



CATALYTIC DEHYDRATION OF ETHYL ALCOHOL

M.S. WAINWRIGHT B.App.Sc.(Hons)

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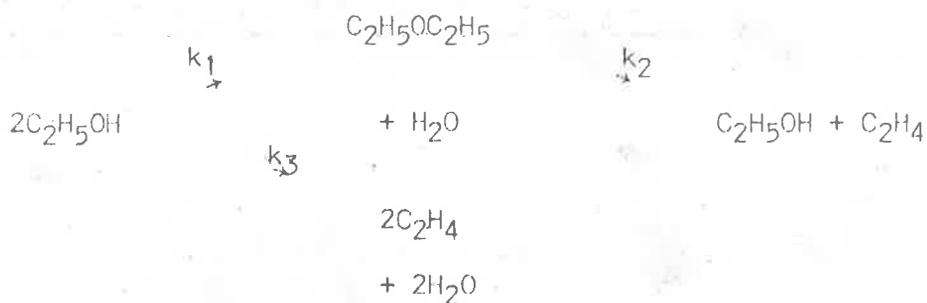
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### SUMMARY

The kinetics of the dehydration of ethyl alcohol on a commercial  $\gamma$ -alumina catalyst have been investigated using a differential flow reactor.

At temperatures below 300°C diethyl ether was formed almost exclusively. The apparent activation energy determined for this reaction was  $28,500 \pm 50$  cal/gm mole. At temperatures above 300°C ethylene was formed simultaneously with diethyl ether. The apparent activation energy determined for ethylene formation was  $29,200 \pm 50$  cal/gm mole. Diethyl ether was decomposed over the catalyst at temperatures between 300 and 400°C the reaction products being ethyl alcohol and ethylene. At 300°C the rates of formation of ethyl alcohol and ethylene from diethyl ether were  $8.3 \times 10^{-5}$  and  $8.5 \times 10^{-5}$  mole/gm min respectively. The rates of diethyl ether and ethylene formation from ethyl alcohol at the same temperature were  $8.3 \times 10^{-5}$  and  $9.9 \times 10^{-6}$  mole/gm min. These results support the hypothesis that during the dehydration of ethyl alcohol ethylene is formed at least partly, by a consecutive mechanism in which diethyl ether acts as an intermediate. As a consequence of these observations a combined parallel - consecutive (simultaneous) mechanism is postulated:



where  $k_1 = k_2 \gg k_3$

The orders of reaction for the formation of both diethyl ether and ethylene were examined by varying the partial pressure of ethyl alcohol in the range, zero to 800 mms Hg. High purity nitrogen was used as the diluent in all cases.

Below 300°C ether formation was found to be zero order with respect to alcohol pressure. The rate of ethylene formation was also found to be zero order. The influence of water on the rate of formation of diethyl ether and of ethylene was studied at various temperatures. Water was found to inhibit both reactions. The results obtained over a range of water and alcohol partial pressures were found to obey a rate law of the form

$$r = k\theta_a = \frac{k \sqrt{K_a p_a}}{1 + \sqrt{K_a p_a} + K_w p_w}$$

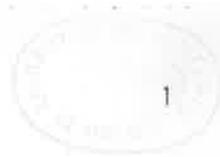
for both ethylene and ether formation. This expression represents the mechanism which applies when an ethyl alcohol molecule is adsorbed on two adjacent catalyst sites to form an intermediate species which then breaks down to form products.

The dehydration of ethyl alcohol in the region of simultaneous ether and ethylene formation has been examined in greater detail than in any previously reported study. The use of a gas chromatograph equipped with a flame ionization detector has enabled accurate product analyses to be made. In general conversions were kept to less than 1 mole percent for all runs. Thus the reactor used in the study was truly differential in character. This accuracy is necessary to study reactions where the products formed may inhibit the reaction. It is

therefore believed that the results presented are of higher accuracy, and cover a wider range of working temperatures and partial pressures of alcohol and water than reported previously. Furthermore, the results for the decomposition of diethyl ether provide stronger evidence than any reported previously for ethylene formation by a consecutive reaction mechanism.

I declare that this thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by any other person, except when due reference is made in the text.

M.S. Wainwright.



## 1. INTRODUCTION

Many papers have discussed the dehydration of alcohols since the beginning of this century.

Early studies were concerned with possible industrial applications of the reaction as a source of olefines. With the advent of petroleum refining, large quantities of olefines, particularly ethylene, became available and practical interest in the reaction declined. However, research has continued in this field in an endeavour to understand more fully the basic processes of vapour-phase catalytic reactions. Although a number of such studies have been made there is little agreement between the results of various workers. Conflicting views consider that ethylene is formed from ethyl alcohol by consecutive, or by parallel, steps. A further view considers ethylene formation to be a combination of these mechanisms. Another question of interest has been whether the rate of diethyl ether formation is first order, or zero order, with respect to ethyl alcohol concentration.

Few studies have considered the influence of water on the rate of formation of diethyl ether and ethylene. No quantitative results have been reported for the formation of ethylene in the presence of water, although Knozinger and Köhn<sub>3</sub> have recently investigated diethyl ether formation at various water partial pressures. The decomposition of diethyl ether on alumina catalysts has received scant attention when one considers its importance in determining the overall mechanism of ethyl alcohol dehydration.

Several attempts have been made to relate substrate structure to the activation energy for the dehydration of alcohols and conflicting

results have been obtained. Some workers have reported a systematic connection between activation energy and chain length, whereas others have found that the same value of activation energy applies to an homologous series of primary alcohols.

In short, there is a lack of understanding of the dehydration reaction.

This study has been made to investigate the mechanism of the dehydration of ethyl alcohol and to determine if ethylene is formed by parallel, consecutive or simultaneous reaction. A full understanding of these aspects of the reaction is necessary before an investigation into the effect of chain length can be made.

The fundamental limitation in most studies has been the use of reactors which were not differential in character. When a product inhibits a reaction it is necessary to keep its concentration as low as possible. However, the literature abounds with rates calculated for conversions of the order of 30 percent. Frequently workers were forced to use such high conversions because they lacked sensitive methods of chemical analysis. To overcome this basic problem a truly differential reactor, in which conversions were generally maintained at less than 1 percent, was used in this study. This was made possible by using a flame ionization gas chromatograph for product analysis. In studies of this sort the method of catalyst preparation is of utmost importance. Many of the conflicting results which appear in the literature may be attributed to inconsistent catalyst preparation. To guard against this source of trouble, during the present investigation a commercial catalyst, which had been used in a

(1)  
recent study was obtained.

## 2. LITERATURE REVIEW

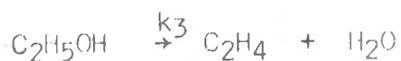
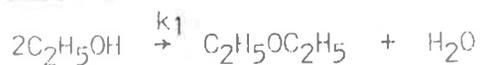
Since there are two recent comprehensive reviews of the dehydration of alcohols, <sup>(2,3)</sup> only references to mechanism and kinetics are reviewed here. The alternative courses of the reaction are reviewed first. This is followed by a review of the mechanisms that have been postulated for diethyl ether and ethylene formation.

There is a brief survey of the decomposition of diethyl ether on  $\gamma$ -alumina catalyst and this section of the thesis is concluded with a review of the effect of temperature on the reaction steps.

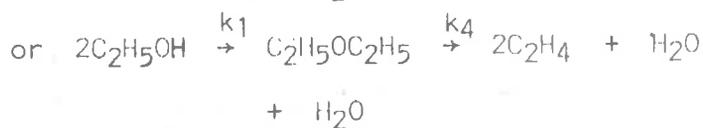
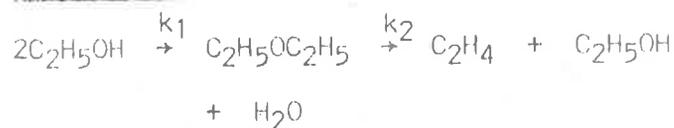
### 2.1 The Various Reaction Schemes

There have been many supporters for the conflicting views that ethylene is formed by consecutive, parallel or simultaneous reaction steps. The three postulated schemes are as follows:

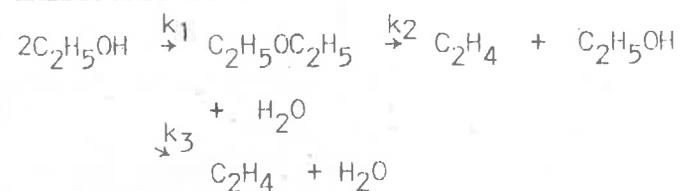
#### 1. Parallel



#### 2. Consecutive



#### 3. Simultaneous





than the formation of ethylene from alcohol, and that with other catalysts and alcohols the formation of ether was not significant. Of course this was an oversimplification of the situation. The fact that ethylene formation is slower from ethyl alcohol than diethyl ether may be explained by the fact that ethyl alcohol is more strongly adsorbed on  $\gamma$ -alumina than diethyl ether. Hence in the presence of alcohol the apparent rate of ether decomposition would be less than the rate found for a pure ether feed. The absence of ether from the products obtained using other catalysts may be attributed to the existence of completely different mechanisms on different solid surfaces. It certainly does not rule out the possibility of consecutive ethylene formation on  $\gamma$ -alumina catalysts.

(7)

Adkins and Perkins also questioned the validity of the consecutive scheme when they studied the dehydration of butanol and found that butyl ether was not a significant intermediate in the formation of the considerable quantities of butene obtained.

(8)

In confirmation of this argument, Adkins and Bischoff showed that whereas ethanol and ether have about the same stability on alumina, the ether is much more stable on titanium dioxide and is therefore not a necessary intermediate in olefine formation.

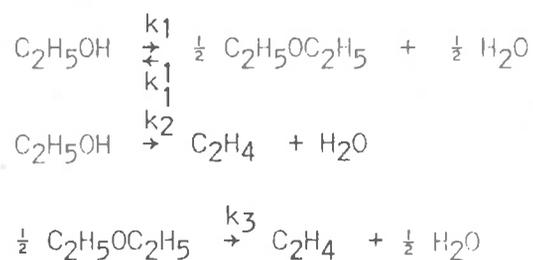
While their findings add interest to the overall study of dehydration reactions, the results do not warrant the conclusions they have drawn, and this aspect will be examined more fully later.

There have been few recent studies in which a parallel



(13,14)

Two recent papers by Isagulyants and co-workers discussed a study of the mechanism of the dehydration reaction using  $C^{14}$  labelled compounds. They claimed that they were able to determine the rates of the individual phases of parallel, consecutive and parallel-consecutive reactions. The second of the papers studied the following simultaneous reactions on alumina, where  $k$  is the rate of reaction.



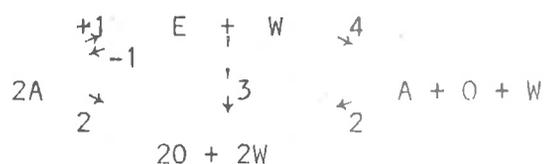
at  $275^\circ C$  they found that  $k_2 = k_3$  and as the temperature was increased  $k_2$  increased more rapidly than  $k_3$ , so that at  $400^\circ C$   $k_2$  dominated the process. When the contact time was increased at various temperatures,  $k_1$  decreased rapidly and  $k_1^1$  increased rapidly to a maximum and then decreased, so that both  $k_1$  and  $k_1^1$  decreased as the concentrations of ethanol and ether decreased. Their results favoured a simultaneous scheme with the parallel ethylene formation being dominant at higher temperatures.

(12)

Knozinger and Köhne have published a comprehensive study of the dehydration of ethanol and other aliphatic alcohols on  $\gamma$ -alumina. In particular they studied the dehydration of ethyl alcohol and diethyl ether for various temperatures and contact times. The programme was in fact a more accurate reassessment of the work of Pease and Yung. Their results

(5)

showed remarkably close agreement with those of Balanceanu and Jungers (10) and the C<sup>14</sup> study of Isagulyants (13). From their results they were able to set up the following reaction scheme where A represents ethanol, E is diethyl ether, W is water, and O is ethylene.



This scheme was postulated on the following findings.

(a) At low temperatures and small conversions the primary reaction step is a bimolecular ether formation. This was shown by the appearance of only ether and water at low temperature (211°C) and an induction period in the plot of olefine partial pressure against contact time at slightly higher temperatures (256°C). At high degrees of conversion the back reaction (-1) becomes important.

(b) With increasing temperatures the induction period disappeared from the olefine curve while at the same time the ether concentration in the contact time plot exhibited a maximum. They concluded that with increasing temperatures a primary olefine elimination (by reaction 2), in addition to the secondary olefine elimination from ether, became important. This was evidence for simultaneous, parallel, and consecutive steps.

The authors also considered the validity of the two schemes for ethylene elimination from ether via steps (3) or (4). The former scheme had been supported by Isagulyants and the latter by

Balaceanu and Jungers. Knozinger and Köhne supported reaction (4), since for reaction (3) to occur four bonds would have to be broken and four new ones formed. On the other hand, only one bond is required to dissociate to give step (4). The validity of their statement regarding the likely step was based on a paper by Rice and Teller<sup>(15)</sup> which postulated the "principle of least motion". This states that from a number of possible reaction mechanisms with a high degree of probability, the mechanism in which the position of the individual atoms and electronic configuration of the reacting system is least altered, is preferred.

#### 2.1.4 Summary

The simultaneous reaction scheme postulated by Balaceanu and Jungers, and Knozinger and Köhne, appears to be the most accurate reported to date. There appears to be little conclusive evidence for independent (parallel) ethylene formation. However, the results do not completely rule out the possibility of a purely consecutive scheme.

## 2.2 Mechanisms for Dehydration Reactions

The overall mechanism of surface catalysis is very complex. In general, vapour-phase catalytic reactions are considered to take place by the following five steps.

1. Diffusion of the reacting molecules to the catalyst surface.
2. Adsorption of the reactants on the surface.
3. Reaction on the surface.
4. Desorption of products.

5. Diffusion of the products into the bulk fluid.

To include all these terms in one rate expression would be a formidable task. However, one of the steps often has a resistance to reaction that is far greater than the others and determines the reaction rate. In order to study catalytic reactions it is desirable to eliminate mass transfer considerations and to make step (3) the rate-controlling step. Various examples of rate expressions for bimolecular and unimolecular reactions, for which chemical reaction is rate determining, will now be presented.

Thus diethyl ether formation from ethyl alcohol is an example of a bimolecular solid-catalyzed reaction whilst ethylene formation is unimolecular.

I Bimolecular Reactions:

1.  $2A \rightarrow E + W$  where an adsorbed molecule of A reacts with a neighbouring adsorbed molecule to form adsorbed species E and W. This is an example of a conventional LANGMUIR-HINSHELWOOD mechanism.

The basic rate equation is

$$r = k\theta_a^2$$

$$r = \frac{k_1 K_a^2 p_a^2}{(1 + K_a p_a + K_w p_w + K_e p_e)^2} \quad (2.1)$$

where  $k_1$  is the specific reaction rate constant.

$K_a$ ,  $K_w$  and  $K_e$  are the equilibrium adsorption coefficients

$p_a$ ,  $p_w$  and  $p_e$  are the partial pressures of A, W and E.

$\theta_a$  is the degree of surface coverage with molecules

of A.

2.  $2A \rightarrow E + W$  where an adsorbed molecule of A reacts with a gas-phase molecule to form an adsorbed species and a gaseous species. This is an example of a RIDEAL-ELEY mechanism.

The rate equation is

$$r = k\theta_a p_a$$

$$r = \frac{k_1 K_a p_a^2}{(1 + K_a p_a + K_w p_w + K_e p_e)} \quad (2.2)$$

#### II Unimolecular Reaction

3.  $A \rightarrow O + W$  where an adsorbed molecule of A breaks down to form products O and W.

The rate equation is

$$r = k\theta_a$$

$$r = \frac{k_1 K_a p_a}{(1 + K_a p_a + K_w p_w + K_e p_e)} \quad (2.3)$$

Equations (2.1), (2.2) and (2.3) may be simplified when initial rates (low conversions) are used to yield

$$r_o = \frac{k_1 p_a^2}{(1 + K_a p_a)^2} \quad (2.4)$$

$$r_o = \frac{k p_a^2}{1 + K_a p_a} \quad (2.5)$$

$$r_o = \frac{k p_a}{1 + K_a p_a} \quad (2.6)$$

2.4 and 2.6 are zero order rate expressions.

2.5 is a first order expression.

### 2.2.1 Mechanism of Diethyl Ether Formation

There have been few attempts in the past to derive a rate expression for the dehydration of ethyl alcohol to diethyl ether in terms of general catalytic theory. However, recently there have been two notable contributions. (16,9) There have also been attempts (17,18) to fit homogeneous rate expressions to the data for ether formation. Most studies have used low alcohol partial pressures in deriving the rate expressions.

There have been conflicting mechanisms postulated in the two recent papers by de Boer and co-workers (9) and Knozinger and Ress. (16) The former have shown that at 307°C diethyl ether is formed simultaneously by Langmuir-Hinshelwood and Rideal-Eley mechanisms with the latter playing the more significant role.

The equation given for ether production was

$$v_{\text{ether}} = k_2 \theta_p + k_3 \theta_a P_a$$

where  $v_{\text{ether}}$  is the rate of ether formation

$\theta_a$  is the degree of coverage with alcohol molecules

$\theta_p$  is the degree of occupation with such pairs of alcohol molecules that reaction can take place by a Langmuir-Hinshelwood mechanism

It was shown that  $\theta_p = \frac{1}{2} n \theta_a^2$  where there are  $n$  possible sites round every adsorbed alcohol molecule so situated that another alcohol molecule can be adsorbed in a position favourable for reaction.

$$\text{Thus } v_{\text{ether}} = \frac{1}{2} k_2 n \theta_a^2 + k_3 \theta_a P_a$$

For saturation conditions  $\theta_a = 1 - \theta_w$   
 and so  $v_{\text{ether}} = k_2 \frac{1}{2} n (1 - \theta_w)^2 + k_3 (1 - \theta_w) p_a$   
 $= k_{II} + k_{III} p_a$

The experimental data fitted this expression very well. However, the study suffered from several limitations. The investigation was carried out at only one temperature and at alcohol partial pressures in the range 0 to 110 mm Hg. An extension of the concentration range may have given greater evidence for their postulated mechanism.

There was no attempt made to evaluate the influence of water on the reaction.

(16)

Knozinger and Röss studied the influence of both ethanol and water concentrations for dehydration of ethyl alcohol in the temperature range 174°C - 193°C. Their results showed that between 80 and 320 mm Hg ethanol pressure the rate of ether formation was independent of alcohol concentration. They also studied the effect of water partial pressure for several alcohol pressures at temperatures from 174°C to 193°C. Small partial pressures of water appreciably inhibited the reaction. The extent of this inhibition decreased with increased temperature. At 175 torr alcohol pressure a water pressure of 10 torr reduced the rate by 71% at 174°C, by 64% at 184°C and by 53% at 193°C. For low conversions (initial rates) they were able to describe their results by the expression

$$r = r_0 \theta_a = \frac{r_0 \sqrt{p_a}}{\sqrt{p_a} + b p_w} \quad (2.7)$$

where  $r$  is the rate in mole/gm sec

$r_0$  is the zero order rate at  $p_w = 0$

$p_a$  and  $p_w$  are the partial pressures of alcohol and water respectively

$\theta_a$  is the relative surface coverage of ethanol in the presence of inhibiting water

$b$  in terms of LANGMUIR theory, is the relative adsorption coefficient of water to ethanol.

$b$  had values of 4.0 at 174°C, 2.7 at 184°C and 1.4 at 193°C.

The surprising feature of equation (2.7) is that the surface concentration of ethanol is only linear and not squared as would be expected for a bimolecular surface reaction according to the conventional Langmuir-Hinshelwood mechanism.

(19)

Knozinger had previously published a theoretical paper on ether formation by ethanol dehydration on aluminium oxide in which he postulated a "double-centred mechanism". He suggested that a stable surface complex (possibly in the form of a surface aluminate) was necessary for ether formation.

He further postulated that the surface concentration of such a species was constant and that the rate equation should therefore be independent of it. Hence the concentration or pressure dependence of the reaction was thought to depend on the surface concentration of a second reaction partner which was less

strongly held and occupied a fraction,  $\theta_a$ , of the catalyst surface.

In this case a rate expression of the form

$$r = k \theta_a$$

$$\text{or } r = \frac{k K_a p_a}{1 + K_a p_a + K_w p_w}$$

would apply if the weakly-held alcohol molecule occupied one catalyst site. In fact, presence of the square root of the alcohol partial pressure in the rate equation (2.7) was attributed to a two-point alcohol adsorption. Infrared investigations by Knozinger<sup>(20)</sup> showed that in the range of temperatures which applied to the dehydration study the preferred mode of alcohol adsorption was by two non-linear hydrogen bonds. A further study<sup>(21)</sup> showed that water, in the presence of excess alcohol is adsorbed by means of only one passive hydrogen bond to a surface hydroxyl group. The existence of a thermally stable surface alcoholate group has been proved by infrared spectroscopy.<sup>(22,23,24)</sup>

There has therefore been considerable support for the "two-centred mechanism" postulated by Knozinger.<sup>(10)</sup>

Balaceanu and Jungers studied the dehydration of ethyl alcohol at 300°C and found that ether was formed by a bimolecular reaction. However, they concluded that the secondary ether break down to ethylene limited the usefulness of the results and extended the study to consider the dehydration of methanol, for which only a stable ether forms. The mechanism which they found best fitted their data was

$$r = \frac{k_1 K_a^2 p_a^2}{(1 + K_a p_a + K_e p_e + K_w p_w)^2}$$

which conforms to the conventional LANGMUIR-HINSHELWOOD concept. They also studied the influence of water and concluded that water inhibited the reaction. In fact at 300°C they found that 30% water in alcohol reduced the rate by 37%.

From these three studies, which have considered the mechanism from the adsorption viewpoint, three different rate expressions have been postulated for the dehydration of ethanol to diethyl ether. The three mechanisms which have been advanced are a Langmuir-Hinshelwood bimolecular reaction (zero order), a double-centred mechanism (zero order), and a combined Langmuir-Hinshelwood-Rideal-Eley mechanism (combined zero and first order). Obviously this aspect of the dehydration reaction merits re-examination.

### 2.2.2 Mechanism of Ethylene Formation

As in the case of ether there have been few mechanistic studies of ethylene formation.

(25)

Brey and Krieger derived the following rate equation for the dehydration of ethanol on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 350°C to 400°C.

$$22,400R = \frac{k L K_a p_a}{K_a p_a + K_w p_w} \quad (2.8)$$

The equation was based on the assumption that surface reaction was rate-controlling, that ethanol and water were strongly adsorbed while ether and ethylene were not, that one active site was involved per molecule of ethanol reacted, and that the reverse

reaction could be neglected because of the magnitude of the equilibrium constant. In equation (2.8)

$R$  is the rate in moles of ethylene/cm<sup>3</sup> of catalyst bed/second

$k$  is the rate constant

$L$  is the number of active sites per cm<sup>3</sup> of catalyst bed

$K_a$  and  $K_w$  are the equilibrium adsorption constants for alcohol and water respectively

$p_a$  and  $p_w$  are partial pressures of alcohol and water.

Equation (2.8) is a general expression for a reaction of the type  $A \rightarrow R + S$ . Similar equations have been used by Miller (26) and Kirk (27) and Butt, Bliss and Walker (9) for the dehydration of primary alcohols to olefines over alumina.

de Boer and co-workers have also found that their results for ethylene formation fit conventional catalytic rate expressions. They wrote their rate equation in the form

$$v_{\text{ethylene}} = k_1 \theta_a$$

which at high alcohol pressures became

$$v_{\text{ethylene}} = k_1$$

No attempt was made in either of these studies to determine the effect of water on the rate of ethylene formation. Since (16,18) Knozinger has proposed that ether is produced by a double-centred mechanism, a study of ethylene production at various alcohol and water concentrations might reveal a similar mechanism

for that reaction thus providing support for his hypothesis.

### 2.2.3 Mechanism of Diethyl Ether Decomposition (10)

Balaceanu and Jungers studied the decomposition of diethyl ether on  $\gamma$ -alumina and found that the results fitted the rate expression

$$V = \frac{k b_{\text{ether}} C_{\text{ether}}}{b_{\text{ether}} C_{\text{ether}} + b_{\text{water}} C_{\text{water}}}$$

using initial reaction rates.

Where  $V$  is the rate of reaction

$k$  is the rate constant

$b_{\text{ether}}$  and  $b_{\text{water}}$  are the adsorption coefficients of ether and water

$C_{\text{ether}}$  and  $C_{\text{water}}$  are the concentrations of ether and water.

### 2.3 Adsorption Studies

It is impracticable to measure the adsorption coefficient for ethanol on  $\gamma$ -alumina at high temperatures because the alcohol under goes rapid dehydration. For this reason "relative adsorption coefficients" have often been obtained from kinetic measurements by solving rate expressions based on the Langmuir adsorption theory. In general these coefficients have been quoted relative to water.

(28)

Topchieva has determined the adsorption coefficient of water, diethyl ether and ethylene by adsorption studies.

The following values were obtained:

Substrate	Temperature (°C)	Ads. Coeff. (atm <sup>-1</sup> )
Water	250	90
Diethyl ether	250	20
Water	430	2.0
Ethylene	430	0.8

Thus in the catalytic dehydration of ethanol on alumina the water formed inhibits the reaction more strongly than ether or ethylene.

(10)

Balaceanu and Jungers dehydrated ether-water mixtures over alumina catalyst at various temperatures. Assuming a unimolecular surface reaction they obtained the relative adsorption coefficients by solving the rate equation for various ether-water compositions. They then repeated the study for ether-ethanol mixtures. The results for the two systems are presented below.

Temperature °C	Relative Adsorption Coefficient	
225	$\frac{K_w}{K_e} = 13.0$	$\frac{K_a}{K_e} = 7.0$
245	$\frac{K_w}{K_e} = 9.5$	$\frac{K_a}{K_e} = 3.5$
260	$\frac{K_w}{K_e} = 5.8$	$\frac{K_a}{K_e} = 2.5$

These results suggest that ethanol and water are strongly adsorbed, whilst ether and ethylene are weakly adsorbed. This would account for the inhibiting effect of water upon the dehydration of ethanol on

$\gamma$ -alumina.

#### 2.4 The Effect of Temperature

The literature on the temperature dependence of the various dehydration reactions is inconsistent for two main reasons. Firstly, different authors have employed different methods of catalyst preparation and pretreatment. Secondly, in many cases the activation energy has been found by plotting the logarithm of the rate and not the logarithm of the specific rate constant against reciprocal temperature. One may only plot the logarithm of the rate in the case of a zero order reaction, when in fact the rate constant is equal to the initial rate of reaction. However, in the case of a reaction which is not zero order, or in the case of a zero order reaction where large conversions are used to calculate the rate of reaction, the reaction rate is dependent upon concentration and so cannot be used to determine the value of the apparent activation energy.

Some values of the apparent activation energies for the various steps of ethanol dehydration and diethyl ether decomposition on  $\gamma$ -alumina catalysts are tabulated below.

Reactant	Product	$E_a$ (Kcal/gm mole)	Reference
Ethanol	Diethyl Ether	14.0	(10)
"	"	22.6	(11)
"	"	14.2	(17)
"	"	25.9	(16)
Ethanol	Ethylene	38.0	(10)
"	"	14.5	(11)
"	"	11.2	(17)
"	"	30.8	(1)
Diethyl Ether	Ethylene	24.0	(10)
"	"	14.5	(11)

The results of Topchieva<sup>(11)</sup> showed that the activation energy for ethanol and diethyl ether dehydration to ethylene was the same for both reactants. From this he concluded that the one surface intermediate was formed when either ethanol or diethyl ether was decomposed. However, he did not explain why the higher value was obtained for diethyl ether formation from ethanol.

Another explanation of the temperature dependence of dehydration reactions was advanced by Stauffer and Kranich<sup>(1)</sup> who obtained a value of 30.8 K cal/gm mole for ethylene formation, the same value that Kabel and Johanson<sup>(29)</sup> had obtained for ether production from ethanol on Dowex 50-ion-exchange resin.

They suggested that the breaking of the same bond may be rate controlling over a wide temperature range and over widely different catalysts whether the product is olefine or ether.

Several studies have been made to determine the influence of substrate structure on the apparent activation energy for the reaction.

Stauffer and Kranich<sup>(1)</sup> and Miller and Kirk<sup>(26)</sup> have found that for the dehydration of a series of primary alcohols from ethanol to hexanol, the activation energy is the same for all alcohols on the same catalyst. The latter pair determined a value of  $16.0 \pm 0.7$  K cal/gm mole for dehydration on an alumina-silica catalyst, whereas the former obtained a value of 30.8 K cal/gm mole on a  $\gamma$ -alumina catalyst. Since the activation energies for the homologues were the same, the conclusion was drawn that the bond rupture energy was important. Different conclusions were reached by Dohse<sup>(30)</sup> and Bork<sup>(31)</sup> who found a systematic connection between activation energy and chain length or chain branching.

The limitation in all four studies was that rates were calculated without a clear appreciation of the mechanism or reaction scheme. Until the mechanism of the reaction is completely understood, no useful conclusions can be reached concerning the effect of substrate structure. In fact, because of the complicated "simultaneous" reaction scheme that has gained most support recently, it would appear that the dehydration of alcohols on  $\gamma$ -alumina is not a good reaction on which to study such effects. More useful results should be obtained by using a catalyst, such as thoria, which produces olefine as the sole reaction product.

## 2.5 Conclusions

A review of the literature suggests that a detailed study of the dehydration of ethanol over a wide range of temperatures, and ethanol and water partial pressures, may be rewarding. In particular it will check the applicability of the theory of Knozinger (16,19,24,32) to ethylene formation. It may provide evidence to discriminate between the parallel, consecutive, or simultaneous reaction schemes, about which there has been so much conflicting literature. All of these aspects of the reaction must be investigated fully before studies of fundamental properties such as substrate structure can be attempted.

### 3. EXPERIMENTAL

This section describes the nature and manner of preparation of the materials used, the differential reactor system, and the gas chromatographic technique used for product composition analysis. It also summarises the procedures used to study various aspects of the reaction mechanism.

#### 3.1 Materials

##### 3.1.1 Diluent Gas

Oxygen-free, dry nitrogen (Commonwealth Industrial Gases Pty. Ltd.) was used as a diluent in the reactant and product streams. The impurities quoted by the supplier were oxygen (20 p.p.m.) and water (10 p.p.m.). No attempt was made to lower the oxygen level. However, the water content was reduced by passing the gas through a 5A molecular sieve drier. It was considered essential that any water be removed because of the many reports of water inhibiting the dehydration reaction.

##### 3.1.2 Ethyl Alcohol

"Anhydrous" ethyl alcohol (supplied by F.H. Faulding and Co. Ltd.) was shown by gas chromatography to have only water as an impurity. This was removed by drying over 3A molecular sieves. The ethyl alcohol was then distilled and stored over 5A molecular sieves until used.

##### 3.1.3 $\gamma$ -Alumina Catalyst

The  $\gamma$ -alumina catalyst was supplied by the Harshaw Chemical

Company (U.S.A.) in the form of  $\frac{1}{8}$ " cylinders. The sample (Type Al-0104 T  $\frac{1}{8}$ " - Lot 159) was 99% pure  $\gamma$ -alumina. The surface area ( $80 \text{ m}^2/\text{gm}$ ) and pore volume ( $0.3 \pm 0.02 \text{ cc/gm}$ ) were determined by the manufacturer using a BET apparatus and a mercury porosimeter respectively.

### 3.2 Apparatus

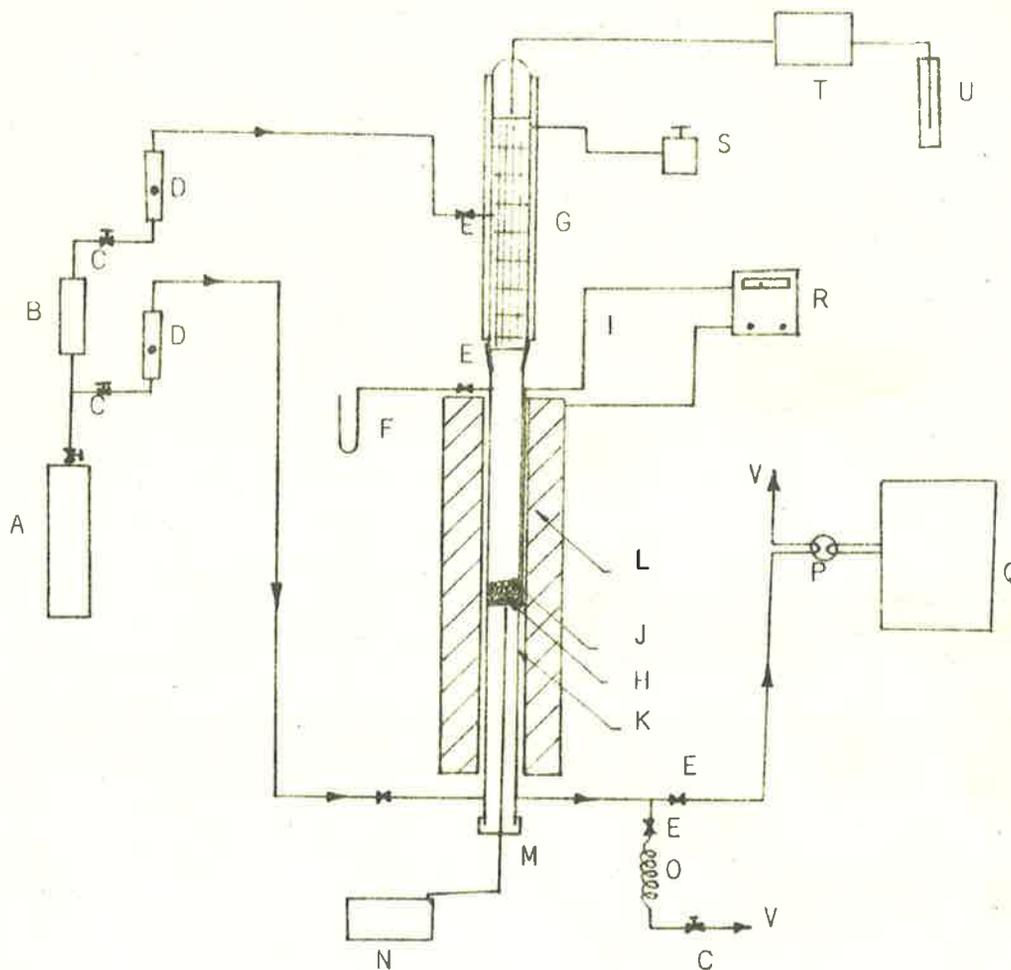
A flow diagram of the apparatus is shown in Figure 1.

#### 3.2.1 Differential Reactor System

An all-glass reactor was constructed from 24 mm bore borosilicate glass. The catalyst support was a sintered glass disc of porosity 1, located at the centre of the reactor tube. The support gave minimal channeling and pressure drop. The reactor was heated by a tube furnace. An electrically heated vaporizer and preheater was situated above the reactor. It was constructed from the same tubing as the reactor and was packed with  $\frac{1}{4}$ " glass Raschig rings. The temperature of the preheater was controlled manually through an autotransformer.

Ethyl alcohol was admitted to the top of the vaporizer by a metering pump. The pump, which has been described elsewhere,<sup>(3)</sup> was driven by a variable speed motor, with a maximum speed of 400 r.p.m. through a 1 to 10 reduction gearbox. Solvent resistant tubes with bores from 0.02 to 0.08 inches were used. These tubes produced flows from 0.1 gm/min to 3.0 gm/min.

In those runs in which the ethyl alcohol feed was diluted with nitrogen, the gas was metered into the preheater through a needle valve and rotameter after passing through molecular sieve



- |                          |                             |
|--------------------------|-----------------------------|
| A. Nitrogen cylinder     | L. Furnace                  |
| B. Molecular sieve drier | M. Measurement thermocouple |
| C. Needle valve          | N. Potentiometer            |
| D. Rotameter             | O. Condenser                |
| E. Teflon stopcock       | P. Heated gas sample valve  |
| F. Manometer             | Q. Gas chromatograph        |
| G. Preheater             | R. On-off controller        |
| H. Sintered glass disc   | S. Auto-transformer         |
| I. Control thermocouple  | T. Metering pump            |
| J. Catalyst bed          | U. Alcohol feed tank        |
| K. Reactor               | V. Vent                     |

FIGURE 1 Flow diagram of the apparatus.

driers. For all runs a second nitrogen stream, which was metered in the same way, was mixed with the product stream from the reactor. This was done for two reasons. Firstly, it lowered the partial pressure of the condensable material in the reactor effluent and so reduced the likelihood of condensation of the product stream prior to analysis by the gas chromatograph. Secondly, it reduced the alcohol concentration in the product stream so that the amount of alcohol introduced into the gas chromatograph during an analysis was within the linear range of the flame ionization detector.

The lines from the reactor to the gas chromatograph were made from borosilicate tubing and were heated to prevent condensation of ethyl alcohol, water, or ether. Heating tapes, which were regulated by autotransformers, were used to heat these lines.

The total reaction pressure was found by summing the pressure in the system and the atmospheric pressure. The pressure of the system (differential pressure) was measured using a mercury-filled U-tube manometer. The line to the manometer was electrically heated to prevent any condensation of alcohol.

All on-off valves in the glass-ware of the reaction system had teflon keys. This type of stopcock was used to prevent contamination of the product stream with grease and to enable efficient operation in heated lines.

### 3.2.2 Temperature Measurement and Control

The temperature of the tube furnace heating the reactor was

controlled by a Honeywell-Brown Pyrovane indicating on-off controller, which actuated an external relay thus switching between an autotransformer supplying high voltage and one at a lower voltage. The voltage difference between the high power and low power transformers was generally maintained at 10 volts in order to produce a minimum amplitude in the temperature cycle within the reactor. The thermocouple which actuated the controller was located in the air-space between the reactor and the tube furnace, the bead of the thermocouple being level with the catalyst bed. This positioning of the thermocouple gave better control of the temperature in the reactor than when the thermocouple was located in the catalyst bed. In the latter case the lags in the system greatly affected the quality of the control.

The reaction temperature was measured with a calibrated chromel-alumel thermocouple which was located in the outlet gas stream about  $\frac{1}{8}$ " from the bottom of the catalyst bed. The measured reaction temperatures had a variation of less than  $\pm 1^{\circ}\text{C}$  from the average value quoted for a particular run.

### 3.3 Analysis by Gas Chromatography

Comprehensive gas chromatography facilities were available for this study. The instrument used was a Shimadzu GC 1C gas chromatograph, a dual column device, which had thermal conductivity and flame ionization detectors connected in series. The unit is pictured in Figure 2. Other facilities included a heated gas sample valve, a non-linear temperature programmer, and a preparative attachment. A sample of the product stream could be introduced onto the column simply by turning a



FIGURE 2 Photograph of the gas chromatograph.

valve. The valve and sample loop were housed in an oven which could be maintained at temperatures between ambient and 200°C by means of an on-off controller. To ensure that there was no condensation of water, ethanol or ether from the gas mixture, the valve was maintained at 150°C during all runs. The valve was equipped with three sample loops which had capacities of 1, 2, and 5 cm<sup>3</sup>. Calibration of the flame ionization detector for ethanol showed that the 1 cm<sup>3</sup> loop admitted a sample which contained ethanol in an amount outside the linear range of the detector. Hence, a 0.4 cm<sup>3</sup> loop was constructed to ensure that the analysis was made within the linear range.

### 3.3.1 Choice of Detector

Many studies of dehydration reactions have employed gas chromatographs equipped with thermal conductivity detectors. Generally this detector has been used in order to obtain a quantitative estimate of the water concentration in the product stream. In this study there was a choice of two detector systems. The flame ionization detector was chosen since the thermal conductivity method was considered to be not sensitive enough to determine compositions when conversions of less than 1 mole percent were expected. Although the flame ionization detector is insensitive to water, the amount of water could be estimated knowing the amounts of ether and ethylene formed. In fact, the rates of reaction were calculated using the mole fractions of ethylene and diethyl ether. Flame ionization had several other advantages over thermal conductivity. Firstly, it allowed the use of nitrogen as carrier gas in place of the more expensive helium which is required

for use with thermal conductivity detectors. Secondly, the flame ionization device has a linear response range that exceeds (33) by several orders of magnitude that of any other detector.

### 3.3.2 Choice of Separation

Several columns were investigated. Poropak Q which consists of porous polymer beads, was found to give excellent separation of ethylene, diethyl ether and ethanol. A comprehensive report of the use of this packing material to separate the three components has been given earlier. (3) Using Poropak Q the order of elution is ethylene, ethanol and diethyl ether. Whilst this separation was adequate for analyses when high conversions to ether were maintained, difficulties arose at low ether concentrations. At the sensitivities required to determine the low ether concentrations, a small amount of ethanol could be detected that was being eluted from the column. This appeared on the recorder trace as quite a large "tail". Thus the ether peak was superimposed on the trailing edge of the ethanol peak. An alternative column material was then investigated.

(1)

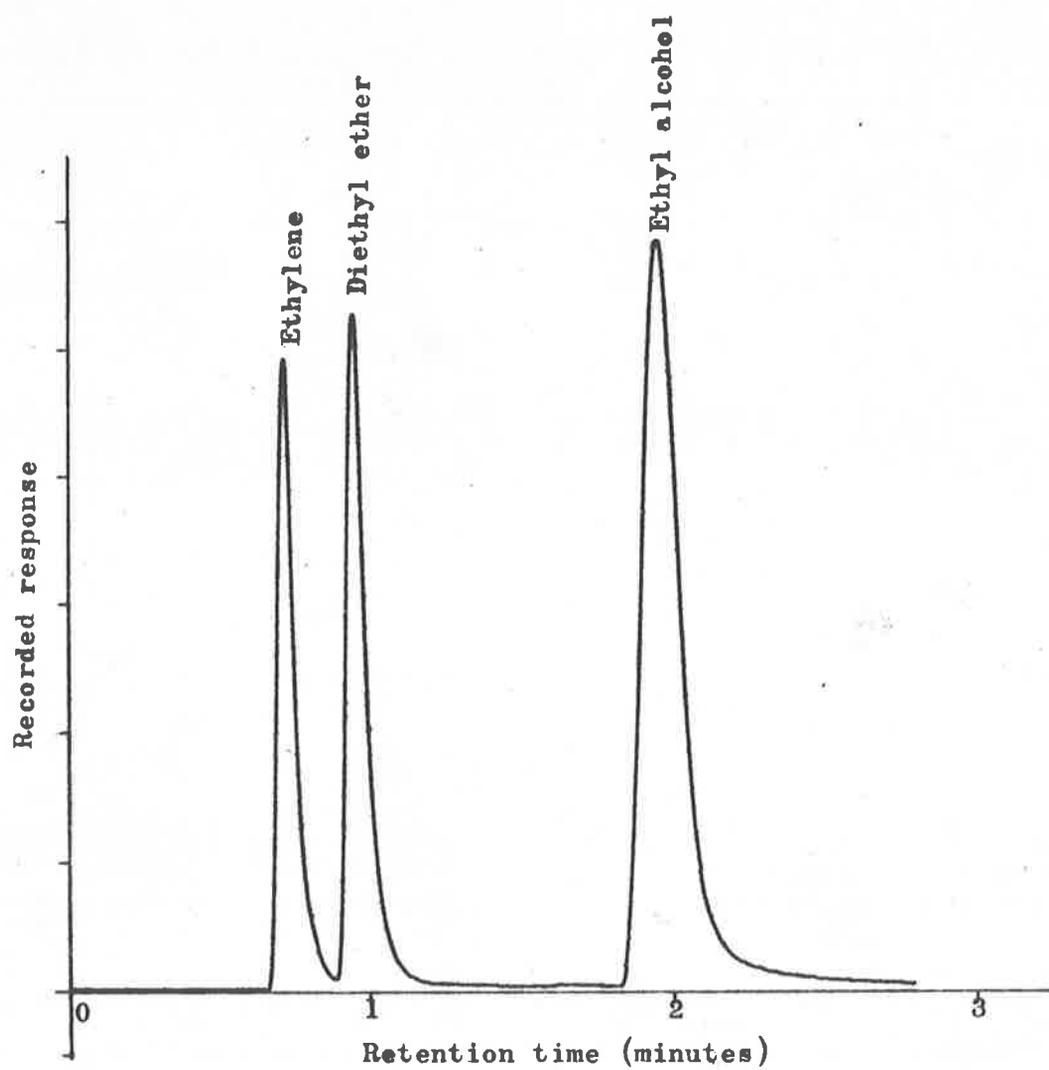
Stauffer and Kranich (1) reported the use of Renex 678, a polyoxyethylene alkyl aryl ether, as a stationary phase for the GLC separation of alcohol, olefine and ether mixtures. A column of Renex 678 (10 wt %) on 80-100 mesh Chromosorb W (90 wt %) was prepared using acetone as solvent. This packing provided an excellent separation of the three components, the order of elution being ethylene, diethyl ether and ethyl alcohol. Acetaldehyde, a reported by-product for some studies, was eluted between

diethyl ether and ethanol. Renex 678 on Chromosorb W was therefore chosen as the column packing for all product analysis in this study. A typical chromatogram of the product stream is presented in Figure 3. The details of conditions used in the separation are presented below.

<u>Column</u>	Material	: Stainless Steel
	Internal Diameter	: 3 mm
	Length	: 1.5 m
<u>Packing</u>	Renex 678 (10 wt %) on Chromosorb W (90 wt %)	
<u>Carrier Gas</u>	Nitrogen	
	Flow rate	: 40 cm <sup>3</sup> /min
<u>Hydrogen</u>	Flow rate	: 40 cm <sup>3</sup> /min
<u>Air</u>	Flow rate	: 1,000 cm <sup>3</sup> /min
<u>Temperatures</u>	Column	: 75°C
	Injection Port	: 150°C
	Heated Gas Sampler	: 150°C
	Detector	: 250°C
<u>Reference Column</u>	Same as separating column	
<u>Retention Times</u>	Ethylene	: 0.75 min
	Diethyl Ether	: 1.0 min
	Ethanol	: 2.0 min

### 3.3.3 Calibration of the Detector

The flame ionization detector shows a regularity in its response to related compounds. (33) Onkiahong (34) introduced a "C-factor" which eliminated the need to calibrate this detector.



**FIGURE 3** Chromatogram of product analysis

He defined the factor as

$$\underline{C} = \frac{\text{molecular weight}}{12 \times \text{number of carbon atoms}}$$

The ratio molecular weight/12 was introduced to give composition measurement in weight. The factor as defined by Onkiehong, converts the response per gram of sample to the response per gram of carbon. When mole fractions are required the M.W./12 ratio can be omitted. Onkiehong found that when the components contain oxygen, a good approximation was to split off as many CO<sub>2</sub> groups as possible from the parent molecule and to use only the residual carbon atoms for calculation purposes. He showed, by measurement of their responses relative to hydrocarbons, that this approximation could be applied to ethyl alcohol and diethyl ether.

Calibrations for diethyl ether, ethylene and ethyl alcohol present certain difficulties. The high volatility of ether at ambient temperature makes it difficult to inject reproducible amounts of that component. Ethylene, because it is a gas, must be calibrated independently of the two liquid components. Hence both gas and liquid syringes must be used and this places great importance on their accuracy of calibration. The Onkiehong C-factor approach to quantitative product analysis was adopted to overcome the difficulty of calibration for these three components. However, conventional calibration procedures using syringes, were done to check that product analysis was made within the linear range of the detector. The calibration graphs for diethyl ether, ethyl alcohol and ethylene are shown in Figures 4, 5 and 6 respectively. These

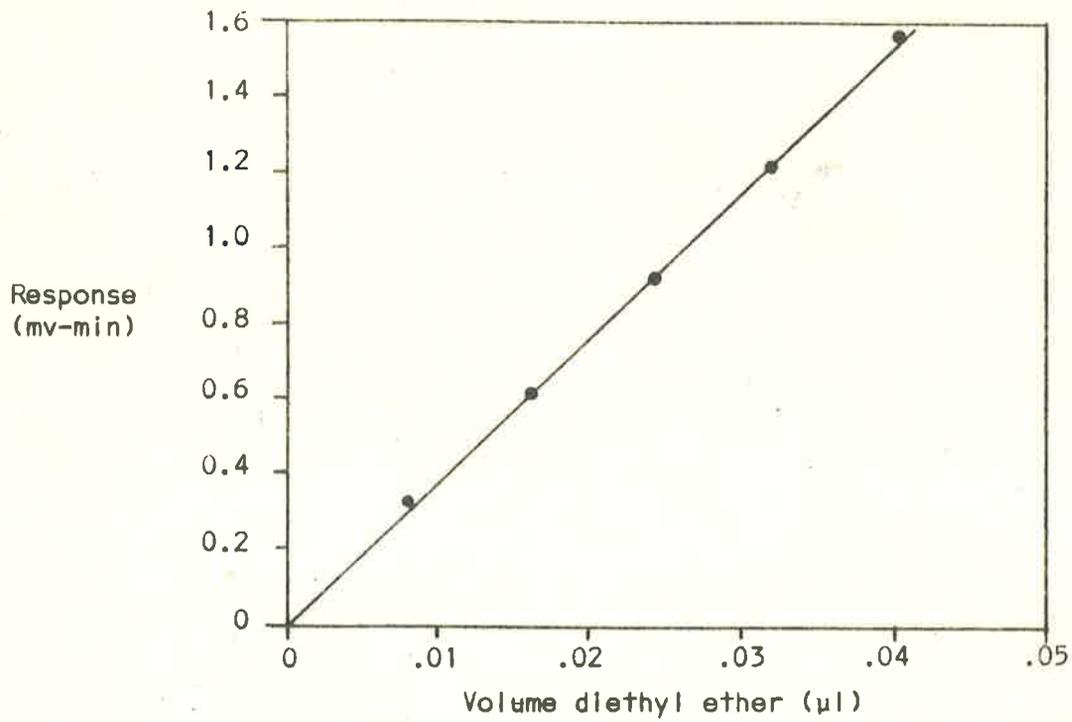


FIGURE 4 Chromatograph calibration for ether.

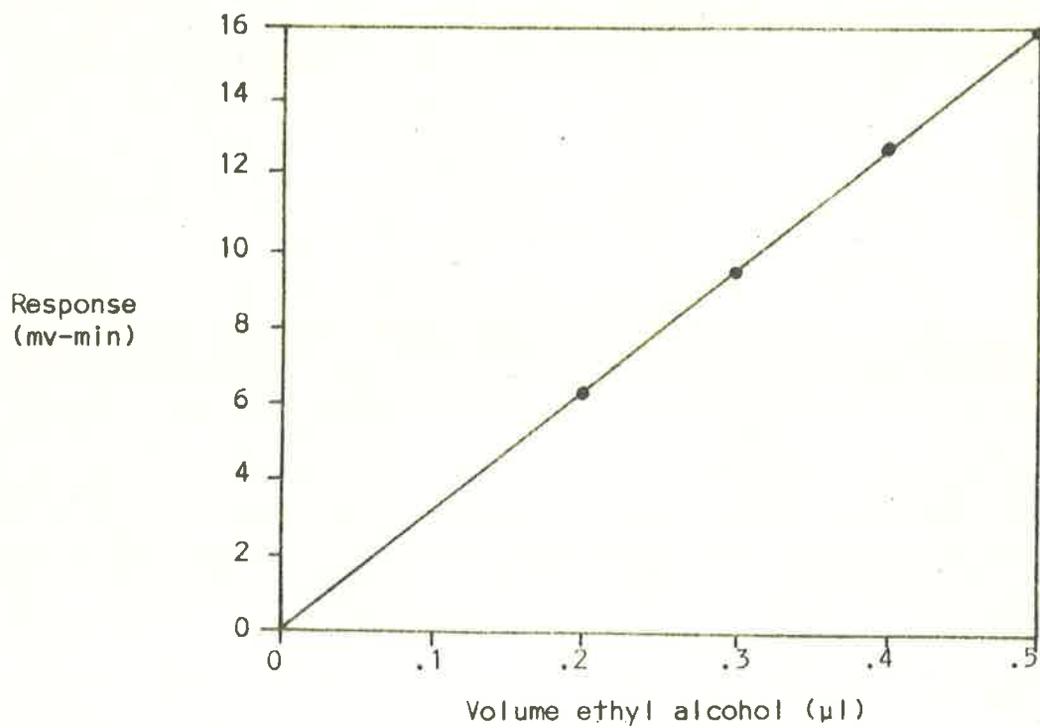


FIGURE 5 Chromatograph calibration for ethanol.

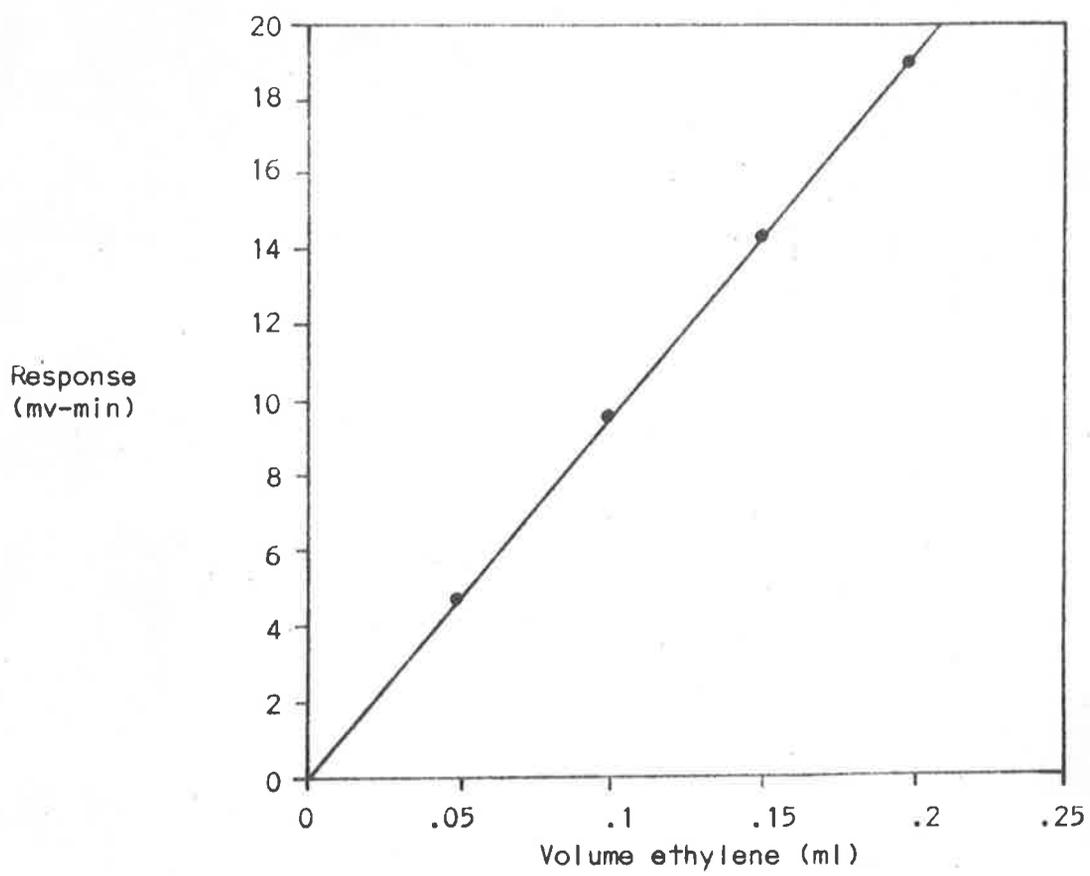


FIGURE 6 Chromatograph calibration for ethylene.

graphs show that the response was linear for all three components for the sample volumes investigated.

### 3.3.4 Quantitative Analysis

Quantitative interpretation of the chromatogram was done by the internal normalization method. In this method, also known as the total peak area method, the concentration of each component in the sample is calculated. The first step in the procedure is to calculate the area of each peak in the chromatogram. The area of each peak is proportional to the amount of the respective component:

$$A_i = f_i(C_i)$$

where  $f_i$  is the detector response factor which corresponds to the  $C_i$ -factor defined by Onkiehong. The values of  $f$  used in this study were

ethyl alcohol	$f_a = 1.5$
diethyl ether	$f_e = 3.5$
ethylene	$f_o = 2.0$

These values were determined using the expression

( $f_i = \text{no. of C atoms in component } i - \text{no. of CO}_2 \text{ groups in component } i$ ). The relative amounts of each component were then determined by summing the  $\frac{A_i}{f_i}$  terms and using expressions of the form

$$C_e = \frac{\frac{A_e}{f_e}}{\frac{A_o}{f_o} + \frac{A_a}{f_a} + \frac{A_e}{f_e}}$$

to calculate the relative amounts of ethylene, diethyl ether and ethyl alcohol.

The peak areas were determined by multiplying the height of each peak by the width at half height. This method was first recommended by Cremer and Müller. (35) A study by Gill and Tao (36) reported an error of 2.58% in the area of individual peaks using this method. This was compared with an error of 0.44% using an electronic integrator and 4.06% using planimetry.

### 3.4 Experimental Techniques used to investigate mechanisms

A general description of the reaction system was presented in Section 3.2.1. The following section reports the procedures used to investigate various aspects of the reaction mechanism.

#### 3.4.1 Temperature dependence of Ethanol Dehydration

The rates of diethyl<sup>2</sup> ether formation were determined in the temperature range 214°C to 319°C using 10.0 grams of catalyst. The ethanol molal flow rate was increased as the reaction temperature was increased so that initial reaction rates were obtained for all temperatures studied. This ensured that approximately the same low conversions were obtained for all runs. The calculation of initial rates of reaction is necessary in a system where a product species inhibits the reaction.

The rates of formation of ether and ethylene were determined over 0.4 grams of catalyst at temperatures from 305°C to 436°C using the same procedure.

#### 3.4.2 Temperature dependence of Diethyl Ether Decomposition

The decomposition of diethyl ether was investigated in the temperature range 300°C - 400°C using 1.0 grams of catalyst. The high volatility of diethyl ether caused difficulty in the calibration of the metering pump for that compound. In fact, the feed reservoir had to be immersed in an ice-bath to cool the ether sufficiently to prevent vaporization in the pump. When this procedure was used the ether flow rate was constant for all temperatures studied. Conversions of ether varied from 2.4% at 300°C to 28% at 400°C.

Therefore the rates obtained were not the initial reaction rates.

#### 3.4.3 The influence of Ethanol partial pressure

The rates of diethyl ether formation were determined at 248°C and 295°C for alcohol pressures in the range 40 mm Hg to 800 mm Hg. In all runs 2.0 grams of catalyst was used. The alcohol flow rate was held constant and the partial pressure was varied by dilution of the alcohol vapour with nitrogen.

The influence of ethanol partial pressure on rates of diethyl ether and ethylene formation was studied at 357°C and 393°C using 0.4 grams of catalyst and the above procedure.

#### 3.4.4 The influence of Water partial pressure

The effect of water on the rates of formation of diethyl ether was studied at 261°C and 312°C using 10.0 grams of catalyst. Similar studies were carried out at 348°C and 386°C for the

formation of ethylene and ether over 0.4 grams of catalyst. The water partial pressure was varied by metering ethanol-water mixtures into the reactor. The water composition in these feeds varied from 2 to 30 weight percent and produced water vapour pressures varying from approximately 40 mm Hg to 400 mm Hg.

## 4. RESULTS

### 4.1 Treatment of Results

The rates of reaction were calculated from the experimental results by means of the equation,

$$r_i = \frac{F_a x_i}{W} \quad (4.1)$$

where  $r_i$  is the rate of formation of  $i$  (moles/gm min)

$x_i$  is the mole fraction of  $i$  in the product stream

$W$  is the mass of catalyst (gm)

$F_a$  is the flow rate of reactant  $a$  (moles/min)

Equation (4.1) is the expression used to calculate reaction rates from differential reactor data when the feed to the reactor is free from product component  $i$ . The rates of reaction were calculated using a Control Data Corporation 6400 digital computer. The mole fractions of the product species were determined from gas chromatographic analysis using the technique described in Section 3.3.4. The data fed to the computer included the heights and widths at half height of individual peaks, the mass of catalyst used, and the reactant flow rate. The programme also calculated partial pressures of water and ethanol in the runs where those parameters were varied.

### 4.2 The rate controlling step

The effect of mass transfer phenomena was investigated by measuring the reaction rates when the space velocity of the feed was varied. It was found in all runs that the chemical reaction was the rate-controlling step. The activation energies for both diethyl ether and ethylene

formation were found to be approximately 30 K cal/gm mole, a value which is much greater than those for diffusion processes. The space velocities used in this study were greater than those reported in similar investigations of the reaction mechanism. (9,16) Chemical reaction may therefore be assumed to be the controlling mechanism in this study.

#### 4.3 Temperature dependence of Diethyl Ether Formation

The rates of diethyl ether formation were determined in the temperature range 214°C to 319°C. Reaction rates varied from  $8.62 \times 10^{-7}$  moles/gm min at 214°C to  $1.74 \times 10^{-4}$  moles/gm min at 319°C, indicating that the reaction is highly activated. The rates and corresponding temperatures are given in Table 4.1

TABLE 4.1 : The temperature dependence of ethanol dehydration at temperatures from 214°C to 319°C.

Temperature (°C)	Rate of diethyl ether formation (mole/gm min)
214	$8.62 \times 10^{-7}$
220	$1.27 \times 10^{-6}$
224	$1.84 \times 10^{-6}$
229.5	$2.76 \times 10^{-6}$
236.5	$4.01 \times 10^{-6}$
242	$5.13 \times 10^{-6}$
251	$8.37 \times 10^{-6}$
255.5	$1.13 \times 10^{-5}$
261	$1.29 \times 10^{-5}$
266	$1.76 \times 10^{-5}$
274.5	$2.87 \times 10^{-5}$
280.5	$3.55 \times 10^{-5}$
287.5	$5.00 \times 10^{-5}$
294	$6.03 \times 10^{-5}$
301.5	$8.29 \times 10^{-5}$
311	$1.34 \times 10^{-4}$
319	$1.74 \times 10^{-4}$

Complete details of the experimental runs are tabulated in Appendix 2. Finally, the results are presented as an Arrhenius plot in Figure 7.

#### 4.4 Temperature dependence of the dehydration of ethyl alcohol in the range 305°C to 436°C

The rates of simultaneous diethyl ether and ethylene formation were determined in the temperature range 305°C to 436°C. These results are presented in Table 4.2.

**TABLE 4.2** : The temperature dependence of ethanol dehydration at temperatures from 305°C to 436°C.

Temperature (°C)	Rate of diethyl ether formation (mole/gm min)	Rate of ethylene formation (mole/gm min)
305	$1.38 \times 10^{-4}$	$1.00 \times 10^{-5}$
308	$1.59 \times 10^{-4}$	$1.32 \times 10^{-5}$
315.5	$2.28 \times 10^{-4}$	$1.97 \times 10^{-5}$
321	$2.84 \times 10^{-4}$	$2.45 \times 10^{-5}$
328	$3.74 \times 10^{-4}$	$3.64 \times 10^{-5}$
334	$4.36 \times 10^{-4}$	$4.42 \times 10^{-5}$
339.5	$5.00 \times 10^{-4}$	$5.36 \times 10^{-5}$
345.5	$5.99 \times 10^{-4}$	$6.67 \times 10^{-5}$
352.5	$7.18 \times 10^{-4}$	$9.06 \times 10^{-5}$
356	$7.95 \times 10^{-4}$	$9.96 \times 10^{-5}$
364	$8.55 \times 10^{-4}$	$1.17 \times 10^{-4}$
373.5	$1.11 \times 10^{-3}$	$1.66 \times 10^{-4}$
378	$1.26 \times 10^{-3}$	$1.96 \times 10^{-4}$
385	$1.39 \times 10^{-3}$	$2.36 \times 10^{-4}$
392	$1.70 \times 10^{-3}$	$3.25 \times 10^{-4}$
399	$2.18 \times 10^{-3}$	$4.27 \times 10^{-4}$
404	$2.55 \times 10^{-3}$	$5.46 \times 10^{-4}$
409	$2.59 \times 10^{-3}$	$6.20 \times 10^{-4}$
414	$2.59 \times 10^{-3}$	$6.64 \times 10^{-4}$
420	$2.71 \times 10^{-3}$	$7.64 \times 10^{-4}$
426	$3.05 \times 10^{-3}$	$9.46 \times 10^{-4}$
431.5	$3.30 \times 10^{-3}$	$1.17 \times 10^{-3}$
436	$3.61 \times 10^{-3}$	$1.41 \times 10^{-3}$

Complete data for the runs are presented in Appendix 3. Finally, the results have been plotted as the natural logarithm of the rate versus reciprocal absolute temperature in Figure 8.

#### 4.5 Temperature dependence of Diethyl Ether decomposition

The rates of formation of ethylene and ethyl alcohol were calculated from the results for diethyl ether decomposition at temperatures from 300°C to 400°C. At 300°C the conversions to ethanol and ethylene were approximately equal. However, as the temperature was increased, the rate of ethylene production increased at a greater rate than ethanol formation. So marked was this effect that at 400°C the ethylene rate was almost double the ethanol rate. The results are given in Table 4.3 and full experimental details are presented in Appendix 4. The logarithms of the rates of ethylene and ethanol formation are plotted against reciprocal absolute temperature in Figure 16.

TABLE 4.3 : Rates of diethyl ether decomposition in the temperature range 300°C to 400°C.

Temperature (°C)	Rate of ethanol formation (mole/gm min)	Rate of ethylene formation (mole/gm min)
300	$8.56 \times 10^{-5}$	$8.36 \times 10^{-5}$
312	$1.08 \times 10^{-4}$	$1.22 \times 10^{-4}$
324	$1.46 \times 10^{-4}$	$1.75 \times 10^{-4}$
337	$2.06 \times 10^{-4}$	$2.68 \times 10^{-4}$
354	$2.82 \times 10^{-4}$	$4.06 \times 10^{-4}$
368	$4.02 \times 10^{-4}$	$5.92 \times 10^{-4}$
378	$4.76 \times 10^{-4}$	$7.44 \times 10^{-4}$
390	$6.10 \times 10^{-4}$	$1.04 \times 10^{-3}$
400	$6.98 \times 10^{-4}$	$1.28 \times 10^{-3}$

#### 4.6 Calculation of apparent activation energies

The activation energies and frequency factors have been calculated for both diethyl ether formation and ethylene formation. These results are presented in Table 4.4

TABLE 4.4 : Activation energies and frequency factors for the formation of diethyl ether and ethylene

Reaction	Diethyl ether Formation	Ethylene Formation
Temperature Range ( $^{\circ}\text{C}$ )	214 - 319	305 - 436
Apparent activation energy $E_a$ (cals/gm mole)	$28,500 \pm 50$	$29,200 \pm 50$
Frequency factor (mole/gm min)	$6.10 \times 10^6$	$1.34 \times 10^6$

The activation energy for diethyl ether formation was calculated using rate data determined in the temperature range  $214^{\circ}\text{C}$  to  $319^{\circ}\text{C}$ . In this range the formation of diethyl ether was found to be independent of alcohol pressure at pressures approaching one atmosphere (Section 4.7). Thus, under those conditions, the reaction was zero order and the rate constant was equal to the rate of reaction. However, at higher temperatures (Section 4.8) the reaction was no longer independent of alcohol concentration and the rate constant differed from the rate of reaction. Since the reaction rates were concentration dependent, the activation energy was not calculated for the higher temperature range.

In Section 4.8 ethylene formation has been shown to be zero order for the temperature range 305°C to 436°C, hence the activation energy has been determined for that reaction.

The activation energies for the formation of ethanol and ethylene, by the decomposition of diethyl ether, were not determined for two reasons. Firstly, no attempt was made in this study, to determine the order or reaction rate constant for the reaction. Secondly, high conversions were obtained. Consequently the reaction rates were concentration dependent. Although the plots of  $\ln$  rate versus  $\frac{1}{TOK}$  are straight lines for both ethylene and ethanol formation, values of activation energies calculated from those plots would have little meaning.

A digital computer programme was written to calculate the activation energies and frequency factors. The data required for the programme were reaction rate constants and temperature. The computer calculated and tabulated the natural logarithms of the rate constants and the reciprocal absolute temperatures. A linear least squares fit of the data to the Arrhenius equation  $\ln k = \ln A - \frac{E_a}{RT}$  was made and the least squares values of  $\ln k$  were calculated and tabulated for every temperature. The activation energy was determined by multiplying the negative value of the slope of the least squares fit of the data by the gas constant  $R$ . The frequency factor was found by taking the anti-logarithm of the intercept. Appendices 13 and 14 present the results of the least squares fit of the data.

The reliability of the estimates of the activation energies was evaluated using the standard statistical analysis procedures recommended (37) in the Chemical Engineers Handbook. The activation energies had a

95% probability of being within  $\pm 45$  cal/gm mole and  $\pm 28$  cal/gm mole of the values determined for diethyl ether and ethylene respectively. The values of the functions used in the statistical analyses are given in Table 4.5.

TABLE 4.5 : Statistical analysis of activation energy values.

Reaction	Diethyl ether Formation	Ethylene Formation
True value of $E_a$ (cals/gm mole)	28,490	29,220
No. of points n	17	23
No. of degrees of freedom df	16	22
Standard deviation s	109	76
Probability	95%	95%
Distribution t	1.75	1.72
Confidence Interval (cals/gm mole)	$\pm 45$	$\pm 28$

#### 4.7 The influence of Ethanol pressures on the dehydration of Ethanol at 248°C and 295°C

The rates of diethyl ether formation were determined for various ethyl alcohol partial pressures at 248°C and 295°C. The results are presented in Tables 4.6 and 4.7 respectively. The results of Table 4.6 show that the rate of diethyl ether formation at 248°C is independent of ethyl alcohol pressure at pressures above 328 mm Hg. Similarly Table 4.7 shows that at 295°C the reaction is zero order for

ethanol pressures greater than 647 mm Hg. As the temperature is increased the region of zero order behaviour is decreased.

TABLE 4.6 : The influence of ethanol partial pressure on the rate of ethanol dehydration at 248°C

Ethanol Pressure (mm Hg)	Rate of Diethyl Ether formation (mole/gm min) $\times 10^6$
734.8	7.20
627.3	7.09
537.7	7.20
423.0	7.10
328.0	7.23
212.5	5.59
178.8	4.90
154.7	4.62
137.5	4.19
114.0	3.72
68.6	2.74
46.7	2.01

TABLE 4.7 : The influence of ethanol partial pressure on the rate of ethanol dehydration at 295°C

Ethanol Pressure (mm Hg)	Rate of Diethyl Ether formation (mole/gm min) $\times 10^5$
791.2	6.30
759.3	6.21
704.4	6.45
647.4	6.35
583.8	5.90
519.8	5.68
466.9	5.33
423.2	5.12
359.1	4.88
320.3	4.81
278.2	4.63
232.2	4.19
199.1	3.76
160.6	3.45
110.2	3.01
78.9	2.74
48.9	2.16

The results of Tables 4.6 and 4.7 are plotted in Figures 17 and 18.

Complete details of the runs are given in Appendices 5 and 6.

#### 4.8 The influence of Ethanol pressures on the dehydration of Ethanol at 357°C and 393°C.

The results for these runs are presented in Tables 4.8 and 4.9. The rate of diethyl ether formation at 357°C depends on ethyl alcohol pressures at pressures up to 772 mm Hg. However, the dependence is inversely proportional to the pressure. At the same temperature and the same alcohol pressures, ethylene formation is zero order for ethanol pressures in excess of 300 mm Hg.

TABLE 4.8 : The influence of ethanol partial pressure on the rate of ethanol dehydration at 357°C

Ethanol partial pressure (mm Hg)	Rate of ether formation $\times 10^4$ (mole/gm min)	Rate of ethylene formation $\times 10^5$ (mole/gm min)
771.8	9.99	12.1
717.6	9.79	12.1
636.4	9.48	12.3
554.8	9.26	12.5
476.3	8.67	12.1
417.6	8.47	12.4
370.5	7.90	12.0
330.1	7.53	11.7
304.2	7.39	12.0
281.5	7.21	11.6
268.6	6.86	11.3
239.4	6.66	10.9
222.6	6.45	10.8
188.8	6.18	9.95
161.9	5.33	9.71
145.2	5.03	9.52
131.0	4.90	9.82
115.4	4.25	8.59
52.8	1.72	5.46

Table 4.9 presents similar results for the 393°C runs.

TABLE 4.9 : The influence of ethanol partial pressure on the rate of ethanol dehydration at 393°C

Ethanol partial pressure (mm Hg)	Rate of ether formation $\times 10^3$ (mole/gm min)	Rate of ethylene formation $\times 10^4$ (mole/gm min)
748.0	2.28	4.58
698.8	2.23	4.54
660.3	2.19	4.70
617.6	2.18	4.78
579.9	2.10	4.73
548.6	2.03	4.70
517.6	1.91	4.58
492.6	1.86	4.46
454.5	1.87	4.59
415.5	1.79	4.44
348.6	1.67	4.53
312.2	1.54	4.34
273.7	1.46	4.41
217.8	1.22	4.43
173.3	.985	4.08
129.0	.798	3.74
81.3	.370	2.40
65.7	.250	2.26
25.3	.133	2.21

The results given in Tables 4.8 and 4.9 are plotted as Figures 19 and 20 respectively. Full details of the runs are presented in Appendices 7 and 8.

#### 4.9 The influence of water pressure on the rate of ethanol dehydration at 261°C and 312°C

The rates of diethyl ether formation for various water and ethanol partial pressures are presented in Tables 4.10 and 4.11 for runs at 261°C and 312°C respectively.

TABLE 4.10 : The influence of water partial pressure on the rate of ethanol dehydration at 261°C.

Ethanol partial pressure (mm Hg)	Water partial pressure (mm Hg)	Rate of ether formation $\times 10^6$ (mole/gm min)
552.6	2.4	13.3
530.7	29.1	8.05
509.3	55.2	6.37
489.9	80.5	5.36
470.9	105.3	4.72
451.8	128.7	4.00
434.6	151.7	3.58
418.1	173.8	3.03
401.0	195.3	2.64
381.2	213.8	2.39
353.0	254.4	2.06
324.0	291.1	1.71

TABLE 4.11 : The influence of water partial pressure on the rate of ethanol dehydration at 312°C.

Ethanol partial pressure (mm Hg)	Water partial pressure (mm Hg)	Rate of ether formation $\times 10^5$ (mole/gm min)
687.3	4.6	6.28
658.0	37.1	4.11
629.5	69.0	3.17
602.2	99.7	2.55
575.4	129.1	2.20
550.0	157.0	1.81
525.5	184.1	1.54
502.6	209.1	1.29
479.8	234.0	1.14
458.2	257.2	1.00
437.5	279.6	.945
417.5	300.8	.936
398.2	321.5	.836
379.8	341.4	.789

The inhibiting effect of water is readily seen from these results. A full interpretation of these results is presented in the Discussion Section of the text. Complete details of the experimental runs are presented in Appendices 9 and 10.

#### 4.10 The influence of water pressure on the rate of ethanol dehydration at 348°C and 386°C

The inhibiting effect of water on the rates of diethyl ether and ethylene formation at 348°C and 386°C is apparent in the results presented in Tables 4.12 and 4.13.

TABLE 4.12 : The influence of water partial pressure on the rate of ethanol dehydration at 348°C

Ethanol partial pressure (mm Hg)	Water partial pressure (mm Hg)	Rate of ether formation $\times 10^4$ (mole/gm min)	Rate of ethylene formation $\times 10^5$ (mole/gm min)
758.1	3.0	6.86	8.69
723.9	40.1	5.87	7.29
685.7	75.0	5.06	6.41
646.6	107.2	4.71	6.10
611.0	137.1	4.19	5.51
583.1	166.6	3.69	5.00
551.5	193.3	3.50	4.82
528.1	220.3	3.03	4.31
502.4	245.1	2.78	4.14
475.0	266.8	2.52	3.84
472.5	302.0	2.25	3.49
429.6	347.3	2.30	3.24
404.1	362.7	1.58	2.88

TABLE 4.13 : The influence of water partial pressure on the rate of ethanol dehydration at 386°C

Ethanol partial pressure (mm Hg)	Water partial pressure (mm Hg)	Rate of ether formation $\times 10^3$ (mole/gm min)	Rate of ethylene formation $\times 10^4$ (mole/gm min)
762.5	5.2	2.00	3.83
727.4	42.9	1.83	3.62
694.5	77.7	1.60	3.27
627.3	142.3	1.36	3.10
599.3	172.3	1.23	2.85
542.6	227.5	1.05	2.63
518.1	253.6	.982	2.55
494.4	278.4	.869	2.29
471.6	302.2	.791	2.16
449.6	325.0	.773	2.13
434.9	351.3	.691	1.98
412.9	371.4	.672	1.95
393.1	390.7	.605	1.83
366.1	424.7	.533	1.69

Fuller details of the results of these runs are presented in Appendices 11 and 12. An interpretation of the results in terms of the mechanisms for ethylene and ether formation is presented in the Discussion Section of the thesis.

#### 4.11 The accuracy of the rate determinations

Equation 4.1 was used to calculate reaction rates. Therefore the rates are proportional to the flow rate of reactant, to the mole fraction of product, and to the inverse of the catalyst mass. Since small conversions were obtained in the reactor, the mole fraction of product may be approximated to  $\frac{\text{moles of ether}}{\text{moles of alcohol}}$  for estimation of errors in ether mole fraction. An accuracy and a reproducibility of approximately

$\pm 1$  percent per component can be attained using a well designed gas chromatography system. Errors in calibration of the metering pump are estimated at  $\pm 0.5$  percent. The same figure may be applied to the mass of catalyst bed. The overall error in individual rate measurements under isothermal conditions is therefore approximately  $\pm 3$  percent. However, the bed temperature fluctuated by approximately  $\pm 0.5^{\circ}\text{C}$ . This represented a  $\pm 3$  percent error in the rate at the lower temperatures studied. At higher temperatures the magnitude of this error was reduced. Thus the maximum overall error in individual rates is  $\pm 6$  percent. The two major sources of error in the study were temperature fluctuations in the catalyst bed and quantitative product analysis by gas chromatography.

## 5. DISCUSSION

### 5.1 Experimental Technique

The experimental procedures used in the present study had many advantages over those used in previous studies. Firstly, the use of a commercial catalyst sample from a single batch enabled an accurate study of the reaction mechanism to be carried out without the complications arising from non-uniformity of catalyst samples. Secondly, the apparatus was designed so that reaction mechanisms could be examined over a wider range of temperatures and concentrations than has yet been reported. The use of a porous glass disc as the catalyst support is considered to be superior to the method employed by Knozinger et al<sup>(12)</sup> in similar studies. The reactor used by the workers was a horizontal glass reaction tube which held a "boat" crucible containing the catalyst sample. In the present study initial reaction rates were determined by ensuring low conversions in the reactor.<sup>(1)</sup> During a previous study, using the same catalyst as in the present programme rate data was obtained using a recycle reactor. The author considers the recycle reactor to be unsuitable for a study of dehydration reactions, since the principle of operation relies on the recirculation of most of the product stream. Conversions in the reactor therefore approach equilibrium values. This build-up in the concentration of product species is totally undesirable in the case of dehydration reactions, because water, which is one of the products, strongly inhibits the reaction.

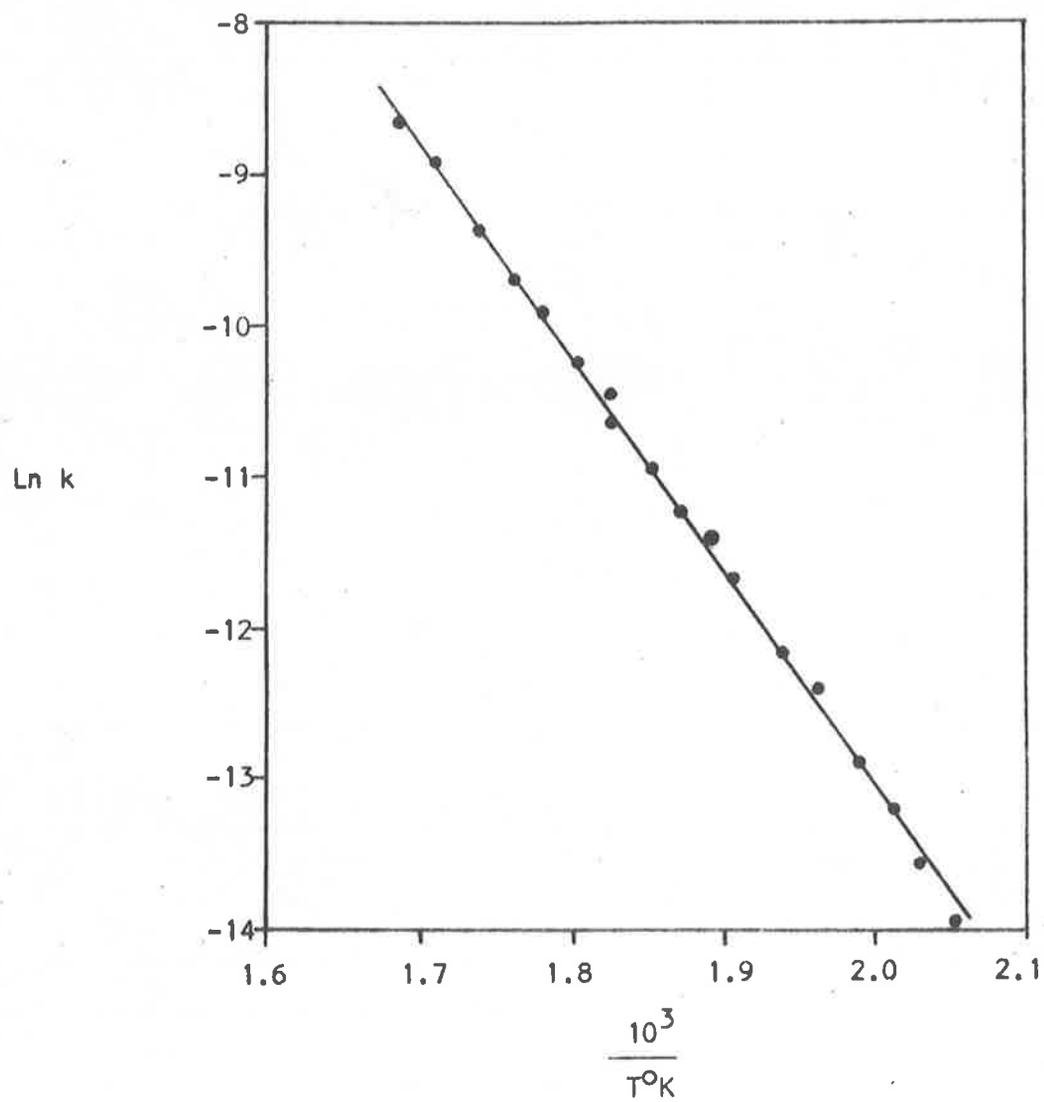
Every precaution was taken to ensure that the chemical reaction was the rate determining step. Mass transfer effects were eliminated by using high space velocities. Uncatalyzed runs were carried out for

temperatures in the range of the study, and it was found that thermal dehydration was not significant. Checks on catalyst deactivation were made by repeating the initial run of a series after completing the other runs. There was no evidence of catalyst deactivation during the study.

## 5.2 Temperature Dependence of Ethanol Dehydration

An Arrhenius plot of the rate data for ethanol dehydration at temperatures from 214°C to 319°C is presented in Figure 7. A similar plot for rates obtained in the range 305°C to 436°C is presented in Figure 8. The reliability and accuracy of the results are high. In Figure 7 the plot of the natural logarithm of the rates of diethyl ether formation against reciprocal absolute temperature is a straight line. This line is continued in Figure 8 for temperatures up to approximately 330°C. Above that temperature the rates of ether formation fall below the values for the extrapolated line. This decreased rate above 330°C is associated with a corresponding formation of ethylene. These results are interpreted as implying the formation of ethylene, at least partly, by a consecutive mechanism involving the decomposition of diethyl ether.

A reduction in reaction rates at high temperatures may often be attributed to the effect of gas diffusion phenomena. The high rates of chemical reactions at high temperatures frequently cause mass transfer effects to be rate controlling. However, in the current study errors from this source were eliminated by use of sufficiently high space velocities. Another possible reason for reduced rates of ether formation at high temperatures is due to inhibition by water. This is a possibility when conversions are increased as the temperature is increased.



**FIGURE 7** Plot of the natural logarithm of the rate constant  $k$  for diethyl ether formation vs. reciprocal absolute temperature  $T^\circ\text{K}$  for temperatures from  $214^\circ\text{C}$  to  $319^\circ\text{C}$ .

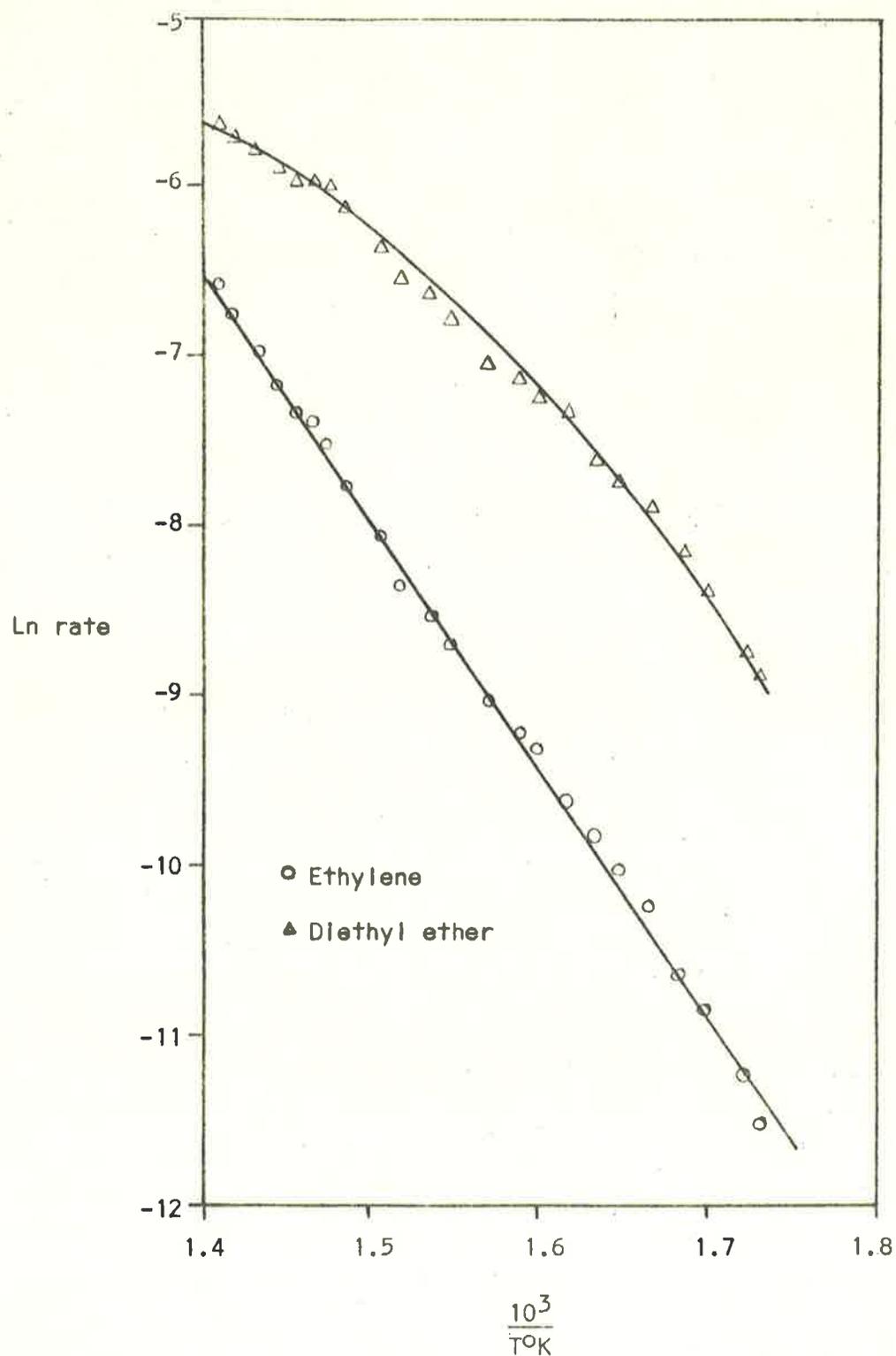


FIGURE 8 Plot of the natural logarithms of the rates of diethyl ether and ethylene formation vs. reciprocal absolute temperature  $T^{\circ}\text{K}$  for

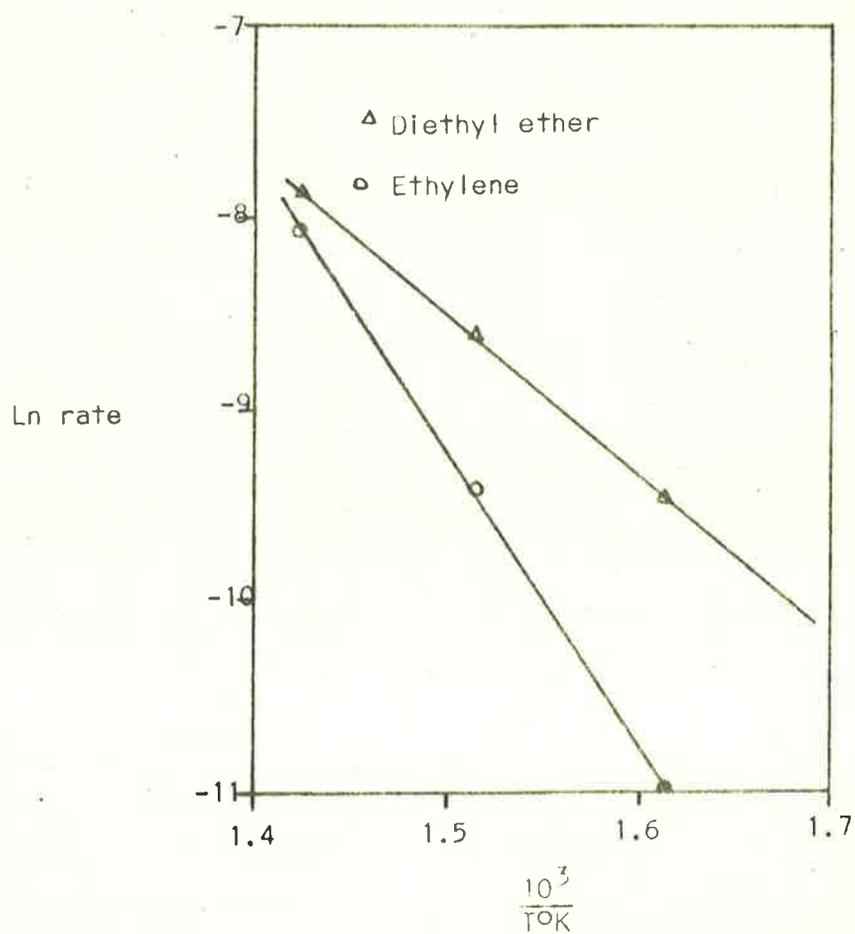


FIGURE 9 Plots of the natural logarithms of the rates of diethyl ether and ethylene formation vs. reciprocal absolute temperature T<sup>o</sup>K at temperatures from 343<sup>o</sup>C to 429<sup>o</sup>C for the results of Stauffer and Kranich (1).

However, in the present study alcohol molal flow rates were adjusted so that conversions were kept approximately the same for all temperatures studied. The postulation that the apparent reduced rate of diethyl ether formation is due to a decomposition of ether to ethylene is therefore a reasonable one.

The results of Figure 8 may be compared with those of Stauffer and (1) Kranich, which are presented in Figure 9. The catalyst used in their study was identical with that used in the current study. The rates for both studies are expressed in mole/gm min. From a comparison between the results of Figures 8 and 9 it is obvious that the rates obtained by Stauffer and Kranich for both diethyl ether and ethylene formations were considerably lower than the values obtained in the present study. The table below shows the rates of ethylene and diethyl ether formation obtained in this study, expressed as a ratio of those found by Stauffer and Kranich.

Temperature (°C)	Ratio of reaction rates obtained in the current study to those obtained by Stauffer and Kranich.	
	Ether Formation	Ethylene Formation
351°C	9.28	3.86
394°C	8.33	3.86

The lower values obtained by Stauffer and Kranich may be attributed to their use of a recycle reactor. The relatively high equilibrium conversions obtained for the dehydration reactions lead to high water

concentrations and subsequent inhibition of the reaction. Another limitation of their study was the restricted range of temperatures investigated. Further evidence for a reduction in rate due to water inhibition, is provided by the greater inhibition by water in the case of ether formation. Results obtained during the current study show that ether formation is more affected by the presence of water than ethylene formation. These results are presented in Table 5.2. It was also shown that the influence of water was reduced at high temperatures. This effect can also be seen in the results of Stauffer and Kranich. Their results are not regarded as a particularly significant contribution to the field due to the fundamental limitations in their study.

(12)

The results of Knozinger and Köhne are presented in Figures 10 - 14. Their results show the same effects as those of Stauffer and Kranich. (1) At low temperatures ether is formed exclusively. As the temperature is increased the rate of ether formation goes through a maximum at approximately 270°C. This has been interpreted as the effect of a consecutive ethylene formation. However, the reduced rate with increased temperature could be attributed to the high water concentrations present in their reactor. Unlike the present study, where space velocities were increased as the temperature was increased, Knozinger and Köhne used one space velocity at all temperatures. This resulted in both increased conversions and increased water concentrations. They concluded, from their results, that ethylene is formed by a combination of consecutive and parallel steps.

It is proposed, as a consequence of the current work, that the dehydration of ethanol in the temperature range 214°C to 436°C takes

FIGURE 10

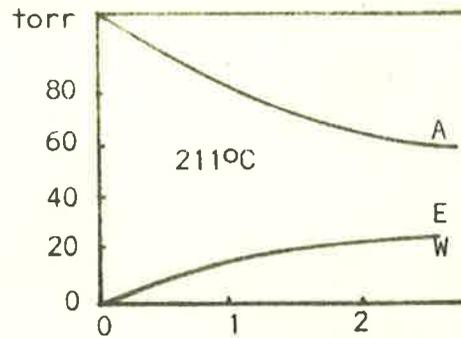


FIGURE 11

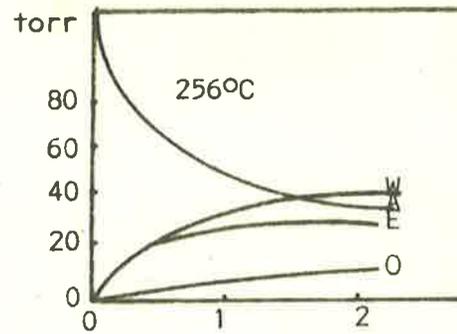


FIGURE 12

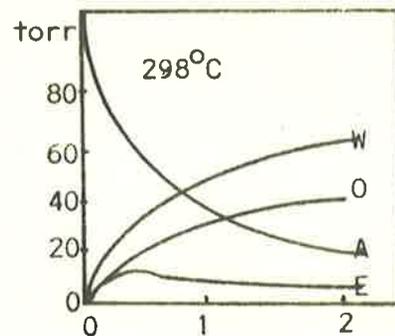
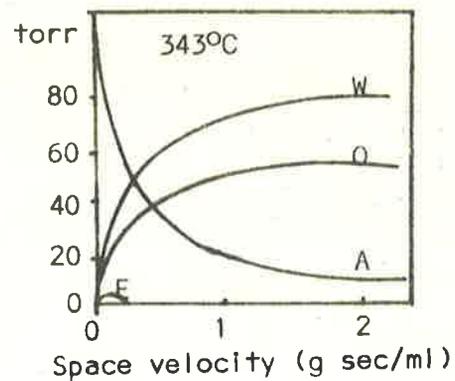


FIGURE 13

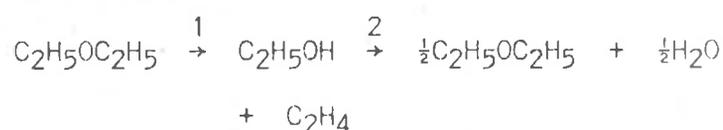


FIGURES 10-13 Dependence of ethanol decomposition on contact time at temperatures indicated for the results of Knozinger and Kohne (12).

place by a consecutive mechanism, with the parallel ethylene formation being less significant.

### 5.3 Temperature Dependence of Diethyl Ether Decomposition

In Figure 16 the natural logarithms of the rates of ethylene and ethanol formations from diethyl ether (in moles/gm min) are plotted against reciprocal absolute temperature. At 300°C equimolar amounts of ethanol and ethylene are formed. As the temperature is increased, in the range 300°C to 400°C, the ratio of moles of ethylene to moles of ethanol is increased from unity to 1.8. This reduced ethanol formation can be interpreted in several ways. Firstly, because of the experimental difficulties already discussed, the same molal ether flow rate was used at all temperatures. Thus initial rates were not determined and subsequent dehydration of the ethanol most likely took place at higher temperatures. The reaction scheme proposed is represented below.



Step 2 of this reaction would be more significant at higher temperatures. Thus the observed rate of ethanol formation from ether would be lower than the actual rate, due to the subsequent dehydration of some of the alcohol into the reactant, diethyl ether. Another theory on the mechanism for the decomposition of diethyl ether is that it breaks down to ethylene by an independent reaction



(15)

However, the "principle of least motion", postulated by Rice and Teller,

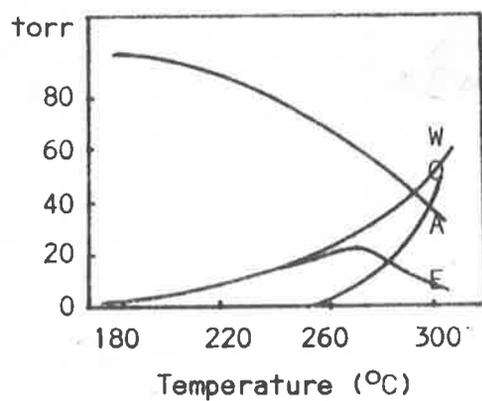


FIGURE 14 Dependence of ethanol decomposition on catalyst temperature for the results of Knozinger and Kohne(12).

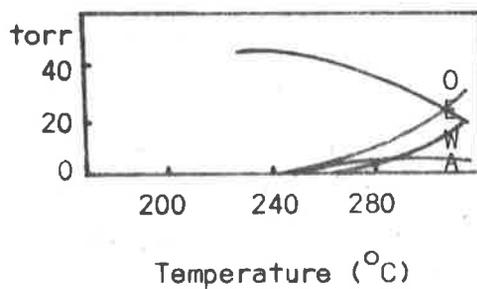
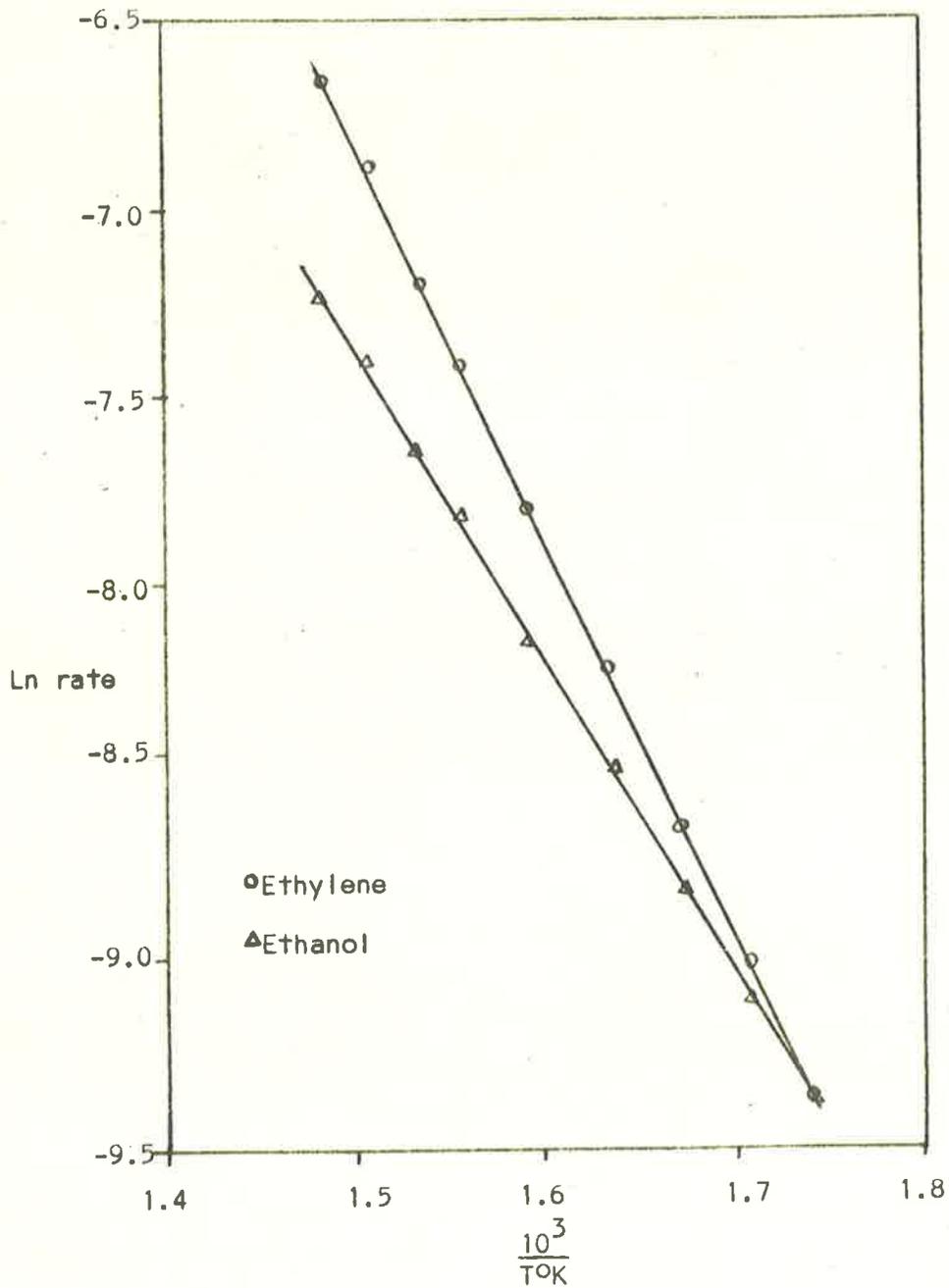


FIGURE 15 Dependence of diethyl ether decomposition on catalyst temperature for the results of Knozinger and Kohne(12).



**FIGURE 16** Plot of the natural logarithms of the rate of decomposition of diethyl ether to ethylene and ethanol vs. reciprocal absolute temperature  $T$  K at temperatures from  $300^\circ\text{C}$  to  $400^\circ\text{C}$ .

makes this an unlikely reaction path.

The use of an improved apparatus to determine initial rates of ether decomposition would provide more conclusive results for this section of the study. An explanation of the experimental problems encountered in accurately metering ether into the apparatus has been given earlier in the thesis.

The results of Knozinger and Köhne, for the decomposition of diethyl ether on  $\gamma$ -alumina, are given in Figure 15. Their results were similar to those found in this study. They also used the same space velocities at all temperatures. Reference to Figure 15 shows equimolar ethylene and ether formation at low temperatures, and an increased molar ratio of ethylene to ethanol as the temperature is increased. They also noted simultaneous water formation when the ethanol rate was reduced. They did not consider that the reaction



was a likely one.

#### 5.4 The Reaction Scheme

The results obtained for the dehydration of ethanol and the decomposition of diethyl ether, suggest that ethylene is formed from ethanol by a consecutive reaction. However, the results do not entirely rule out the possibility of a simultaneous ethylene formation by direct dehydration,



An interesting comparison can be drawn for the results of the

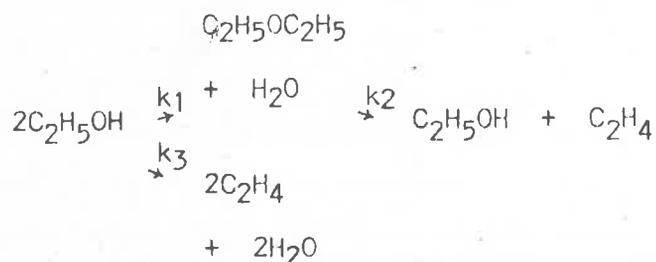
dehydration of ethanol, and the decomposition of diethyl ether, at 300°C. The results are presented in Table 5.1 below.

TABLE 5.1 : The rates of dehydration of ethanol and decomposition of diethyl ether on  $\gamma$ -alumina at 300°C

Reaction	Rate (mole/gm min) $\times 10^5$
Ethanol $\rightarrow$ Ether	8.3
Ethanol $\rightarrow$ Ethylene	0.99
Ether $\rightarrow$ Ethanol	8.3
Ether $\rightarrow$ Ethylene	8.5

These results were obtained from the graphs in Figures 7, 8 and 16. They show that the rate of ethylene formation from diethyl ether is 8.5 times faster than from ethyl alcohol. The consecutive ethylene formation is therefore much faster than the parallel step.

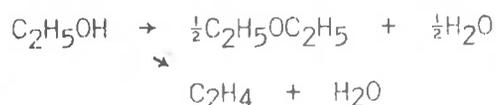
The results for the two reactions support a reaction scheme of the type postulated by Knozinger and Köhne. (12) The reaction mechanism proposed is :



where  $k_1 \approx k_2 \gg k_3$

The fact that  $k_3$  is so much less than the constants for the other steps,

suggests that any ethylene formed from ethanol results from the decomposition of ether as it forms. However, evidence to support such a proposal is difficult to obtain. Several unsuccessful attempts have been made. Isagulyants (13,14) attempted to elucidate the mechanism by using C<sup>14</sup> tracer methods on two occasions. However, these attempts failed because the three species, ethylene, ether and ethanol, all contain carbon and the C<sup>14</sup> is distributed between them. The results obtained in the current study agree with those reported by Balaceanu and Jungers (10) and Knozinger and Köhne, but conflict with those obtained by de Boer et al, (9) who concluded that ethylene was not formed from diethyl ether. Stauffer and Kranich, (1) using the same catalyst as in the present study, supported the parallel scheme favoured by de Boer.



However, the validity of the results of Stauffer and Kranich has already been questioned in Section 5.2 on the grounds of the unsatisfactory experimental technique used in their study.

### 5.5 Apparent Activation Energy Values

Activation energy values of  $28,500 \pm 50$  cal/gm mole and  $29,200 \pm 50$  cal/gm mole were found for diethyl ether and ethylene formation respectively. The closeness of the values suggests that the same rate-determining process applies in both reactions. The value for ethylene formation compares with an activation energy of  $30,800$  cal/gm mole obtained by Stauffer and Kranich (1) for the dehydration of ethanol on the same catalyst as used in the current

(16)  
study. Knozinger and Ress found that the activation energy was 25,900 cal/gm mole for diethyl ether formation by the dehydration of ethanol on  $\gamma$ -alumina. These reported values suggest that the activation energies obtained in the present study are of the right order.

## 5.6 Mechanisms of Dehydration Reactions

### 5.6.1 Reaction Order

The effects of substrate partial pressure on the rate of dehydration of ethyl alcohol are shown in Figures 17 - 20. The formation of diethyl ether is zero order at temperatures of 248°C and 295°C. However, at the increased temperature, the concentration range for which the reaction is zero order is greatly reduced. Figures 19 and 20 show that in the region of simultaneous diethyl ether and ethylene formation, the rate of ether formation is pressure dependent within the range zero to 800 mm Hg pressure. However, in the same range and at the same temperatures, ethylene formation is a zero order reaction. The mechanism of ether formation in this higher temperature region is complicated by the simultaneous breakdown to alcohol and ethylene.

The results of the current study may be compared with those recently reported by Knozinger and Ress, (16) and de Boer et al. (9). The results of Knozinger and Ress, presented in Figure 24, show that diethyl ether formation is zero order in the temperature range 175°C to 193°C. They also show that the region of zero order reaction is less at 193°C than at 175°C. A limitation of their results was that rates were determined within a relatively low

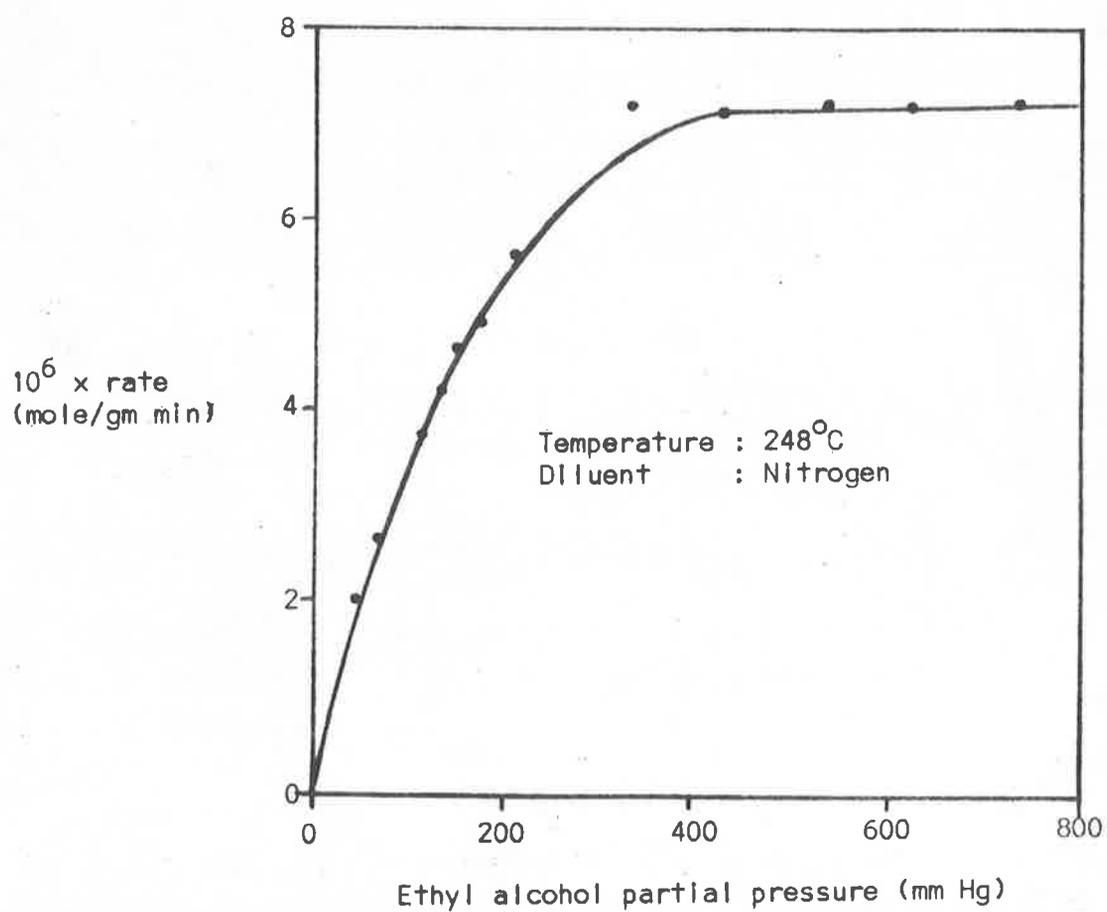
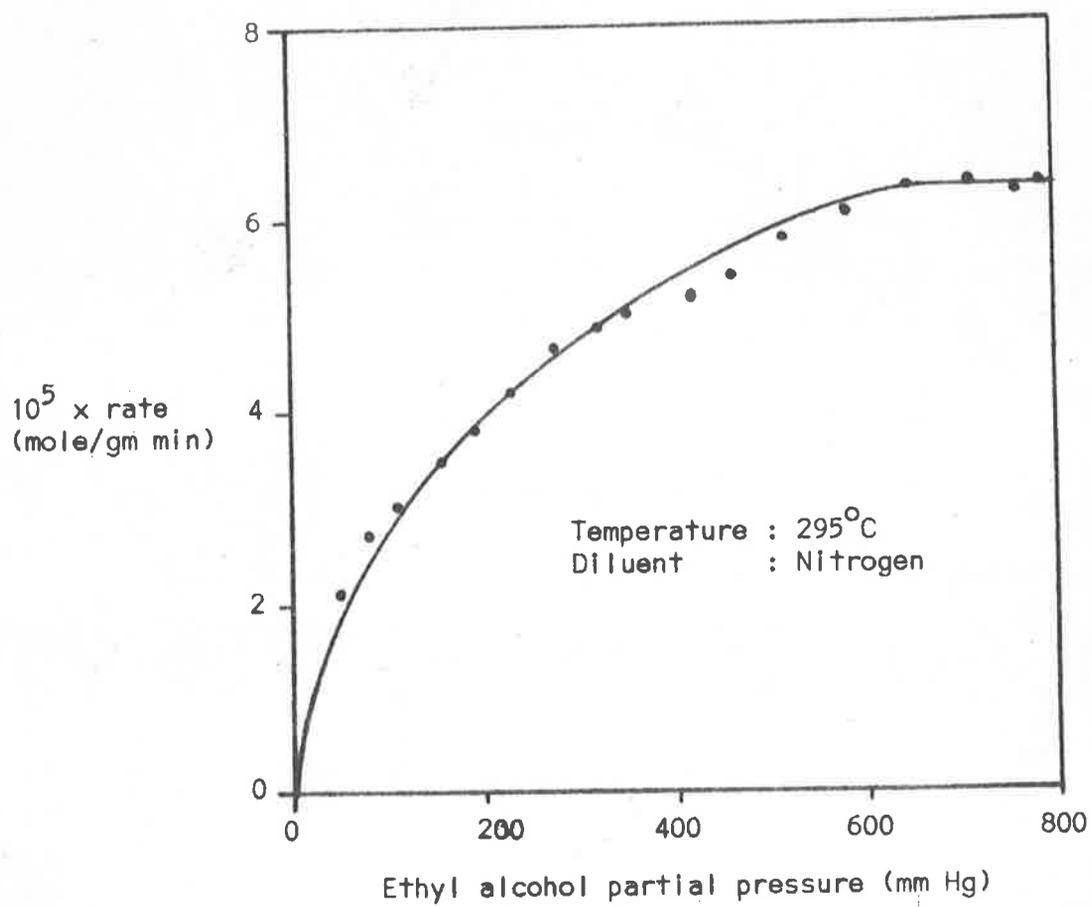


FIGURE 17. Dependence of rate of diethyl ether formation on ethyl alcohol partial pressure at 248°C.



**FIGURE 18** Dependence of rate of diethyl ether formation on ethyl alcohol partial pressure at 295°C.

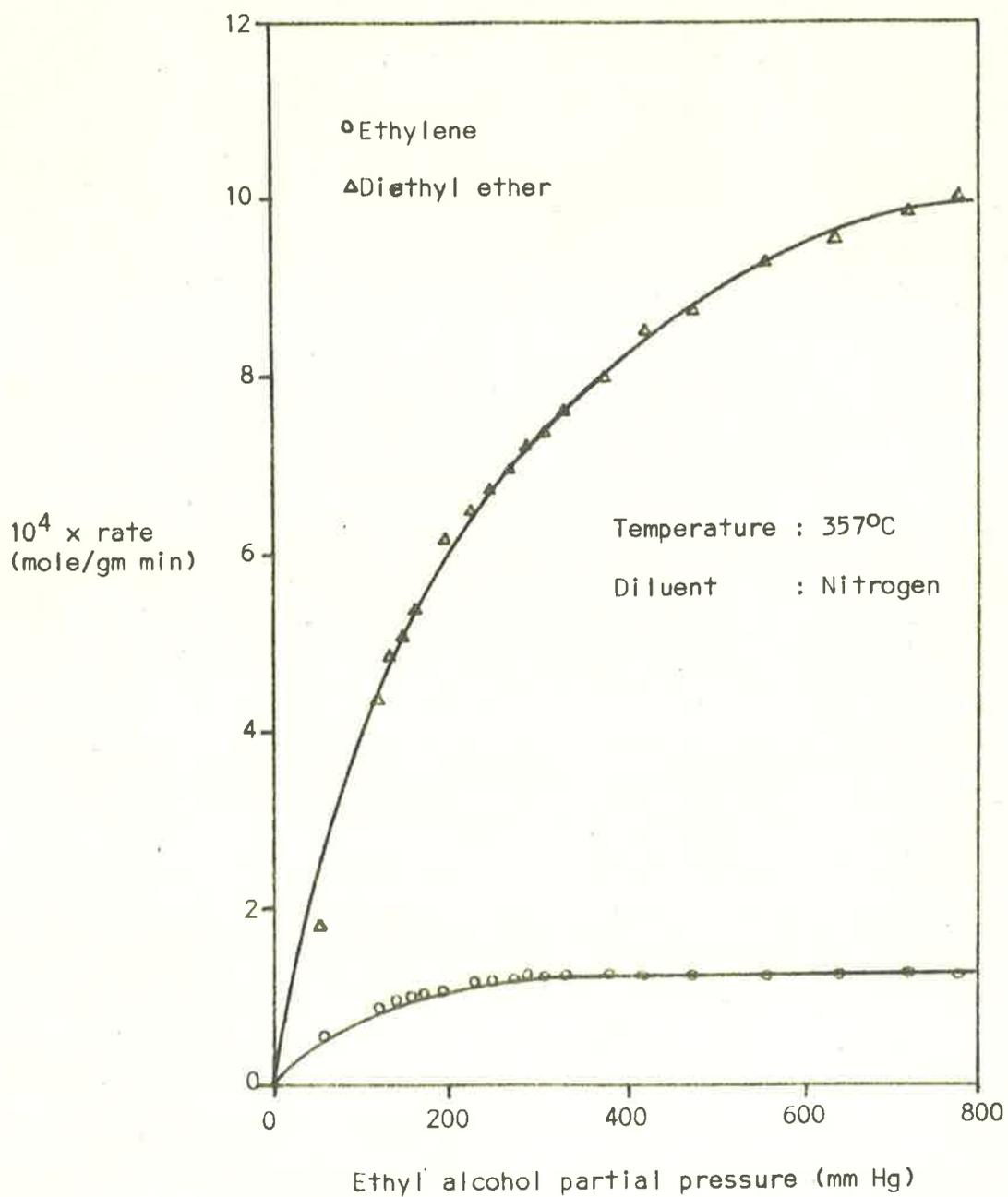
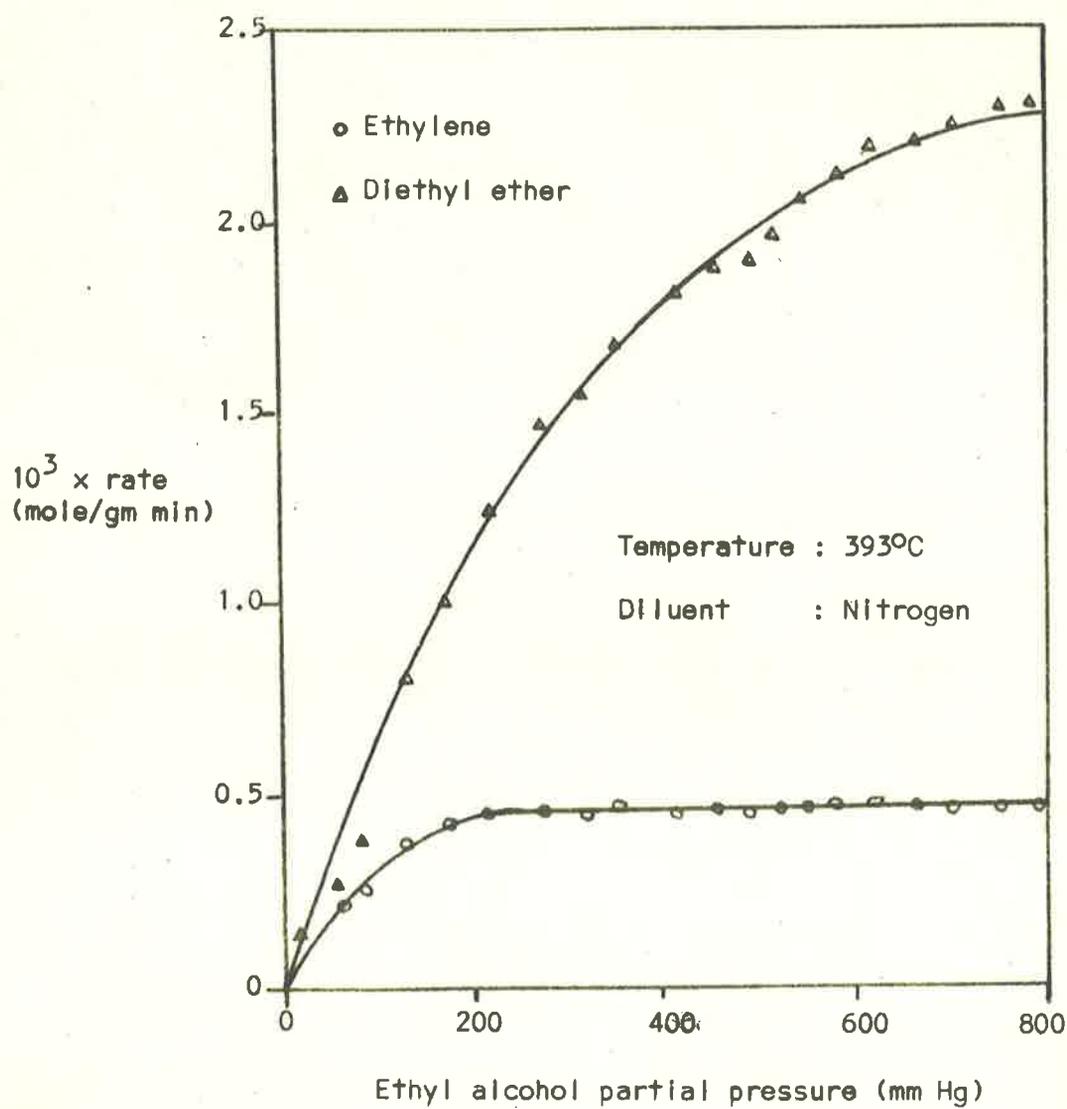


FIGURE 19 Dependence of rate of formation of diethyl ether and rate of formation of ethylene on ethyl alcohol partial pressure at  $357^\circ\text{C}$ .



**FIGURE 20** Dependence of rate of formation of diethyl ether and rate of formation of ethylene on ethyl alcohol partial pressure at 393°C.

range of ethanol pressures.

(9)

de Boer et al studied simultaneous ether and ethylene formation at 307°C for a very small range of ethyl alcohol pressures. Their results, presented in Figure 21, show that ethylene formation is zero order. Ether formation was interpreted as a combined zero and first order reaction. An explanation of this combined mechanism for ether formation is presented in Figure 22. Curve A represents a first order RIDEAL-ELEY mechanism, while Curve B represents a conventional LANGMUIR-HINSHELWOOD zero order, dual-site, mechanism. Curve C, a combination of curves A and B, has a similar form to the experimental curve for ether formation. Their results were obtained for the ethanol pressure range 0 to 110 mm Hg. Figures 19 and 20 for the current study, show that ether formation in that pressure range may be approximated to a straight line graph similar to that obtained by de Boer. However, the overall curve is certainly not linear. The results of de Boer, although fitting the postulated combined zero and first order mechanism, possibly have only a limited range of application.

There have been no reported studies concerning the effect of ethanol partial pressure on dehydration using  $\gamma$ -alumina, for the complete pressure range to one atmosphere. However, Jain and Pillai<sup>(38)</sup> have studied the dehydration of isopropyl alcohol on  $\gamma$ -alumina for various alcohol concentrations, using cyclohexane as diluent. Their results, presented in Figure 23, are similar to those in Figures 19 and 20. They found that olefine formation is zero order over a wide concentration range, but that ether formation

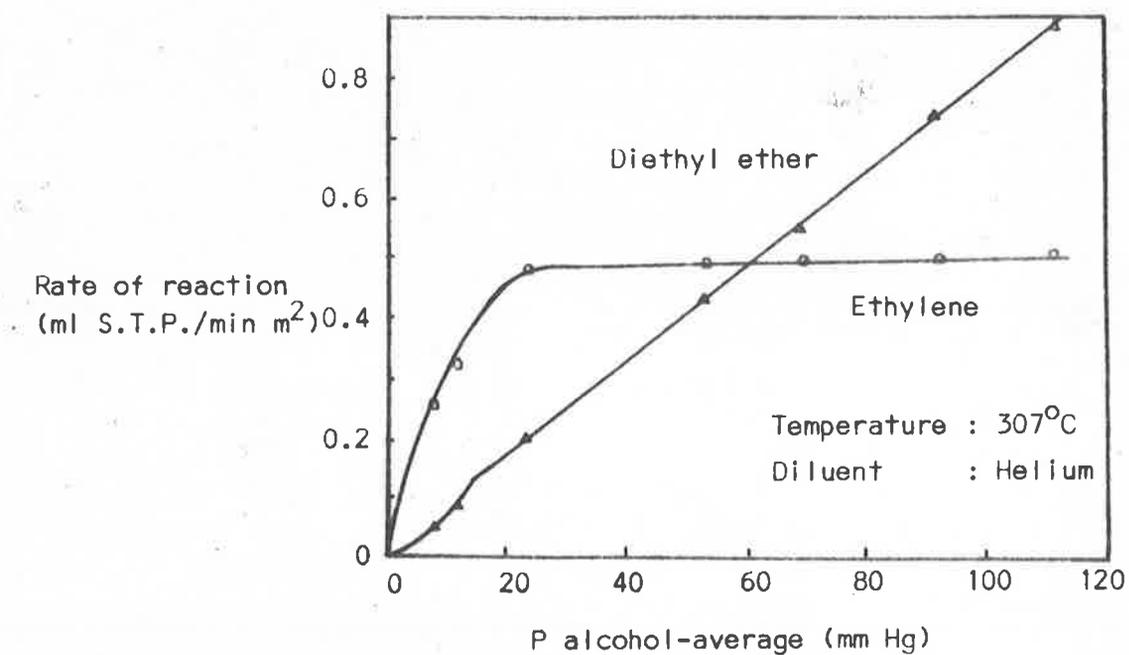


FIGURE 21 Dependence of rate of formation of diethyl ether and rate of formation of ethylene on ethyl alcohol partial pressure at 307°C for the results of de Boer et al (9).

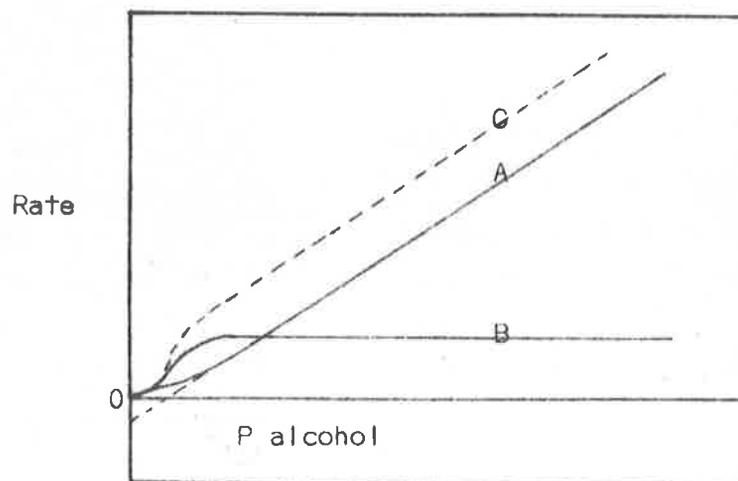


FIGURE 22 Schematic explanation of the curve of ether production in Figure 21.

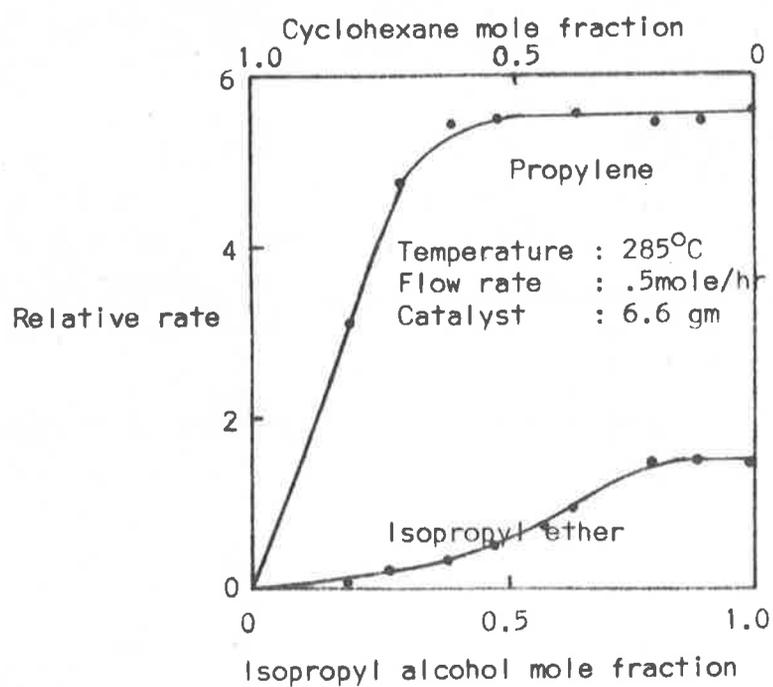


FIGURE 23 Dependence of rate of formation of isopropyl ether and rate of formation of propylene on isopropanol mole fraction for the results of Jain and Pillai (38).

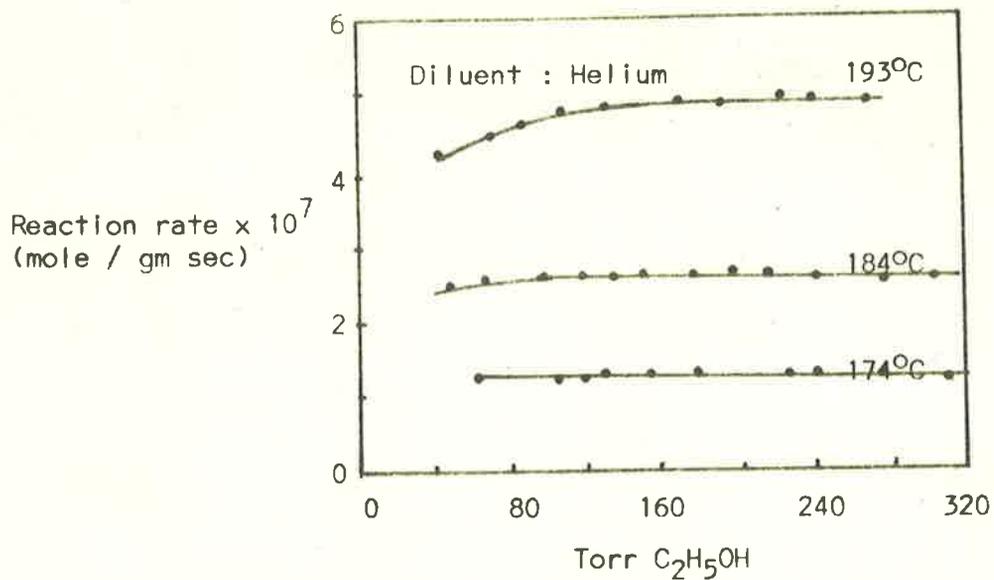


FIGURE 24 Dependence of rate of diethyl ether formation on ethanol pressure for the results of Knozinger and Röss (16).

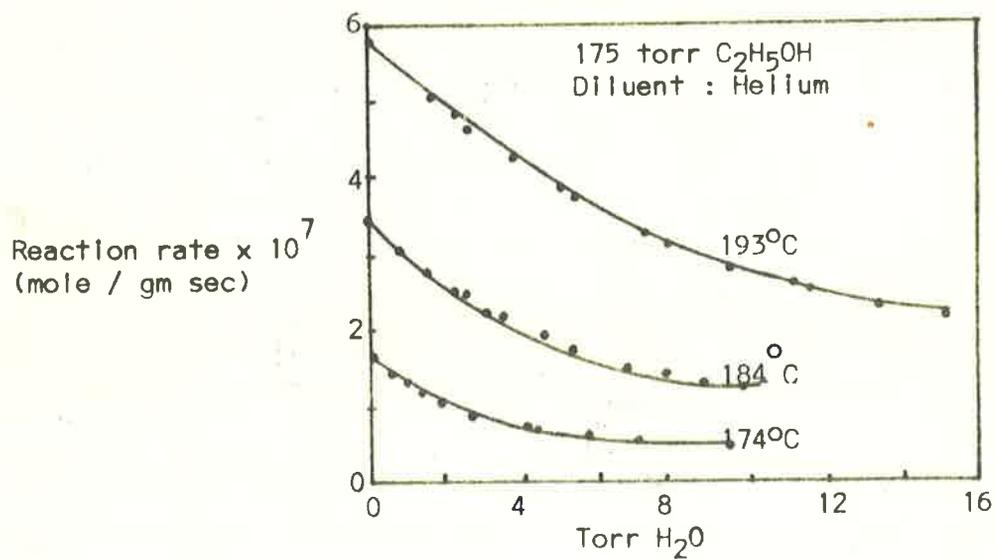


FIGURE 25 Effect of water on rate of diethyl ether formation for the results of Knozinger and Röss (16).

is independent of alcohol concentration only in a limited range approaching 100 percent alcohol.

### 5.6.2 Influence of Water on Reaction Rates

The results given in Tables 4.10 - 4.13 show that water strongly inhibits both the rates of ether and ethylene formation. The extent of the inhibition is reduced at higher temperatures. The experimental technique used in the study required that ethanol pressures were decreased when water pressures were increased. This had an advantage over the method of Knozinger and Ress who varied the water pressure at a constant alcohol pressure. The results so obtained are presented in Figure 25.

### 5.6.3 Rate Expressions for Dehydration Reactions

As mentioned earlier various mechanisms have been proposed for the dehydration of ethanol to form diethyl ether and ethylene. In the case of ether formation it is a zero order bimolecular reaction. The general rate expression for such a reaction is the LANGMUIR-HINSHELWOOD equation

$$r = k \theta_a^2 = \frac{r_0 K_a^2 p_a^2}{(1 + K_a p_a + K_w p_w + K_e p_e)^2}$$

For low conversions to ether this can be written,

$$r = r_0 \left( \frac{K_a p_a}{1 + K_a p_a + K_w p_w} \right)^2$$

At relatively high alcohol concentrations it may be further modified to

$$r = r_0 \left( \frac{K_a p_a}{K_a p_a + K_w p_w} \right)^2$$

$$\text{or } \sqrt{\frac{r_0}{r}} = 1 + \frac{K_w p_w}{K_a p_a} \quad 5.1$$

Another possible mechanism for ether formation has been postulated by Knozinger and Röss. (16) It is a bimolecular reaction between a surface alcoholate and an alcohol molecule held to the catalyst by two hydrogen bonds. The alcoholate molecule is thought to have a constant concentration. Hence the rate expression is written

$$r = r_0 \theta_a = \frac{r_0 \sqrt{K_a p_a}}{1 + \sqrt{K_a p_a} + K_w p_w + K_e p_e}$$

For initial rates, and high alcohol pressures,

$$r = \frac{r_0 \sqrt{K_a p_a}}{\sqrt{K_a p_a} + K_w p_w}$$

$$\text{or } \frac{r_0}{r} = 1 + \frac{K_w p_w}{\sqrt{K_a p_a}} \quad 5.2$$

A modification of the Knozinger-Röss postulate is the reaction between an alcohol molecule adsorbed on a single site and a surface alcoholate.

The rate expression for this mechanism would be

$$\frac{r_0}{r} = 1 + \frac{K_w p_w}{K_a p_a} \quad 5.3$$

The three possible mechanisms were tested by plotting the rates of dehydration of ethanol-water mixtures for the linearised equations 5.1, 5.2 and 5.3. The results are plotted in Figures

26 - 28 for the rates determined at 261°C and Figures 29 - 31 for the rates determined at 312°C. Figures 26 and 29 are the plots for a conventional LANGMUIR-HINSHELWOOD, bimolecular reaction. The graphs, at both temperatures, are non-linear. Therefore, the conventional dual-site mechanism does not apply to the results. The plots for equation 5.3 are presented in Figures 27 and 30. The mechanism applies for low concentrations, but at high water pressures the values of ratio  $\frac{r_0}{r}$  become less than those necessary to satisfy the reaction model. The results using the Knozinger-Ress mechanism are plotted in Figures 28 and 31. These plots are linear over the complete concentration ranges studied, and intercept the  $\frac{r_0}{r}$  axis at 1. Therefore, the results obtained in this study best fit the Knozinger-Ress "double-centred" mechanism. It has been shown to apply over a wider range of alcohol and water pressures and at higher temperatures than those investigated by Knozinger and (16) Ress.

The results for ether formation at 348°C and 386°C are plotted in Figures 36 - 41 using equations 5.1, 5.2 and 5.3. These plots do not have the same significance as those obtained at lower temperatures. The reaction has been shown to be concentration-dependent at these high temperatures, hence one cannot assume zero order behaviour. The results show that all three possible mechanisms give straight line plots; therefore no conclusive results can be obtained from the high temperature ether formations.

Ethylene is formed by a zero order, unimolecular reaction, in the range of temperatures studied. Conventional single-site

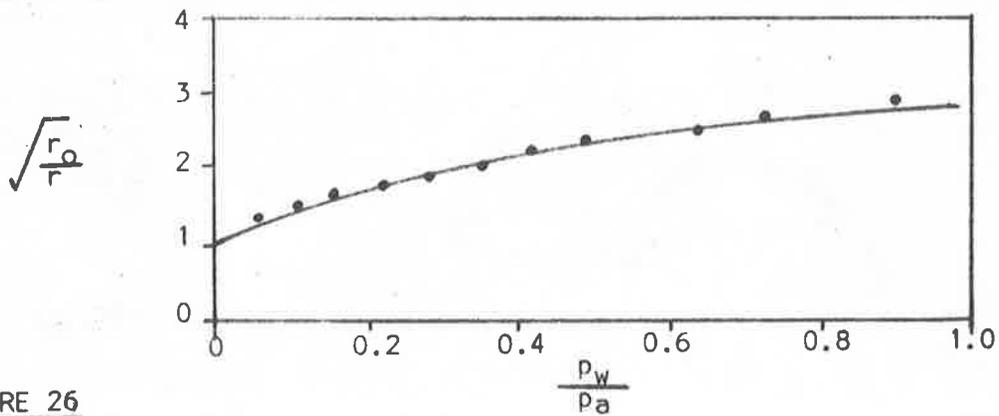


FIGURE 26

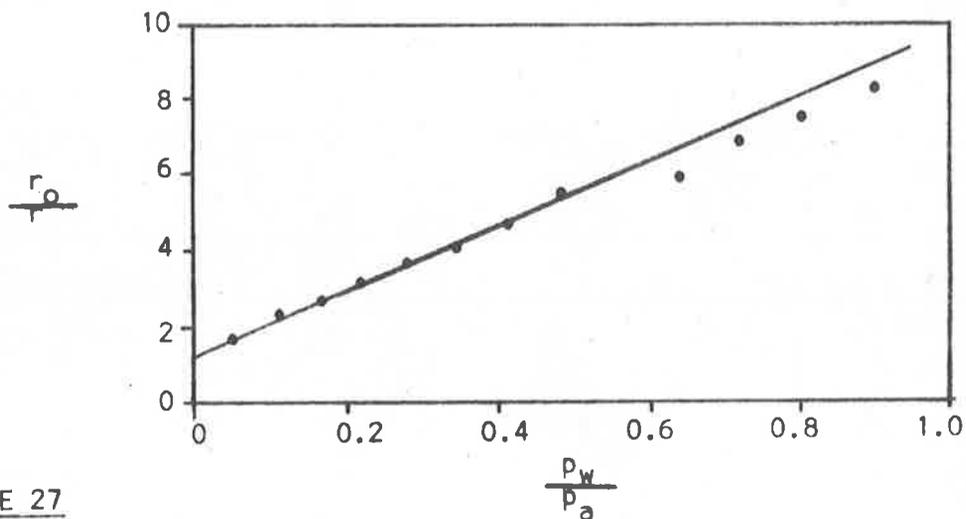


FIGURE 27

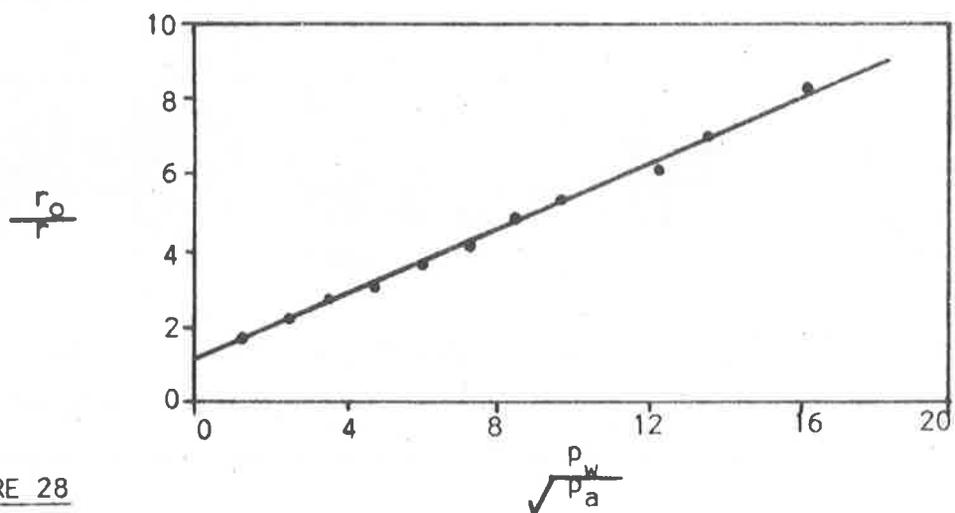


FIGURE 28

FIGURES 26-28 Influence of water on rate of ether formation at 261°C.  
 FIGURE 26 Langmuir-Hinshelwood dual-site mechanism.  
 FIGURE 27 Langmuir-Hinshelwood single-site mechanism.  
 FIGURE 28 Knozinger-Ress mechanism.

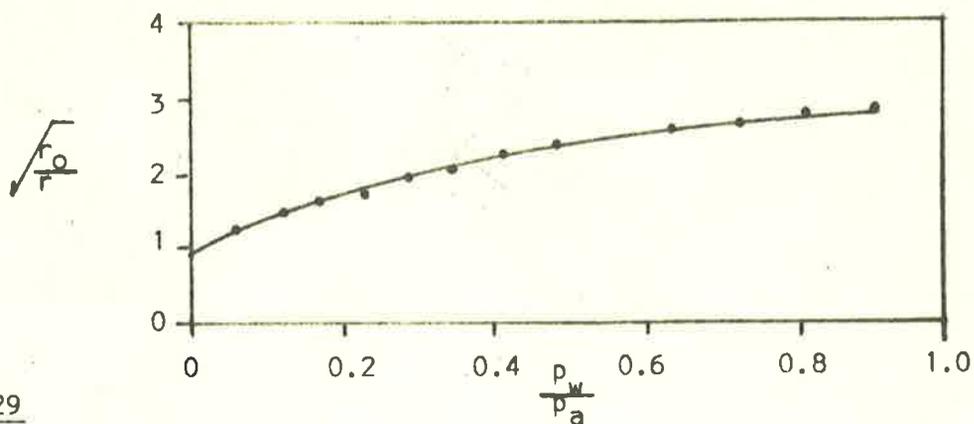


FIGURE 29

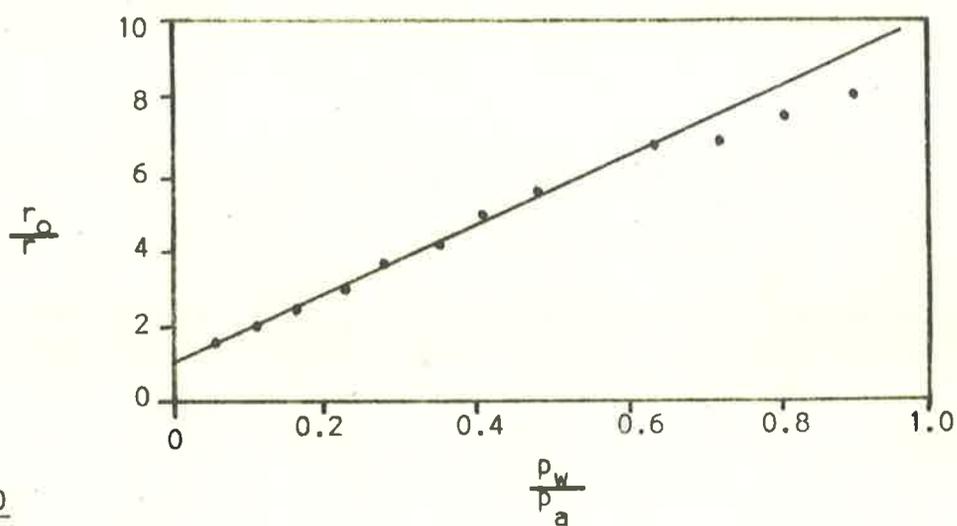


FIGURE 30

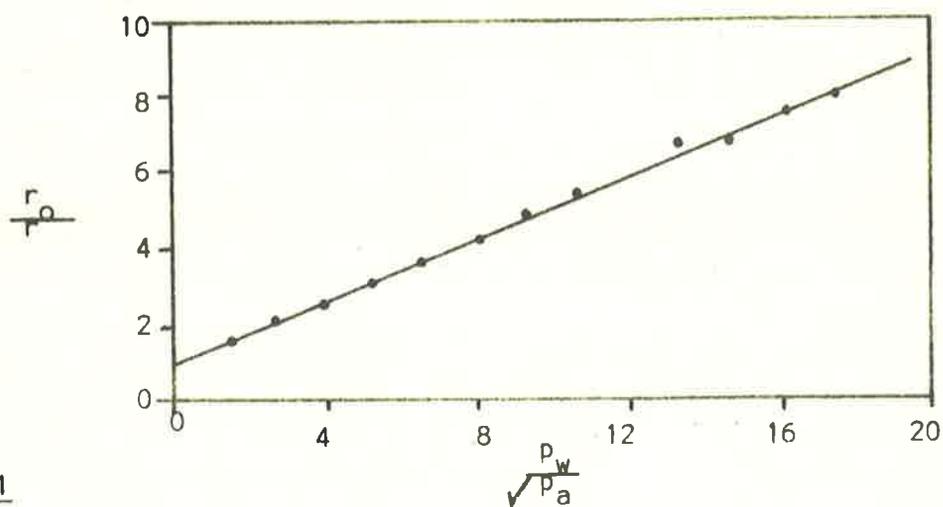


FIGURE 31

FIGURES 29-31 Influence of water on rate of ether formation at 312°C.

FIGURE 29 Langmuir-Hinshelwood dual-site mechanism.

FIGURE 30 Langmuir-Hinshelwood single-site mechanism.

FIGURE 31 Knozinger-Ress mechanism.

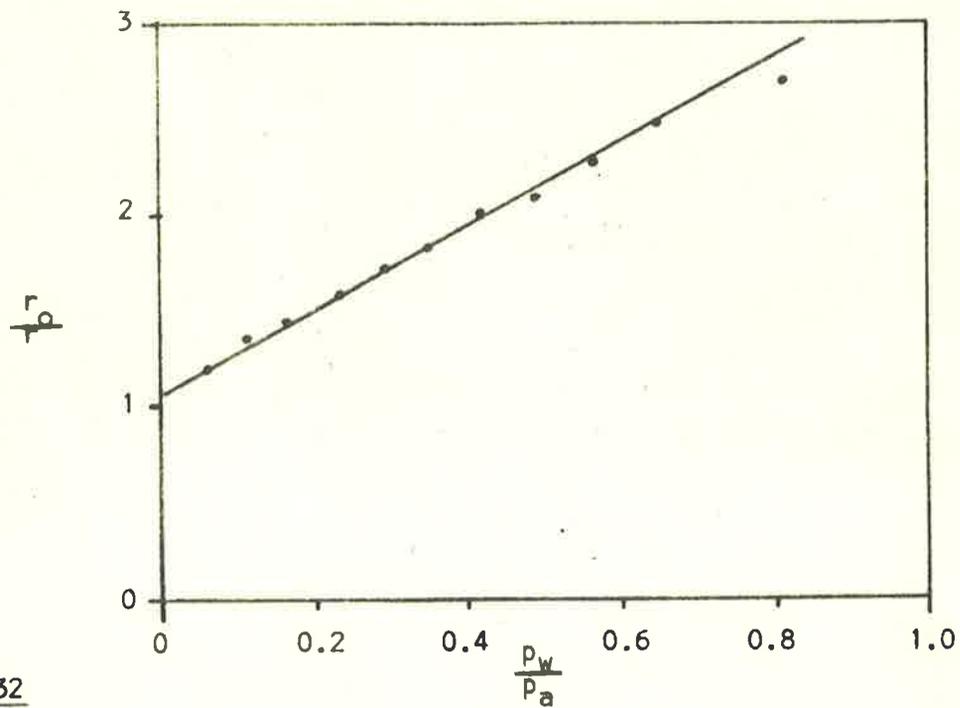


FIGURE 32

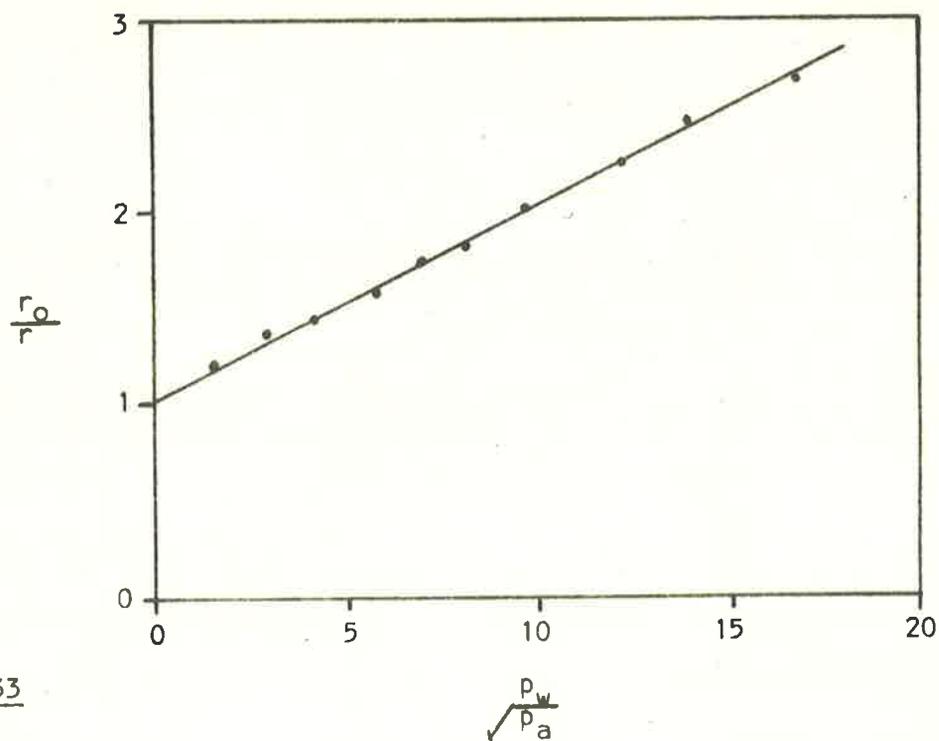


FIGURE 33

FIGURES 32&33 Influence of water on rate of ethylene formation at 348°C.  
 FIGURE 32 Langmuir-Hinshelwood single-site mechanism.  
 FIGURE 33 Knozinger-Ress mechanism.

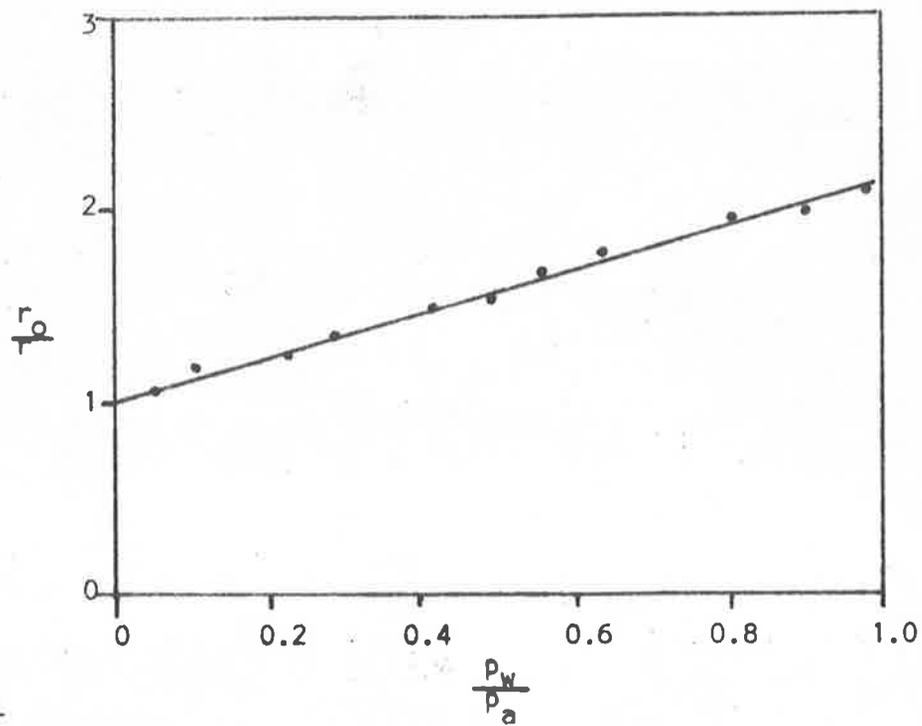


FIGURE 34

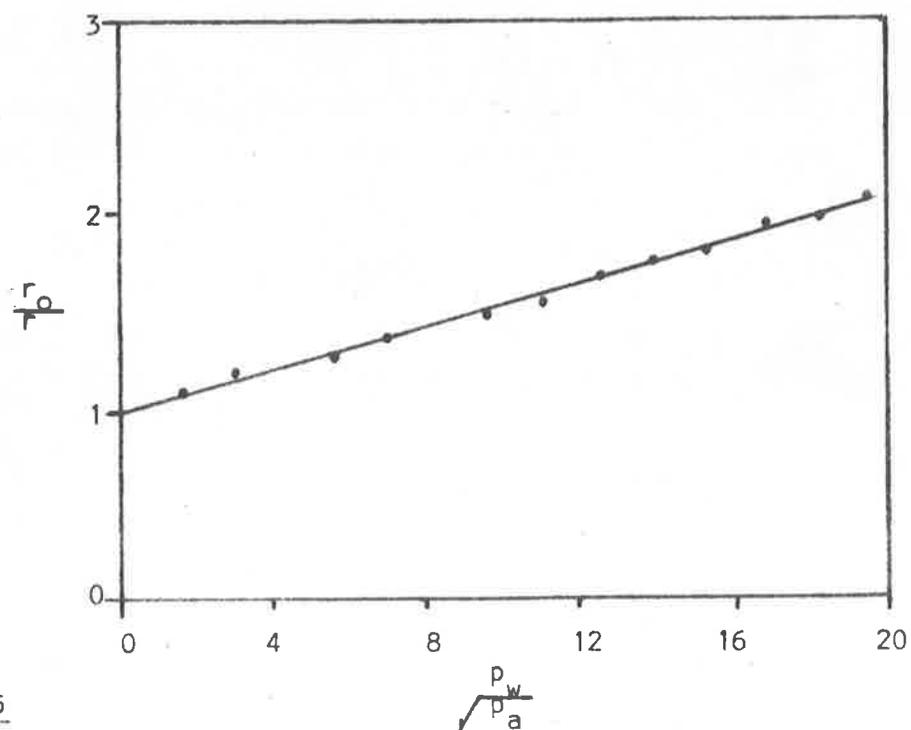


FIGURE 35

FIGURES 34&35 Influence of water on rate of ethylene formation at 386°C.  
 FIGURE 34 Langmuir-Hinshelwood single-site mechanism.  
 FIGURE 35 Knozinger-Ress mechanism.

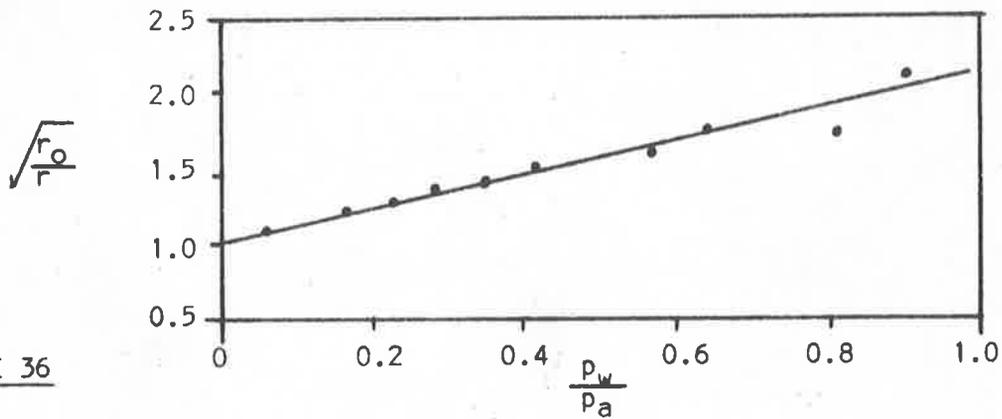


FIGURE 36

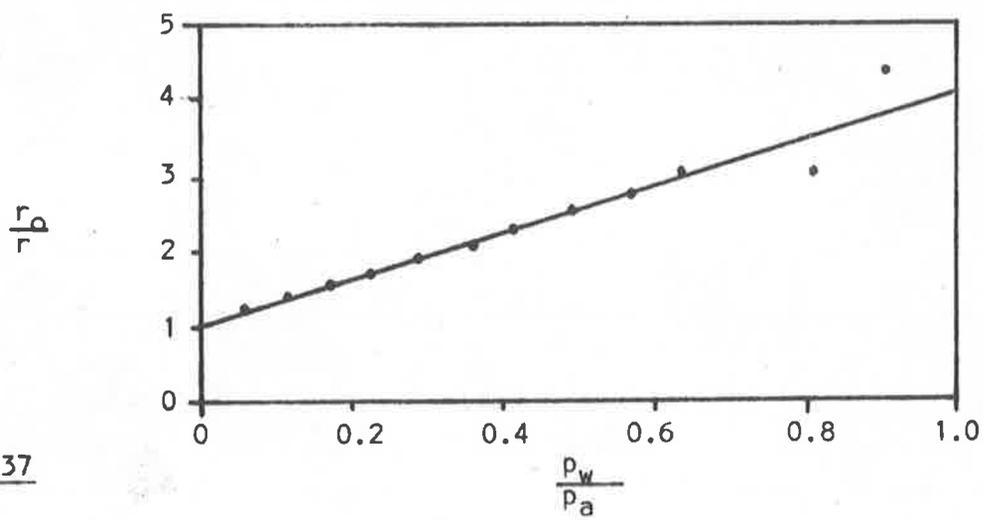


FIGURE 37

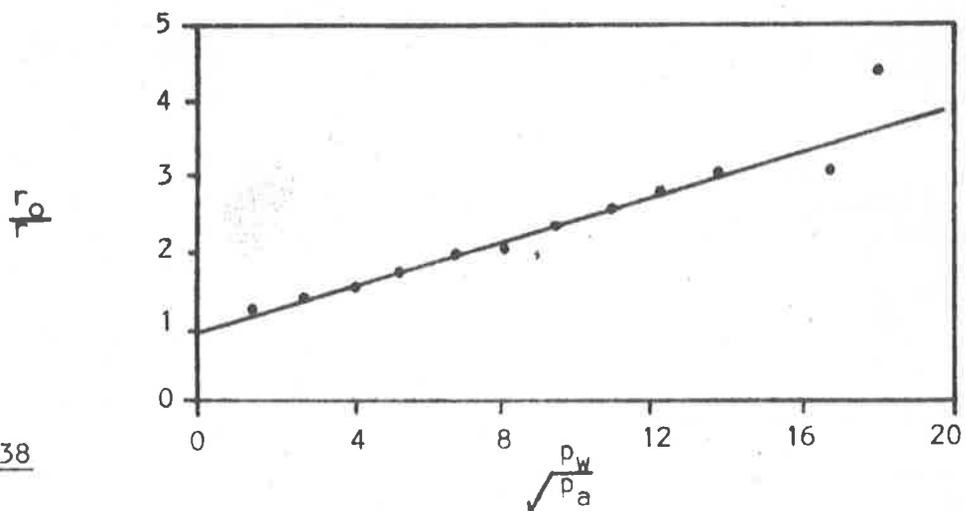


FIGURE 38

FIGURES 36-38 Influence of water on rate of ether formation at 348°C.  
 FIGURE 36 Langmuir-Hinshelwood dual-site mechanism.  
 FIGURE 37 Langmuir-Hinshelwood single-site mechanism.  
 FIGURE 38 Knozinger-Ress mechanism.

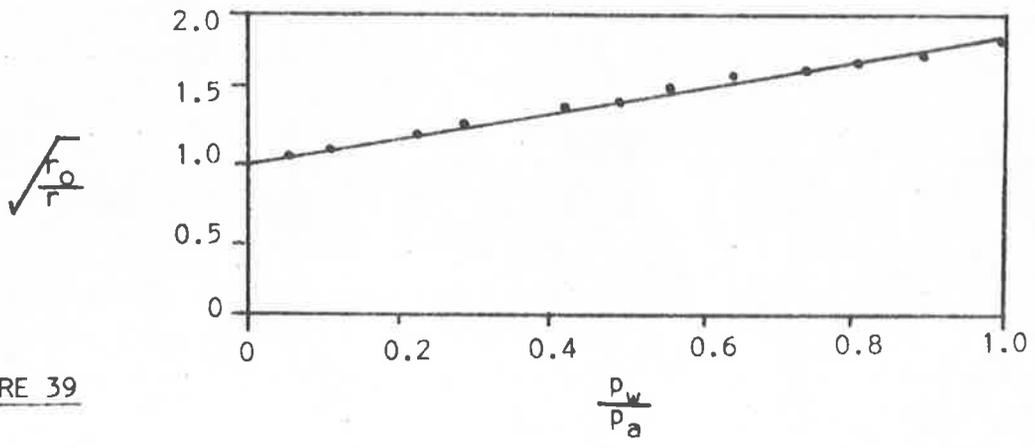


FIGURE 39

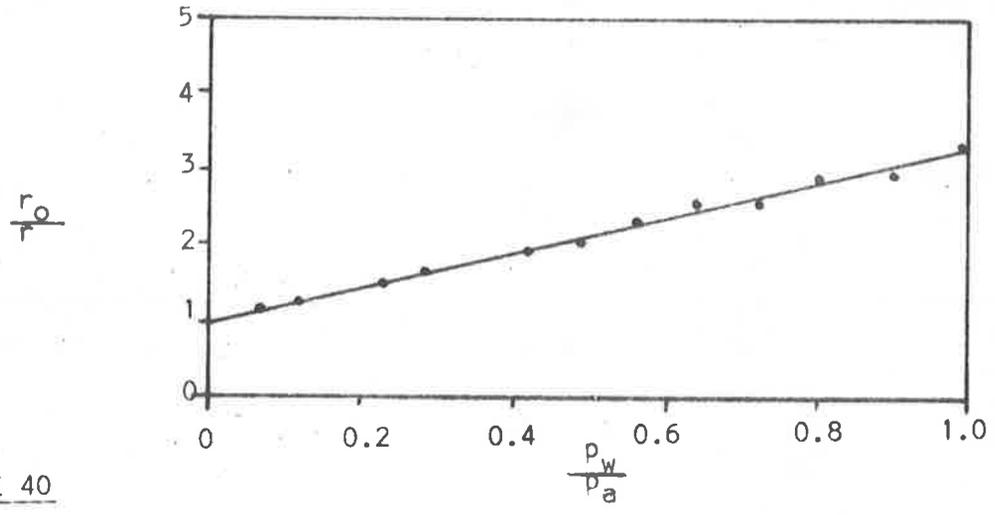


FIGURE 40

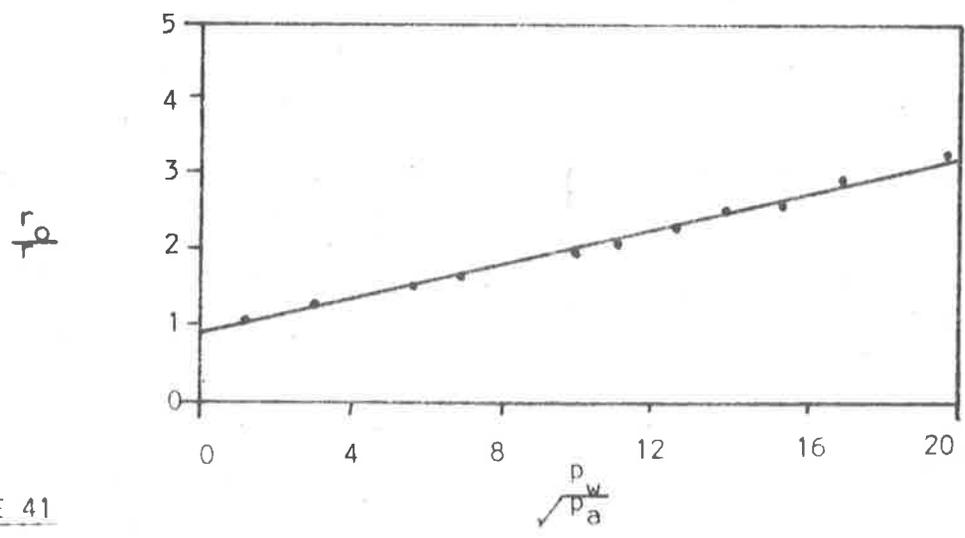


FIGURE 41

FIGURES 39-41 Influence of water on rate of ether formation at 386°C.  
 FIGURE 39 Langmuir-Hinshelwood dual-site mechanism.  
 FIGURE 40 Langmuir-Hinshelwood single-site mechanism.  
 FIGURE 41 Knözinger-Ress mechanism.

reaction theory postulates a rate equation

$$r = k \theta_a = \frac{r_0 K_a p_a}{1 + K_a p_a + K_w p_w + K_o p_o}$$

For high alcohol pressures and initial rates this becomes

$$r = \frac{r_0 K_a p_a}{K_a p_a + K_w p_w}$$

$$\frac{r_0}{r} = 1 + \frac{K_w p_w}{K_a p_a} \quad 5.4$$

Another possible mechanism is an extension of the Knozinger-Ress mechanism to ethylene formation. They have shown the existence of an alcohol molecule which is weakly held to the catalyst surface by two hydrogen bonds. The rate expression for the formation of ethylene from such an adsorbed species would be

$$\frac{r_0}{r} = 1 + \frac{K_w p_w}{\sqrt{K_a p_a}} \quad 5.3$$

which is the same as for ether formation. However, in the case of ethylene formation, there is no reaction with an alcoholate molecule.

The results for ethylene formation at 346°C and 386°C are plotted according to equations 5.3 and 5.4 in Figures 32 to 35. The data fit both rate expressions for the two temperatures studied. However, since the double-centred mechanism has been shown to apply for ether formation there is a greater possibility that it is the mechanism for ethylene formation.

#### 5.6.4 Relative Adsorption Coefficients

Computer programmes were written to plot the rate equations 5.1, 5.2, 5.3 and 5.4 using data which was linearized by a least squares technique, and hence calculate the slopes of the linearized plots. For the "double-centred" mechanism the slope is the numerical value of  $\frac{K_w}{\sqrt{K_a}}$ . This ratio is a measure of the relative inhibition of the dehydration reaction by water. The relative adsorption coefficients found for diethyl ether and ethylene formation are presented in Table 5.2 below.

TABLE 5.2 : Relative adsorption coefficients  $\frac{K_w}{\sqrt{K_a}}$  for diethyl ether and ethylene formations at the temperatures indicated.

Temperature (°C)	Product	$\frac{K_w}{\sqrt{K_a}}$ ((mm Hg) <sup>-1/2</sup> )
261	Diethyl Ether	0.432
312	Diethyl Ether	0.414
348	Diethyl Ether	0.162
386	Diethyl Ether	0.125
348	Ethylene	0.104
386	Ethylene	0.058

These results show that the relative adsorption term is decreased as the temperature is increased. They also show that at the same temperature, water inhibits ether formation more than ethylene formation. This effect has been described earlier in the text

when discussing limitations of the results of Stauffer and Kranich.

#### 5.6.5 Summary

The present study has extended the range of alcohol and water pressures beyond those used by Knozinger and Röss (16) who postulated the "double-centred" mechanism. A higher temperature range has been investigated in this study also. The work on simultaneous ethylene and ether formation shows that the same rate equation

$$r = \frac{r_0 \sqrt{K_a p_a}}{\sqrt{K_a p_a} + K_w p_w}$$

applies to both reactions. In the case of ether formation the mechanism postulated by Knozinger and Röss has been verified. The results for ethylene formation have been interpreted as involving the break-down of an alcohol molecule which is held to the catalyst surface by two hydrogen bonds. However, the overall mechanism of ethylene formation cannot be fully elucidated until a similar rate expression is derived for the decomposition of diethyl ether on  $\gamma$ -alumina. Kinetic studies using ether-water mixtures would yield results necessary for such a derivation. Infrared adsorption studies would also be necessary in order to determine the mechanism fully.

#### 5.7 Catalyst Activity

A direct comparison has already been drawn between the results obtained for dehydration of ethanol in this study, and those obtained by Stauffer and Kranich (1) using the same catalyst. The rates obtained in

the present study were approximately four times higher for ethylene formation and nine times higher for ether formation. However, the lower rates obtained by Stauffer and Kranich have been attributed to poor experimental technique and not lower catalyst activity. The results of the current study can be compared with those obtained by Knozinger and Ress<sup>(16)</sup> who found that at 193°C ether was formed at a rate of  $4.8 \times 10^{-7}$  mole/gm sec. The activation energy was found to be 25.9 K cal/gm mole. By using these values, the rate of reaction at 250°C can be estimated. The value so obtained is  $5.7 \times 10^{-4}$  mole/gm min. The rate of ether formation at 250°C for the present study was found to be  $8.1 \times 10^{-6}$  mole/gm min. The large difference between the two values may be attributed to a greater activity for the catalyst used by Knozinger and Ress. Their catalyst samples, prepared in the laboratory, had surface areas of approximately 110 m<sup>2</sup>/gm, whereas the commercial catalyst used in the present study had an area of 80 m<sup>2</sup>/gm. On the other hand, the commercial catalyst, despite the lower activity, provided uniformity of sample.

## 6. CONCLUSIONS AND RECOMMENDATIONS

1. A differential reaction apparatus, designed by the author, enabled a more comprehensive study of the dehydration of ethyl alcohol to be made than any reported previously. In particular, the mechanisms of diethyl ether and ethylene formations were studied for large ranges of ethanol and water pressures and over a wide temperature range. As discussed in detail earlier, the use of initial rate data avoided the difficulties of equilibrium considerations and inhibition by water which had affected the results of other workers. A gas chromatograph equipped with a flame ionization detector was used to determine product compositions accurately.

2. The dehydration of ethyl alcohol obeyed the following rate expression for both ethylene and diethyl ether formation

$$r = \frac{r_0}{1 + K \frac{p_w}{\sqrt{p_a}}} \quad (6.1)$$

where  $r_0$  is the zero order rate when no water is present  
(moles/gm min)

$r$  is the reaction rate (moles/gm min)

$p_w$  and  $p_a$  are the partial pressures of water and alcohol  
respectively (mm Hg)

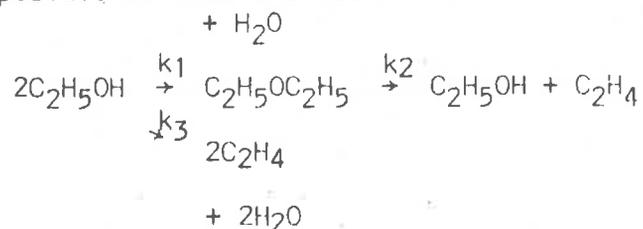
$K$  is the relative adsorption term

This expression has been previously derived for diethyl ether formation  
(16)  
by Knozinger and Röss. In the case of ethylene formation the rate  
expression describes a unimolecular surface reaction in which an

ethanol molecule is adsorbed to the catalyst by two hydrogen bonds. For diethyl ether formation it represents a bimolecular reaction between a stable surface alcoholate and an alcohol molecule held to the surface by two hydrogen bonds. (16) A complete mechanism for ethylene formation cannot be postulated until the mechanism of diethyl ether decomposition on  $\gamma$ -alumina has been fully elucidated.

The constant K in equation 6.1 is a measure of the extent by which the reactions are inhibited by water. At the same temperature ether formation was inhibited more than ethylene formation. The effect of inhibition by water was reduced as the reaction temperature was increased, for both ether and ethylene formation.

3. The dehydration of ethanol has been studied at temperatures between 305°C and 436°C. Diethyl ether decomposition over the catalyst was studied in the temperature range 300°C to 400°C. The results obtained in both these investigations showed that ethylene is formed from ethanol, at least in part, by a consecutive mechanism. The following reaction scheme was postulated from the results for the two reactions.

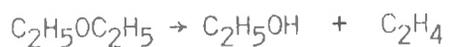


where  $k_1 \approx k_2 \gg k_3$ .

The parallel reaction was therefore considered to play an insignificant role in ethylene formation.

4. The apparent activation energies were calculated for diethyl ether and ethylene formations. The values obtained were 28,500 cal/gm mole and 29,200 cal/gm mole respectively. The closeness of the values suggests that the same process is the rate determining step in both reactions. This is supported by the fact that the same rate expression applies for the two reactions.

5. The decomposition of diethyl ether on  $\gamma$ -alumina has been shown to take place by the reaction



and not by the water elimination reaction



reported by other workers.

6. The results show that the commercial catalyst was not as active as the catalyst preparation used in another study. (16) However, the same mechanism of ether formation was shown to apply in both cases and the activation energies for ether formation were similar in magnitude.

7. A limited study was made of the decomposition of diethyl ether on  $\gamma$ -alumina. A more comprehensive examination of that reaction is necessary before the complete reaction mechanism for alcohol dehydration can be elucidated. This requires the construction of a reaction apparatus which overcomes the problem of accurately metering an ether feed into the reactor. Such an apparatus is currently being developed in this laboratory.

8. Originally, it was intended to investigate the effect of substrate structure on the rate of alcohol dehydration in an attempt to resolve the conflicting views expressed on the subject in the technical literature. However, a detailed review of the literature showed a basic lack of understanding of the reaction mechanisms for the formation of ethers and olefines, hence the current study was deemed necessary before an examination of any effects due to substrate structure could be undertaken. In fact, because of the complex mechanism that applies for the dehydration of alcohols on  $\gamma$ -alumina, the reaction does not appear to be an ideal one to use for such studies. A more profitable study might be to use thorium oxide as catalyst, since it has been reported to form olefine as the sole reaction product. Little is known about dehydration reactions using thorium oxide catalysts, and investigations using that catalyst appear to be the logical extensions of this work on the catalytic dehydration of alcohols.

APPENDIX 1

## Nomenclature used in the Appendices

- $R_e$  : rate of diethyl ether formation (mole/gm min)  
 $R_o$  : rate of ethylene formation (mole/gm min)  
 $R_a$  : rate of ethyl alcohol formation (mole/gm min)  
 $P_a$  : ethyl alcohol partial pressure (mm Hg)  
 $P_w$  : water partial pressure (mm Hg)  
 $P_t$  : total pressure (mm Hg)  
 $T_c$  : reaction temperature ( $^{\circ}\text{C}$ )  
 $W_c$  : mass of catalyst (gm)  
 $F_a$  : alcohol feed rate (moles/min)  
 $F_e$  : ether feed rate (moles/min)  
 $X_e$  : mole fraction of ether  
 $X_o$  : mole fraction of ethylene  
 $X_a$  : mole fraction of ethyl alcohol  
 $k_e$  : specific rate constant for diethyl ether formation  
 $k_o$  : specific rate constant for ethylene formation

In the Appendices certain variables have their values expressed in 'E format'. This has been done since the results have been calculated by computer. For example, a value  $8.62 \times 10^{-7}$  is expressed as 8.62E-07.

## APPENDIX 2

Results for Diethyl Ether formation at temperatures from 214°C to 319°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
8.62E-07	0.	782.7	.3	783.0	214.0	10.0	.00564	.00076	0.00000
1.27E-06	0.	782.6	.4	783.0	220.0	10.0	.00564	.00113	0.00000
1.84E-06	0.	782.4	.6	783.0	224.0	10.0	.00564	.00163	0.00000
2.76E-06	0.	782.1	.9	783.0	229.5	10.0	.00569	.00243	0.00000
4.01E-06	0.	781.6	1.4	783.0	236.5	10.0	.00575	.00349	0.00000
5.13E-06	0.	781.3	1.7	783.0	242.0	10.0	.00575	.00446	0.00000
8.37E-06	0.	780.2	2.8	783.0	251.0	10.0	.00584	.00717	0.00000
1.13E-05	0.	779.2	3.8	783.0	255.5	10.0	.00584	.00965	0.00000
1.29E-05	0.	778.7	4.3	783.0	261.0	10.0	.00584	.01102	0.00000
1.76E-05	0.	777.1	5.9	783.0	266.0	10.0	.00584	.01507	0.00000
2.87E-05	0.	779.0	4.0	783.0	274.5	10.0	.01404	.01023	0.00000
3.55E-05	0.	778.1	4.9	783.0	280.5	10.0	.01404	.01264	0.00000
5.00E-05	0.	779.3	3.7	783.0	287.5	10.0	.02639	.00947	0.00000
6.03E-05	0.	778.6	4.4	783.0	294.0	10.0	.02639	.01142	0.00000
9.29E-05	0.	779.3	3.7	783.0	301.5	10.0	.04341	.00954	0.00000
1.34E-04	0.	777.0	6.0	783.0	311.5	10.0	.04341	.01541	0.00000
1.74E-04	0.	775.3	7.7	783.0	319.0	10.0	.04363	.01989	0.00000

## APPENDIX 3

Results for Diethyl Ether and Ethylene formation at temperatures from 305°C to 436°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
1.38E-04	1.00E-05	768.6	1.4	770.0	305.0	.4	.00862	.00319	.00046
1.59E-04	1.32E-05	768.8	1.2	770.0	308.0	.4	.01237	.00257	.00043
2.28E-04	1.97E-05	768.6	1.4	770.0	315.5	.4	.01480	.00309	.00053
2.84E-04	2.45E-05	768.6	1.4	770.0	321.0	.4	.01884	.00301	.00052
3.74E-04	3.64E-05	768.2	1.8	770.0	328.0	.4	.01884	.00397	.00077
4.36E-04	4.42E-05	768.1	1.9	770.0	334.0	.4	.02145	.00407	.00082
5.00E-04	5.36E-05	767.8	2.2	770.0	339.5	.4	.02145	.00466	.00100
5.99E-04	6.67E-05	768.0	2.0	770.0	345.5	.4	.02811	.00426	.00095
7.18E-04	9.06E-05	767.5	2.5	770.0	352.5	.4	.02811	.00511	.00129
7.95E-04	9.96E-05	767.8	2.2	770.0	356.0	.4	.03484	.00456	.00114
8.55E-04	1.17E-04	767.6	2.4	770.0	364.0	.4	.03484	.00491	.00135
1.11E-03	1.66E-04	767.4	2.6	770.0	373.5	.4	.04246	.00522	.00156
1.26E-03	1.96E-04	767.0	3.0	770.0	378.0	.4	.04246	.00594	.00185
1.39E-03	2.36E-04	767.0	3.0	770.0	385.0	.4	.04814	.00576	.00196
1.70E-03	3.25E-04	766.3	3.7	770.0	391.7	.4	.04814	.00706	.00270
2.18E-03	4.27E-04	766.6	3.4	770.0	399.0	.4	.06787	.00642	.00252
2.55E-03	5.46E-04	765.9	4.1	770.0	405.0	.4	.06787	.00750	.00322
2.59E-03	6.20E-04	765.6	4.4	770.0	409.0	.4	.06729	.00771	.00369
2.59E-03	6.64E-04	765.5	4.5	770.0	414.0	.4	.06729	.00769	.00395
2.71E-03	7.64E-04	765.2	4.8	770.0	420.0	.4	.06729	.00806	.00454
3.05E-03	9.46E-04	764.4	5.6	770.0	426.0	.4	.06729	.00906	.00562
3.30E-03	1.17E-03	763.6	6.4	770.0	431.5	.4	.06729	.00980	.00694
3.61E-03	1.42E-03	762.7	7.3	770.0	436.0	.4	.06729	.01073	.00841

APPENDIX 4

Results for Ethyl Alcohol and Ethylene formation for the decomposition of Diethyl Ether at temperatures from 300°C to 400°C.

Weight of catalyst :  $W_C = 1.00$  gm

Total Pressure :  $P_T = 781$  mm Hg

Feed Composition : 100% Diethyl Ether

$T_C$	$F_e$	$X_a$	$X_o$	$R_a$	$R_o$
300.0	.00715	.01196	.01166	8.56E-05	8.34E-05
312.0	.00715	.01507	.01711	1.08E-04	1.22E-04
324.0	.00715	.02037	.02448	1.46E-04	1.75E-04
337.0	.00715	.02881	.03757	2.06E-04	2.69E-04
354.0	.00715	.03940	.05666	2.82E-04	4.05E-04
368.0	.00715	.05633	.08285	4.03E-04	5.92E-04
378.0	.00715	.06664	.10398	4.77E-04	7.43E-04
390.0	.00715	.08532	.14558	6.10E-04	1.04E-03
400.0	.00715	.09773	.17954	6.99E-04	1.28E-03

APPENDIX 5

Results for formation of Diethyl Ether for varying partial pressures of Ethyl Alcohol at 248°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_T$	$T_C$	$W_C$	$F_a$	$X_e$	$X_o$
7.20E-06	0.	734.8	.4	817.0	248.0	2.0	.00538	.00134	0.00000
7.09E-06	0.	627.3	.4	817.0	248.0	2.0	.00538	.00132	0.00000
7.20E-06	0.	537.7	.4	822.0	248.0	2.0	.00538	.00134	0.00000
7.10E-06	0.	423.0	.3	822.0	248.0	2.0	.00538	.00132	0.00000
7.23E-06	0.	328.0	.2	823.0	248.0	2.0	.00538	.00134	0.00000
5.59E-06	0.	212.5	.1	823.0	248.0	2.0	.00551	.00101	0.00000
4.90E-06	0.	178.8	.1	824.0	248.0	2.0	.00551	.00089	0.00000
4.62E-06	0.	154.7	.1	821.0	248.0	2.0	.00551	.00084	0.00000
4.19E-06	0.	137.5	.1	821.0	248.0	2.0	.00551	.00076	0.00000
3.72E-06	0.	114.0	.0	815.0	248.0	2.0	.00551	.00067	0.00000
2.74E-06	0.	68.6	.0	790.0	248.0	2.0	.00560	.00049	0.00000
2.01E-06	0.	46.7	.0	785.0	248.0	2.0	.00560	.00036	0.00000

## APPENDIX 6

Results for formation of Diethyl Ether for varying partial pressures of Ethyl Alcohol at 295°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
6.30E-05	0.	791.2	1.0	794.0	295.0	2.0	.02286	.00276	0.00000
6.21E-05	0.	759.3	1.0	794.0	295.0	2.0	.02286	.00272	0.00000
6.45E-05	0.	704.4	1.0	793.0	295.0	2.0	.02286	.00282	0.00000
6.35E-05	0.	647.4	.9	792.0	295.0	2.0	.02286	.00278	0.00000
5.90E-05	0.	583.8	.8	792.0	295.0	2.0	.02286	.00258	0.00000
5.68E-05	0.	519.8	.6	792.0	295.0	2.0	.02292	.00248	0.00000
5.33E-05	0.	466.9	.5	790.0	295.0	2.0	.02292	.00233	0.00000
5.12E-05	0.	423.2	.5	791.0	295.0	2.0	.02292	.00223	0.00000
4.88E-05	0.	359.1	.4	792.0	295.0	2.0	.02292	.00213	0.00000
4.81E-05	0.	320.3	.3	793.0	295.0	2.0	.02299	.00209	0.00000
4.63E-05	0.	278.2	.3	782.0	295.0	2.0	.02299	.00201	0.00000
4.19E-05	0.	232.2	.2	784.0	295.0	2.0	.02299	.00182	0.00000
3.76E-05	0.	199.1	.2	782.0	295.0	2.0	.02303	.00163	0.00000
3.45E-05	0.	160.6	.1	778.0	295.0	2.0	.02303	.00150	0.00000
3.01E-05	0.	110.2	.1	777.0	295.0	2.0	.01463	.00206	0.00000
2.74E-05	0.	78.9	.1	777.0	295.0	2.0	.01001	.00274	0.00000
2.16E-05	0.	48.9	.1	777.0	295.0	2.0	.00595	.00364	0.00000

## APPENDIX 7

Results for formation of Diethyl Ether and Ethylene for varying partial pressures of Ethyl Alcohol at 357°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
9.99E-04	1.21E-04	771.8	6.4	862.0	357.0	.4	.01496	.01336	.00323
9.79E-04	1.21E-04	717.6	5.8	859.0	357.0	.4	.01504	.01301	.00322
9.48E-04	1.23E-04	636.4	5.0	854.0	357.0	.4	.01519	.01248	.00323
9.26E-04	1.25E-04	554.8	4.3	853.0	357.0	.4	.01532	.01208	.00326
8.67E-04	1.21E-04	476.3	3.5	853.0	357.0	.4	.01528	.01135	.00317
8.47E-04	1.24E-04	417.6	3.0	852.0	357.0	.4	.01532	.01106	.00324
7.90E-04	1.20E-04	370.5	2.5	849.0	357.0	.4	.01532	.01031	.00313
7.53E-04	1.17E-04	330.1	2.1	854.0	357.0	.4	.01528	.00985	.00306
7.39E-04	1.20E-04	304.2	1.9	851.0	357.0	.4	.01530	.00966	.00313
7.21E-04	1.16E-04	281.5	1.8	851.0	357.0	.4	.01530	.00942	.00302
6.86E-04	1.13E-04	268.6	1.6	862.0	357.0	.4	.01548	.00887	.00293
6.66E-04	1.09E-04	239.4	1.4	825.0	357.0	.4	.01548	.00860	.00281
6.45E-04	1.08E-04	222.6	1.2	825.0	357.0	.4	.01541	.00836	.00281
6.18E-04	9.95E-05	188.8	1.0	809.0	357.0	.4	.01535	.00806	.00259
5.33E-04	9.71E-05	161.9	.8	788.0	357.0	.4	.01524	.00699	.00255
5.03E-04	9.52E-05	145.2	.7	788.0	357.0	.4	.01524	.00660	.00250
4.90E-04	9.82E-05	131.0	.6	786.0	357.0	.4	.01524	.00643	.00258
4.25E-04	8.59E-05	155.4	.5	786.0	357.0	.4	.01524	.00558	.00226
1.72E-04	5.46E-05	52.8	.2	786.0	357.0	.4	.00638	.00540	.00343

## APPENDIX 8

Results for formation of Diethyl Ether and Ethylene for varying partial pressures of Ethyl Alcohol at 393°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
2.28E-03	4.58E-04	748.0	5.1	779.0	393.0	.4	.04693	.00973	.00391
2.23E-03	4.54E-04	698.8	4.7	779.0	393.0	.4	.04693	.00948	.00387
2.19E-03	4.70E-04	660.3	4.4	779.0	393.0	.4	.04693	.00933	.00400
2.18E-03	4.78E-04	617.6	4.1	779.0	393.0	.4	.04702	.00925	.00407
2.10E-03	4.73E-04	579.9	3.8	779.0	393.0	.4	.04702	.00892	.00402
2.03E-03	4.70E-04	548.6	3.4	779.0	393.0	.4	.04760	.00853	.00395
1.91E-03	4.58E-04	517.6	3.1	779.0	393.0	.4	.04760	.00803	.00385
1.86E-03	4.46E-04	492.6	2.8	779.0	393.0	.4	.04760	.00782	.00375
1.87E-03	4.59E-04	454.5	2.6	779.0	393.0	.4	.04788	.00780	.00383
1.79E-03	4.44E-04	415.5	2.3	779.0	393.0	.4	.04788	.00748	.00371
1.67E-03	4.53E-04	348.6	1.9	779.0	393.0	.4	.04788	.00698	.00378
1.54E-03	4.34E-04	312.2	1.6	779.0	393.0	.4	.04808	.00641	.00361
1.46E-03	4.41E-04	273.7	1.3	779.0	393.0	.4	.04808	.00607	.00367
1.22E-03	4.43E-04	217.8	1.3	783.0	393.0	.4	.03419	.00716	.00518
9.85E-04	4.08E-04	173.3	1.2	781.0	393.0	.4	.02529	.00779	.00645
7.98E-04	3.74E-04	129.0	1.1	781.0	393.0	.4	.01754	.00910	.00854
3.70E-04	2.40E-04	81.3	.7	780.0	393.0	.4	.01031	.00718	.00931
2.50E-04	2.26E-04	65.7	.6	779.0	393.0	.4	.00816	.00613	.01110
1.33E-04	2.21E-04	25.3	.5	779.0	393.0	.4	.00297	.00895	.02969

## APPENDIX 9

Results for formation of Diethyl Ether for different Water and Ethyl Alcohol partial pressures at 261°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
1.33E-05	0.	552.6	2.4	763.0	261.0	10.0	.00755	.00879	0.00000
8.05E-06	0.	530.7	29.1	763.0	261.0	10.0	.00742	.00542	0.00000
6.37E-06	0.	509.3	55.2	763.0	261.0	10.0	.00729	.00437	0.00000
5.36E-06	0.	489.9	80.5	763.0	261.0	10.0	.00723	.00371	0.00000
4.72E-06	0.	470.9	105.3	763.0	261.0	10.0	.00716	.00330	0.00000
4.00E-06	0.	451.8	128.7	763.0	261.0	10.0	.00703	.00285	0.00000
3.58E-06	0.	434.6	151.7	763.0	261.0	10.0	.00699	.00256	0.00000
3.03E-06	0.	418.1	173.8	763.0	261.0	10.0	.00695	.00218	0.00000
2.64E-06	0.	401.0	195.3	763.0	261.0	10.0	.00684	.00193	0.00000
2.39E-06	0.	381.2	213.8	763.0	261.0	10.0	.00645	.00185	0.00000
2.06E-06	0.	353.0	254.4	763.0	261.0	10.0	.00645	.00160	0.00000
1.71E-06	0.	324.0	291.1	763.0	261.0	10.0	.00623	.00137	0.00000

## APPENDIX 10

Results for formation of Diethyl Ether for different Water and Ethyl Alcohol partial pressures at 312°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
6.28E-05	0.	687.3	4.6	776.0	312.0	10.0	.02323	.01353	0.00000
4.11E-05	0.	658.0	37.1	776.0	312.0	10.0	.02312	.00890	0.00000
3.17E-05	0.	629.5	69.0	776.0	312.0	10.0	.02310	.00686	0.00000
2.55E-05	0.	602.2	99.7	776.0	312.0	10.0	.02310	.00552	0.00000
2.20E-05	0.	575.4	129.1	776.0	312.0	10.0	.02288	.00480	0.00000
1.81E-05	0.	550.0	157.0	776.0	312.0	10.0	.02266	.00399	0.00000
1.54E-05	0.	525.5	184.1	776.0	312.0	10.0	.02249	.00343	0.00000
1.29E-05	0.	502.6	209.1	776.0	312.0	10.0	.02223	.00289	0.00000
1.14E-05	0.	479.8	234.0	776.0	312.0	10.0	.02192	.00259	0.00000
1.00E-05	0.	458.2	257.2	776.0	312.0	10.0	.02149	.00233	0.00000
9.45E-06	0.	437.5	279.6	776.0	312.0	10.0	.02112	.00224	0.00000
9.36E-06	0.	417.5	300.8	776.0	312.0	10.0	.02056	.00228	0.00000
8.36E-06	0.	398.2	321.5	776.0	312.0	10.0	.02012	.00208	0.00000
7.89E-06	0.	379.8	341.4	776.0	312.0	10.0	.01971	.00200	0.00000

APPENDIX 11

Results for formation of Diethyl Ether and Ethylene for different Water and Ethyl Alcohol partial pressures at 348°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
6.86E-04	8.69E-05	758.1	3.0	860.0	348.0	.4	.02177	.00630	.00160
5.87E-04	7.29E-05	723.9	40.1	860.0	348.0	.4	.02142	.00548	.00136
5.06E-04	6.41E-05	685.7	75.0	852.0	348.0	.4	.02134	.00475	.00120
4.71E-04	6.10E-05	646.6	107.2	842.0	348.0	.4	.02085	.00452	.00117
4.19E-04	5.51E-05	611.0	137.1	833.0	348.0	.4	.02045	.00410	.00108
3.69E-04	5.00E-05	583.2	166.6	832.0	348.0	.4	.02016	.00366	.00099
3.50E-04	4.82E-05	552.5	193.3	825.0	348.0	.4	.01982	.00353	.00097
3.03E-04	4.31E-05	528.1	220.3	825.0	348.0	.4	.01960	.00309	.00088
2.78E-04	4.14E-05	502.4	245.1	822.0	348.0	.4	.01917	.00290	.00086
2.52E-04	3.84E-05	475.0	266.8	814.0	348.0	.4	.01869	.00270	.00082
2.25E-04	3.49E-05	472.5	302.0	848.0	348.0	.4	.01828	.00247	.00076
2.30E-04	3.24E-05	429.6	347.3	844.0	348.0	.4	.01819	.00253	.00071
1.58E-04	2.88E-05	404.1	362.7	835.0	348.0	.4	.01687	.00188	.00068

APPENDIX 12

Results for formation of Diethyl Ether and Ethylene for different Water and Ethyl Alcohol partial pressures at 386°C.

$R_e$	$R_o$	$P_a$	$P_w$	$P_t$	$T_c$	$W_c$	$F_a$	$X_e$	$X_o$
2.00E-03	3.83E-04	762.5	5.2	821.0	386.0	.4	.04066	.00983	.00377
1.83E-03	3.62E-04	727.4	42.9	821.0	386.0	.4	.04083	.00896	.00355
1.60E-03	3.27E-04	694.5	77.7	821.0	386.0	.4	.04042	.00794	.00324
1.36E-03	3.10E-04	627.3	142.3	814.0	386.0	.4	.04013	.00676	.00309
1.23E-03	2.85E-04	599.2	172.3	814.0	386.0	.4	.04009	.00615	.00284
1.05E-03	2.63E-04	542.6	227.5	809.0	386.0	.4	.03964	.00529	.00265
9.82E-04	2.55E-04	518.1	253.6	809.0	386.0	.4	.03944	.00498	.00259
8.69E-04	2.29E-04	494.4	278.4	809.0	386.0	.4	.03881	.00448	.00236
7.91E-04	2.16E-04	471.6	302.2	809.0	386.0	.4	.03814	.00415	.00227
7.73E-04	2.13E-04	449.6	325.0	809.0	386.0	.4	.03723	.00415	.00229
6.91E-04	1.98E-04	434.9	351.3	820.0	386.0	.4	.03660	.00378	.00216
6.72E-04	1.95E-04	412.9	371.4	817.0	386.0	.4	.03588	.00375	.00217
6.05E-04	1.83E-04	383.1	390.7	816.0	386.0	.4	.03469	.00349	.00211
5.33E-04	1.69E-04	366.1	424.7	822.0	386.0	.4	.03332	.00320	.00203

## APPENDIX 13

Results for the dehydration of Ethyl Alcohol at temperatures from 214°C - 319°C.

T(°C)	$k_e$ (mole/gm min)	$\frac{1}{T}$ (°K)	$\ln k_e$	$\ln k_e^*$
319.0	1.74E-04	1.69E-03	-8.66E+00	-8.59E+00
311.5	1.34E-04	1.17E-03	-8.92E+00	-8.90E+00
301.5	8.29E-05	1.74E-03	-9.40E+00	-9.33E+00
294.0	6.03E-05	1.76E-03	-9.72E+00	-9.66E+00
287.5	5.00E-05	1.78E-03	-9.90E+00	-9.95E+00
280.5	3.55E-05	1.81E-03	-1.02E+01	-1.03E+01
274.5	2.87E-05	1.83E-03	-1.05E+01	-1.06E+01
266.0	1.76E-05	1.85E-03	-1.09E+01	-1.10E+01
261.0	1.29E-05	1.87E-03	-1.13E+01	-1.12E+01
255.5	1.13E-05	1.89E-03	-1.14E+01	-1.15E+01
251.0	8.37E-06	1.91E-03	-1.17E+01	-1.17E+01
242.0	5.13E-06	1.94E-03	-1.22E+01	-1.22E+01
236.5	4.01E-06	1.96E-03	-1.24E+01	-1.25E+01
229.5	2.76E-06	1.99E-03	-1.28E+01	-1.29E+01
224.0	1.84E-06	2.01E-03	-1.32E+01	-1.32E+01
220.0	1.27E-06	2.03E-03	-1.36E+01	-1.34E+01
214.0	8.62E-07	2.05E-03	-1.40E+01	-1.38E+01

$k_e^*$  is least squares value of  $k_e$

Activation energy (calories/gm mole) =  $28,500 \pm 50$

Frequency factor =  $6.10 \times 10^6$  (mole/gm min)

## APPENDIX 14

Results for the dehydration of Ethyl Alcohol, at temperatures from 305°C - 436°C.

T(°C)	$k_e$ (mole/gm min)	$\frac{1}{T}$ (°K)	$\ln k_o$	$\ln k_o^*$
305.0	1.00E-05	1.73E-03	-1.15E+01	-1.13E+01
308.0	1.32E-05	1.72E-03	-1.12E+01	-1.12E+01
315.5	1.97E-05	1.70E-03	-1.08E+01	-1.09E+01
321.0	2.45E-05	1.68E-03	-1.06E+01	-1.06E+01
328.0	3.64E-05	1.66E-03	-1.02E+01	-1.04E+01
334.0	4.42E-05	1.65E-03	-1.00E+01	-1.01E+01
339.5	5.36E-05	1.63E-03	-9.83E+00	-9.89E+00
345.5	6.67E-05	1.62E-03	-9.62E+00	-9.66E+00
352.5	9.06E-05	1.60E-03	-9.31E+00	-9.39E+00
356.0	9.96E-05	1.59E-03	-9.21E+00	-9.26E+00
364.0	1.17E-04	1.57E-03	-9.05E+00	-8.97E+00
373.5	1.66E-04	1.55E-03	-8.71E+00	-8.63E+00
378.0	1.96E-04	1.54E-03	-8.54E+00	-8.47E+00
385.0	2.36E-04	1.52E-03	-8.35E+00	-8.23E+00
391.7	3.25E-04	1.50E-03	-8.03E+00	-8.01E+00
399.0	4.27E-04	1.49E-03	-7.76E+00	-7.77E+00
404.0	5.46E-04	1.48E-03	-7.51E+00	-7.61E+00
409.0	6.20E-04	1.47E-03	-7.39E+00	-7.45E+00
414.0	6.64E-04	1.46E-03	-7.32E+00	-7.29E+00
420.0	7.64E-04	1.44E-03	-7.18E+00	-7.10E+00
426.0	9.46E-04	1.43E-03	-6.96E+00	-6.92E+00
431.5	1.17E-03	1.42E-03	-6.75E+00	-6.76E+00
436.0	1.42E-03	1.41E-03	-6.56E+00	-6.63E+00

$k_o^*$  is least squares value of  $k_o$

Activation energy (calories/gm mole) =  $29,200 \pm 50$

Frequency factor =  $1.34 \times 10^6$  (mole/gm min)

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