GAS-SOLID CHROMATOGRAPHIC STUDIES
OF TWO WELL-KNOWN CATALYSTS

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ROBERT PETER MASON

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SUMMARY

This work was initiated to explore the scope and feasibility of using a gas chromatograph to study catalytic reactions. Various methods have been proposed in the literature and it was decided to investigate various possible systems.

Two catalysts were chosen for study.

The dehydration of alcohols over alumina catalysts has been extensively studied and found to be ideally suited to studies by gas chromatography. The effect of modification of the catalyst by inorganic ions and by water was investigated. The dehydration of ethanol and pentanol were studied. Results indicated that alumina has two types of active sites responsible for the dehydration of alcohols.

Zeolite catalysts are well-known and in this work the catalytic cracking of alkanes over zeolite Y was studied. The reaction mechanism was found to be complex and catalyst deactivation due to build-up of highly carbonaceous deposits occurred.

All components of the reaction products were produced at similar rates to the overall reaction rate indicating that desorption of alkane product species was not the rate determining step.

Between 150° and 300°C propane was the smallest product formed. Only alkanes were found in the product spectrum which was temperature dependent.

Addition of hydrogen gas greatly increased the amount of detectable products. Heptane was found to react significantly above about 200°C, hexane above 225°C and pentane above 250°C. Hexane and cyclohexane reacted at similar temperatures.

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NOTATION

A	Peak area
A_E	frequency factor
a	initial amount of reactant
Ea	activation energy
f	fraction of molecules on the surface
g	defined as $\frac{V_R}{V_m}$ in [21].
h	peak height
k	(with subscripts), various reaction rate constants
L	column length
N	number of theoretical plates
n_{in}	number of moles input
n_{out}	number of moles output
S	detector sensitivity
t	(with subscripts) retention time (also time spent in a specific phase)
V_R	retention volume
V_m	dead volume (retention volume of a non-absorbed species)
2V	length of step interval
W	mass or weight of sample
W_x	peak width
x	amount of reactant that has reacted

CHAPTER 1 : INTRODUCTION

In this research a gas chromatograph is used as a chemical reactor for the study of heterogeneous catalysis. The chromatograph is used both as a reactor and a separator. The products and unreacted reactant can be separated and in most instances the catalyst itself is a suitable stationary phase for such separations. Chromatography has been used in this research to study the dehydration of alcohols over alumina catalysts and also the catalytic cracking of alkanes over zeolite Y.

Various methods have been used to study reactions and reaction kinetics by gas chromatography (fig 1). Methods that rely on the chromatograph to separate the product components only may be classified as "microreactor" techniques. Pulses of reactant are added to the microreactor and the products swept immediately into the chromatograph for separation.

A variation of this precolumn technique is "sample vacancy chromatography".[16] This technique employs a continuous reactant feed but allows periodic separation of the products formed. It has, however, the disadvantage of requiring fairly extensive modification to the chromatograph.

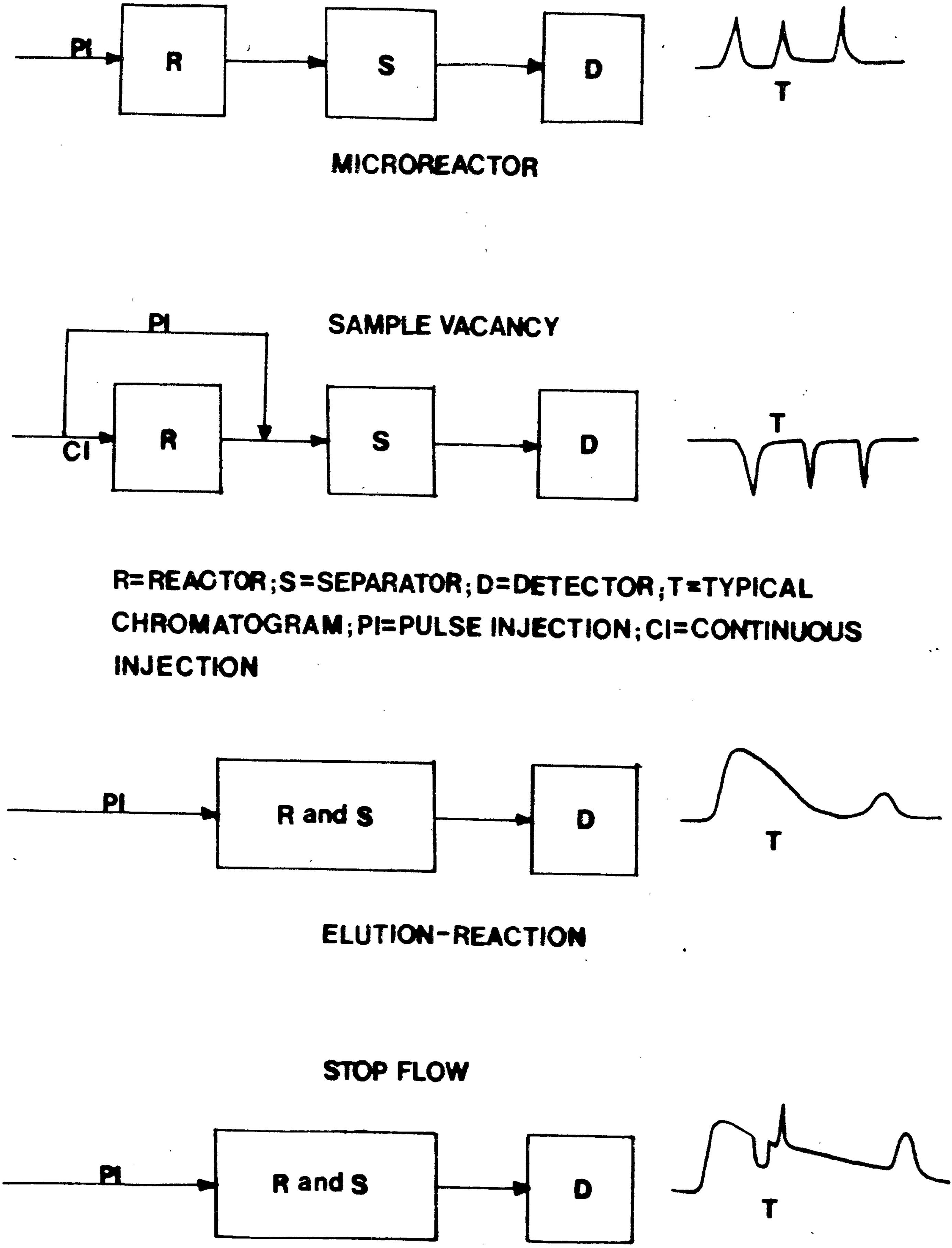

Figure 1.

Diagram showing the basic types of reaction chromatography used in catalytic studies.

Methods which use the chromatographic column as a dual purpose reactor and separator are classified as "on-column" techniques. Information may be gained from elution studies using the catalyst (or a reactant) as the stationary phase and using pulses of reactant. These elution techniques have been extensively used.[4]

If the gas flow is periodically stopped for a defined interval, sharp peaks superimposed on the elution profiles are found on restarting the gas flow. These sharp peaks are due to products formed during the "stop-flow interval".[21] These "stop-flow peaks" give clear information concerning the reaction kinetics. This technique has been termed "stop-flow chromatography".[21]

The methods and classifications overlap and a combination of two or more techniques is often required. For instance, there are certain advantages in using a microreactor and performing stop-flow chromatography, thus obtaining only one stop-flow peak per pulse of reactant. In any event, to obtain an exact and comprehensive survey of the system under study it is advantageous to combine the results of various techniques as the information obtained by any particular technique has its own unique aspects.

The main objectives of this research were:

1. To investigate the feasibility of studying catalytic reactions by gas chromatography.

2. To investigate the applicability and scope of the different methods mentioned above by comparison of the data obtained by the various techniques.

3. To study a well-characterised catalytic system which is easily adaptable to gas chromatography investigation and which has been previously studied by gas chromatography. The dehydration of alcohols over alumina catalyst was chosen as it has been extensively investigated by Lane et al.[22]

4. To study some aspects of alcohol dehydration by alumina which have not been fully investigated.

5. To study a catalyst which has not previously been extensively studied by gas chromatographic methods but which has nevertheless been fairly well characterised. The catalytic cracking of alkanes over zeolite Y was chosen.

6. To investigate the possibility of obtaining other information (eg rate of deactivation and poisoning) as well as kinetic data from gas chromatographic studies.

7. To investigate the applicability of the various methods to different reaction systems.

Stop-flow chromatography was chosen as the principal method of studying the catalysts. Other methods used were on-column elution techniques and microreactor stop-flow chromatography.

A variety of gas chromatographic methods have thus been used in this research to study catalytic reactions.

CHAPTER 2

DEVELOPMENT OF REACTION CHROMATOGRAPHY AND RELATED THEORY.

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CHAPTER 2

DEVELOPMENT OF REACTION CHROMATOGRAPHY AND RELATED THEORY.

2.1 Introduction

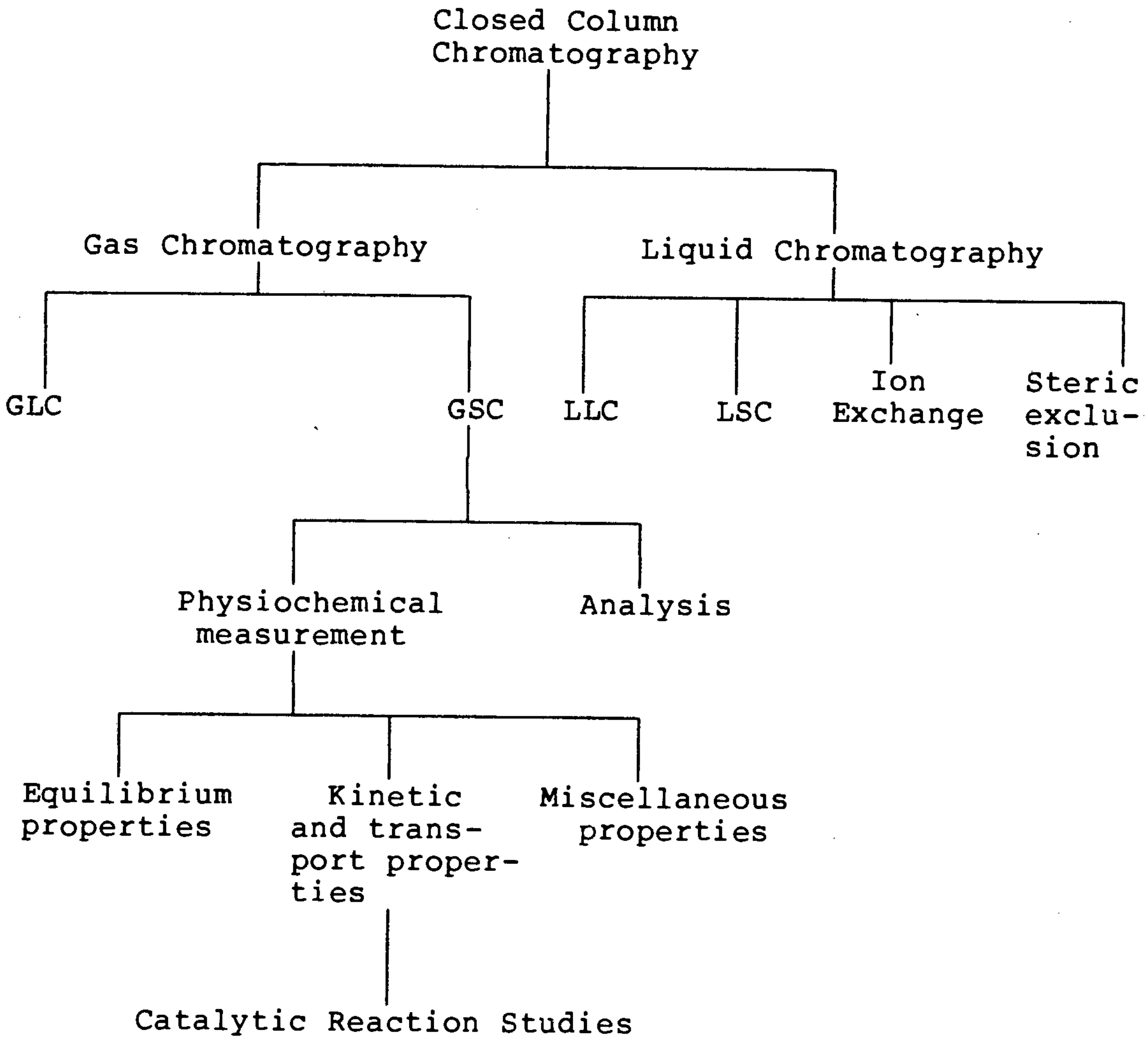
The term "chromatography" was first used by Mikhail Tswett, a botanist, to describe his experiments by which he separated plant pigments. In the eighty years since his discovery, chromatography has expanded dramatically. Today any separation method in which a mixture is applied as a narrow initial zone to a stationary porous sorbent and in which the components of the mixture are caused to undergo differential migration by the flow of a mobile phase, may be termed chromatography.

Chromatography generally employs two phases to effect a separation; a stationary phase and a mobile phase. The mobile phase is either liquid or gas. Gas chromatography (GC), employing a gaseous mobile phase, is the method used in this research.

In particular, gas-solid chromatography (GSC) with a solid stationary phase is the method used as the catalysts studied were solid and in most instances they performed as the stationary phase as well. The study of reaction kinetics by chromatography is only a small part of a whole range of physiochemical measurements which can be carried out by chromatography. The area of this research is put into overall perspective in fig. 2.

Figure 2

Diagram showing the relationship between studies of catalytic reaction and other uses and other forms of chromatography.



The theory of chromatography is well developed[1-4], and will not be discussed here. The theory relating to reaction chromatography will be discussed later. Both analytical and physiochemical measurement by chromatography rely on the same principles and it is not surprising that the two uses of chromatography were developed simultaneously. A short historical overview of the development of chromatography is, therefore, appropriate as it illustrates the development of the methods used in chromatographic studies of chemical reactions.

2.2 Historical Development of Chromatography

Mikhail Tswett is usually acknowledged as the discoverer of chromatography. He wrote in 1903:

"When a petroleum ether solution is filtered through a column of adsorbent, the pigments are resolved, according to the adsorption sequence, from top to bottom into various coloured zones, since the more strongly adsorbed pigments displace the more weakly adsorbed ones and force them farther downwards" (translated in[1]).

Another important pioneer was David Talbot Day who, between 1898 and 1903, separated crude oil and its various fractions by passing it through finely pulverised Fuller's earth[1].

Thus chromatography had its origins in two very diverse fields of science. Both the above separations relied on liquid adsorption by a solid to separate the mixture. These discoveries were virtually ignored until the early 1930's when they were redeveloped and refined.

A liquid stationary phase was first used in 1942 by Martin and Synge[3]. Besides introducing liquid-liquid chromatography (LLC), they also developed a chromatographic plate theory and measured liquid-liquid partition coefficients. This was the earliest use of chromatography for physiochemical measurement.[3]

The first use of gas as a mobile phase was made when Turner in 1943 used gas-solid adsorption chromatography (GSC) to separate a hydrocarbon mixture. Cremer and Prior measured free energies by GSC in 1947 and James and Phillips in 1954 measured adsorption isotherms.[4] The 1940's and 1950's saw a very rapid development of GSC for both analytical and physiochemical measurements.[2, 3]

It is interesting to note that the method most used today, gas-liquid chromatography (GLC) was developed much later than the other methods. James and Martin first used the technique in 1954. However, its development has been the most dramatic.[2]

It was very quickly used for a wide range of physiochemical measurements by James and Martin, Hoare and Purnell, Littlewood and co-workers, Porter and co-workers, Anderson, and by many others[2, 4].

Martin stated in 1956 that "the method of gas chromatography provides perhaps the easiest of all means of studying the thermodynamics of the interaction of a volatile solute with a non-volatile solvent and its potential value for providing this type of data should be great".[4]

So analytical chromatography and physiochemical measurement by chromatography have similar origins and were developed almost simultaneously. In the last thirty years the scope of both fields of chromatography has blossomed and the amount of literature devoted to these subjects is now enormous.

GLC finds much wider application in physiochemical measurement than does GSC. However, as far as studying reactions by chromatography is concerned, GSC is more often used. The development of reaction chromatography has, to a large extent, been due to the need to study and develop catalysts, especially in the petro-chemical fields. Reaction GSC is well suited for the study of catalytic reactions and it allows calculation of both kinetic and thermodynamic data.

2.3 Development of Reaction Chromatography

As previously mentioned, the usefulness of chromatography in the study of reactions and reaction kinetics has led to a rapid development of various techniques. The techniques can be divided into two groups according to the function of the chromatograph.

The first group essentially relies on the chromatograph as a separator only and as such is essentially an analytical application. It was soon realised after the introduction of chromatography that the effluent from a chemical reactor could be sampled and injected into a chromatograph for separation and quantification. The use of a precolumn "microreactor" joined directly to the chromatograph and the injection of pulses of reactant was a logical development of the original concept.

The second group may be termed as "on-column reaction" techniques. This is loosely taken to define those methods where the chromatographic column performs a dual function as a chemical reactor and as an analytical separator. This grouping includes "on-column" reactions under elution conditions and the method of "stop-flow" chromatography development by Phillips et al[21].

A number of excellent review articles describe the various techniques and uses of gas chromatography in catalytic research. Beroza and Coad[5] review mainly microreactor techniques. Choudhary and Doraiswamy[6] devote a large part of their review to the determination of catalyst characteristics (eg pore size, number of active sites) as well as reviewing microreactor and on-column reaction studies. Langer et al[7] discuss the definitions and equations of a generalised "ideal chromatographic reactor". They also review the various studies made with both microreactor and on-column techniques. A more recent comprehensive review has been made by Saha and Mathur[8]. They divide their review into analytical applications (eg analysis of catalyst and poisons), measurement of physio-chemical properties and studies using the chromatograph as a reactor.

As can be seen from the above reviews, considerable research has been done using chromatographic reactors. The various groups and techniques will be discussed below and the relevant theory used in this research will be reported.

2.3.1 Microreactor techniques

Microreactor techniques are generally not regarded as falling under the definition of reaction chromatography. However, a brief description of this technique is required as it indirectly relates to the other techniques.

The microreactor technique was introduced by Kokes et al.[9] A small precolumn containing the catalyst is connected directly to the chromatograph (or separating column). In early procedures the precolumn was housed outside the chromatographic oven (eg Hall et al[10]). Recently Grob and Leasure[11] have used the front section of a chromatographic column as the "microreactor" : it is thus housed inside the chromatographic system. Semi-automatic[10] and automatic systems (eg Harrison et al[12]) have been devised. Detailed microreactor design systems have been reported (eg, Choudhary[13], Cho et al[14],). A high pressure system has been designed by Steingasner and Pines[15].

As mentioned previously, the technique has been adequately reviewed[5-8]. The work mentioned here gives some indications of the scope of the technique as well as showing the extent of interest in the technique. It is very widely used, especially as it resembles closely a conventional chemical reactor.

Generally a pulse of reactant is injected and the products formed and the remaining reactant separated by the chromatograph (analytical column). By varying the gas flow rate and other parameters, it is possible to obtain reaction kinetics and other data.

It is possible to use a microreactor-stop-flow technique to increase the contact time between reactant and catalyst or for other reasons. This technique will be discussed under section 2.3.4.

Phillips and McIllwrick[16] developed a microreactor technique which they called "sample vacancy chromatography". A fixed amount of reactant and carrier gas is fed into the microreactor and separating column. When a plateau signal is recorded (ie a steady state), a sample of pure carrier gas is injected onto the column. The resulting chromatogram is a series of negative peaks, one for each component of the effluent mixture. Phillips and McIllwrick compared this technique to stop-flow chromatography.

In this research, neither of the above microreactor techniques were used. However, in certain circumstances it is useful to use a microreactor combined with stop-flow chromatography. This method will be discussed under 2.3.4.

The microreactor techniques are still largely used as they closely simulate pulse reactors which are widely used to study reaction kinetics. However, they have disadvantages which include the extensive modification of equipment and the time required to obtain kinetic information.

2.3.2 The "ideal chromatographic reactor"

Both on-column elution reactions and stop-flow chromatography assume that the chromatographic column behaves as an "ideal reactor". It is instructive at this point to consider the various criteria required for the system to be "ideal" .

Conder and Young[4] and Langer et al[7] list the following criteria. The conditions necessary to approach ideality will be discussed.

Firstly, it is assumed that any products are instantaneously separated as soon as the reaction has occurred. This implies an infinite difference in retention volumes. Generally a reactant and its products have substantially differing retention times so this criterion is usually satisfied.

The fact that products are rapidly removed from the reaction site allows studies to be made of reversible reactions - and also reactions where autocatalysis and product inhibition occur. With stop-flow chromatography, products are not rapidly removed during the stop interval (no carrier gas flow). Thus autocatalysis, product inhibition or the reverse reaction are not restricted. However Lane et al[22] have shown that by varying stop interval lengths, it is possible to measure the kinetics of the competing processes.

The column is assumed to be homogeneous in composition and that the composition of the phases does not change. The gas velocity is assumed to be linear throughout the column. If the difference in inlet and outlet pressure is small, the gas flow approaches linearity. If the stationary phase is solid, it is easily uniformly distributed throughout the column.

Peak spreading and axial diffusion due to effects other than the reaction are assumed to be negligible. This means an infinite number of theoretical plates. Also the distribution isotherm is assumed to be linear.

In stop-flow chromatography with strongly adsorbed reactants (eg alcohols on alumina) the above criteria concerning normal chromatographic processes are less important as the reactant is essentially immobile on the column. Thus the catalyst is for the most part a separator of products where normal chromatographic effects can be tolerated.

As the pressure in the chromatographic column is not uniform throughout the column, the system is limited to studying first-order or pseudo-first-order reactions.

Other assumptions are that the column is isothermal, the reaction rates are chemically controlled and that partition between phases is constant.

If small samples are used, the criteria for an ideal reactor are approached. Advantages of the chromatographic reactor are the small samples required, easy control of temperature and flow rate; and that reactions with competing side reactions can be studied.

However, the technique is usually limited to volatile reactants, first-order or pseudo-first-order reactions and generally only one reactant. If the stationary phase is a liquid, the solid support and its effects must be carefully considered.

The theory of an ideal chemical reactor has been discussed[4, 7]. The purpose here is to indicate the viability of the two methods to be discussed and the advantages and disadvantages of each.

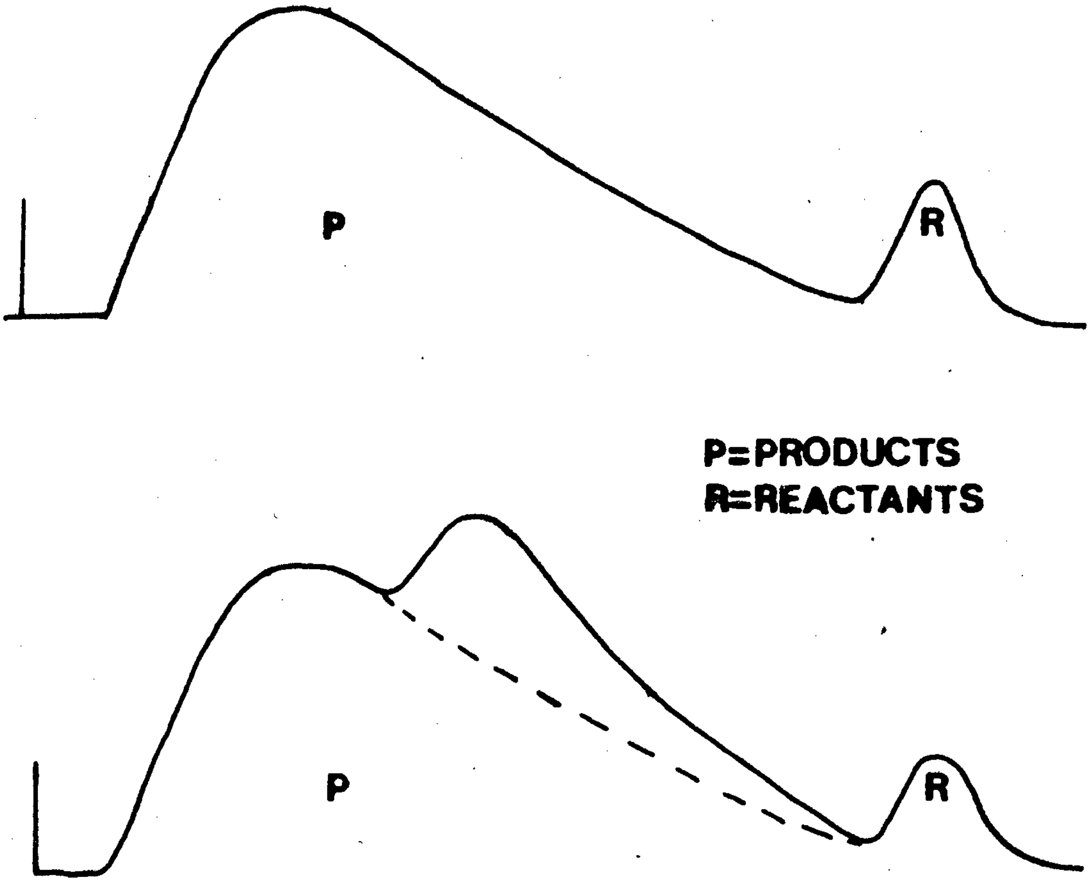
2.3.3 On-column elution reactions

If as the reactant is passing through the chromatographic column it is being both converted to product(s) and simultaneously separated, the method is considered to be an on-column elution reaction technique. The gas flow is continuous and pulses of reactant are injected. Kinetic information can be deduced from the shape and/or areas of the resulting peaks. The products are either more or less strongly retained than the reactant.

If the products are less strongly retained, the recorded chromatogram would consist of a broad product(s) peak followed by the unreacted reactant peak (fig 3). If more than one product is observed, the interpretation would differ, depending on the processes occurring. For example, a consecutive set of reactions (A --> B --> C) would require different interpretation to one reactant forming two products (A --> B + C).

Figure 3

Chromatograms of typical elution reactions yielding one and two products (reactant more strongly adsorbed than products).



Bassett and Habgood[17] in 1960 derived an equation relating the first-order heterogeneous rate constant for the irreversible isomerization of cyclopropane to the fractional conversion, flow rate and retention time assuming a linear isotherm.

Magee[18] derived an equation involving only one dependent variable using a simplified model. Gil-Av and Herzberg-Minzly and later Berezkin and co-workers studied bimolecular reactions as pseudo-first-order reactions by using one reactant as the stationary phase[4]. Berezkin and Shiryaeva[19] used more than one column and a circulation technique to increase contact time.

A large amount of work has been done recently by Langer, Yurchak, Patton and co-workers while Roginskii, Rozental, Gaziev and co-workers published many papers in the 1960's (see Chapter 13[4]).

Langer, Patton and co-workers[4, 7, 20] used material balance equations to derive a continuous flow model for first order reactions. Their equation is derived for a gas-liquid situation:

$$\frac{N_{in}}{N_{out}} = \exp\,(k_l t_l + k_g t_g) \quad \ldots. \quad (2.1)$$

where N = number of moles, t_l = time spent in the liquid phase, t_g = time spent in the gas phase and k_l and k_g are the appropriate rate constants.

By using an inert standard and taking into account detector sensitivity, the equation may be modified to:

$$\ln \frac{A_I}{A_R} = (k_l + \frac{t_g k_g}{t_l}).t_l + \ln \frac{W_I/S_I}{W_R/S_R} \quad \ldots. \quad (2.2)$$

where A = peak area, W = weight, S = detector sensitivity and subscripts I and R refer to the inert standard and reactant respectively. Thus a plot of

$$\ln \frac{A_I}{A_R} \quad \text{versus } t_l$$

will have a slope of $k_l + \frac{t_g}{t_l}.k_g$

which is referred to as k_{app}. When the stationary phase is the solid catalyst, it can be assumed that reaction in the gas phase is negligible and equation 2.2 becomes:

$$\ln \frac{A_I}{A_R} = k_s t_s + \text{constant} \qquad \ldots\ldots (2.3)$$

where s implies a solid stationary phase.

Further it can be shown that a plot of ln (recorder response) against time, t, for the diffuse edge of the product peak will have a slope of - $k^1{}_{app}$ where

$$k^1{}_{app} = \frac{k_{app} \quad t_{l,R}}{t_{l,R} - t_{l,p}}$$

where R stands for reactant, P for product.

If the reactant is strongly retained and the product fairly weakly retained we see that $k^1{}_{app} \dashrightarrow k_{app}$. Also from equation 2.3 we can see that $k^1{}_{app} \dashrightarrow k_{app} = k_s$ for systems where the solid catalyst is the stationary phase, ie

$$k^1{}_{app} = k_s\ t_R/t_R - t_p \qquad \ldots. (2.4)$$

This method is useful if normal band-broadening processes are negligible as they tend to "smooth out" the product curve. Reverse reactions, even if small, cannot be tolerated.

In this work, equation 2.4 and plots of ln (recorder response) versus time were used to obtain kinetic data. The data was compared with other methods to determine its applicability to catalytic reactions.

2.3.4 Stop-flow Chromatography

This method has been developed mainly by Phillips and co-workers[21-24]. It is a modification of the elution reaction techniques discussed in 2.3.3. The data obtained is the same, however stop-flow chromatography can also separate the products obtained.

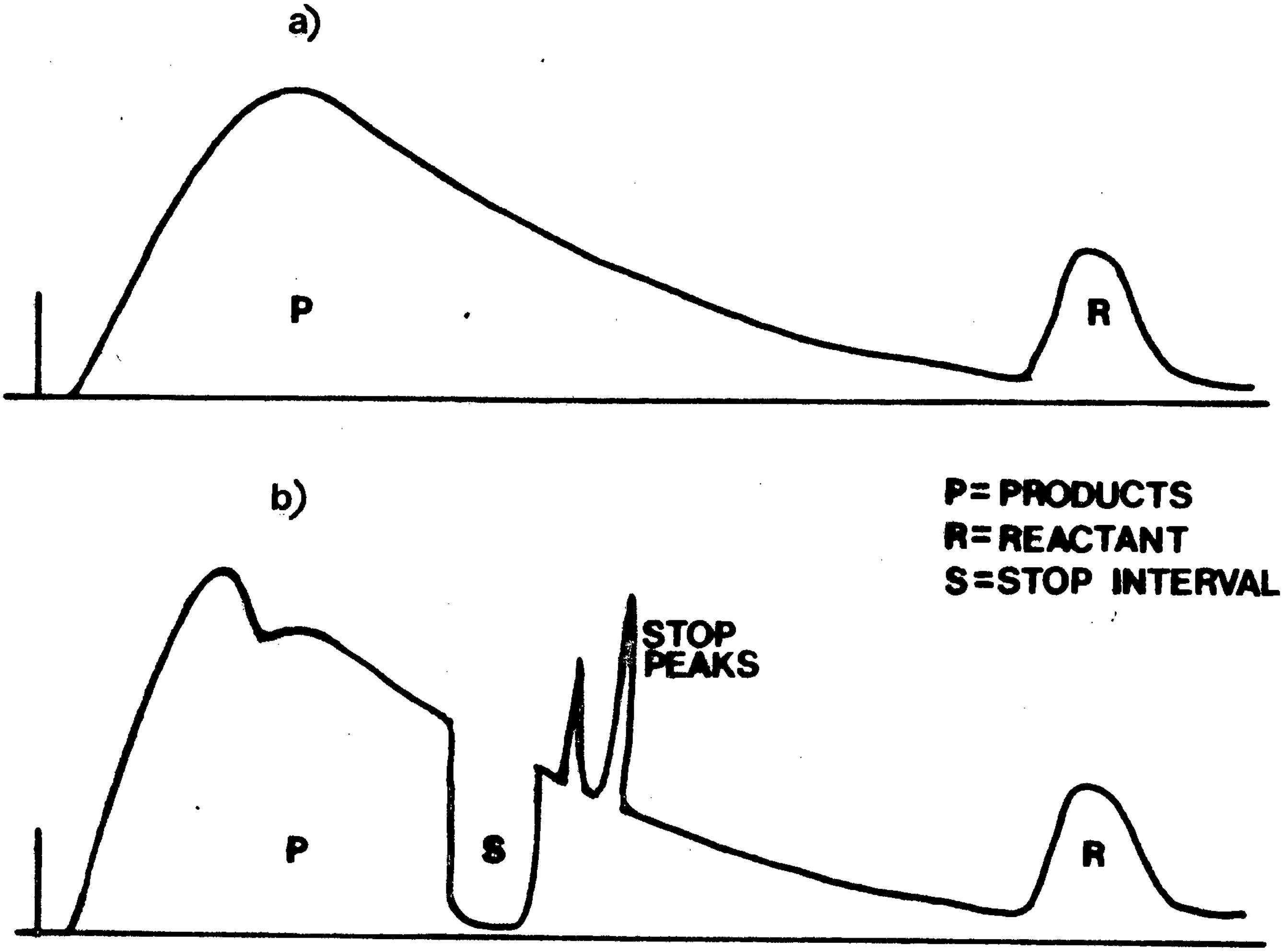
Again the catalyst is usually used as both reactor and separator. An injection of reactant is allowed to elute under normal flow conditions, producing the broad reaction chromatograms mentioned in 2.3.3. However, in addition, the gas flow is periodically stopped for short intervals of time. During this "stop-time" the reaction proceeds resulting in a localised concentration of products. On restarting the flow, these products are separated from each other and are eluted as sharp peaks superimposed on the broad reaction chromatogram. The sharp peaks produced are comparable to what would be obtained if the product mixture had been analytically separated on the column used.

These sharp peaks are easily quantified and allow reaction kinetics to be calculated. Let us consider the case if the reactant is strongly retained on the column while the products are much less strongly retained. Other possibilities lead to similar conclusions[4].

The broad reaction chromatogram is pictured in fig 4(a) for elution conditions while fig 4(b) shows the resulting chromatogram from stop-flow chromatography.

Figure 4

Chromatograms of (a) a typical elution reaction and (b) a stop-flow experiment (reactant more strongly adsorbed than products).



Considering the reaction occurring as:

$$A \xrightarrow{k} B$$

we can write:

$$\frac{dx}{dt} = kf\ (a - x) \qquad \text{.....}\ (2.5)$$

for a first-order reaction where x is the amount of reactant reacted; t is the reaction time; k the rate constant; a the initial amount of reactant and f the fraction of the reactant molecules on the surface.

If the stop-interval has length 2V (secs) and A is the corrected peak area (for attenuation changes) it can be seen that [4,21]:

$$\ln \frac{A}{kfv} = kft + \text{constant} \qquad \text{....}\ (2.6)$$

Thus a plot of $\ln \frac{A}{fv}$ against t will have a slope of -kf from which k can be calculated. If $f \rightarrow 1$, and stop-intervals are kept constant then a ln (area) versus t plot will give k directly.

Phillips and co-workers[21] state that for symmetrical elution peaks, f will be constant for a particular column, reactant and temperature where f is defined as:

$f = \frac{g - 1}{g}$ where $g = \frac{V_R}{V_m}$ where V_R is the retention volume of reactant and V_m is the retention volume of an unretained species (dead time). Substituting and manipulating we see that:

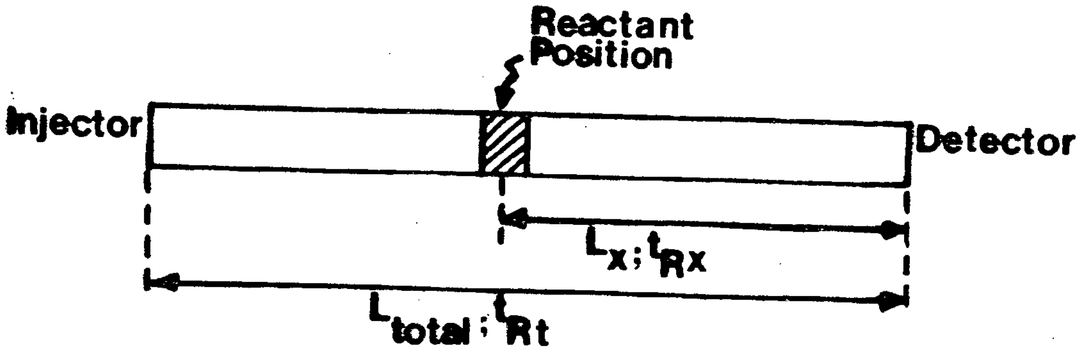
$$f = \frac{V_R - V_m}{V_R} \qquad \text{.... (2.7)}$$

Therefore as V_R increases, f approaches unity for a particular column and temperature. Also any parameter which affects V_R will also affect f. In most catalytic studies f should be close to unity as the reactant interacts in a complex way with the catalyst, resulting in a large retention volume. To a certain extent, experimental factors can be controlled to ensure that f is fairly close to unity (for example, by using low temperatures and flowrates, but short columns to reduce analysis time).

In most cases, the stop-flow results in sharp, easily defined peaks. In some instances, the reactant is totally adsorbed (f is essentially one) and can be taken to be stationary on the column. If this is the case, then peak heights may be used instead of peak area. If the reactant has a finite retention time, peak areas must be calculated as the peak width of the eluted product peaks decreases as the reactant moves through the column.

Figure 5

Diagrammatic representation of the general position of reactant during a stop interval and its related parameters.



However, it is sometimes difficult to estimate area if the peak width is constantly changing. A method of calculating relative areas has been devised. Considering the diagram (fig 5) we see that after any stop interval, the product peak will have an elution time, t_{RX} which is dependent on the distance the reactant has travelled along the column ($L_{total} - L_X$). Assuming a constant height equivalent of a theoretical plate H throughout the column we see that:

$$\frac{L_X}{N_X} = H = \text{constant} \qquad \text{.... (2.8)}$$

where N_X is the number of theoretical plates in length, L_X. The number of theoretical plates is related to the retention time and peak width by:

$$N_X = 16 \left[\frac{t_{RX}}{W_X} \right]^2 \qquad \ldots. \ (2.9)$$

where W_X is the peak width for retention time t_{RX}. This equation is defined in the literature[1-4]. Also if all other parameters are kept constant, t_{RX} is directly related to L_X by:

$$t_{RX} = L_X \cdot \frac{t_{Rt}}{L_{total}} \qquad \ldots. \ (2.10)$$

where t_{Rt} and L_{total} refer to the entire column length. Rearranging and substituting we find:

$$(W_X)^2 = \frac{16\ H\ (t_{RX})^2}{L_X}$$

$$= \frac{16\ H\ .\ (t_{RX})^2 . t_{RX}}{t_{RX} \cdot L_{total}}$$

$$= \text{constant} \ \ x \ \ t_{RX}$$

so

$$W_X = C \ . \sqrt{t_{RX}} \qquad \ldots. \ (2.11)$$

where $C = \dfrac{16\ H\ .\ t_{Rt}}{L_{total}}$

Thus the peak width is directly related to the square root of the retention time. Now if we assume that the peak area can be represented by a triangle then:

$$\text{Area} = \tfrac{1}{2}\ \text{base x height, h}$$

$$= \tfrac{1}{2}\ C \cdot \sqrt{t_{RX}} \cdot h \qquad \ldots.\ (2.12)$$

Thus a plot of log $\sqrt{t_{RX}}$. h versus total reaction time will allow calculation of the rate of the reaction.

Besides conventional stop-flow chromatography where the column is packed with catalyst which is used as reactor and separator, microreactor-stop-flow techniques were used. In these instances a small "plug" of zeolite was packed into a column, the rest of the column being filled with a stationary phase used to separate the products formed.

This was found advantageous where the retention time of the product was large or where only one stop per run was required. Studies of the effect of stop time, rate of catalyst deactivation and effect of temperature on amount of reaction were all easily studied using this technique.

The accuracy is somewhat limited, especially when complex reaction systems are studied. This fact is discussed further in 4.8.

The accuracy of data obtained from stop-flow chromatography is governed mainly by normal chromatographic parameters. The factor involves the retention time, t_r, which is assumed to be constant. Thus any changes in flowrate, especially, will affect the data obtained. Also as mentioned in 2.3.2, consecutive reactions, autocatalysis and product poisoning all affect the resultant peak area from a particular stop. However, to find if these processes are occurring, it is only necessary to use different stop time lengths and ascertain if a linear response is observed.

Stop-flow chromatography is a versatile technique which requires little modification to standard chromatography equipment. Although it has not been much used it is, however, a powerful and very useful tool for studying a wide range of reaction systems.

CHAPTER 3

DEHYDRATION OF ETHANOL AND PENTANOL USING UNMODIFIED AND MODIFIED ALUMINA.

3.1 Introduction

3.2 Reaction of Ethanol on Unmodified Alumina

3.2.1 Results and Discussion

3.2.2 Conclusions

3.3 Reaction of Pentanol on Alumina

3.3.1 Results and Discussion

3.3.2 Conclusions

3.4 Conclusive Comments

3.1 Introduction

The dehydration reactions of alcohols over various catalysts have been extensively studied. Alumina and modified aluminas (containing inorganic salts) have been found to be suitable catalysts for the dehydration of alcohols[22, 26]. The reaction usually produces an alkene and water.

Lane et al[22] have studied the reactions of a large variety of alcohols on alumina modified with 10% KCl. Their results supported a trans-elimination mechanism and suggest that alumina has two types of active sites. Autocatalysis by water and olefin polymerization were found to be side reactions.

Knözinger and Ratnasamy[27] have reviewed catalytic aluminas extensively and have related the surface characteristics and catalytic activity to the structure of the aluminas.

Jirátová and Béranek[26] studied the dehydration of 1-butanol at 573K on modified aluminas. They found that acidity depended on the introduced ion in the order $SO_4^{2-} > F^- > PO_4^{3-} > Cl^- > Zn^{2+} >$ none $> Mg^{2+} > Na^+$. They also found that activity and reaction rate were affected by addition of ions whereas the mechanism was unaffected.

Dehydration of alcohols is easily studied by reaction gas chromatography. If a flame ionization detector is used, the water is not detected and thus only one product peak (ignoring any polymerization or cracking peaks) is detected. This makes the system ideal for stop-flow chromatography when coupled with the fact that alcohols are almost irreversibly adsorbed by alumina.

Although Lane et al[22] have comprehensively studied dehydration reactions by stop-flow chromatography and the catalytic activity has been extensively studied[27], there still seems some doubt about the nature of the active sites and the reaction mechanisms. Also there seems some confusion as to the effect of catalyst modification with Lane et al[22] finding deactivation of the alumina with KCl and Jírátová and Béranek[26] finding Cl^- increased activity.

The writer thus decided to study some of the aspects of the reactions of alcohols on alumina. In this work two alcohols were studied. Ethanol was chosen as an alcohol which might produce unexpected products whereas pentanol was expected to produce mainly pentene and water. Comparison of the results obtained could help explain the reaction mechanisms. The effects of KCl, KF and water on the activity of alumina were also investigated.

3.2 Reaction of Ethanol on Unmodified Alumina

The experimental methods are outlined in Appendix I. A 5 µl mixture containing a 18:1 molar ratio of ethanol : pentane was used. Stop flow intervals were three minutes unless otherwise stated. Injector temperature was 300 °C. Nitrogen flow-rate was 30 ml/min. A flame ionization (FID) detector was used. All peak areas were recorded in mm^2 after attenuation correction.

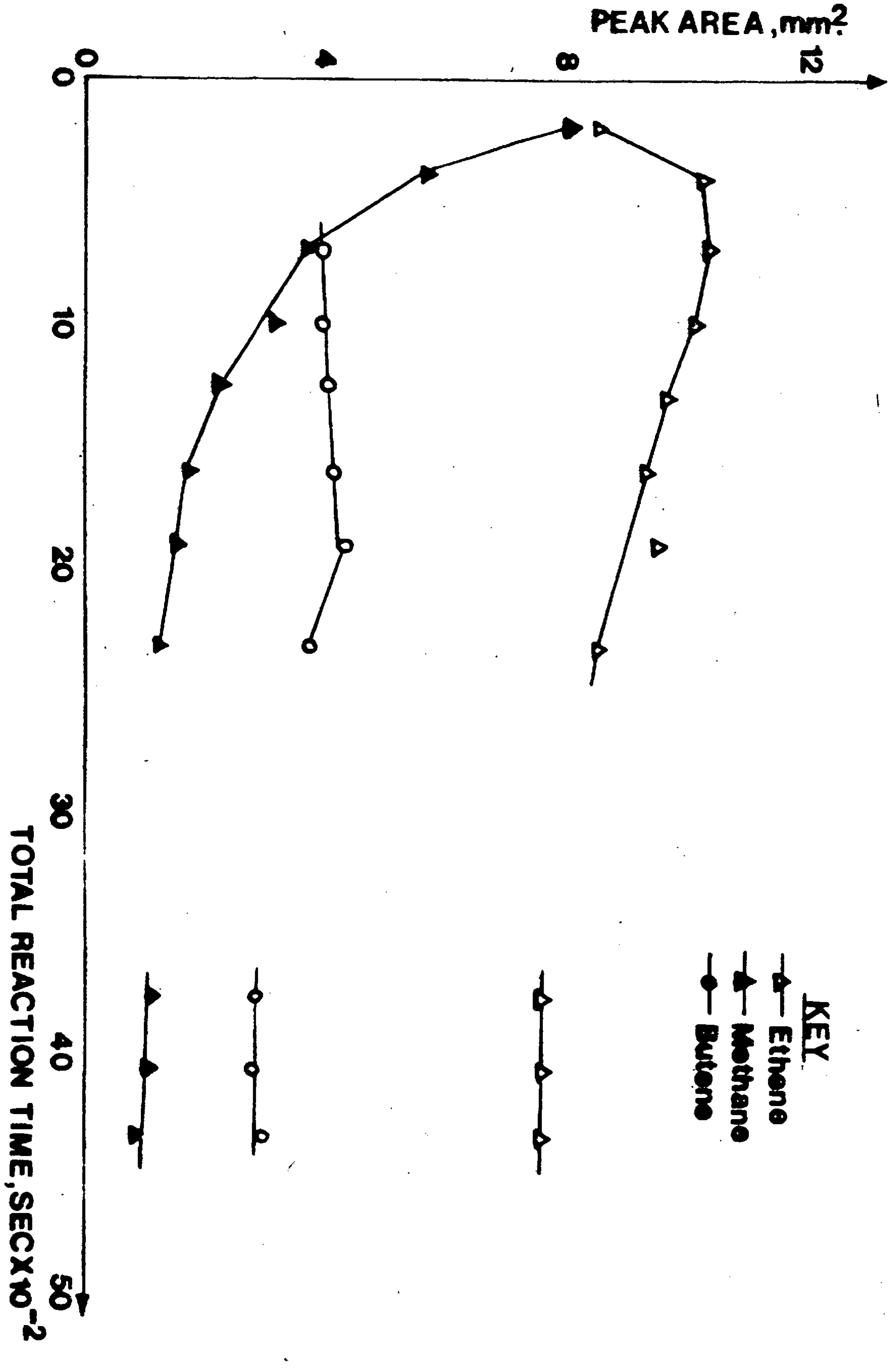
3.2.1 Results and Discussion

Six product peaks were found after each stop-flow interval. Besides a main peak due to ethene, a series of polymerization products were found. Peaks were identified by injection of pure hydrocarbons and from the linear relationship between log (retention time) and carbon number.

The reaction initially produced a large proportion of methane which rapidly decreased in relative amount. The results for a reaction temperature of 300°C are gathered in table 1, appendix 2 and displayed graphically in fig 6. The products were identified as most likely, in order of elution, to be methane, ethene, butane, butene and possibly pentene.

Figure 6

Change in various products with reaction time for the dehydration of ethanol on unmodified alumina at 300°C.



It can be seen that initially there is an increase in ethene and butene production with time and a large, rapidly decreasing production of methane. After about 25 minutes the reaction reaches a steady state. At this stage ethene made up 54% of the total detected product area produced during a stop interval, methane 10% and butene 24%, the rest (12%) being other polymerization products. Assuming a proportional detector response to the number of carbon atoms per molecule a molar ratio of 10:27:6 (methane:ethene:butene) can be calculated.

Reaction rates were calculated from plots of ln (peak area) versus reaction time. Reaction time is the total time from reactant injection to the midpoint of a particular stop-flow interval. The theory related to the extraction of rate constants from stop-flow data is discussed in Chapter 2. In these reactions, f is essentially one as the alcohol is totally adsorped onto the column. The calculated data is gathered in tables 1 and 2 and represented graphically in fig 7.

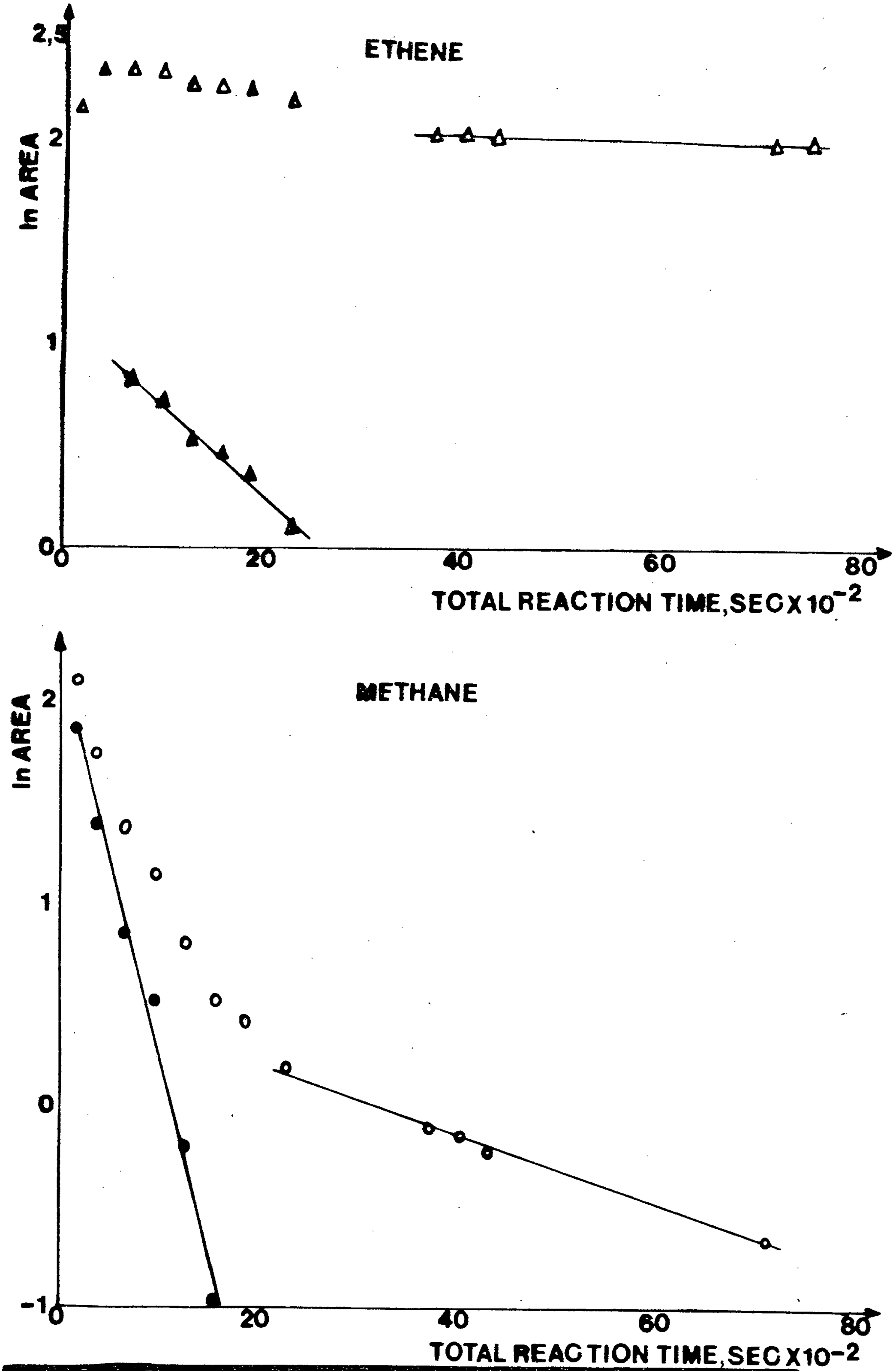


Figure 7 Graphs showing the rates of production of both ethene and methane on the different active sites (solid points indicate calculated data)

TABLE 1

Data for the rate of production of ethene from ethanol dehydration at 300°C on unmodified alumina.

Total reaction time (secs)	Ethene peak area (mm^2)	ln Area	Calculated area due to slow reaction	ln Area due to fast reaction
180	8,60	2,15	8,18	
390	10,30	2,33	8,15	
690	10,35	2,34	8,10	0,81
990	10,15	2,32	8,07	0,73
1290	9,70	2,27	8,02	0,52
1590	9,55	2,26	7,98	0,45
1890	9,35	2,24	7,93	0,35
2310	8,98	2,19	7,87	0,10
3750	7,62	2,03	7,68	
4050	7,68	2,04	7,64	
4320	7,59	2,03	7,60	
7110	7,25	1,98	7,23	
7500 (6 min stop)	7,18	1,97	7,18	

TABLE 2

Data for the rate of production of methane from ethanol dehydration at 300°C.

Total reaction time (secs)	Methane peak area (mm^2)	ln Area	Calculated area due to slow reaction	la Area due to fast reaction
180	8,12	2,09	1,69	1,86
390	5,64	1,73	1,63	1,39
690	3,92	1,37	1,55	0,86
990	3,16	1,15	1,47	0,52
1290	2,22	0,80	1,40	-0,20
1590	1,70	0,53	1,33	-0,99
1890	1,53	0,43	1,26	-1,31
2310	1,21	0,19	1,17	
3750	0,90	-0,11	0,91	
4050	0,87	-0,14	0,87	
4320	0,80	-0,22	0,83	
7110	0,52	-0,65	0,51	

Lane et al[12] and Katsanos and co-workers[28-31] have shown that modified and unmodified aluminas have more than one type of active site. Lane et al found three different active sites for n-heptanol dehydration at high concentrations on unmodified alumina at 305,5°C. For ethanol dehydration at 300°C there seems to be a number of differing active sites. Stop peak areas are plotted as log values against total reaction time. If first-order kinetics is assumed, the plotted curves may be broken down into a series of reactions occurring simultaneously on different sites. (A similar situation is the well-known simultaneous decay of radioactive isotopes). The rate constants calculated in this work are listed in table 3.

Two different sites for methane production as well as two for ethane production are indicated. It seems likely that there is conversion to methane on the more active sites.

Lane et al[22] found three different types of active sites for the dehydration of n-heptanol at 305,5°C when high amounts of the alcohol were injected. They used 3 and 30 ul (about 0,2 mmoles) of n-heptanol. Their results are reproduced below (table 4).

TABLE 3

Kinetic data for the dehydration of ethanol over unmodified alumina at 300°C.

	Rate const X10^4 (S^{-1})	Correlation coefficient	Intercept a_x	$\frac{a_1}{a_2}$	Number of data points	Symbol used
Methane	1,72	0,996	0,56	0,19	5	k_{M1}
	18,8	0,995	2,20		7	k_{M2}
Ethene	0,18	0,985	2,10	2,66	5	k_{E1}
	4,31	0,990	1,12		6	k_{E2}
Butene	0,73	0,926	1,34	-	5	k_B

TABLE 4

Dehydration of n-heptanol on unmodified alumina at 305.5°C (Reproduced from Lane et al, J Cat, 18, (1970), 281-296[22]

ul Heptanol injected	k_3 x10^4 (S^{-1})	k_{fast} x10^4 (S^{-1})	k_{slow} x10^4 (S^{-1})	$\frac{a_{fast}}{a_{slow}}$
3	-	8,45	1,13	1,53
30	20,4	9,31	2,24	0,95
30	33,8	12,0	2,86	2,2

Before comparing data with their work it is also worth noting that in their work activation of the catalyst was done at 400°C whereas 450° was used in the present work.

The review article of Knözinger and Ratnasamy[27] collects strong evidence that the catalytic activity of alumina is not directly related to the normal Lewis acid-base pairs created by regular dehydroxylation (removal of water from two neighbouring hydroxyl groups). They state that on heating (activation) at 400°C, 50% dehydroxylation has occurred and, therefore, the catalyst should have substantial activity. The data of many authors reported in the review show that substantially higher temperatures are required to produce highly active catalysts. The catalytic sites are thought to be "defect sites" created by irregular dehydroxylation processes.

Therefore, heating at 450°C to activate could produce some "defect sites" which would not be present if activation was done at 400°C.

Lane and co-workers[22] also provide information that ethanol is adsorbed differently to other alcohols. Only the carbon atom carrying the hydroxyl group is adsorbed onto the surface and thus the methyl group could be easily desorbed as methane leaving a species doubly bonded to the alumina surface. This process would occur on the more active sites.

Reaction of primary alcohols leads to the formation of the corresponding olefin. Ethene is the least stable alkene and, therefore, it is possible that methane is a preferred product. Lane et al do not mention the formation of methane in their work.

However, their work shows that when comparing the "slow reaction" rates, n-propanol is more reactive than ethanol, but the reaction rate then decreases to a constant value as the chain length increases. n-Pentanol was found to be less reactive than ethanol. Results presented later (3.3) for the dehydration of pentanol at 300°C indicated a slow reaction rate of $0{,}14 \times 10^{-4}\ S^{-1}$. Thus it would seem that the corresponding sites for ethanol reaction produce ethene ($k_{E2} = 0{,}18 \times 10^{-4}\ S^{-1}$).

However, when considering the "fast reaction" sites (for pentanol, $k_{fast} = 20{,}1 \times 10^{-4}\ S^{-1}$) it seems that slightly differing types of sites are actually involved. It seems possible that the "fast reaction" sites are a combination of sites which produce methane (k_{M1} = 18,8 x 10^{-4} S^{-1}) and ethene (k_{E1} = 4,31 x 10^{-4} S^{-1}).

The relative amounts of the various active sites can be obtained from the intercepts of the corresponding log (peak area) plots (table 3). From equation 2.5 we can see that

$$\frac{dx}{dt} = kf\ (a - x)$$

and that the constant in equation 2.6 is directly related to a, the initial concentration of reactant. As the alcohol is totally adsorbed, the various intercepts give the initial amount of reactant present on each type of site in the catalyst. Also it must be remembered that the detector response depends on the number of carbon atoms. (It is assumed to be a linear response). The comparison is tabled below (table 5).

TABLE 5

Relative concentrations of various active sites for ethanol dehydration over unmodified alumina at 300 °C.

Reaction rate $X10^4(S^{-1})$	Intercept	Corresponding area (mm^2)	Relative number of sites	Product
18,8	2,20	9,03	9,03	Methane
1,72	0,56	1,75	1,75	Methane
4,31	1,12	3,06	1,53	Ethene
0,18	2,10	8,17	4,09	Ethene
0,73	1,34	3,82	0,95	Butene

It can also be seen that the number of "fast reaction" sites producing ethene is relatively small and also that the number of "slow reaction - methane sites" is also small. Thus the main active sites are methane producing

$$(k_{fast} = 18,8 \times 10^{-4} S^{-1})$$

and ethene producing

$$(k_{slow} = 0,18 \times 10^{-4} S^{-1}).$$

When compared with the data obtained for n-pentanol at 300°C (3.3) we find a similar k_{fast} value of $20,1 \times 10^{-4}$ S^{-1}.

The amount of ethanol injected per run was about 0,1 mmols. Although this is a higher concentration than used in the pentanol reaction (0,04 mmol) (3.3) , we believe that the hypothesis of Lane and co-workers (viz three differing active sites) need not be evoked. It is also interesting to note the differences between the activites of the aluminas used. In the work of Lane and co-workers, the rate of the fast reaction is 5 - 10 times the rate of the slow reaction. In this work the rate comparison is about 100 times. This is possibly due to the higher activation temperature used, causing slow reaction sites to be converted into more active sites. Of course, it might just be due to differences in the samples of alumina used.

It can be seen from table 5 that the amount of polymerization is relatively small. As a variety of products was observed in the product spectrum in addition to ethene and methane, it is assumed that this process is a complex polymerization - depolymerization process. "Coking" was visually noted. Coking is the term used to describe the build-up of high molecular weight, hydrogen deficient carbonaceous species on the catalyst surface. It is assumed to result from the combination of adsorbed carbon species remaining after methane production. This would also account for the initial increase in butene product (fig 4) followed by the measured decrease in amount (k_B = 0,73 x 10^{-4} S^{-1}). It is possible that both ethene and methane could also be produced from desorption of species from these sites.

3.2.2 Conclusion

Ethanol is dehydrated over an alumina catalyst at a reaction temperature of 300°C. The major products formed are methane and ethene. Minor products are mainly polymerization products, butene being the most abundant species.

Alumina seems to have two types of active sites which occur in different relative abundance. They produce methane ($k = 18{,}8 \times 10^{-4}\ S^{-1}$) and ethene ($k = 0{,}18 \times 10^{-4}\ S^{-1}$). Methane and ethene are also produced in much smaller amounts with corresponding rates of reaction of $k = 1{,}72 \times 10^{-4}\ S^{-1}$ for methane, and $k = 4{,}31 \times 10^{-4}\ S^{-1}$ for ethene.

The favoured production of methane is probably due to it being a more thermodynamically stable product. The expected product olefin (viz ethene) is a less favoured product.

The ratio of "slow" to "fast" reaction rates (as defined by Lane et al[22]) is an order of magnitude higher than found in their work. This is probably due to either the higher activation temperature used or due to the aluminas having different properties.

Higher product formation and catalyst coking seem to be interrelated. It is proposed that the methane producing sites are the centres of coking activity.

The dehydration of ethanol over alumina at 300°C leads to a number of products being formed. The mechanisms and nature of the sites seem to be related to activation temperature and also depend on the alcohol which has reacted. The results are essentially in agreement with the work of Lane et al[22].

3.3 Reaction of pentanol on alumina

The dehydration of pentanol was studied as an example of a "typical" primary alcohol. It was hoped that the postulates put forward to explain the dehydration of ethanol could be further examined. Also it was hoped that the effect of water and the effects of added ions to the catalyst could be investigated. There is some controversy concerning the effect of the chloride ion[22, 26]. A mixture containing pentanol and internal standards pentane, pentene and hexane was used. Each injection contained about 0,04 mmol pentanol. Using pentene as an internal standard it was calculated that about $0{,}02 \times 10^{-3}$ mmol of pentene was produced initially during a three minute stop at 350 °C. Ignoring polymerization reactions, this is a conversion rate of $0{,}3 \times 10^{-3}\%$ per second.

For each run, 4 μl of the above mixture was used. Stop flow intervals were usually 3 minutes. Injector temperature was 300 °C, detector 350 °C, column 300 and 350 °C. Nitrogen flow was 30 ml/min and a FID was used for detection. All peak areas were recorded in mm^2 after correction for attenuation.

Inorganic ions were added by dissolving the ions in water, slurrying with the alumina and heating to dryness. In all cases, the catalyst was activated by heating it at 450°C for at least one hour prior to experimentation.

3.3.1 Results and Discussion

The raw stop-flow data are tabulated in Appendix 2, table 2 for a typical reaction of pentanol on unmodified alumina at 300° and 350°C. Polymerization products were found but in relatively small quantities. No "cracking products" (as with methane production from ethanol) were observed. The polymerization products were ignored in kinetic calculations. The kinetic data are gathered in table 6.

TABLE 6

Kinetics for the dehydration of pentanol over unmodified alumina at 300°C

Temp °C	Measured rate $X10^4$ (S^{-1})	Correlation Coefficient for curve	Inter-cept, a_x	$\frac{a_1}{a_2}$
300	20,1	0,993	3,42	0,97
300	0,14	0,945	3,45	
350	0,64	0,997	7,07	

As observed in 3.2 the reaction rates in this work differ fairly substantially from those reported by Lane et al[22]. Also it is possible to calculate an activation energy from the two sets of data for the slow reaction. The calculation yields:

$\frac{Ea}{R} = 10852$ or $Ea = 90 \text{ kJ mol}^{-1}$;

$\ln A_E = 16{,}97$ or $A_E = 23 \times 10^6 S^{-1}$.

These values are about half the magnitude of those obtained by Lane et al [22] for n-hexanol on 10% $^w/w$ KCl on Al_2O_3 (Ea 177 $kJmol^{-1}$, A_E 5 x $10^{11}S^{-1}$).

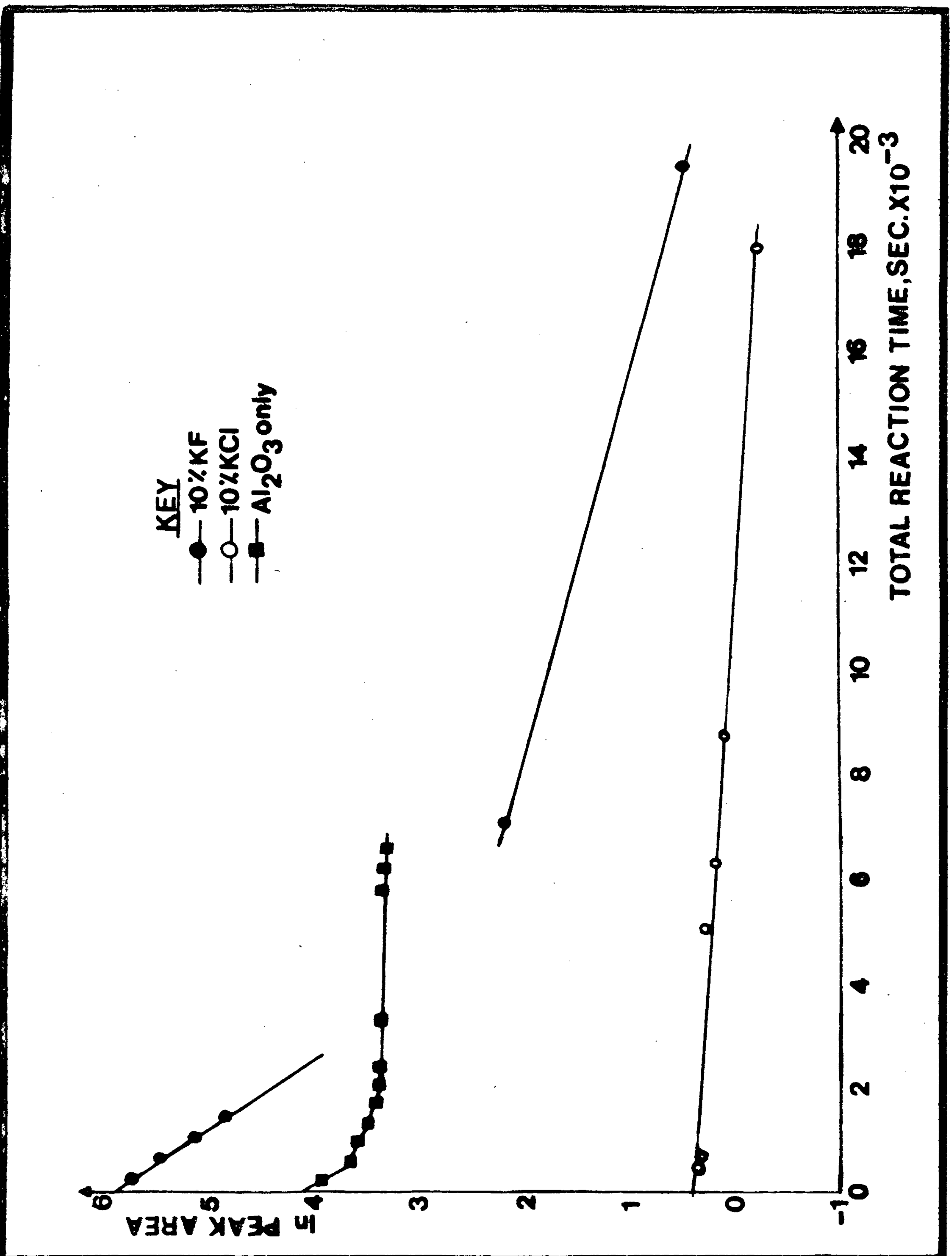
Before discussing the differences between these values, it is necessary to discuss the effects of inorganic ions on the activity of alumina. Results for runs with 10% $^w/w$ KF on Al_2O_3 and 10% $^w/w$ KCl on Al_2O_3 are gathered in Appendix 2, table 3. They are shown graphically in fig 8.

The following observations can be made. Firstly KF greatly enhances the activity of the catalyst. It can also be seen that no "slow reaction" site is evident even after 18 000 seconds of reaction. Although the less active site is still probably present, the effect of KF seems to be to convert "slow" sites into much more active sites. It seems unlikely that this increased activity is due to the K^+ cation, especially when Jirátová and Beránek[26] found deactivation with Mg^{2+} and Na^+.

They found that unmodified alumina had only strong and weak acid sites, with no intermediate acidity. Addition of Cl^- resulted in conversion of both strong and weak sites into sites of intermediate acidity. The overall acidity increased.

FIGURE 8

Effect of added ions on the activity of alumina to pentanol dehydration at 300°C



Addition of F^- resulted in an increase in the number of strong acid sites while the weak acid sites were converted into sites of intermediate acidity. The overall acidity increased.

Sodium, however, caused a disappearance of all strong acid sites coupled with a decrease in the number of weak acid sites. The overall acidity dropped dramatically. It is felt that K^+ would behave similarly.

According to Jirátová and Beránek[26] the reactivities (reaction rate) of the modified aluminas followed the following sequence for the conversion of 1- butanol at 573 K:

$F^- \simeq SO_4^{2-} \gg Cl^- > PO_4^{3-} \simeq Zn^{2+} \simeq \text{none} > Mg^{2+} > Na^+$.

This is slightly different to the sequence of acidity:

$SO_4^{2-} > F^- > PO^{3-} > Cl^- > Zn^{2+} > \text{none} > Mg^{2+} > Na^+$.

Therefore, even though Cl^- modified alumina has increased acidity compared with unmodified alumina, the reactivity is not enhanced to any great extent. Generally then, Cl^- and Na^+ cause disappearance of strong acid sites while F^- causes a large increase in the number of highly acid sites.

Thus it would be expected that the addition of KCl would cause disappearance of strong acid sites with some increase in acid sites of intermediate activity. Equating strong acid sites to "fast" reaction sites shows that this seems to occur, ie addition of KCl cause a marked decrease in the number of "fast" reaction sites (here they are almost totally eliminated) while the number of "slow" reaction sites is relatively unchanged.

On the other hand, the presence of KF would lead to a decrease in the number of "slow" sites accompanied with an increase in the number of "fast" sites. The results of Jirátová and Beránek[26] also tend to indicate that the increase in activity due to the presence of F^- is much larger than the decrease in activity due to the presence of alkali ions.

Therefore it can be seen that the results of this work, the work of Lane et al[22] and Jirátová and Beránek[26] are all in agreement.

The presence of KCl could result in an increase in the required activation energy. The activation energy for pentanol reaction on "slow" sites at 300°C is about half that found by Lane et al[22] for n-heptanol at 305°C for 10% KCl-modified alumina. However this difference could also just be due to differences in the aluminas used. However Cl^- could form an ion pair with strong acid sites reducing the overall acidity of the site. Thus more energy would be required to form an activated complex (adsorbed alkoxide species).

Not only does KCl change the ratio of active sites, it also causes a decrease in the rate of reaction. This fits the observation of a higher activation energy being needed.

Thus the effect of KCl on alumina is to deactivate the catalyst, reduce drastically the number of "fast" reaction sites, and to cause a twofold increase in the activation energy required for reaction.

Finally, the effect of water on the reaction rate was investigated. The raw results are gathered in appendix 2, table 4, and shown graphically in fig 9.

The relative increase in reaction was calculated for each injection of water (table 7).

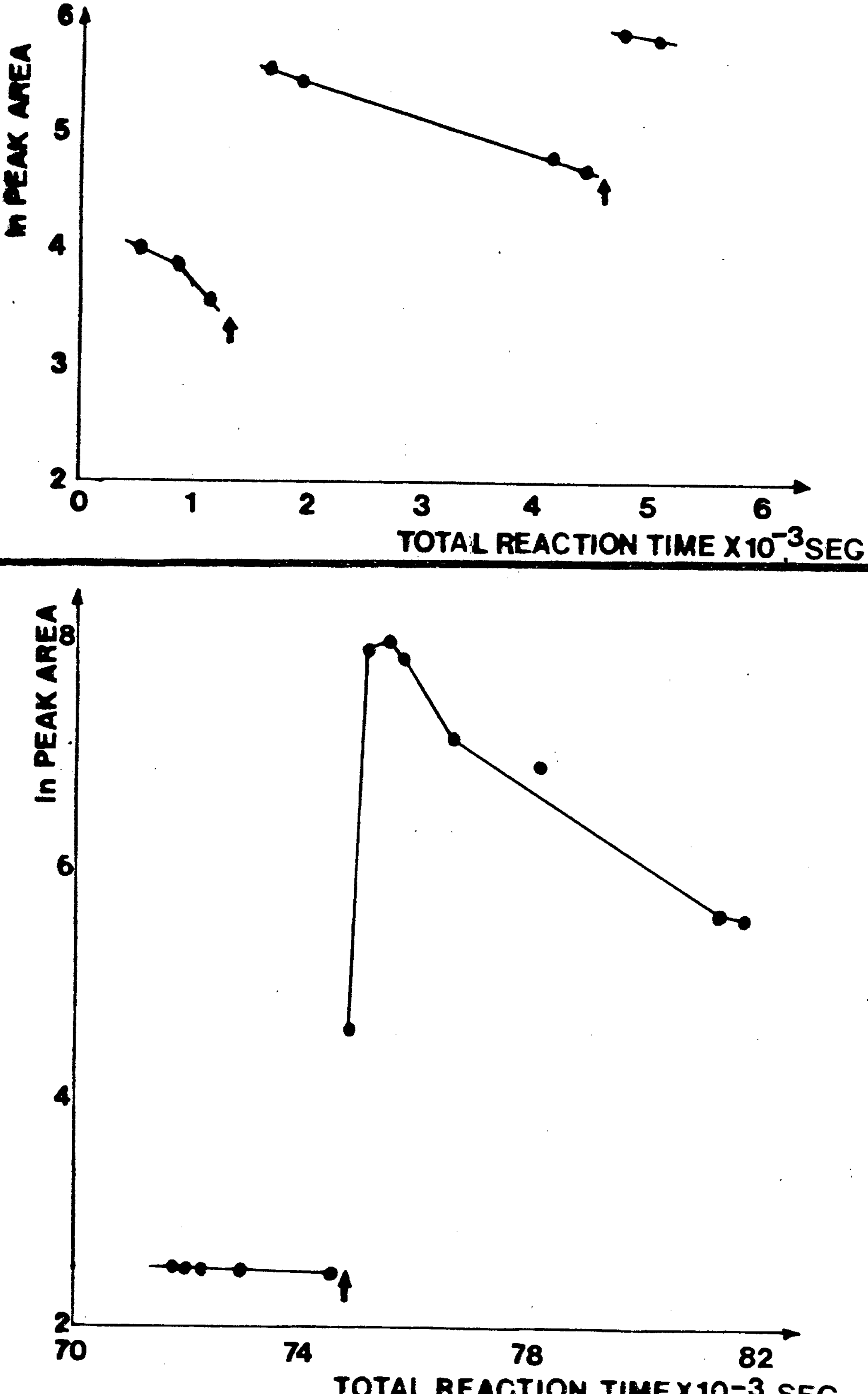
TABLE 7

Effect of water on the relative amount of pentene produced during the dehydration of pentanol over unmodified alumina at 300 °C

ul H_2O injected	Pentene peak area prior to injection (mm^2)	Maximum pentene peak area after injection (mm^2)	Difference in area (mm^2)	Relative Change in area
4	109,4	362,3	252,9	0,23
8	35,4	263,0	227,6	0,64
100	11,7	2 851,2	2 839,5	24,3

FIGURE 9

Effect of water on the activity of unmodified alumina to pentanol dehydration at 300°C



The effect of water is of relatively long duration when it is considered that water has a relatively short retention time in an alumina column. Thus the effect of water must be to activate sites which were previously inactive although the alcohol has been adsorbed onto the surface. The tremendous increase in reaction when 0,1 mls of water was injected indicates how few adsorption sites on the alumina are catalytically active under normal conditions. The rate of decrease of reaction after addition of water seems to indicate that the effect of water is to convert the "slow" reaction sites into "fast" reaction sites.

3.3.2 Conclusions

Pentanol is dehydrated to pentene at 300° and 350°C over an alumina catalyst. Two broad types of active sites are indicated which produce pentene. Other products are produced in small amounts. The energy of activation for the conversion of pentanol is 90 $kJmol^{-1}$. This is lower than the value obtained by Lane et al[22] for a KCl-modified alumina catalyst.

Modification with KCl reduces catalytic activity while addition of KF enhances activity. More specifically K^+ seems to reduce activity drastically, Cl^- seems to deactivate the active or "fast reaction" sites and F^- greatly enhances the activity of the catalyst, mainly by increasing the number of "fast reaction" sites.

Water has a large effect on the amount of products produced but does not seem to enhance the rate of reaction. It seems likely that water transforms inactive sites into very active ("fast") sites.

It can, therefore, be seen that the activity of the alumina catalyst can be significantly affected by the presence of inorganic ions as well as the presence of water.

Similar reactive sites are involved in the dehydration of ethanol and of pentanol.

3.4 Concluding comments

Two major types of active sites exist for the dehydration of alcohols over alumina catalysts. These sites are very sensitive to the presence of inorganic ions. Anions tend to enhance catalytic activity while cations affect the catalyst adversely.

The dehydration of pentanol follows the expected pattern of conversion into the corresponding olefin and water. With ethanol however, the more active sites cause "cracking" of the adsorbed species resulting in the production of methane as well as ethene.

The addition of KCl leads to a decrease in reaction rate. This seems to result from an increase in the activation energy required for reaction in the presence of KCl.

It can be seen that the activity of alumina catalysts can be radically altered by various means. Thus any investigations need to take into account any differences in the catalyst used.

CHAPTER 4

THE REACTION OF ALKANES OVER ZEOLITE Y. SOME ASPECTS OF THE REACTION

4.1 Introduction

During initial investigations of various catalysts and various reactions, it was found that hexane was cracked on zeolite Y at high temperatures. It was decided that this system be studied even though a review of the literature showed that the reactions of alkanes on zeolites and other catalysts have been fairly extensively studied.

However, even though there is a large volume of literature on the subject, there is a general lack of consensus over various factors. It was hoped that reaction chromatography and especially stop-flow chromatography could provide information concerning the reaction and the reaction mechanism. Most work to date has involved the use of chemical reactor systems.

Scott, Phillips and co-workers[23-25] have studied the hydrocracking of alkanes over a $Ni-SiO_2$ catalyst using various chromatographic techniques. They found a fairly simple reaction mechanism. The alkane is chemisorbed and a terminal carbon "split-off". The resulting species is then desorbed. This process may recur. Thus a range of products is produced. Most mechanisms proposed for reaction on zeolite catalysts are complex. It was hoped that this work would help elucidate the mechanisms involved.

Zeolite is a complex heterogeneous surface with a large range of active sites. Whan[32] states that removal of ammonia from the ammonium-exchanged form of a zeolite produces Brönsted sites while removal of water (dehydroxylation) creates Lewis sites (fig 10).

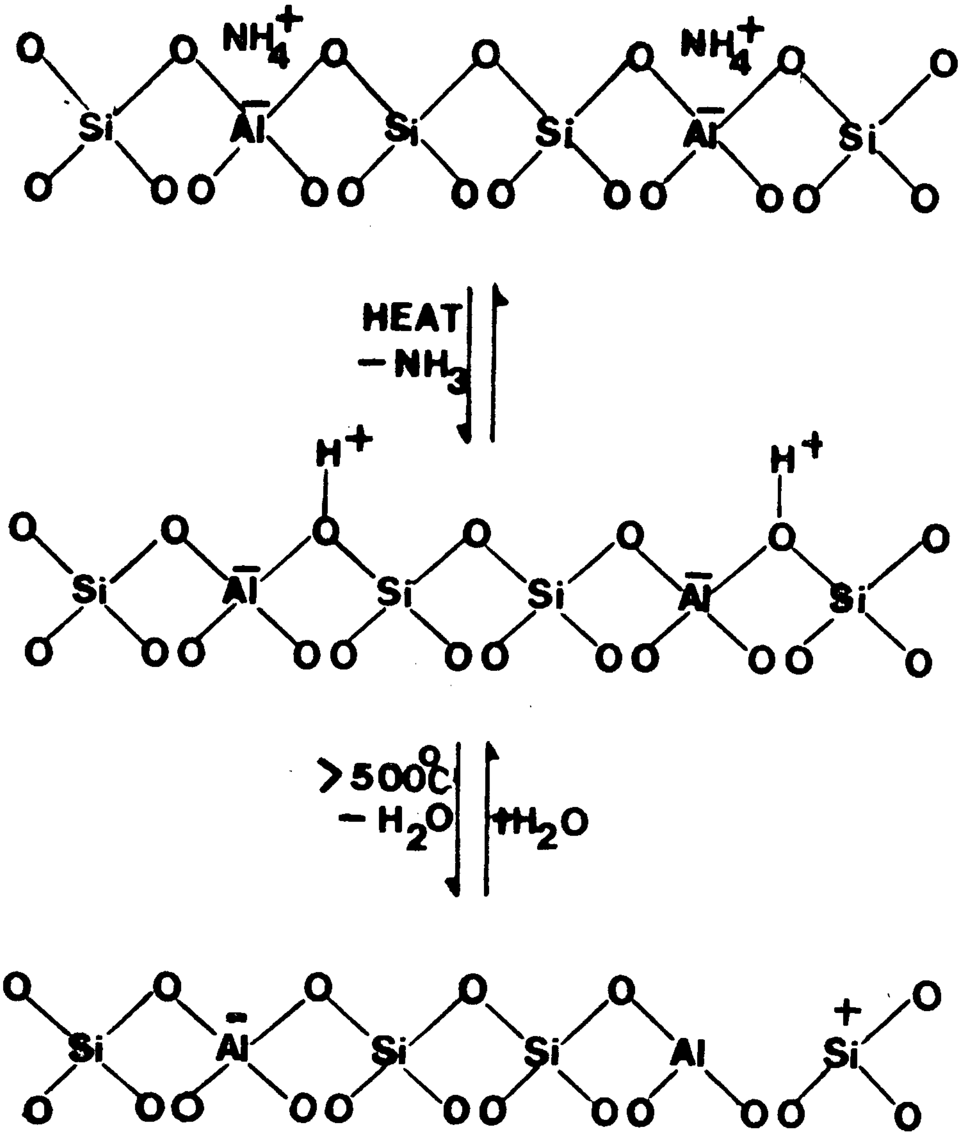


FIGURE 10

Diagram showing the effect of heating the ammonium exchanged form of a zeolite

A large volume of literature has been devoted to the nature of the active sites, the effects of various factors and the mechanisms of reactions over zeolite catalysts.

Catalytic activity has been related to the acidity of the catalyst. For instance, Barthomeuf and Beaumont[33] have found that the active sites are strongly acidic aluminium sites. Selectivity depends on the sodium ion content of the catalyst.

Increasing the sodium ion content also decreases catalyst activity[34] and decreases the number of Brönsted acid sites and their acidity[35]. In fact, Fejes et al[36] totally deactivated zeolites with sodium vapour.

The mode of catalyst preparation also affects its activity[37-41]. The ammonium exchanged form of zeolite Y releases ammonia when heated to between 400° and 500°C. Both Benesi[37] and Hopkins[39] found that zeolite Y became totally inactive to alkanes if pretreated at a temperature of 650°C or higher. Hopkins found that the maximum activity for craking of n-hexane and n-heptane at a reaction temperature of 350°C could be obtained by activation at about 550°C. This seems to indicate that partial dehydroxylation (550°C) increases activity but removal of too much water destroys the activity of the catalyst (possibly as a result of destruction of the zeolite structure).

Hopkins[39] also found differences in ammonia removal depending on the surrounding atmosphere (oxygen or nitrogen).

On the basis of this information it was decided to pretreat the catalyst by heating to 450°C under nitrogen for at least one hour. Although this would not result in the most active catalyst it would be suitable for comparative work. Also at this temperature the number of Lewis sites should be small and any activity should be due to Brönsted sites caused by the removal of ammonia.

Many proposals concerning the reaction mechanisms have been put forward[42-48]. Tung and Mininch[42] proposed a carbonium ion mechanism via a surface bound olefin. The mechanism applies both to alkanes[42,43,45] and alkenes[44]. Weitkamp and Schultz[45] studied the reaction of a n-dodecane (250-500°C; a feed molar ratio of H_2:n-dodecane of 20). They found the ratio of small to large products increased with temperature. No significant amounts of olefins were found in the reactor effluent. John et al[47,48] came to similar conclusions.

Weeks et al[49] and Daage and Fajula[50] used ^{13}C- labelled alkanes to study the reaction mechanism. Weeks et al studied the reaction of n-nonane at 230°C after activation in vacuum at 500°C. Their results led them to conclude that the observed product distribution was a result of a "temperature dependent random desorption and cracking of a complex precursor". Major products were pentane, iso-pentane, butane, iso-butane and propane, the lightest product formed. Insignificant quantities of products are formed from simple scission of the reactant.

Daage and Fajula[50,51] studied the reaction of branched hexanes over H-mordenite at 170°C (after activation at 550°C in dry air) in a hydrogen stream. Propane was the lightest product and only traces of olefins were found. Cracking was seen to be a result of a complex polymerization-depolymerization process. B-scission of a 2-methyl-pentenium-4 cation is the proposed initiator. Intramolecular isomerization involves a complex series of reactions. Alkyl shifts, branching rearrangements and interchange between internal and external carbon atoms are mechanisms proposed.

Coke formation is directly related to product formation. Langner[52] studied the reaction of olefins on NaH-Y zeolites at 250°-400°C after activation at 350°C under nitrogen. No hydrogen gas was mixed with the reactant. He proposed the participation of coke precursors (cyclic aromatics) in the reaction sequence.

The reaction of butene led to a mixed olefin and paraffin product spectrum. The ratio of olefin to paraffin decreased with increasing carbon number. An "induction period" was found prior to the formation of alkanes indicating the role of coke formation in the reaction sequence.

Catalyst deactivation was quicker at lower temperatures. He showed[53] that below 300°C, catalyst deactivation was caused by strongly absorbed species in the pore system while at higher temperatures the blocking of entrances with macromolecules occurred.

The nature of the coke seems to be independent of the reactant species[59]. Rollman and co-workers[54-57] also showed that the amount of coking depends on the zeolite pore structure. A mixed feed was reacted in the presence of hydrogen at 316-528°C after activation at 500°C. Zeolite Y had the highest coke yield. They proposed that alkylation of aromatics is the first step in the coking process. Composition and crystal size of the zeolite seem to be of secondary importance. Intercrystalline coke is seen to be a shape selective reaction directly controlled by the zeolite pore structure.

Hano et al[58] have found that burning the coke formed in air is not dependent on the origins of the coke and is almost independent of particle size.

As can be seen the reactions of alkanes and alkenes on zeolite catalysts have received much attention. A carbonium ion mechanisms involving olefinic intermediates is proposed and, therefore, alkanes and alkenes crack via similar mechanisms.

The reaction mechanism is complex and probably involves formation of coke species prior to formation of product alkanes. Only traces of olefin products are found from the reaction of alkanes and the product spectrum is temperature dependent.

Deactivation of the catalyst by coking increases with a decrease in temperature and the nature of the coke seems to be independent of the reactant used. Coke formation seems to be a shape selective process controlled mainly by the zeolite pore structure.

It was hoped that reaction chromatography could help clarify the reaction mechanisms involved in cracking of alkanes over zeolite catalysts.

4.2 Effect of temperature on the reactivity of various alkanes

The method of microreactor-stop-flow chromatography seemed suitable for studying the change in reaction rate with temperature. If the same stop interval is used throughout the series of experiments the resulting product peaks from the stop interval are representative of the reaction rate and can be used to compare the reaction at different temperatures.

Flowrates were adjusted for each run so that the reaction occurred on a similar part of the zeolite plug in all cases. Although this would eliminate any errors due to differing activities in different parts of the column it did not take into account any deactivation of the catalyst (4.4).

Prior to the series of experiments the catalyst was activated for one hour under nitrogen at 450°C. 5 µl of the reactant was used in all cases with 200 second stops. The detector (FID) temperature was 350°C, injector temperatures were varied (usually 10°C higher than column temperature). The total injected area of reactant was calculated from the peak area of a similar injection onto a squalane column.

As high temperatures were used no suitable commercially available stationary phase could be found. Thus the analytical columnn consisted of 10% zeolite Y on chromosorb W. However, as reaction would occur on this part of the column as well, runs without a stop were performed in each case to calculate the amount of reaction during elution. The raw data is collected in appendix 3, table 1. Chromatograms recorded for pentane, hexane and heptane at 240°C are shown in fig 11. The calculations required to determine the extent of reaction are collected in appendix 4. The calculated results are contained in table 8 and shown graphically in fig 12.

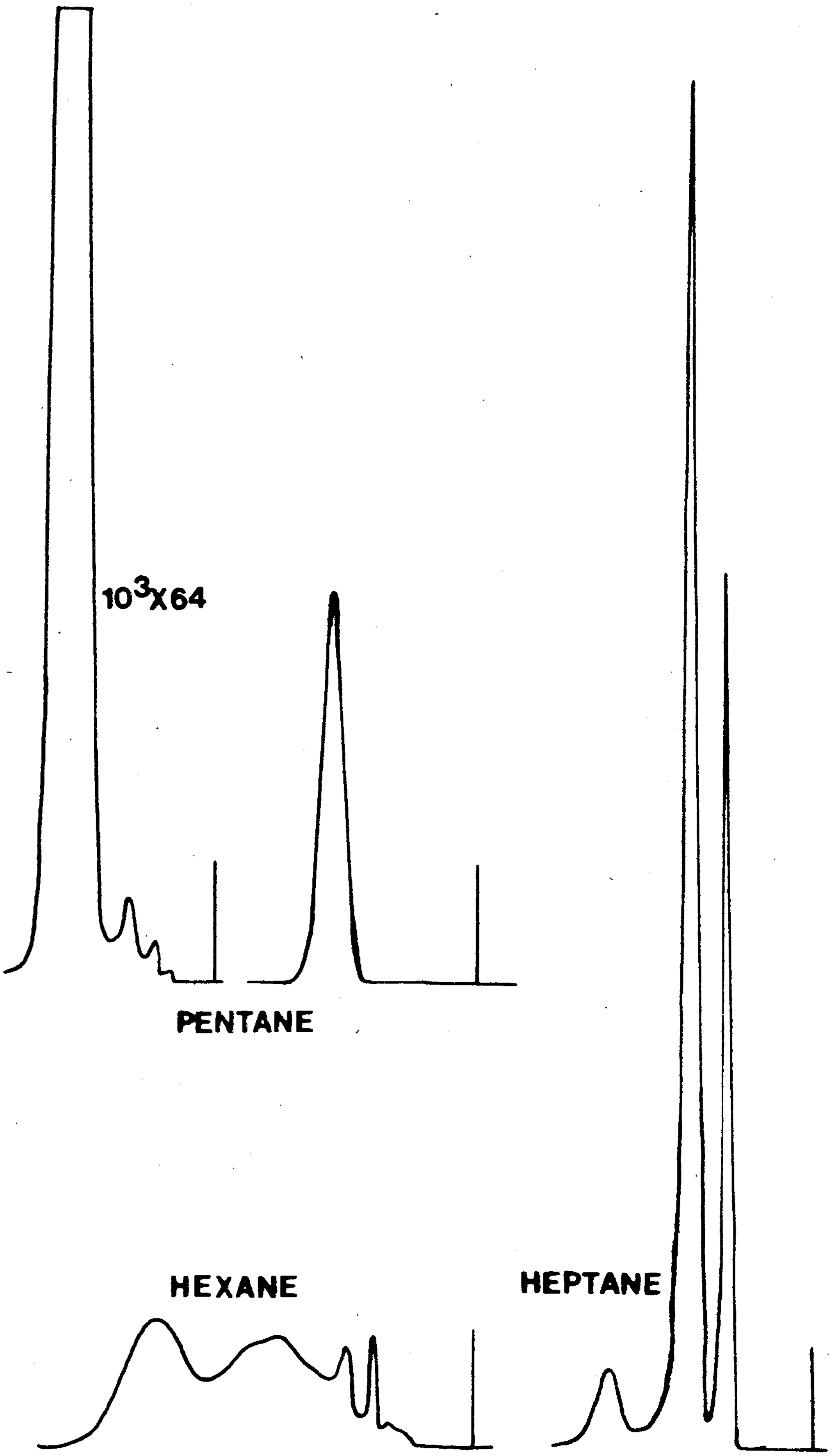


FIGURE 11

Chromatograms showing the difference in the reactivity of pentane, hexane and heptane at 240°C; all conditions the same. Attenuation $10^3 \times 256$.

TABLE 8

Calculated data showing the effect of temperature on the reactivity of various alkanes over zeolite Y

Temp °C	Total product area after a stop-flow run	Calculated product area due to stop interval only	Calculated Nonvolatile products produced during stop interval	% Volatile products produced during stop	% Nonvolatiles produced during stop
Pentane					
240	4	4	8	96	1
260	184	156	92	22	13
275	349	289	64	41	9
290	501	477	112	68	16
Hexane					
210	5	5	108	0,4	9
220	50	28	131	2	10
230	136	103	60	8	5
240	500	479	200	38	16
250	622	583	319	47	26
260	502	452	552	36	44
Cyclohexane					
220	61	44	122	3	9
230	225	202	268	16	21
235	349	320	423	25	33
240	595	561	500	43	38
260	733	691	443	53	34

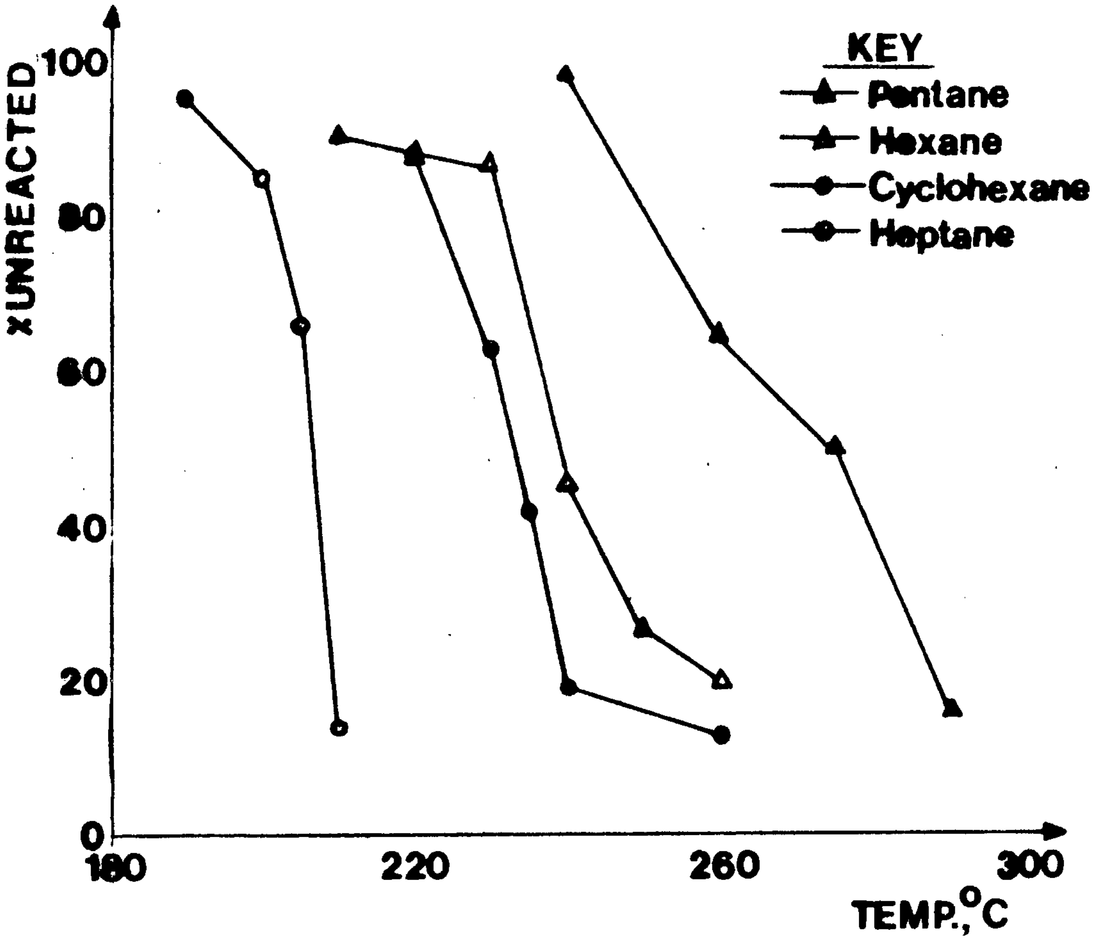
continued/...

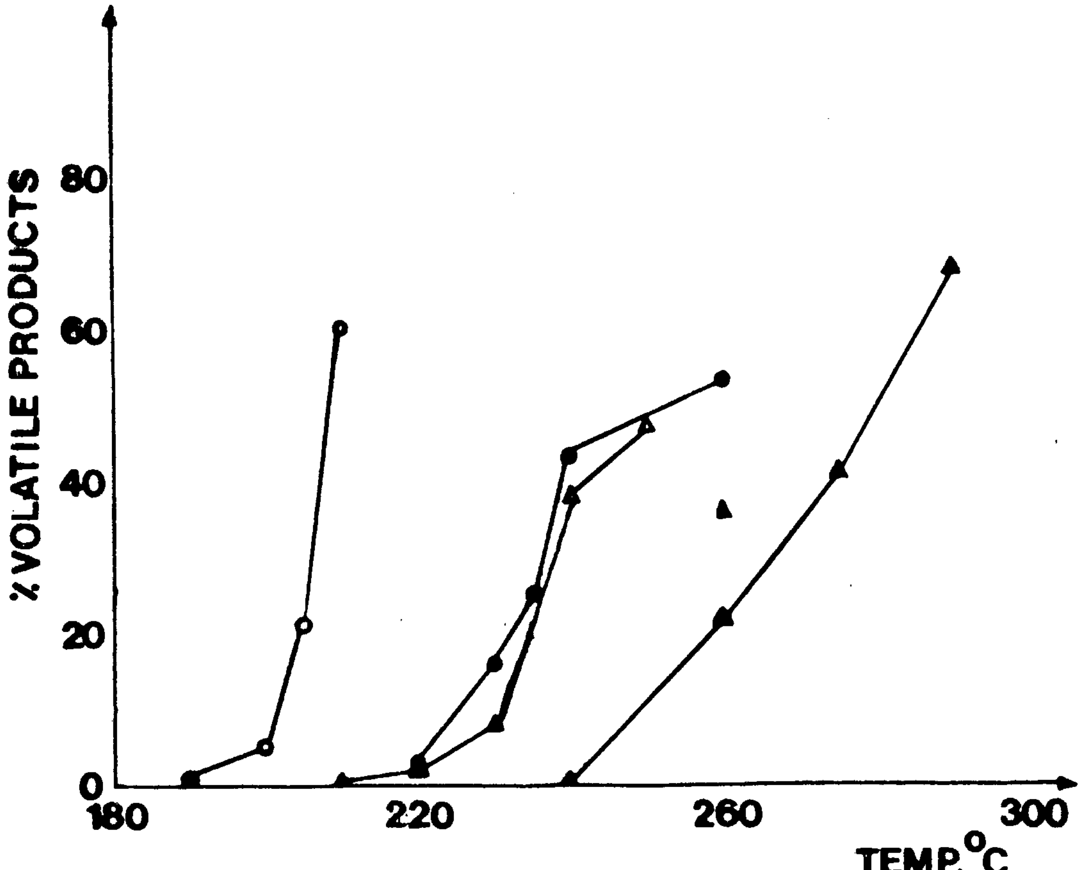
TABLE 8 continued ...

Temp °C	Total product area after a stop-flow run	Calculated product area due to stop interval only	Calculated Nonvolatile products produced during stop interval	% Volatile products produced during stop	% Nonvolatiles produced during stop
Heptane					
190	27	18	61	1	4
200	86	65	146	5	10
205	335	301	183	21	13
210	876	839	359	60	26

FIGURE 12

Graphs showing the effect of temperature on amount of reaction for various alkanes on zeolite Y





All profiles show a rapid increase over a fairly small temperature range. It can also be seen that the curves become increasingly steep as the size of the reactant molecule increases. Cyclohexane seems to be more susceptible to cracking reactions than hexane. The retention time of cyclohexane is longer than that of hexane on a zeolite column. Thus cyclohexane is more strongly adsorbed by zeolite, and this could account for its slightly higher reactivity.

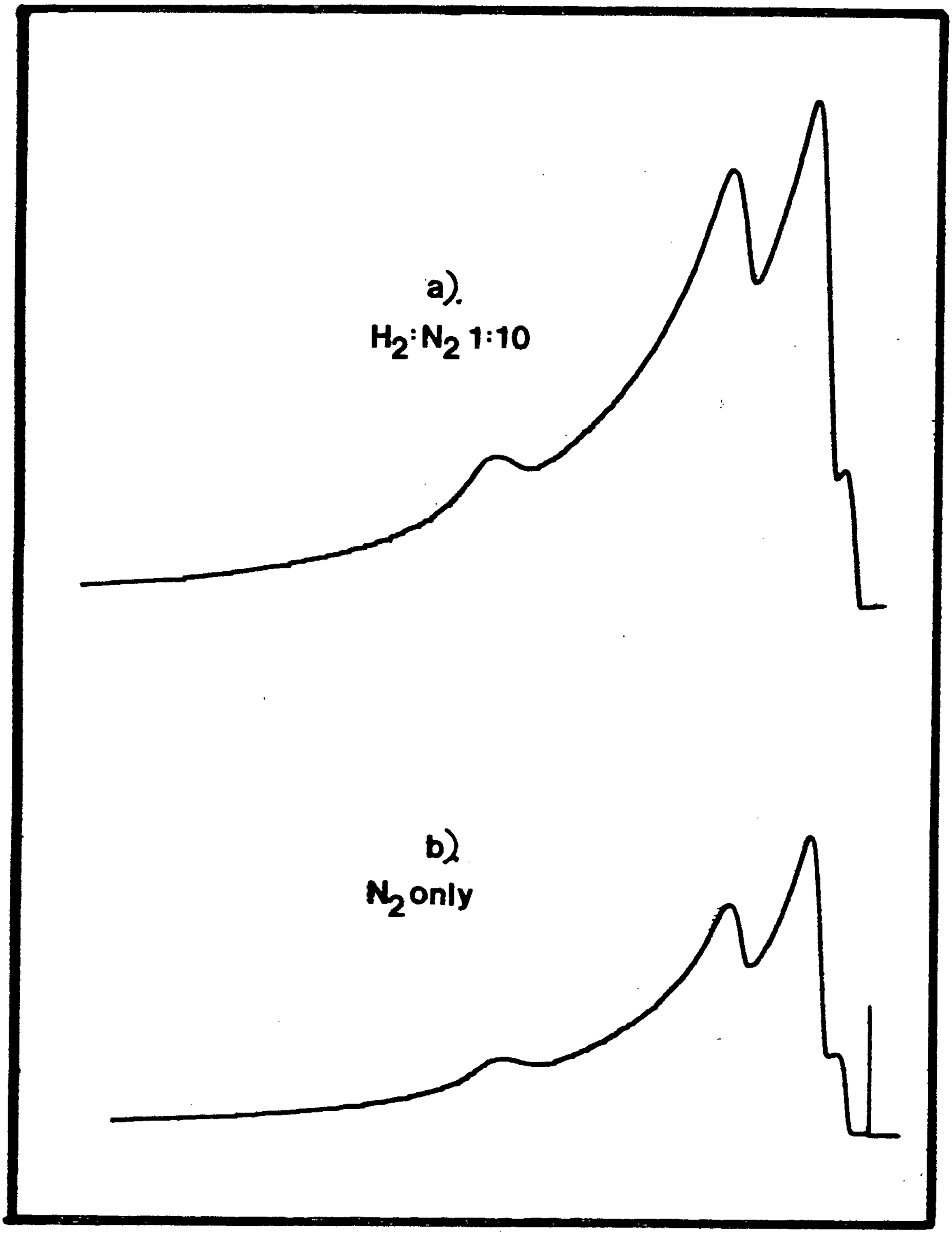
It can be seen that heptane is fairly reactive above 200°C, hexane and cyclohexane above 225°C, and pentane above 250°C. This might explain to some extent the complex reaction mechanisms observed by some authors. High temperatures would result in the products themselves being highly reactive and result in a complex range of products not easily interpreted.

Hexane and cyclohexane gave three product peaks which were identified as probably propane, butane and pentane. Hexane, as well, was observed from the reaction of heptane. Pentane cracked to propane and butane.

It is also worth noting that these reactions occurred in a nitrogen atomosphere. It is expected that in a hydrogen atmosphere there would be more reaction. Fig 13 shows two elution chromatograms for 5 µl injections of heptane onto a 0,5 m zeolite column at 170°C in the presence of hydrogen and nitrogen. Attenuation, chart speed, flowrate, temperature and amount of heptane injected are constant in both runs. An increase in the amount of volatile products is found. Hydrogen probably causes hydrogenation of adsorbed unsaturated species leading to more volatile products being formed. The remaining heptane peak was not recorded. Peaks evident are due to the four cracking products.

FIGURE 13

Elution chromatograms for heptane under similar conditions except that a) has hydrogen (10%) in the carrier gas (nitrogen).



Langner[53] states that coking increases with decreasing temperature. For each species there seems to be a general trend that the amount of totally adsorbed products increases relative to the volatile products with decreasing temperature. The results are not conclusive. However results obtained on a 0,5 m zeolite column at 160°- 180°C show an increase in the ratio of volatile products to nonvolatile products with increasing temperature for the reaction of heptane (table 9).

In these studies the catalyst was reactivated prior to each run by heating at 450°C under air for one hour followed by one hour under nitrogen at the same temperature.

Catalyst deactivation (4.5) with reaction time probably accounts for the inaccurate data obtained using reactor stop-flow chromatography.

Thus as the temperature increases, the relative amount of nonvolatile products decreases.

In conclusion, heptane becames fairly reactive on zeolite Y (pretreated at 450°C under nitrogen) at about 200°C, hexane and cyclohexane at about 225°C and pentane at 250°C. Volatile products are alkanes of lower carbon number. Propane was the lightest product found. A hydrogen atmosphere greatly enhances the amount of volatile products formed when compared with a nitrogen atmosphere.

Coking tends to increase as temperature decreases for the reaction of a particular reactant species.

TABLE 9

Effect of temperature on the products formed during the reaction of heptane over zeolite Y. Total injected area was 1260 (porapak column 170°C).

Temp °C	Area of volatile products	% Volatile products	Area of remaining heptane	% Hexane remaining	% Nonvolatile products	% Volatiles / % Nonvolatiles
160	441	35	156	12	53	0,66
170	501	40	240	19	41	0,98
180	796	63	83	7	30	2,10

4.3 Effect of stop time and temperature on the product spectrum of hexane

Lane et al[22] have shown that any polymerization or sequential reaction and also any autocatalytic effects can be easily monitored if stop-flow chromatography with varying stop times is used.

If no sequential reactions are present, the ratios of the various products formed during the reaction should be independent of stop interval length. Thus it could be possible to gain information concerning the reaction mechanisms by studying the product spectrum after different stop lengths.

Most authors have found that the reaction of alkanes on zeolites occurs via complex mechanisms. It was hoped that this study could help to elucidate the mechanisms involved.

Reactor-stop-flow chromatography provides a quick and easy method for obtaining data for different stop lengths. Hexane was chosen as it was hoped that the ratios of the various products formed would be easily interpreted.

A series of runs were performed where the stop time was varied while all other parameters were kept constant. As it was strongly suspected that the catalyst was deactivated by coke formation, the stop time lengths were chosen in a random rather than sequential order to remove any bias in the results. The time from injection to the beginning of the stop was kept constant and it was therefore assumed that the reaction occurred in the same section of the reactor plug during each experiment.

2 µl injections of hexane were used. Prior to the series of experiments, a newly packed column of catalyst was activated by heating for one hour under nitrogen at 450°C. On changing temperature, the catalyst was reactivated by heating at 450°C under air for one hour followed by an hour at 450°C under nitrogen. Experiments were done at 250° and 260°C. Results are listed below (table 10) and shown graphically in fig 14. Raw data obtained is collected in appendix 3, table 2.

At both temperatures, the ratio of products 2 (butane) and 3 (pentane) relative to product 1 (propane) follow similar trends. At 260° C the ratio of butane to pentane increases sharply with stop time while it is relatively unaffected by stop time at the lower temperature (250°C).

The results indicate that the amount of propane increases relative to that of butane; propane increases relative to pentane and butane increases relative to pentane as the stop time increases. In other words, as the stop time increases the smaller products are being formed at the expense of the larger products. The amount of smaller products formed also increases with temperature.

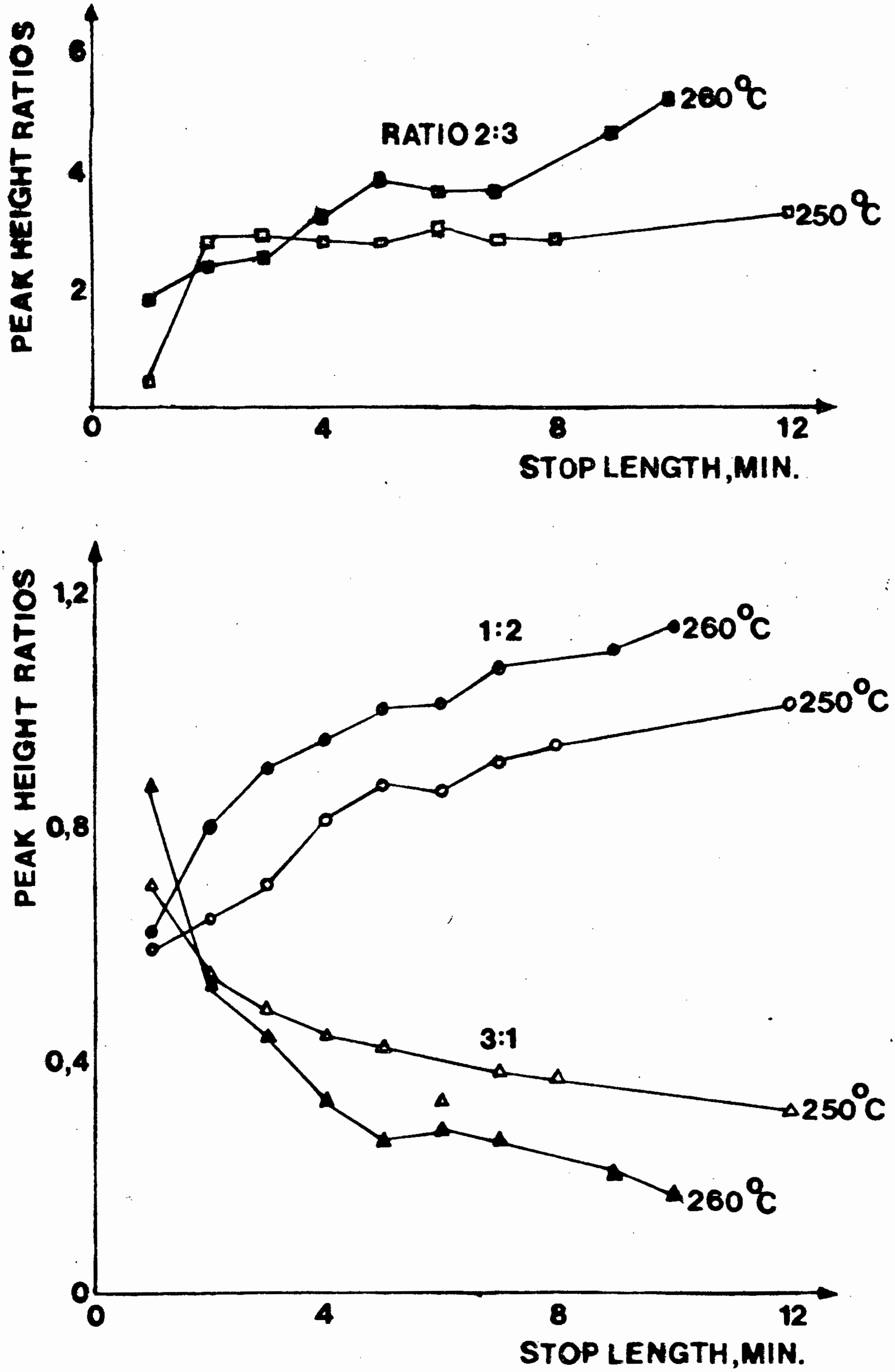
TABLE 10

Effect of stop time and temperature on the relative ratios of the cracking products of hexane over zeolite Y

Temp °C	250			260		
Peak Height Ratios	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{3}{1}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{3}{1}$
Stop-time interval (mins)						
1	0,59	0,42	0,70	0,62	1,85	0,87
2	0,64	2,80	0,55	0,80	2,36	0,53
3	0,70	2,90	0,49	0,90	2,50	0,44
4	0,81	2,79	0,44	0,95	3,17	0,33
5	0,87	2,74	0,42	1,00	3,87	0,26
6	0,86	2,99	0,33	1,01	3,59	0,28
7	0,91	2,88	0,38	1,07	3,65	0,26
8	0,94	2,85	0,37	-	-	-
9	-	-	-	1,10	4,60	0,20
10	-	-	-	1,14	5,12	0,17
12	1,01	3,16	0,31			

FIGURE 14

Effect of stop length on the relative amounts of products formed from hexane reacting on zeolite Y at 250° and 260°C



The rapid increase of ratio $\frac{2}{3}$ at 260°C combined with the more rapid decrease of $\frac{3}{1}$ at 260°C seems to indicate that at the higher temperature any pentane formed by the reaction is readsorbed and reacted to a higher extent at 260°C. The results of 4.2 shows that penatane is fairly reactive at 260°C.

The fact that the ratios change with stop time is not readily explained by a reaction sequence involving polymerization-depolymerization. It seems that it is also due to further reaction of pentane during the long stop periods. As no flow is occurring, the desorbed pentane is in the vicinity of the reaction area (high coke build-up) and could easily react further. Also as the amount of pentane increases, its further reaction would tend to increase the production of further products.

The rate of change of ratio $\frac{2}{1}$ at both temperatures is remarably similar. Log plots of product peak ratio versus stop time length gave the rate of change to be 0,050 at 250°C ($r = 0,92$) and 0,055 at 260°C ($r = 0,89$) and this tends to indicate that any butane and propane that is produced does not further react, even at the higher temperature.

Thus there seems to be little indication that a series of sequential reactions is occurring except to a small extent where the pentane formed is further cracked.

The fact that the amount of propane (peak 1) formed is not a major product indicates that no cleavage of hexane into two propane molecules occurs to any significant extent. Also the fact that no ethane or methane is produced indicates that for each hexane molecule that reacts only part of it is converted into volatile products. This is also indicated by the results of 4.2 where a large amount of coking was found.

The fact that the ratio $\frac{1}{2}$ increases with stop time tends to indicate that the pentane reacting preferentially produces propane to butane.

Thus the results tend to indicate that hexane is adsorbed, reacts and forms an intermediate species which releases cracking products pentane, butane and propane. The pentane produced further reacts to form mostly propane and butane to a lesser extent. There seems to be no direct evidence of a molecular cleavage mechanism or a stripping mechanism (whereby terminal carbon groups are sequentially removed from the parent substance).

It was noticed that the hexane peak height seemed to decrease at a constant rate as stop time increased. It was realised that a plot of stop interval length (seconds) against log of the remaining hexane peak height could give a measure of the rate of disappearance of the reactant. In this experiment results obtained are not precise due to two factors. Firstly, as the "analytical" section of the column was 10% w/w zeolite on Chromosorb W further reaction would occur during elution. Also, as catalyst deactivation was continually occurring results for later runs are less than would be expected for an active catalyst.

This method of determining reaction rates can be used when polymerization or other sequential reactions are occurring. However, it is not suitable if, for example, autocatalysis or product inhibition is occurring. Calculation of kinetic data yielded reaction rates of $26,4 \times 10^{-4}$ S^{-1} ($r = 0,975$) at 250°C and $46,9 \times 10^{-4}$ S^{-1} ($r = 0,973$) at 260°C. These results are discussed further in section 4.7.

4.4 EFFECT OF THE AMOUNT OF HEXANE INJECTED ON THE AMOUNT OF PRODUCTS FORMED

A series of runs were performed using the microreactor stop-flow chromatography system already described to study the effects of amount of reactant injected. A 1,5 m column was used and as products were not entirely separated, a total product area was calculated. The results are collected in table 11 and shown graphically in fig 15.

The trends found are what would be expected. At higher concentrations the amount of products formed would be greater, assuming that the reaction has first order kinetics.

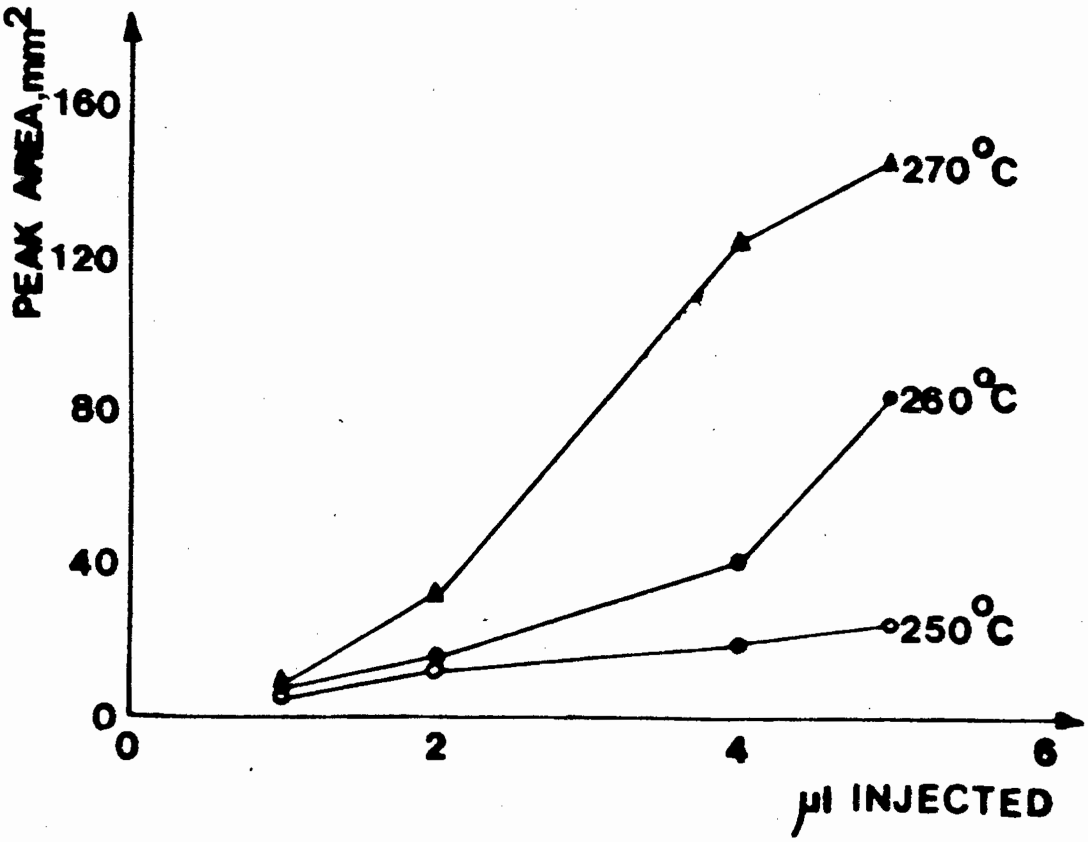
TABLE 11

Effect of the amount of hexane injected on the amount of reaction at various temperatures over zeolite Y

Temp °C	Total Product Area for a 2 min Stop for various injected amounts			
	1 µl	2 µl	4 µl	5 µl
250	5	12	19	25
260	7	16	41	83
270	9	31	122	146

FIGURE 15

Effect of injected volume on the relative amount of reaction at various temperatures for hexane on zeolite Y



4.5 Studies of catalyst deactivation

During initial investigations into the reactions of alkanes over a zeolite Y catalyst it soon became apparent that catalyst deactivation occurred to a significant extent.

Initially microreactor-stop-flow chromatography was used to study the effect of reaction time (total stop time for a series of injections) on the catalyst activity. Parameters were controlled so that the reaction during the stop was always on the same section of the microreactor "plug". These runs were done in conjunction with the runs reported in 4.3.

Stop-flow chromatography runs were also performed and the effects of deactivation and reactivation were monitored for the reaction of heptane.

Although both methods led to similar conclusions, the results will be treated separately for the sake of clarity.

4.5.1 Microreactor - stop-flow results

The raw results are gathered in appendix 3, table 3. 3 µl injections of a 2:1 hexane : pentane mixture ($^{V}/v$) were used with two minute stops. Remaining hexane height after the stop was monitored. As injections were of fairly varying volume, the pentane-hexane mixture was used. It was hoped that relative height of hexane remaining to pentane could be calculated. It was not known at this stage that pentane would react at 250° and 260°C. As no suitable internal standard could be found, the runs were not repeated. The results obtained would give some indication of the rate of deactivation although the errors, mainly due to different injection volumes, could be large.

Data for the change in catalyst activity with total stop time was calculated. A "no stop" run yielded a peak height of 10,6 cm^2. The amount of hexane reacted was calculated as (10,6 - remaining hexane height) cm^2. The data is collected in appendix 3, table 3.

Calculated rates of deactivation were found to be 1,57 x 10^{-4} sec^{-1} (r = 0,703) at 250°C and 1,75 x $10^{-4} sec^{-1}$ (r = 0,991) at 260°C. The rates of deactivation are remarkably similar. The effect of temperature is small as the "coke products" are large molecules which would be relatively unaffected by temperature changes at such low reaction temperatures.

The rate of deactivation is much slower than the rate of reaction. However the calculated rate of deactivation assumes that any nonvolatile products are "coke". Some strongly adsorbed species could be present which do not react or inhibit reaction. The results of 4.5.2 show that coking processes are rather complex. Other published data[53] shows that it is possibly a function of temperature.

4.5.2 Studies using stop-flow chromatography

In these studies a 0,5 m column packed with zeolite was used. The reaction of heptane at 170°C was studied. As the heptane moved through the column at a measurable rate (t_R for 0,5 m column is about 45 minutes), peak areas of products rather than peak heights were monitored. The method discussed in 2.3.4 (equation 2.12) was used to calculate relative areas for the product peaks.

4 stops per run were done, in each case the same time after injection, so that the rate of change of activity as well as rate of reaction could be calculated.

Reactivation of the catalyst involved heating for 1 hr at 450°C in air followed by 1 hr at 450°C in nitrogen.

It was assumed that each injection was of the same size. No internal standard was used. The large errors found in earlier sections of this chapter were attributed to errors in volumes delivered by the syringe. A new syringe was used in these runs.

The detector temperature was 300°C throughout. Injector temperature was 180°C. Gas flow was maintained at a constant rate. A flame ionization detector (FID) was used. 5 µl injections were made and stop times during all runs were 90 seconds.

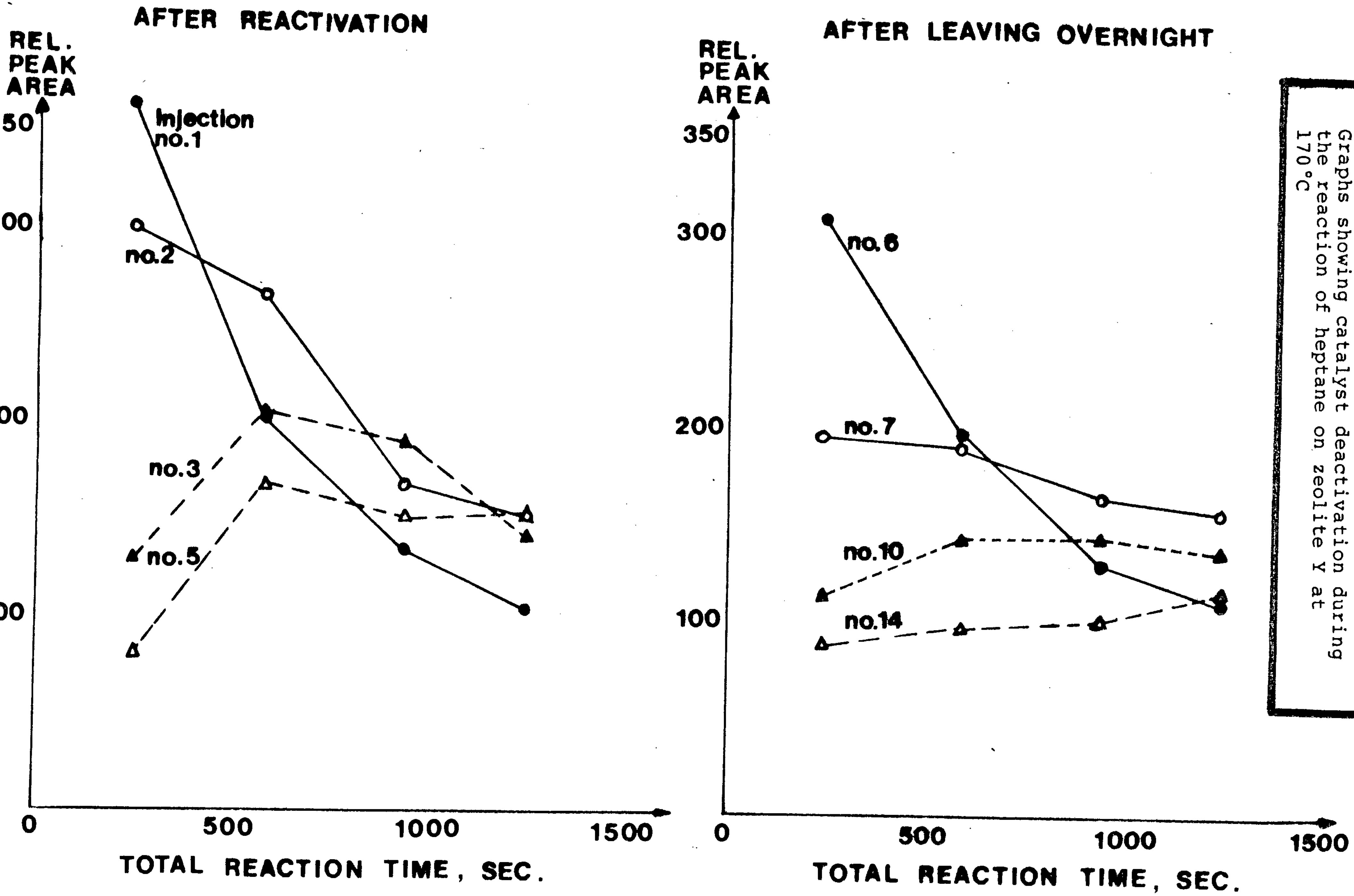


FIGURE 16

Graphs showing catalyst deactivation during the reaction of heptane on zeolite Y at 170°C

Initially a series of experiments was done where there was no reactivation of the catalyst inbetween runs. However, the effect of leaving the column overnight (15 hrs) under a nitrogen stream was demonstrated. The raw data is collected in appendix 3, table 4 and shown graphically in fig 16.

Log plots of relative area against total reaction time for the 1st and 6th injections resulted in reaction rates of, respectively, $12{,}6 \times 10^{-4}\ S^{-1}$ (r = 0,988) and $10{,}6 \times 10^{-4}\ S^{-1}$ (r = 0,984). Thus leaving the catalyst at the reaction temperature for 15 hours under a stream of nitrogen resulted in the catalyst (almost totally) regaining its reactivity. This tends to indicate that the cause of deactivation (coking of active sites, probably) is not an irreversible process and that the coke tends to break down (depolymerize) releasing relatively volatile components (volatile at 170°C). As the concentration of species in the gas phase decreases, adsorbed species on the catalyst would tend to desorb. Also if desorption of depolymerization species occurs, more depolymerization should occur. In contrast to the initial products of the reaction (alkanes) these species would tend to be highly unsaturated and possibly aromatic or olefinic in nature. As only five injections were made prior to leaving the catalyst for 15 hours, it is also possible that the "coking" reactions had not proceeded to a sufficient extent to produce large unsaturated hydrocarbons.

In both series of runs (1-5 and then 6-14) rapid deactivation is evident. The reaction position of the first stop is "totally deactivated" after three injections. It is noticed that after initial rapid deactivation, the rate of deactivation becomes slow, even negligible. The more active sites must be readily coked and become inactive, while coking of less active sites is much slower.

The observed curves for a series of runs are easily explained. For example, the amount of heptane reaching the second stop position in the second run is more than that which reached the second stop position during the first run. Comparing areas from the first stop position for runs 1 and 2 we see that the reaction has decreased by about 20% of the initial activity, ie 20% more heptane is reaching stop position two. Also the rate of deactivation is related to the amount of reaction so the second position will not deactivate as quickly as the first position. Therefore, in the second run, more heptane is reaching position two and this position is not as deactivated as position one, so more reaction occurs on position two than on position one. Similar arguments explain the changes for the other runs and also for the other stop positions.

Assuming that the sections of the catalyst where no stop occurs are less rapidly deactivated, we can say that the amount of hexane reaching the first stop position is constant for each injection. We may get an estimate of the rate of deactivation then from a log plot of ln peak height versus total stop time prior to the injection. The results are collected below for the first 5 injections (table 12).

TABLE 12

Data showing the rate of deactivation of the catalyst during the reaction of heptane at 170°C (over zeolite Y)

Injection number	Total stop time prior to injection (secs)	Monitored rel peak area	ln area
1	0	362	5,89
2	100	299	5,70
3	200	128	4,85
4	300	84	4,43
5	400	81	4,39

The calculated deactivation rate is 42,6 x 10^{-4} S^{-1} (r = 0,957) which is much larger than the calculated reaction rate (12,6 x 10^{-4} S^{-1}). This is opposite to the results of 5.4.1 where rate of reaction was greater than the rate of deactivation for hexane at 250°C and 260°C.

This difference is possibly due to the fact that coking generally increases with decreasing temperature whereas the rate of reaction depends on both temperature and the species being reacted.

Also, results discussed in 4.2 show that the relative amount of volatile products increases with temperature (ie reactivity). The hexane is relatively more reactive at 250°C than the heptane at 170°C, thus the amount of nonvolatile products (or coking) would, therefore, be less for hexane at 250°C than for heptane at 170°C.

Thus the catalyst would be deactivated more slowly for hexane reaction at 260°C.

A series of experiments was also performed where the catalyst was reactivated prior to each run. All parameters were kept constant. The raw data is collected in appendix 3, table 4. The various rate constants calculated are shown in table 13.

TABLE 13

Kinetics for the rate of heptane cracking at 170°C for repeated regenerations of the catalyst

Regeneration number	Rate constant (S^{-1})	r
1	$12,6 \times 10^{-4}$	0,988
2	$11,8 \times 10^{-4}$	0,984
5	$11,8 \times 10^{-4}$	0,979

It can be seen that the regeneration method used (1 hour at 450°C under air) was sufficient to regain almost complete activity. These results, when combined with long term effects noticed (but not quantified), show that there is a small loss in activity with each regeneration. As the "coke" is mainly a carbon-hydrogen mixture it can be assumed that it is converted to carbon oxides and water by oxygen. The water produced could cause changes in the zeolite structure. Carbides or similar species could also be formed with the zeolite structural aluminium or silicon.

The results of 4.5.1 indicate that over a long reaction time, the rate of deactivation is slow. This is also shown by the results of 4.5.2 where there is an initial rapid deactivation followed by slower deactivation.

This tends to indicate that there are some more active sites which are rapidly deactivated whereas the majority of the sites which are less active are deactivated more slowly. A closer look at the data of run 1, (1st regeneration) shows that in actual fact more active sites are present as indicated by the calculations below (table 14):

TABLE 14

Rates of change of reaction for each set of data points for heptane reaction at 170 °C over zeolite Y

Total reaction time (secs) (x)	Product area found	ln area (y)	$\frac{y}{x} \times 10^4$
245	362	5,89	17,4
585	201	5,30	11,4
935	124	4,90	8,56
1245	103	4,63	

Thus all active sites on zeolite Y are not equivalent and there are indications that a range of activities are present. This is expected, especially when data for Al_2O_3 is considered and coupled with the fact that both Brönsted and Lewis sites are probably present in the activated zeolite.

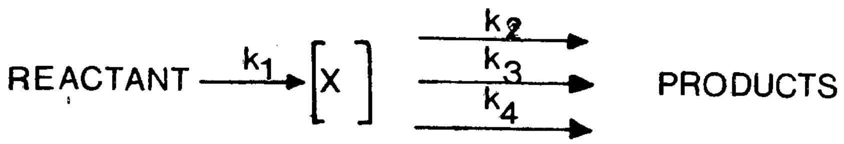
Thus the rapid deactivation of the catalyst seems to be the result of rapid coking of more active sites followed by slow deactivation of less active sites. No difference in products from each type of site is envisaged as the difference between the more active and less active sites is not seen to be great.

4.6 Calculation of activation energies

The reaction of heptane was studied at 160-180°C using conventional stop-flow chromatography. The peak height of one of the products, butane, was monitored for calculation of reaction rates. Although the reaction involves formation of four products via different paths, it was assumed that the relative amounts of each product species would not significantly change with temperature and thus the rate of butane formation is representative of the rate of heptane reacting. All products (hexane, pentane, butane, propane) are unreactive at 170°C (4.2) and therefore product ratios are not expected to change with temperature as observed in 4.3.

For hexane, an overall rate constant was calculated from an elution reaction chromatogram using the technique of Langer et al[4] (described on page 563 and in section 2.3.3; equation 2.4) where the diffuse slope of the product spectrum is used to calculate a rate constant. In this case three product species are present. However, this does not affect the calculation of an overall constant, even though the product peaks are eluted at different times from injection. The calculated constant ($k^1{}_{app}$) overall is directly related to the actual rate constant. The formation of the various products is not seen to be the rate determining step (4.7). In other words, overall rate constants and constants determined from changes in individual product species are equivalent.

Activation energies were calculated from log plots of ln k versus $^1/T$ (Arrhenius equation). The reaction mechanism, although not entirely known can be represented as:



where k_1 is the rate determining step (4.7). Thus the calculated activation energies are for the formation of the intermediate species [x].

The results are collected in table 15:

TABLE 15

Data for the calculation of activation energies for the reaction of hexane and heptane on zeolite Y

Temp °C	$\frac{1}{T} \times 10^3$	$k \times 10^4$ (S^{-1})	ln k	Parameters from log plot
Hexane				
513	1,95	17,6	2,87	slope = $1,5 \times 10^4$
512	1,91	25,0	3,22	intercept = 31,0 r = 0,976
533	1,88	53,0	3,97	
Heptane				
433	2,31	7,3	1,99	slope = $9,6 \times 10^3$
443	2,26	12,6	2,53	intercept = 24,2 r = 0,9996
453	2,21	19,4	2,97	

Thus the calculated activation energies are 125 kJ mol^{-1} for hexane and 80 kJ mol^{-1} for heptane. The corresponding values for A are $82 \times 10^{12} S^{-1}$ and $33 \times 10^9 S^{-1}$.

It seems that the results obtained using stop-flow chromatography (heptane) are more precise (r = 0,9996) than those found using the method of Langer et al (hexane; r = 0,976).

The relatively small activation energies obtained seem justified when the reaction temperature required is considered. These temperatures are relatively small when compared with usual catalytic temperatures (about 400°C).

The activation energy of heptane is less than that for hexane as would be expected considering their relative stabilities in the presence of a highly acidic catalyst.

4.7 Some observations concerning the mechanism of the cracking reaction

A combination of data obtained for heptane using both stop-flow chromatography and elution chromatography gives important information concerning the reaction mechanism. When combined with other data obtained during this study and with published data of other authors, some relevant comments can be made concerning the reaction of alkanes on zeolite Y and also the reaction of hydrocarbons on zeolites in general.

Heptane reaction was studied using stop-flow chromatograpy (4.5, 4.6). The rate of butane formation during each stop interval was measured. It was found to be 12,6 x $10^{-4}S^{-1}$ (r = 0,988). Similar calculations can be made for the other products, propane and pentane. The amount of hexane formed during the stop interval was too small to allow measurement of the resulting broad peak. The calculations are shown below (table 16). The calculation procedure is discussed in 4.6 and 2.3.4.

TABLE 16

Calculations of rate constants for various products formed during the reaction of heptane on zeolite Y at 170 °C

Total reaction time (s)	Product peak height	t_x $(S^{\frac{1}{2}})$	relative area	ln area	Parameters from log plot
Propane					
245	84,0	3,74	314	5,75	slope = 12,7 x $10^{-4}s^{-1}$
585	57,5	3,46	199	5,29	intercept = 6,05
935	43,5	3,00	131	4,87	r = 0,998
1245	33,0	2,65	87,5	4,47	
Pentane					
245	6,8	12,40	84,3	4,43	slope = 21,4 x 10^{-4} s^{-1}
585	3,1	11,09	34,4	3,54	intercept = 4,87
935	1,6	9,70	15,5	2,74	r = 0,992
1245	1,2	8,43	10,1	2,31	

It can be seen that the rates of formation of propane and butane are very similar (12,7 x $10^{-4}s^{-1}$ and 12,6 x $10^{-4}s^{-1}$ respectively). Comparison of data contained in appendix 3, table 4, and table 15 show that for each stop the relative areas of propane and butane are very similar (eg after 2455, areas are respectively 314 and 362). However, considering that the detector responds to the number of carbon atoms per molecule relative amounts of propane and butane in this case are 105 and 90. For pentane, the relative amount is 17. Swimbourne in his book[60] on the analysis of kinetic data states that rate constants should be equal to the ratio of the product species for a series of concurrent reactions (p 87). Here the ratio of rate constants for propane : butane is 1,01 while the ratio of amounts is 1,17.

Pentane, which is produced in only relatively small amounts seems to have the largest reaction rate. This seems to indicate that the mechanism of pentane formation is not similar to the mechanisms of butane and propane formation.

However, if formation of a product species is independent of the other species then the rate of reaction of heptane should be equivalent to the total sum of all the individual rates for each product[60].

Calculation of an apparent rate constant, k^1_{app} from an elution-reaction chromatogram using the method of Langer et al [46] gave the following data (table 17):

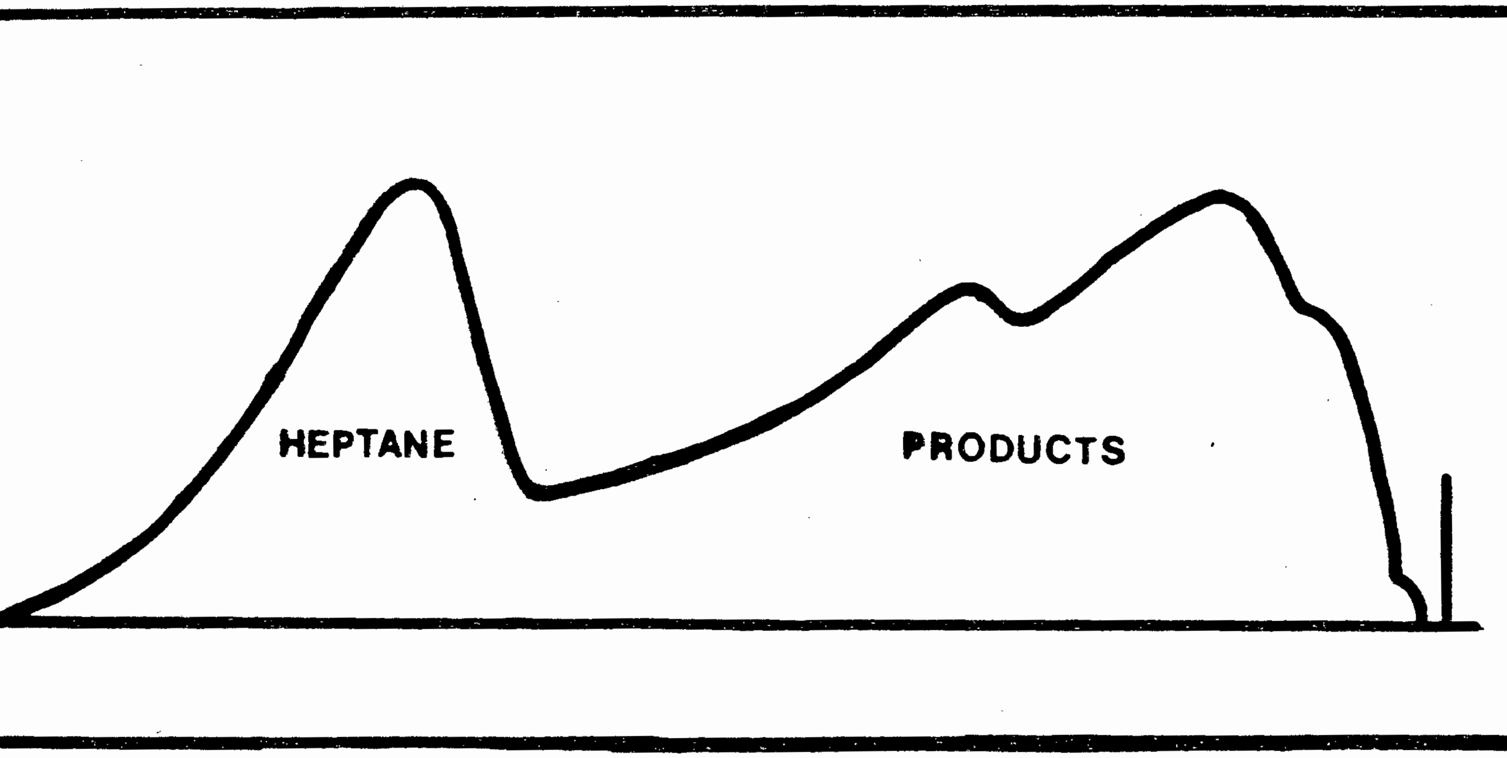
TABLE 17

Calculation of an overall rate constant, k^1app for the reaction of heptane on zeolite Y at 170°C

Total reaction time (secs)	height of peak tail	ln height	Parameters obtained from log plot
895	34,9	3,55	slope = $14,3 \times 10^{-4} s^{-1}$
1015	28,5	3,35	intercept = 4,82
1135	24,1	3,18	r = 0,999
1255	20,3	3,01	
1375	17,5	2,86	

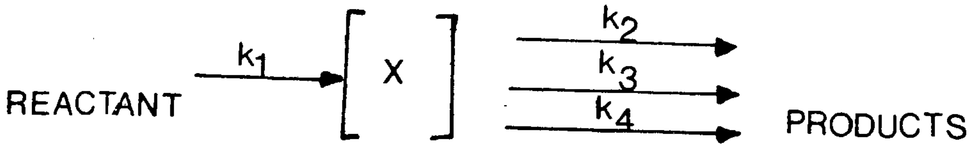
FIGURE 17

Elution chromatogram for heptane on zeolite Y at 170°C



The portion of the reaction chromatogram after elution of all the product peak maxima gave an apparent rate constant k^1_{app} of $14,3 \times 10^{-4} s^{-1}$ ($r = 0,999$). A typical elution-reaction chromatogram is shown in fig 17. Equation 2.4 shows that the actual overall rate constant is less than k^1_{app}.

This tends to indicate that the overall rate constant is of similar magnitude to the individual rate constants. Thus a reaction mechanism consisting of a series of concurrent reactions does not occur. However it is possible that formation of an intermediate species prior to desorption of the various products is the rate determining step and that the desorption of products is fast by comparison. This would account for the various reaction rates observed; that is that they are all equivalent in magnitude. The reaction mechanism is presented below:



Mechanisms proposed by other authors involved carbonium ion formation and isomerization[51, 52] prior to cracking. Olefinic intermediates are proposed[45] and the product spectrum seems to be independent of the starting material (alkane or alkene).

Weeks et al[49] however found that the mechanism of β-scission of carbonium ions did not fit their observations using ^{13}C-labelled n-nonane. They speculate that the product distribution is to a large extent dependent on the reaction temperature for any given reactant. Also the reactivity of the species at the temperature is an important consideration. It is felt that as the reactivity of the species increases (ie the reaction temperature increases) the reaction mechanisms become more complicated as products formed themselves react and the amount of coke formed increases. This results in product spectrums and reaction pathways that are not easily interpreted.

Some initial studies with iso-octane showed that it was substantially cracked at 110°C. Thus the studies of Weeks et al[49] at 230°C with n-nonane, Weitkamp and Schultz[45] at 250°-500°C with n-C_{12}, for example, are carried out under conditions where the reactant is highly reactive.

It was initially thought that a simple mechanism might predominate at a lower reactivity. The equal amounts of butane and propane could result if the heptane is "split" by the catalyst to form butane and propane, this being the major reaction. This seems highly unlikely when the results of 4.2 and 4.5 are considered. A large proportion of the reactant species is retained on the column, presumably as species of relatively high molecular weight when compared with the reactant.

Also, if the predominant mechanism is a cleavage reaction, the product spectrum of hexane should consist almost entirely of propane. This was found not to be the case. In fact, the amount of butane formed is greater than the amount of propane formed. This is also supported by the observation that the product spectrum is dependent to a large extent on the reaction temperature with the average number of carbons per molecule decreasing with increasing temperature. Finally as no olefins are found in the product spectrum, a source of hydrogen is necessary to convert the reactant alkane into product alkanes. Coking has been cited by many authors as the source of the required hydrogen[52-59].

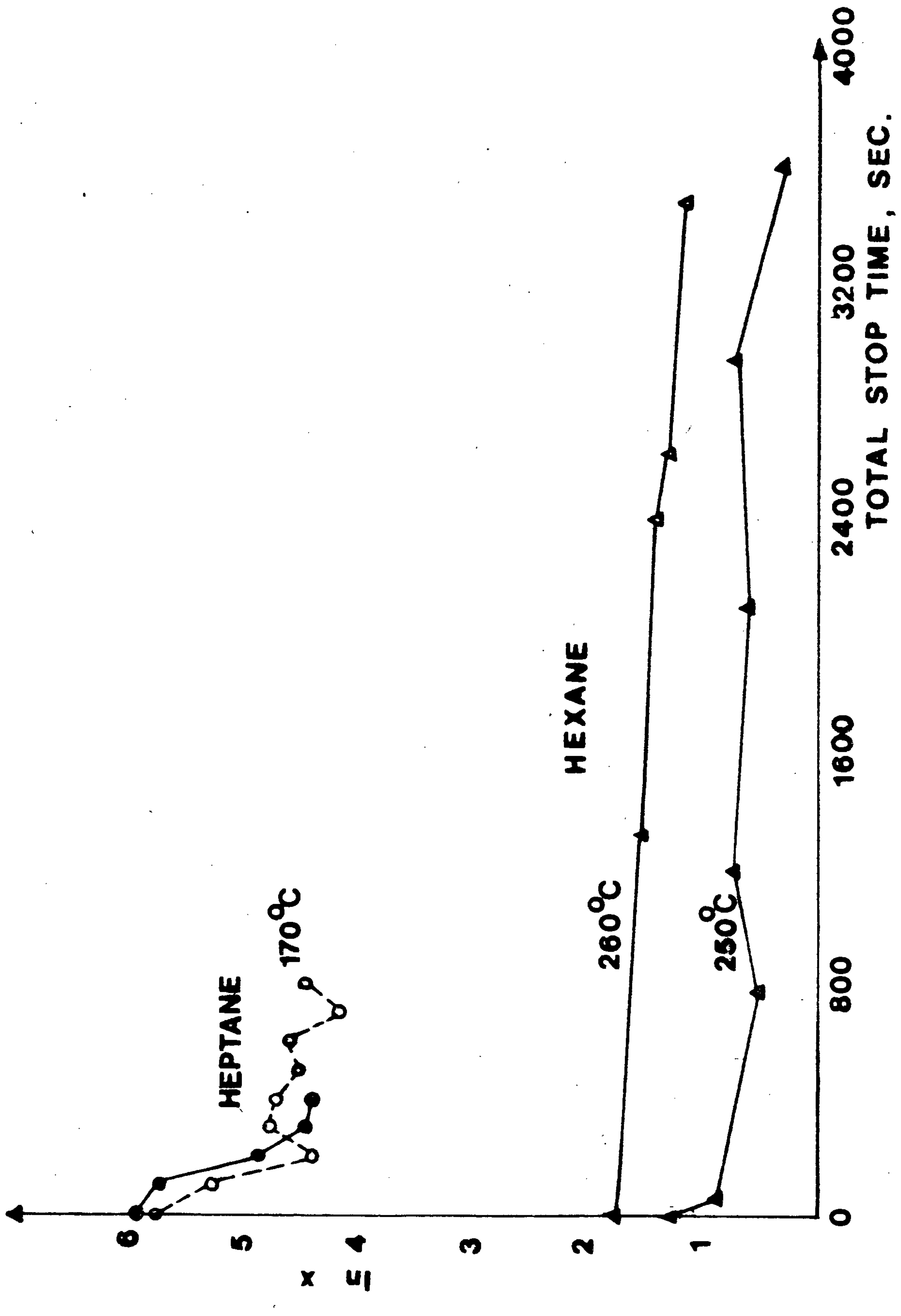
Langner[52, 53] extensively studied coke formation using the reaction of propene on $NaNH_4$-Y. Analysis of coke found that after reaction at 200°C, 35 mg coke/g catalyst was soluble in hexane. Further analysis led him to conclude that the species present were cyclic polyolefinic hydrocarbons with conjugated double bonds. At a reaction temperature of 400°C, less than 3 mg coke/g catalyst was soluble in hexane. The coke formed at this high temperature was seen to be large aromatic compounds with fused rings. The carbon/hydrogen ratio of the coke increased with reaction time at 400°C. At 200°C the ratio remained almost constant with reaction time.

He also found that generally the rate of conversion decreased as pore volume decreased due to coking. However, he found that at high temperatures the catalyst was still active even after total loss of pore volume. The possibility that the large, strongly absorbed, aromatic and hydrogen deficient species have a significant effect on the reaction is indicated. Possibly these "coke centres" could be reactive sites due to the large electron densities resulting from many double bonds.

As reported in 4.5 the rates of deactivation were calculated for heptane reaction at 170°C and hexane reaction at 250°and 260°C. The results of those experiments are gathered together in fig 18. The heptane results show that there is initially a rapid decrease in activity of the catalyst followed by a slower decrease. The hexane results show the general decrease but less initial rapid decrease. As the hexane results were in some respects initial investigations it was not known to what extent the deactivation occurred and thus only a small amount of data was gathered in the initial stages of the reaction.

FIGURE 18

Rates of catalyst deactivation for heptane and hexane on zeolite Y at different temperatures



The induction period found by Langner was not noted in these experiments. This might be owing to the different activation temperatures used (Langner activated at 350°C, this work activated at 450°C).

The effect of hydrogen in the carrier gas (4.2) is marked. Re-examining the elution-reaction chromatograms we see that the effect of 10% hydrogen in the nitrogen stream is to increase the amount of volatile products by about a factor of 2 (average increase in product peak maxima is 1,8). The flow rate was 15 ml/min, ie 1,5 ml/min hydrogen. As heptane took about 45 mins to elute, 67,5 mls of H_2 was added with the carrier gas (or about 3 mmols). 5 μl (or 0,03 mmols) of heptane was used. Therefore the hydrogen to heptane ratio was about 100. The hydrogen was therefore present in excess.

It is thought that the presence of hydrogen allows desorption of species to occur more quickly. Also depolymerization of any large species would tend to be favoured in the presence of hydrogen. In other words, hydrogen accelerates the desorption reaction but does not alter the rate determining step.

Thus alkane reactions over a zeolite catalyst seem to proceed via formation of a complex intermediate species, probably of fairly high molecular weight which then forms "crack products" via desorption. The rate of formation of the intermediate step is seen to be the rate limiting process and probably involves isomerization and oligimerization processes.

The amount of volatile products increases in the presence of hydrogen. The product spectrum seems to be largely dependent on the reaction temperature.

Alkanes are readily cracked over a zeolite Y catalyst to smaller products. Coking occurs resulting in catalyst deactivation.

4.8 Comparison of methods of obtaining kinetic information using reaction chromatography

In this work three methods have been used to estimate the rate of catalytic reactions by using various methods of reaction chromatography.

In studying a reaction sequence, all three methods could give a different interpretation of the reaction occurring.

The first method uses microreactor-stop-flow chromatography. The rate of disappearance of reactant with increasing stop time length is monitored allowing calculation of an overall rate constant. This method has the advantage of being unaffected by sequential reactions, polymerization and factors which change the relative amounts of products. However, autocatalysis or product inhibition cannot be tolerated. Another disadvantage found in this work is that errors due to changes in catalyst activity (eg deactivation) can be fairly substantial. Further, it requires the reactant to have a short residence time on the reactor "plug" so only reaction during the stop interval occurs. However, if a simple reaction is being monitored, product peaks can be used to calculate rate of reaction. This assumes that no sequential processes are occurring.

The second method is conventional stop-flow chromatography. Product peak (or peaks) are monitored and used to calculate kinetic data. If sequential reactions, polymerization or autocatalysis are occurring these can be minimised and their effects kept constant by using a short constant stop length for each stop interval. If more than one product is formed and a concurrent series of reactions is occurring then individual rates of formation may be obtained from monitoring each peak separately.

The main difference in applicability of these two methods is that in the first case retention time of the reactant should be fairly small whereas in stop-flow chromatography the longer the retention time, the better.

In this work, stop-flow chromatography was found suitable for heptane and microreactor-stop-flow suitable for hexane. The relative average speeds through the column can be defined as:

$$\frac{\text{total column volume}}{\text{retention volume}}$$

They were found to be respectively 0,012 and 0,041. If the products are less retained than the reactants, the author believes that on the basis of the observations in this work that a relative average speed of less than 0,04 is required to obtain meaningful data from stop-flow chromatography.

It is worth noting here that the factor f which appears in the stop-flow equation 2.6 approaches one at relatively small retention time for reactant.

If meaningful stop-flow chromatography can be done, then f is close enough to one to be ignored in the reaction rate calculations. For heptane at 170 °C, $f = 0,997$ while for hexane at 250 °C, $f = 0,990$ for the zeolite column. This error, introduced by ignoring the value of f, is relatively small.

The third method involves the estimation of an apparent rate constant from a plot of ln (recorder response) against elution time. This method has been used successfully by Langer et al for a single product system[4]. This method is fast and convenient, but gives an apparent constant which is larger than the actual value although band broadening tends to "smooth-out" the curve. The curve is easily distorted, for example, by reverse reactions and changes in operating conditions. It is suitable for more than one product species for determining the overall rate constant as long as the section of the curve after elution of all product peak maxima is used.

The results obtained using all three methods are collected together below with the calculated correlation coefficients, r, obtained from each plot (table 18).

TABLE 18

Calculated kinetic data using different methods of reaction chromatography

Reactant	Experimental conditions	$k \times 10^4$ (S^{-1})	r
Hexane	Microreactor-stop-flow 250°C; hexane area monitored	23,3	0,950
Hexane	elution-reaction 250°C; slope of product spectrum	27,1	0,999
Heptane	stop-flow 170°C; rate of production of butane	12,6	0,998
Heptane	elution-reaction 170°C; slope of product spectrum	14,4	0,998

All methods except microreactor-stop-flow gave good, precise results. The lower precision in the microreactor-stop-flow case is probably due to the deactivation of the catalyst by, and during, the reaction. In circumstances where no deactivation is occurring, this method should give results of comparable precision.

The elution-reaction method was defined for the formation of one product only as shown by equation 2.4:

$$k^1{}_{app} = \frac{k_s\ t_R}{t_R - t_p}$$

where t_R is residence time of the unreacted reactant and t_p is the residence time of the product. In this work good agreement between methods indicates that the system also applies to a many product reaction where one reactant is producing four products, which are not produced concurrently. That is, a system where the overall rate constant is equal to the individual rate constants of each product species.

The relationship between $k^1{}_{app}$ and k_s must involve the retention times of the various species. For hexane and heptane:

$k^1{}_{app}/k_s$ values are similar

(heptane $\frac{14,4}{12,6} = 1,143$; hexane $\frac{27,1}{23,3} = 1,120$)

This means that the correction factor for retention times is of this order. At 170 °C, residence times of heptane, hexane and pentane are known and thus residence times for butane and propane may be calculated. Individual values of

$$\frac{t_R}{t_R - t_p}$$

were calculated and an average value calculated (table 19). The similarity between the average value (1,157) calculated and the experimentally found value (1,143) is remarkable. On the basis of these results it is proposed that for a first order reaction producing many product species during a catalytic reaction that:

$$k^1_{app} = \left[\frac{\sum^{n} \frac{t_R}{t_R - t_{Pi}}}{n}\right] \cdot k_s$$

where n is the number of products.

TABLE 19

Calculated values for $\frac{t_R}{t_R - t_p}$ for various species at 170°C for a 0,5m zeolite column at a flowrate of 20 ml/min.

Species	Retention time, s	$\frac{t_R}{t_R - t_p}$
Heptane	2440	-
Hexane	780	1,470
Pentane	250	1,114
Butane	80	1,034
Propane	25	1,010
		4,618 Total
		1,157 Average

In conclusion, the choice of the most relevant method in a particular situation depends on the complexity of the reaction. Use of all three systems can, however, aid in the elucidation of the reaction mechanism as they are all affected differently by different reaction mechanisms. It is felt that use of one method entirely can possibly mask the processes occurring during the reaction.

For first-order heterogeneous catalytic systems involving formation of many products, the elution reaction method of Langer et al[4] involving a plot of ln (recorder response) versus elution time can allow calculation of the overall rate constant.

CHAPTER 5

CONCLUSIONS

A gas chromatograph can be effectively used in the study of heterogeneous catalysis. A wide variety of methods have been proposed, which all differ to some extent in the apparatus required, time required and results obtained. It has been demonstrated in this work that a combination of techniques has advantages in that data obtained from different viewpoints can help to solve complexities in the system.

Three methods of obtaining reaction rates for catalytic reactions were investigated. It was shown that the most applicable method depends on the system being studied. However, the precision of each method tends to be comparable, although stop-flow chromatography is less susceptible to errors due to the chromatographic system. Generally stop-flow chromatography is useful for strongly retained reactant species.

Investigations of the catalytic dehydration of alcohols over alumina and modified-alumina catalysts were done. Pentanol reacted at 300°C forming mainly the dehydration products pentene and water. Ethanol, however, is "cracked" to some extent on the more active sites and a fairly large amount of methane is produced along with ethene and water.

Inorganic ions radically affect the activity of the alumina catalyst. The two types of active sites are affected differently. Potassium (K^+) causes deactivation of both strong and weak sites, chlorine (Cl^-) deactivates strong sites and flourine (F^-) enhances the overall activity by converting weak sites into strong sites. Thus addition of KF causes formation of a catalyst with predominantly strong sites while presence of KCl results in a catalyst with predominantly weak sites.

The presence of KCl seems to increase the required activation energy. Thus the presence of inorganic ions does not influence the reaction mechanism but rather causes changes in active site configuration.

Water dramatically influences the dehydration reaction. Thus alcohol dehydration is an autocatalytic reaction. Water seems to change the catalyst surface in some way as its effects are of relatively long duration.

Alumina, then, has two types of active sites for the dehydration of alcohols. These sites are radically affected by inorganic ions and water.

Zeolite Y, an alumina-silicate has been found to be a highly active catalyst for the craking of alkanes. Alkanes are generally cracked to form a series of products, the spectrum being temperature dependent to some extent.

Hexane was studied at 240°C and heptane at 170°C. The product spectrum of hexane at 240°C was complicated by the fact that pentane, one of the products, is reactive at this temperature. In both cases, propane was the lightest species found in the product spectrum.

Catalyst deactivation due to coke formation was studied. It was found to be temperature dependent to some extent. Rate of deactivation was initially fast, but then decreased at a slow constant rate.

The reaction mechanism is thought to involve formation of an activated species which then produces various alkanes by desorption. The formation of the activated complex possibly requires a number of steps, including isomerization, and one of these is the rate determining step of the reaction mechanism. Individual rate constants for products are similar to the overall rate constant. The catalyst may be reactivated by heating in air to decompose the coke to gases but some activity is lost. The initial coke formed can desorb under reaction conditions and activity is regained if the system is allowed to "stand".

The reaction of alkanes over zeolite Y is, therefore, a complex system which requires further study as the mechanisms involved are not yet fully understood.

Finally, this research has adequately demonstrated the usefulness of gas chromatography in studying catalytic processes. The data obtained provides a wide range of kinetic and thermodynamic information. A variety of well-developed techniques is available allowing the choice of the system most suited to the reaction to being studied.

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APPENDIX I - EXPERIMENTAL PROCEDURES

The Chromatograph

In all experimental work, a Pye Unicam series 304 gas chromatograph was used. Both flame ionization (FID) and thermal conductivity (TCD) detectors were available for use. The chromatograph has a maximum temperature of 450°C. Glass columns were used throughout and carrier gas flowrates were measured using a bubble flowmeter.

All gases used were of the highest purity available (greater than 99,5% pure). The carrier gas was further purified over molecular sieve prior to entering the chromatograph. For catalyst regeneration, high purity "medical" air was used.

All columns were glass of inside diameter 5 mm varying in length from 0,5 m to 2,5 m. All columns were vacuum packed.

Stationary phases and catalysts

For reactor-stop-flow chromatography two different analytical columns were used. For high temperature work (greater than 200°C) a 10% by weight mixture of zeolite Y on Chromosorb W was used as no suitable commercially available stationary phase was found. For lower temperatures a 50% by weight mixture of Porapak Q and Chromasorb W was used. A plug of zeolite Y catalyst was inserted into these columns approximately 10 cmn from the injection end of the column. This was done to ensure that the catalyst plug was unaffected by the injector port conditions. The size of the plug varied from 3-10 cm in length, depending on the residence time of the reactant on the catalyst surface.

For GSC, Al-Thamir et al[61] have found that long columns with a small loading (so-called "dusted columns") give superior separations when compared with short columns with high loadings. The writer has come to a similar conclusion in this research. For the reactor-stop-flow experiments, columns used were 2,5 m long.

In the zeolite catalyst experiments, it was necessary to regenerate the catalyst periodically. It was found that this could be successfully achieved by heating the zeolite in the presence of air at 450°C for at least an hour. A further advantage of the zeolite/Chromosorb stationary phase was that the catalyst regeneration could be performed in situ. Literature states[62] that Porapak Q has a maximum temperature limit of 250°C, so that it was an unsuitable phase if in situ regeneration was required.

The Porapak Q was found to react with the zeolite plug as well so that the plug had to be separated by Chromosorb W from the Porapak/Chromosorb phase. However, at low temperatures (less than 200°C) alkanes larger than heptane are so strongly adsorbed by zeolite Y that even the 10% by weight mixture of zeolite Y with Chromosorb W produces excessive retention times. This makes it very unsuitable as a stationary phase at low temperatures.

The zeolite used was Linde Molecular Sieve zeolite Y, type LZ-1/82. The catalyst was supplied in the NH_4^+ - exchanged form. To obtain an active catalyst it is necessary to remove NH_3 by heating to convert the zeolite to the H-form, providing both Lewis and Brönsted acid sites. In all experiments, the H-form of the catalyst was used. Hopkins[39], Chu and Dwyer[38] and Benesi[37] all agree that activation at temperatures of 400-500°C is required to convert the catalyst to the H-form. In this work the catalyst was heated at 450° C for two hours under nitrogen to activate the catalyst.

As mentioned previously, catalyst regeneration was necessary due to activity lost as a result of carbonaceous build up. Heating at 450°C in the presence of air for at least an hour was found to be sufficient to convert the carbonaceous products to volatile gases and to regenerate the catalyst.

The alumina used for the dehydration of alcohols was activated alumina (70/80 mesh) from Analabs (code GCA-006B). The alumina also required activation at 450°C under nitrogen. This was necessary to remove lattice water and to create an active catalyst.

Experimental method

For stop-flow chromatography, a tap was inserted into the carrier gas line just before the injector port. The carrier gas flow through the column is not instantaneously stopped when the tap is closed due to the pressure in the column. Under normal conditions it was found that retention times of products differed by about twenty seconds from what would have been observed for a straight injection.

In all experiments, samples (usually liquid) were injected using precision microsyringes. Where possible and necessary, internal standards were added. All compounds used were analytical grade and were tested for purity by gas chromatography (squalane or Porapak columns).

Peak areas, when symmetrical, were estimated by triangulation methods. In some instances the "cut and weight" method was used. As discussed in chapter 2, a relative area was also calculated for some experiments where the relative area is equal to the peak height multiplied by the square root of the retention time of the product from the time the flow was restarted.

$$\text{Relative Area} = \sqrt{t_{Rx}} \times h$$

Peak heights could be used in studies of the dehydration of the alcohols as the alcohols are totally adsorbed onto the alumina surface.

APPENDIX 2 : TABLE 1

Results for ethanol dehydration on unmodified alumina at 300°C

Reaction time (secs)	PEAK AREAS IN mm^2 (AFTER CORRECTED)						
	Methane	Ethene	Propene	Butane	Butene	Other peaks	Total
180	8,12	8,60				Est 5,0	21,7
390	5,64	10,30				Est 5,0	20,9
690	3,92	10,35	0,72	0,60	3,95	negl.	19,5
990	3,16	10,15	0,85	0,72	3,90	0,58	19,4
1290	2,22	9,70	0,89	0,88	4,00	0,35	18,0
1590	1,70	9,35	0,89	0,80	4,10	0,35	17,2
1890	1,53	9,55	0,97	1,03	4,31	0,40	17,8
2310	1,21	8,54	0,94	0,93	3,74	0,37	15,7
3750	1,17	7,62	0,92	0,86	2,80	0,22	13,6
4050	1,12	7,68	0,92	0,88	2,78	0,19	13,6
4320	0,80	7,59	0,89	0,87	2,98	0,25	13,4
7110	0,52	7,25	0,99	0,87	2,25	0,30	12,2
*7500	1,34	7,18	0,88	0,75	1,85	0,25	12,3

* 6 minute stop

APPENDIX 2 - TABLE 2

Raw data for the dehydration of pentanol over unmodified alumina at 300 and 350 °C

Total reaction time (sec)	Pentene area (10^3 x 32) mm^2	ln pentene area	Calculated area due to slow reaction	ln corrected area for fast reaction
220	50,7	3,93	31,4	2,96
580	39,5	3,68	31,2	2,12
940	36,7	3,60	31,0	1,74
1300	33,1	3,50	30,9	0,79
1660	31,7	3,46	30,7	0,00
2020	30,8	3,43	30,6	
2380	30,2	3,41	30,4	
3280	29,8	3,39	30,0	
5740	29,3	3,38	29,0	
6100	28,7	3,36	28,8	
6460	28,4	3,35	28,7	

continued/...

APPENDIX 2, TABLE 2 continuation ....

350°C - NO NEW INJECTION

Total reaction time (sec)	Pentene area (10^3 x 32) mm^2	ln pentene area	Calculated area due to slow reaction	ln corrected area for fast reaction
74240	11,5	2,41	10,36	
74620	9,98	2,30	10,11	
74950	9,32	2,23	9,89	
75290	9,42	2,24	9,68	
76440	9,53	2,25	9,00	
76760	8,60	2,15	8,82	
77080	8,64	2,16	8,64	
92680	3,41	1,23	3,20	
93055	3,21	1,17	3,12	
93355	3,04	1,11	3,06	
93655	2,91	1,07	3,01	
93955	2,81	1,03	2,95	

APPENDIX 2 - TABLE 3

Raw data showing the effects of addition of inorganic ions to an alumina catalyst used in the dehydration of pentanol at 300°C

Total (5) reaction time	peak area (mm^2)	ln area
ALUMINA WITH 10% $^w/w$ KF		
240	315	5,75
640	243	5,49
1040	174	5,16
1440	129	4,86
7240	11,3	2,42
18720	1,7	0,53
ALUMINA WITH 10% $^w/w$ KCl		
510	1,41	0,34
860	1,36	0,31
5010	1,34	0,29
6290	1,22	0,20
8760	1,13	0,12
17990	0,82	-0,20

APPENDIX 2 - TABLE 4

Effect of water on the reaction of pentanol on unmodified alumina at 300°C

Total reaction time (sec)	Pentene peak area (mm^2)	ln area
510	54,5	4,00
840	48,3	3,87
1120	35,4	3,57
Injected 8 ul H_2O		
1610	263,0	5,57
1910	237,3	5,47
4110	123,9	4,82
4410	109,4	4,69
Injected 4 ul H_2O		
4750	362,3	5,89
5040	345,6	5,85
71682	12,2	2,50
71992	12,0	2,48
72202	11,9	2,48
72952	11,7	2,46
74252	11,7	2,46
Injected 0,1 ml H_2O		
74802	96,3	4,57
75142	2675,2	7,89
75422	2851,2	7,96
75722	2446,4	7,80
76642	1232,0	7,12
78122	968,0	6,88
81322	270,6	5,60
81712	257,4	5,55

APPENDIX 3 - TABLE 1

Effect of temperature on the reactivity of various alkanes

Temp °C	Total recorded area after a "no-stop" run	Total product area after a "no-stop" run	Total recorded area after a stop-flow run	Total product area after a stop-flow run	Remaining reactant area after a stop-flow run
Pentane					
240	689	Negl	681	4	677
260	666	43	586	184	402
275	621	118	596	349	257
290	565	149	567	501	66
Hexane					
210	1201	Negl	1097	5	1092
220	1190	25	1067	50	1017
230	1157	38	1109	136	973
240	1127	47	993	500	493
250	1045	139	874	622	252
260	1008	255	650	502	148

continued /....

APPENDIX 3 - TABLE 1 cont ......

Temp °C	Total recorded area after a "no-stop" run	Total product area after a "no-stop" run	Total recorded area after a stop-flow run	Total product area after a stop-flow run	Remaining reactant area after a stop-flow run
Cyclohexane					
220	1265	20	1147	61	1086
230	1207	36	973	225	748
235	1202	68	835	349	486
240	1198	184	781	595	186
260	1145	331	837	733	104
Heptane					
190	1381	10	1321	27	1294
200	1247	25	1209	86	1123
205	1302	52	1153	335	818
210	1276	257	1023	876	147

APPENDIX 3 - TABLE 2

Raw data showing the effect of stop time on the products formed from the reaction of hexane over zeolite Y.

Stop length (mins)	Remaining hexane peak height (cm)	ln hexane peak height	Product 1 peak height (cm)	Product 2 peak height (cm)	Product 3 peak height (cm)	Total stop time prior to run (mins)
250°C						
1	10,19	2,32	0,60	1,01	0,42	19
2	10,91	2,38	1,46	2,27	0,81	51
3	10,02	2,30	1,58	2,26	0,78	20
4	8,39	2,13	6,79	8,40	3,01	15
5	7,16	1,97	8,46	9,74	3,55	30
6	4,73	1,55	8,41	9,75	3,26	7
7	5,29	1,67	9,65	10,64	3,69	53
8	3,62	1,29	13,92	14,86	5,22	22
12	2,11	0,75	15,19	15,06	4,77	37
260°C						
1	9,90	2,29	0,55	0,89	0,48	44
2	5,36	1,68	2,68	3,35	1,42	5
3	4,46	1,50	3,34	3,70	1,48	37
4	2,83	1,04	7,60	7,96	2,51	24
5	1,62	0,48	8,79	8,75	2,26	7
6	2,06	0,72	8,62	8,57	2,39	45
7	1,73	0,55	8,39	7,82	2,14	51
9	0,86	-0,15	10,55	9,56	2,08	28
10	0,60	-0,51	11,46	10,04	1,96	12

APPENDIX 3 - TABLE 3

Raw data showing the effect of catalyst deactivation on the amount of hexane reacted during a 2 minute stop

Total stop time prior to injection (mins)	Remaining hexane peak height (cm)	ln peak height	Equivalent peak height of reacted hexane	ln peak height
250°C				
0	7,02	1,95	3,58	1,28
5	8,23	2,11	2,37	0,86
13	8,95	2,19	1,65	0,50
20	8,52	2,14	2,08	0,73
35	8,78	2,17	1,82	0,60
49	8,51	2,14	2,09	0,74
60	9,22	2,22	1,38	0,32
260°C				
0	4,79	1,57	5,81	1,76
22	6,07	1,80	4,53	1,51
40	6,60	1,89	4,00	1,39
42	7,00	1,95	3,60	1,28
58	7,47	2,01	3,13	1,14

APPENDIX 3 - TABLE 4

Raw data on the effect of coking on the reactivity of heptane over a zeolite Y catalyst at 170°C

Injection number	Remaining heptane peak height	Rel peak areas of 2nd product (butane) after a 100 second stop after various reaction times (secs)			
		245	585	935	1245
1	8,0	362	201	134	103
2	13,2	299	264	167	150
3	18,8	128	204	189	140
4	24,2	84	178	178	159
5	-	81	167	150	150
COLUMN LEFT OVERNIGHT (15 hrs) AT 170°C 30 ml/min N_2 FLOWING					
6	15,6	305	195	127	109
7	20.2	193	187	163	155
8	24,2	81	161	148	144
9	26,0	113	135	127	135
10	29,2	111	141	143	135
11	29,5	91	115	120	124
12	30,5	97	105	117	122
13	33,2	63	106	120	126
14	29,0	87	95	99	113

continued ....

APPENDIX 3 - TABLE 4 cont ....

EFFECT OF REGENERATION

Regeneration number	Remaining heptane peak height	Rel peak areas of 2nd product (butane) after a 100 second stop after various reaction times (secs)			
		245	585	935	1245
1		362	201	134	103
2		319	187	120	99
5		407	221	153	124

APPENDIX 4

Derivation of equations used to calculate the amount of reaction occurring in reactor-stop-flow experiments

Two types of experiments were made at each temperature. One experiment involved a straight elution reaction (ie, a "no stop" run) while the other experiment involved a 200 second stop followed by elution. As the size of the reactant peak eluted after the stop is generally smaller than the reactant peak during straight elution, the amount of reaction during elution will be different. However, assuming first order kinetics, the ratio of amount reacted during elution to remaining reactant area should be constant and thus the amount of products formed during elution may be calculated.

Let the following parameters be defined:

A_1 - Total recorded area after a "no-stop" experiment.

A_2 - Product area recorded after a "no-stop" experiment.

A_3 - Total recorded area after a stop-flow experiment.

A_4 - Total product area after a stop-flow experiment.

A_5 - Remaining reactant area after a stop-flow experiment:

then:

the ratio of volatile products to remaining amount of reactant, B =

$$\frac{A_2}{A_1 - A_2}$$

Amount of volatile products formed during elution of a stop-flow experiment, C =

$$B \times A_5$$

Amount of volatile products formed during the stop interval, D = $A_4 - C$

or

$$D = A_4 - \frac{A_2}{A_1 - A_2} \times A_5$$

$$= A_4 - \frac{A_2 A_5}{A_1 - A_2}$$

Now also nonvolatile products are formed. If the total injected area is A_6 then:

Amount of nonvolatile products produced during a "no-stop" experiment, E = $A_6 - A$

Ratio of nonvolatile products to remaining amount of reactant, F = $\frac{A_6 - A_1}{A_1 - A_2}$

Amount of nonvolatile products produced during elution during a stop-flow experiment, G, = F x A_5

Amount of nonvolatile products formed during the stop interval, H = $(A_6 - A_3) - G$

or

$$H = (A_6 - A_3) - A_5 \left(\frac{A_6 - A_1}{A_1 - A_2}\right)$$

Note:

Injection of 5 µl into a squalane column resulted in the following areas:

hexane 1250, cyclohexane 1300, heptane 1400 and pentane 700 (different attenuation). These are values for A_6.

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