Chem. Kinet.*, *20*, 867-875, 1988a.

Wallington, T. J., R. Atkinson, and A. M. Winer, Rate constants for the gas phase reaction of OH radicals with peroxyacetyl nitrate (PAN) at 273 and 297 K, *Geophys. Res. Lett.*, *11*, 861, 1984.

Walraevens, R., P. Trouillet, and A. Devos, Basic elimination of HCl from chlorinated ethanes, *Int. J. of Chem. Kinet.*, *6*, 777-786, 1974.

Wang, W.-C., and G. Molnar, A model study of the greenhouse effects due to increasing CH_4, N_2O, CF_2Cl_2, and $CFCl_3$, *J. Geophys. Res.*, *90*, 12,971-12,980, 1985.

Wang, W. C., D. J. Wuebbles, W. M. Washington, R. G. Isaacs, and G. Molnar, Trace gases and other potential perturbations to global climate, *Rev. Geophys.*, *24*, 110, 1986.

Wantuck, P. J., R. C. Oldenberg, S. L. Baughaum, and K. R. Winn, Removal rate constant measurements for CH_3O by O_2 over the 298-973 K range, *J. Phys. Chem.*, *91*, 4653-4655, 1987.

Ward, P. F. V., R. J. Hall, and R. A. Peters, Fluorofatty acids in the seeds of Dichapetalum toxicarium, *Nature*, *201*, 611-612, 1964.

Warneck, P.,*Chemistry of the Natural Atmosphere*, Academic Press, Inc., San Diego, 1988.

Waskell, L., Study of the mutagenicity of anesthetics and their metabolites, *Mutation Res.*, *57*, 141-153, 1978.

Watson, R. T., A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, A kinetics study of the temperature dependence of the reactions of OH ($^2\Pi$) with CF_3CHCl_2, CF_3CHClF, and CF_2ClCH_2Cl, *Int. J. Chem. Kinet.*, *11*, 187-197, 1979.

Watson, R. T., G. Machado, B. Conaway. S. Wagner, and D. D. Davis, A temperature dependent kinetics study of the reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3, CH_3CF_2Cl, and $CF_2ClCFCl_2$, *J. Phys. Chem.*, *81*, 256-262, 1977.

Watson, R. T., M. J. Prather, and M. J. Kurylo, Present state of knowledge of the upper atmosphere 1988: An assessment report (to Congress), *NASA Reference Publication 1208*, 1988.

Weast, R. C., ed., *CRC handbook of chemistry and physics*, *57th ed.*, CRC Press, Boca Raton, FL, D-194, 1977.

Weber, L. A., Vapor pressures and gas phase PVT data for 1,1,1,2-tetrafluoroethane, *Int. J. Thermophysics*, *10, no. 3*, to be published, 1989.

Weber, L. A., and J. M. H. Levelt-Sengers, Critical parameters and saturation densities of 1,1-dichloro-2,2,2-trifluoroethane, to be published, 1989.

Weinstein, L. H., Fluoride and plant life, *J. Occup. Med.*, *19*, 49-78, 1977.

Weinstein, L. H., D. C. McCune, J. F. Mancini, L. J. Colavito, D. H. Silberman, and P. van Leuken, Studies on fluoro-organic compounds in plants. III. Comparison of the biosyntheses of fluoro-organic acids in Acacia georginae with other species, *Environ. Res.*, *5*, 393-408, 1972.

Weinstock, B., The residence time of carbon monoxide in the atmosphere, *Science*, *166*, 224-225, 1969.

Weinstock, B., and H. Niki, Carbon monoxide balance in nature, *Science*, *176*, 290-292, 1972.

Whytock, D. A., and K. O. Kutsche, *Proc. Roy. Soc. A.*, *306*, 503, 1988.

Wilkness, P. E., and D. J. Bressan, Chemical processes at the sea-air interface: The behavior of fluorine, *J. Geophys. Res.*, *76*, 736-741, 1971.

Wilkness, P. E., and D. J. Bressan, Fractionation of the elements of F, Cl, Na, and K at the sea-air interface, *J. Geophys. Res.*, *77*, 5307-5315, 1972.

Wilmarth, W. K, D. M. Stanbury, J. E. Byrd, H. N. Po, and C.-P. Chua, Electron-transfer reactions involving simple free radicals, *Coord. Chem. Rev.*, *51*, 155-179, 1983.

Wilson, D. P., and R. S. Basu, Thermodynamic properties of a new stratospherically safe working fluid--refrigerant 134a, *ASHRAE Trans. 94 pt. 2*, 1988.

Wilson, S. R., P. J. Crutzen, G. Shuster, D. W. T. Griffith, and G. Hales, *Nature*, 1989.

REFERENCES

Wine, P. H., and W. L. Chameides, Possible atmospheric lifetimes and chemical reaction mechanisms for selected HCFCs, HFCs, CH_3CCl_3, and their degradation products against dissolution and/or degradation in seawater and cloudwater, *AFEAS manuscript*, June, 1989.

Wine, P. H., Y. Tang, R. P. Thorn, J. R. Wells, and D. D. Davis, Kinetics of aqueous phase reactions of the SO_4^-radical with potential importance in cloud chemistry, *J. Geophys. Res., 94*, 1085-1094, 1989.

Winer, A. M., K. R. Darnall, R. Atkinson, and J. N. Pitts, Smog chamber study of the correlation of hydroxyl radical rate constants with ozone formation, *Environ. Sci. Technol., 13*, 822-826, 1979.

Winer, A. M., R. Atkinson, and J. N. Pitts, Jr., Gaseous nitrate radical: Possible nighttime atmospheric sink for biogenic organic compounds, *Science, 224*, 156-159, 1984.

Withnall, R., and J. R. Sodeau, Applications for Fourier transform IR spectroscopy to the determination of photo-oxidation quantum yields for halocarbons, *J. Photochem., 33*, 1-11, 1986.

Witte, L., H. Nau, and J. H. Fuhrhop, Quantitative analysis of trifluoroacetic acid in body fluids of patients treated with halothane, *J. Chromatog., 143*, 329-334, 1977.

WMO, Atmospheric ozone 1985: assessment of our understanding of the processes controlling its present distribution and change, *WMO Report No. 16*, sponsored by WMO, NASA, NOAA, FAA, UNEP, CEC, and BMFT, Washington, DC, 1986.

Wofsy, S. C., and M. B. McElroy, HO_x, NO_x, and ClO_3: Their role in atmospheric photochemistry, *Can. J. Chem., 52*, 1582-1591, 1974.

World Health Organization, Fluorine and fluorides, *36*, 1-136, 1984.

World Meteorological Organization, Atmospheric ozone 1985: assessment of our understanding of the processes controlling its present distribution and change, *WMO Report No. 16,Vol. 1*, 117-150, sponsored by WMO, NASA, NOAA, FAA, UNEP, CEC, and BMFT, Washington, DC, 1986.

Wu, D., and K. D. Bayes, Rate constants for the reactions of isobutyl, neopentyl, cyclopentyl, and cyclohexyl radicals with molecular oxygen, *Int. J. Chem. Kinet., 18*, 547, 1986.

Wuebbles, D. J., The relative efficiency of a number of halocarbons for destroying stratospheric ozone, *Rep. UCID-18924*, Lawrence Livermore Nat. Lab., Livermore CA, 1981.

Wuebbles, D. J., Chlorocarbon emission scenarios: Potential impact on stratospheric ozone, *J. Geophys. Res., 88*, 1433-1443, 1983.

Wuebbles, D. J., and D. E. Kinnison, A two-dimensional study of past trends in global ozone, *Proc. Quadrennial Ozone Symposium*, Univ. of Gottingen, Rep. of Germany, 1988.

Wuebbles, D. J., K. E. Grant, P. S. Connell, and J. E. Penner, The role of atmospheric chemistry in climate change, *J. Air Poll. Control Assoc.*, *39*, 21-28, 1989.

Xing Lin and W. L. Chameides, Model simulations of rainout and washout from a warm stratiform cloud, *submitted to J. Atmos. Chem.*, 1989.

Yamashita, T., H. Kubota, Y. Tanaka, T. Makita and H. Kashiwagi, Measurements of physical properties of new fluorocarbons, *Proc. Ninth Japan Symp. on Thermophysical Properties*, 227-230, 1988.

Zafiriou, O. C., Reaction of methyl halides with sea water and marine aerosols, *J. Marine Res.*, *33*, 75-81, 1975.

Zafiriou, O. C., and M. B. True, Nitrite photolysis in seawater by sunlight, *Mar. Chem.*, *8*, 9-32, 1979.

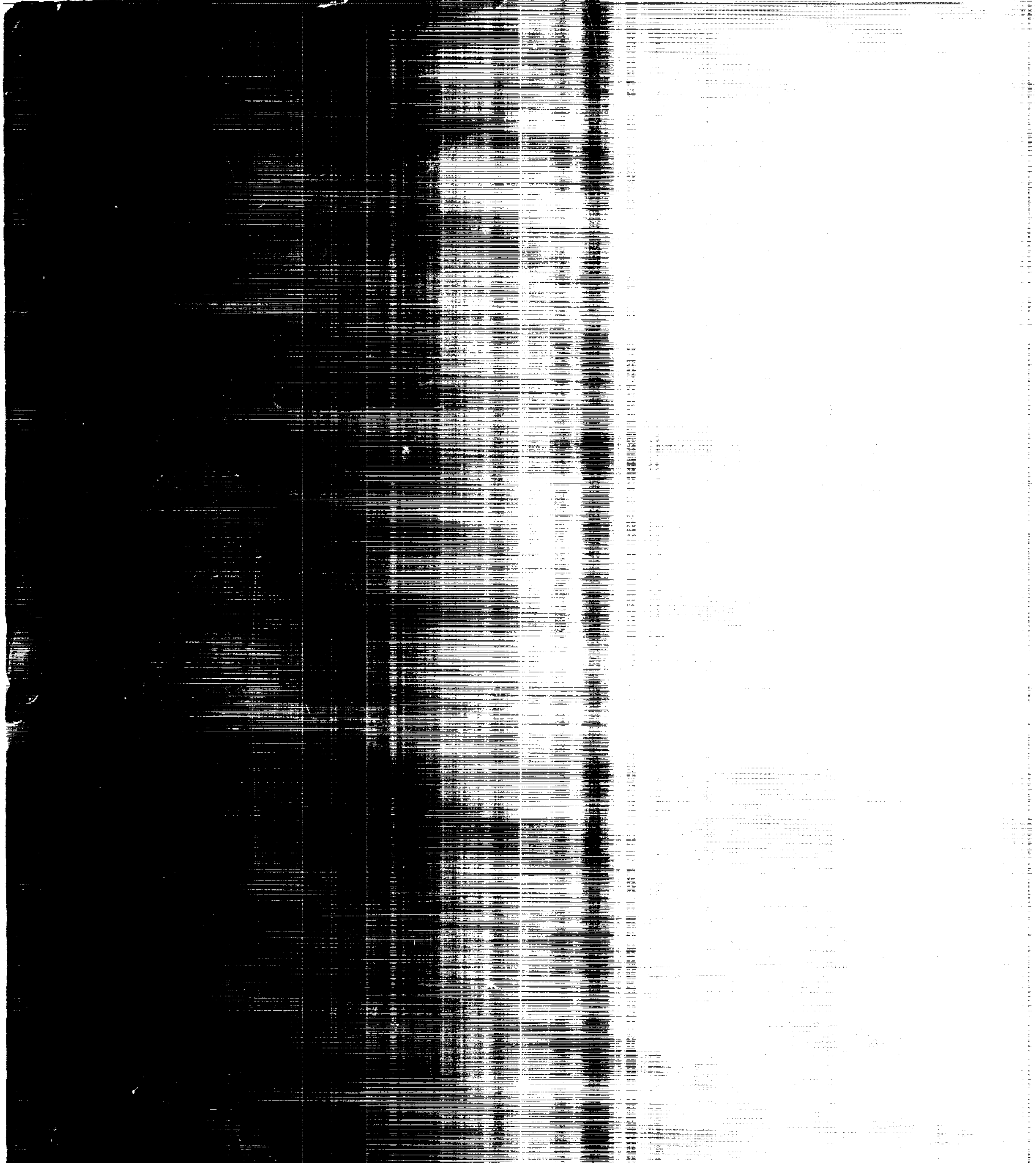
Zander, M., Pressure-volume-temperature behavior of chlorodifluoromethane (Freon 22) in the gaseous and liquid states, *Proc. 4th Symp. on Thermophysical Properties of Gases, Liquids, and Solids, ASME*, 114-123, 1968.

Zellner, R., and L. Jürgens, Photooxidation of $CHClF_2$ under tropospheric conditions, to be published, 1989.

Zepp, R. G., A. M. Braun, J. Hoigne, and J. A. Leenheer, Photoproduction of hydrated electrons from natural organic solutes in aquatic environments, *Env. Sci. Technol.*, *21*, 485-490, 1987a.

Zepp, R. G., J. Hoigne, and H. Bader, Nitrate-induced photooxidation of trace organic chemicals in water, *Environ. Sci. Technol.*, *21*, 443-450, 1987b.

Zhang, K., D. Chen, G. Liu, Y. Xu, and Y. Hu, Solubilities of chloro-difluoromethane and tetrafluoroethylene in aqueous solutions of HCl and NaCl, *Journal of East China Institute of Chemical Technology*, 1985.



WORLD METEOROLOGICAL ORGANIZATION
GLOBAL OZONE RESEARCH AND MONITORING PROJECT

Scientific Assessment of Stratospheric Ozone: 1989