"REACTIONS OF HYDROCARBONS ON METAL FILMS STUDIED BY A COMBINED GAS CHROMATOGRAPH - MASS SPECTROMETER"

A Thesis presented for the degree of Doctor of Philosophy in the Faculty of Science of the University of Edinburgh by

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October 1973

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ABSTRACT

A combined gas chromatograph - mass spectrometer technique has been developed for the study of catalytic reactions in the presence of deuterium. The potential of this analytical combination with respect to elucidation of reaction mechanisms and reactive intermediates has been demonstrated by examining the reactions of saturated hydrocarbons on evaporated films of platinum and iron.

In each G.C.-M.S. experiment, a reaction temperature was chosen at which the reacting paraffin underwent concurrent hydrogenolysis and exchange with the result that the reactant and product hydrocarbons were simultaneously labelled with deuterium. Analysis of such complex reaction mixtures was achieved by separating each hydrocarbon chromatographically before measuring its isotopic distribution directly with a fast-scanning mass spectrometer. The interface between chromatograph and spectrometer was a Biemann-Watson molecular separator which, by preferential removal of helium carrier gas, provided a hydrocarbon-enriched effluent for mass spectral analysis. To allow for partial chromatographic separation of hydrocarbon species with different deuterium contents, it was essential to continue scanning throughout elution of the hydrocarbon peak, and then sum the sequence of intensities recorded for each mass number using Simpson's Rule. Furthermore, in eliminating fragment ion contributions to parent molecule peak heights in the observed spectra, it was found necessary to develop a correction scheme which accounted for the influence of molecular composition on individual C-H or C-D bond dissociations in the spectrometer. Many of the experiments carried out involved chromatographic analysis only and these served to define optimum experimental conditions for the G.C.-M.S. studies and, at the same time, provide
useful information on reaction kinetics.

The reactions of ethane, propane, n-butane, isobutane and neopentane were investigated in the presence of deuterium on platinum films. In the chromatographic studies, reactions were followed to high degrees of conversion and the kinetic behaviour of the hydrogenolysis processes showed a distinct trend in that reactions of ethane were acceleratory, those of propane maintained a constant rate and those of the reactants with four or more carbon atoms, which were also accompanied by reversible skeletal isomerization, tended to decelerate markedly with time, the retardation in rate being more extensive with the branched chain hydrocarbons than with the straight chain n-butane molecule. These kinetic properties were discussed in terms of the nature of the adsorbed species accumulating on the platinum surface, those possessing some carbonium-ion character being likely precursors to the intermediates responsible for the observed poisoning. Combined G.C.-M.S. studies of the n-butane reactions revealed that exchange was multiple in character, much faster than hydrogenolysis or isomerization, and led to rapid isotopic equilibration of each hydrocarbon present with the available hydrogen–deuterium pool; hence for platinum, which was a good exchange catalyst, it was shown that analysis of the deuterium contents of reactant and products provided little additional mechanistic information.

The reactions of ethane, propane, n-butane and neopentane were also studied in the presence of deuterium on iron films. G.C.-M.S. analysis indicated that, for each of these reactants, the initial hydrogenolysis product was almost exclusively CD₄; exchange of each reactant yielded mainly the perdeutero-compound together with lesser amounts of the singly deuterated stepwise exchange product, except in the case of neopentane where neopentane-d₁ and -d₂ were the only deuterated species
formed initially. Exchange of methane on iron was also studied using a
conventional capillary leak - mass spectrometer system; CD₄ was the only exchange
product and the reaction which was slow in rate at each temperature employed also
showed a tendency to poison with time. Taking into account information derived
from chromatographic studies, the order of hydrocarbon reactivity for both
hydrogenolysis and multiple exchange was clearly shown to be n-butane > neopentane >
propane > ethane, while that for the ratio of overall exchange to hydrogenolysis
followed the trend of increasing molecular size. It was concluded from the product
distributions and reaction kinetics that desorption of methane was the likely rate-
determining hydrogenolysis step and the pattern of hydrogenolysis activities was
discussed in terms of the change in relative surface coverages of hydrocarbon and
deuterium with temperature for each of the reactants. The absence of neopentane
exchange products originating from an αγ-adsorbed species suggested that the latter
were irreversibly formed on iron and led directly to carbon-carbon bond rupture;
furthermore, the relative positions of neopentane and n-butane in the activity
series pointed to the relative ease in forming αβ-adsorbed species on iron. The
poisoning of hydrocarbon reactions on an iron surface was accounted for by the
possibilities of carbidizing, sintering and formation of irreversibly adsorbed species.

Lastly, the catalytic properties of iron and platinum displayed in the present
work were reviewed in the context of their respective roles as non-noble and noble
members of the set of Group VIII transition metals.
The studies described in this thesis were undertaken personally in the Chemistry Department of Edinburgh University between October 1969 and October 1972. Much of the work carried out has since become the subject of publications and these have been included for the reader's attention in the closing Appendix.

Of the many people who have helped to make this thesis possible, I am particularly indebted to my academic supervisors Professor C. Kemball F.R.S. and Dr. D.A. Whan for their guidance and encouragement, to my co-workers Dr. J.C. Kempling and Mr. M.C. Gray for their valuable contributions to the study of catalysis on iron, to the Department of Chemistry for providing research facilities, to British Petroleum Ltd. for a generous Research Studentship, to my industrial liaisons Dr. J.J. McCarroll and Mr. K.J. Henderson for their enthusiasm and hospitality, to Messrs. J. Price, J. Broom and A. King for their feats of engineering, glass-blowing and electronic wizardry, respectively, to my parents for their many sacrifices over the years, to my mother-in-law for her profound criticism of the text, to my father-in-law for rescuing the methane exchange results from the dustman and lastly, but not least, to my dear wife and typist, Dorothy, for her endless patience and understanding.

Robert S. Dowie

February, 1973
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APPENDIX
TO

MY WIFE

Sine qua non!
CHAPTER 1

INTRODUCTION TO CATALYSIS

1.1. 'Catalysis' - Quid Est?

Although fundamental chemical studies of catalytic processes have only been pursued for about a hundred and fifty years, there can be little doubt that the influence of catalysis on Man and his environment has existed for a very much longer time - much earlier, for example, than the production of ether from sulphuric acid and alcohol as practised by the alchemists of the middle ages, and quite probably with its true genesis lying in the very depths of the primaeval soup. Indeed, while the all-embracing symbolism of the Biblical creation\(^1\) inevitably precludes any specific mention of our subject, it could conceivably be interpreted, thinking of catalysis as we know it today in its broadest sense, that, perhaps, when Eve tempted Adam to the fruit of the tree of good and evil thus accelerating Man's inescapable intimacy with sin, she was unwittingly behaving as the world's first recorded catalyst!

At the start of the nineteenth century, however, the leading chemical protagonists of the day, in their undying efforts to dispel the myths and magic of alchemy, had shown clearly by careful experimentation\(^2-12\) that there existed 'substances' with the ability to induce chemical changes that did not appear to occur under the same conditions in their absence. In a subsequent review\(^13\) of these observations in 1836, Berzelius highlighted their points of similarity, and by way of establishing a common cause, introduced the concept
of a catalytic reaction, the 'agent provocateur' in each case being christened a 'catalyst'; ignoring the rates of product formation, he concluded that the role of the catalyst was to increase the reaction yield by providing a more favourable chemical environment. In contrast to this, Van't Hoff\(^{(14)}\) later postulated that the function of a catalyst was to greatly enhance the rate of chemical reaction by causing compression of the reactants to a greater than normal concentration, while at the same time having no direct chemical involvement of its own.

The confusion that arose from these conflicting theories was partly erased by Ostwald\(^{(15,16)}\) who proposed that a catalyst acted only by increasing the rate of attainment of, and not the product yield predicted by, the thermodynamically feasible equilibrium position for the reaction; he was also the first to use reaction rate as a measure of catalyst effectiveness or catalytic activity. Attention was then focussed by Sabatier\(^{(17,18)}\) on the specific nature of catalytic reactions and also on the 'poisoning' of catalysts. The idea of specificity was invoked by Van't Hoff's failure\(^{(14)}\) to explain how the same reactant could undergo completely different processes on different catalysts - for example, the decomposition of alcohol vapour to ethylene and water over alumina at 573K or alternatively, to acetaldehyde and hydrogen over copper at the same temperature. Sabatier's poisoning studies illustrated how the longevity of a catalyst could be impaired by loss in activity due to the presence of impurities in a reaction system or to contamination by reaction products.

The concepts introduced by Ostwald and Sabatier are perhaps crystallized in a more recent and comprehensive definition of the catalyst role by Hinshelwood\(^{(19)}\); in essence, this says that a catalyst provides an alternative and faster reaction mechanism than that of the corresponding non-catalysed process, and can undergo
normal chemical reactions with the substrate to form intermediates which may then interact, decompose or rearrange to yield products, together with complete or partial regeneration of the catalyst. Thus, a fundamental understanding of how a catalyst behaves requires a knowledge of the nature and stability of the intermediate species produced between catalyst and substrate, of the reaction steps leading to their formation, and also of those involved in their breakdown to products. Although this pattern is exhibited by all catalysed reactions, there are many possible kinetic mechanisms, rendering a unique theory of catalysis a rather intangible quantity. Instead, it is more practical to divide catalytic systems into two principal categories, namely, homogeneous and heterogeneous, the reaction mechanisms belonging to either of these groups being similar in kind although not in detail.

In a homogeneous process, the reactants and catalyst are both present in the same physical phase; in a heterogeneous catalytic reaction, the catalyst and its substrate are in different phases, the most commonly occurring example - and the one with which this thesis is exclusively concerned - being that involving a solid catalyst and gaseous reactants. The ability of metal surfaces to adsorb gases and form chemically active adsorbed species was first studied by Langmuir\textsuperscript{(20-22)} and the equations he derived\textsuperscript{(23)} relating the amount of gas adsorbed by the surface to its pressure in the gas phase have been fundamental in the interpretation of the kinetics of many catalytic reactions.
1.2. Adsorption Processes

For a heterogeneous catalytic reaction to take place, it is essential that at least one of the gaseous reactants becomes attached in some way, and for a sufficient length of time, to the catalyst surface i.e. the process of adsorption resulting in an enhanced concentration of molecules at the surface must occur. The observed catalytic activity is then considerably dependent on the nature, extent and strength of adsorption, the latter being a measure of the tightness with which the molecules are held to the adsorbent. Experimental studies have shown that all adsorption phenomena conform broadly to one of two descriptions, physical adsorption or chemisorption.

**Physical Adsorption:** In this mode of adsorption, the molecules or atoms are attached to the surface by the resultant attractive force between them and the adsorbent, acting in the direction of the solid. The interactions involved are of the weaker, Van der Waals type, similar in strength to those associated with the liquefaction of a vapour, and only significant enough to contribute to catalytic activity in exceptional cases such as the oxidation of nitric oxide over a silica catalyst\(^{(24)}\).

Heats of physical adsorption are generally comparable in magnitude to the heat of condensation of the adsorbate and normally take values of about 5-20 kJ mol\(^{-1}\). When the adsorbent is easily accessible, the processes of physical adsorption and desorption occur rapidly and reversibly, the activation energy of the latter being only a few kilojoules per mole. On a porous surface, however, adsorption may be slower because diffusion of the adsorbate through the pores can be the rate determining step; in this situation, the equilibrium between adsorption and desorption will be reached less rapidly, a feature also
characteristic of activated chemisorption (vide infra).

Although physical adsorption may not be important from the standpoint of catalytic activity, it has proved extremely effective in the measurement of a catalyst's surface properties by determining the quantity of gas physically adsorbed under various experimental conditions. This technique has been most widely used for the estimation of surface areas by the method of Brunauer, Emmett and Teller \(^\text{(25,26)}\), and also for the determination of pore size distributions of supported or solid catalysts \((27-29)\).

**Chemisorption:** This form of adsorption is equivalent in nature to a chemical reaction in which there is a transfer or sharing of electrons between the adsorbed gas molecules and the solid surface to form bonds similar in kind to those found in chemical compounds; the chemisorbed species produced in this way are now generally accepted as being necessary precursors to, or intermediates in, heterogeneous catalytic reactions. When adsorbed on the surface, the restrictions imposed on molecular motion mean a loss of several degrees of freedom and, consequently, a decrease in entropy of the system. Since chemisorption occurs spontaneously, the change in the free energy will also be negative, which, from the rearranged equation

\[
\Delta H = \Delta G + T \Delta S
\]

indicates a negative heat of adsorption. So chemisorption is an exothermic process, the heat of adsorption values being normally in the range 80-200 k J mol\(^{-1}\).

Chemisorption phenomena can be grouped under three headings according to the observed rates of adsorption. Firstly, there are systems involving rapid chemisorption only \((30,31)\), which have associated activation energies of about
2 k J mol\(^{-1}\); further examples of this include the studies of Wagerer\(^{(32,33)}\) on a series of gas–metal interactions, and those of Becker and Hartman\(^{(34)}\) on the adsorption of nitrogen on tungsten.

Secondly, there are several systems in which the initial chemisorption is activated; this means that the heat of chemisorption at zero coverage is of the order of 40–80 k J mol\(^{-1}\). While the adsorption of a simple gas like hydrogen is found to be activated in only a few cases\(^{(35-37)}\), chemisorptions of larger molecules such as methane and ethane\(^{(38-40)}\) commonly fall into this category. Another specific instance is that of nitrogen whose slow adsorption on fresh surfaces\(^{(41,42)}\), in particular on iron catalysts\(^{(43,44)}\), has been attributed to the difficulty in breaking the nitrogen–nitrogen bond.

Finally, a more frequently observed pattern is that consisting of an initial rapid, non-activated chemisorption followed by a slower, activated uptake of gas. The rates of these two stages may normally be readily distinguishable\(^{(45)}\), although the difference between them is not always so marked\(^{(46)}\). Another important experimental observation has been that surfaces tend to exhibit slower adsorption at relatively high coverages, an example of this effect being the slow uptake of oxygen on tungsten in the later stages of chemisorption, as reported by Rideal and Trapnell\(^{(47)}\).

In general, the velocities of slow chemisorption processes, whether initial or subsequent, can be described by the Elovich equation\(^{(48-50)}\)

\[
\frac{\partial v}{\partial t} = a e^{-bv}
\]

where \(v\) is the volume of gas adsorbed, \(t\) is the time, and \(a\) and \(b\) are constants. Elovichian kinetics have been reported\(^{(51-54)}\) for the adsorption of hydrogen.
and carbon monoxide on iron and nickel films. A further application was pointed out by Taylor and Thon (50) who suggested that, if the value of \( b \) in equation 1.1 was a function of the nature of the surface sites associated with chemisorption, then any sharp changes in the gradient of an integrated Elovich plot could be indicative of adsorption occurring preferentially on different types of site at different surface coverages. This idea was borne out by the studies of Ehrlich (55-58) which showed that, for tungsten, a weakly chemisorbed surface structure could be the precursor to a more strongly bonded arrangement, and also by those of Maxted and Evans (59) for adsorption of hydrogen on clean platinum and platinum exposed to hydrogen sulphide which illustrated how discontinuities could appear in the Elovich slope.

The kinetics of chemisorption may also be influenced by there being more than one possible surface - adsorbate geometry; Eischens and his co-workers (60), in their infrared spectra of carbon monoxide chemisorbed on palladium, have found evidence for carbon monoxide originally bonded to two palladium atoms per adsorbed molecule, converting to a form involving only a single attachment to the surface. Adsorption Isotherms: The first attempts to quantify the adsorption of gases on solids were proposed by Freundlich (61) and Langmuir (23). The former described the dependence of the amount of gas adsorbed on the pressure in the gas phase by the isotherm equation

\[
q = a p^{1/n}
\]

with \( q \), the quantity of adsorbed gas, \( p \), the pressure and \( n \), a constant greater than unity. Langmuir, however, found from his experiments that this theory was inadequate over large ranges of pressure, and went on to derive an alternative isotherm based on the assumptions that there are only a fixed number of surface
sites, any one of which must be vacant before adsorption may occur, and that the heat of adsorption is independent of surface coverage. The resultant equation was

\[ \Theta = \frac{ap}{1 + ap} \]

where \( \Theta \) is the fraction of surface covered by adsorbed species, \( p \) is again the gas pressure and \( a \) is a constant related to the heat of adsorption. Concordance with this simple Langmuir treatment is not always found in practice as it takes no account of lateral interactions on the surface between adjacently adsorbed molecules, and also of the fact that there is often a decrease in the heat of chemisorption with coverage due to surface heterogeneity, as observed by Keier and Roginskii(62).

Various isotherms have been employed to overcome the deficiencies of the Langmuir, including those of Brunauer, Emmett and Teller(25), and Tempkin(63). The B.E.T. theory was derived using the Langmuir assumptions as a basis, but with the concept of a localized monolayer extended to accommodate the possibility of multilayer adsorption; for the second and subsequent layers, the heat of adsorption was considered equal to the heat of condensation of the gas. The isotherm equation takes the form

\[ \frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c - 1)}{v_m c} \cdot \frac{p}{p_o} \]

where \( v \) is the volume of gas adsorbed, \( v_m \) is the volume of adsorbate for monolayer coverage, \( p \) is the partial gas phase pressure, \( p_o \) is the saturated vapour pressure and \( c \) is a constant. By plotting \( p/v(p_o - p) \) against \( p/p_o \), \( v_m \) can be found from the relationship \( v_m = 1 / (\text{gradient} \div \text{intercept}) \) and leads directly to a value for the number of molecules required to cover the surface. The surface area of the solid can then be estimated if the area occupied by one adsorbed molecule is known.
The application of isotherms is one of several major aspects of chemisorption discussed in a relatively recent review by Gundry and Tompkins (64).

1.3. Reaction Mechanisms in Catalysis

For heterogeneous catalysis to take place, there must be chemisorption of at least one of the reactants present. It is generally accepted for saturated hydrocarbons — on the reactions of which, this thesis is entirely concentrated — that formation of a chemisorbed species on the surface requires rupture of at least one of the carbon—hydrogen bonds in the molecule. This form of dissociative adsorption also occurs with unsaturated adsorbates, although an associatively adsorbed olefin is also a possibility.

Dissociatively chemisorbed molecules may undergo chemical reaction on a catalyst surface by one of two well—established mechanisms. Assuming the adsorption and desorption steps are at equilibrium, then the overall catalytic rate can be considered entirely a function of the interactions between chemisorbed species, and, consequently, proportional to their fractional surface coverages (equivalent to concentration terms). For the case of a saturated hydrocarbon reacting with deuterium on a suitable catalyst, this mechanism, involving only chemisorbed intermediates, would proceed according to the reaction scheme

\[
\begin{align*}
\text{C}_n\text{H}_{2n+2} & \quad \text{D} \quad \text{H} \rightarrow \text{C}_n\text{H}_{2n+1} \quad \text{D} & \quad \text{R} & \quad \text{C}_n\text{H}_{2n+1}\text{D} \\
\text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S}
\end{align*}
\]

where the continuous and dotted lines denote chemisorption and physical adsorption, respectively. This mode of reaction path, developed by Langmuir (65–68) and Hinshelwood (69–70), has adequately accounted for the rate expressions of many
catalytic decomposition and bimolecular reactions.

The alternative is the Eley - Rideal mechanism\(^{(71)}\) in which one of the reacting species is either physically adsorbed or still in the gas phase; for the above hydrocarbon/\(\text{D}_2\) example, the corresponding reaction scheme here is

\[
\begin{align*}
\text{C}_n\text{H}_{2n+1} \quad \text{D}_2 & \quad \text{or} \quad \text{C}_n\text{H}_{2n+1} \quad \text{D}_2 \\
| \quad | & \quad | \quad | \\
\text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S}
\end{align*}
\]

Evidence for this mechanism arose from the experiments of Bonhoeffer and Farkas\(^{(72,73)}\) on hydrogen - deuterium exchange reactions and also the reversible interconversion of ortho and para hydrogen, both of which occurred with adsorption of hydrogen as atoms followed by exchange or conversion upon desorbing. The rates of these reactions at 193K were much greater, however, than that observed by Roberts\(^{(31)}\) for the desorption of hydrogen from tungsten at a similar low temperature, which prompted Rideal to suggest that the reacting species were chemisorbed atoms together with molecules either attached physically to the surface by weak Van der Waals forces or present in the gas phase.

Close analyses of both mechanisms have failed to establish that either the Langmuir - Hinshelwood or Eley - Rideal operates to the total exclusion of the other.

**Kinetics:** The overall rate of a catalytic process may be controlled by any of the following five constituent reaction steps:

1. The diffusion of reactant molecules to the catalyst surface.
2. Chemisorption of reactant molecules by the surface.
3. Chemical reaction between adsorbed species on the surface.
4. Desorption of molecules from the surface.
5. The diffusion of product molecules away from the catalyst.
For a static catalytic reaction system, as used in this present study, steps (1) and (5) are not normally rate-determining, the total pressure in the reactor and the size of the particles present both being small enough to permit rapid diffusion to and from the catalyst. Also, the temperature dependence of reaction rate should be $T^{1/2}$ in the case of diffusion control, but $e^{-E/RT}$ for stages (2), (3) or (4) which are essentially chemical phenomena; so Arrhenius plots can be applied to eliminate diffusion as the rate-determining process. In practice, reaction on the catalyst between adsorbed intermediates is more frequently the slow stage than the adsorption and desorption steps. Sometimes it is possible to pinpoint the rate-controlling process by comparison of available kinetic measurements; thus, Kummer and Emmett deduced that the dissociative chemisorption of nitrogen was the slow step in the formation of ammonia from nitrogen and hydrogen, the rate of which was comparable with that of the exchange of $^{14}_N-^{14}_N$ with $^{15}_N-^{15}_N$.

**Exchange Reactions:** As already indicated, 'tracer' techniques involving replacement of one isotope by another of the same element, e.g. $^{14}_N$ by $^{15}_N$, have often been instrumental in the elucidation of catalytic mechanisms and the nature of adsorbed intermediates (see also Section 1.5.). The principal application of this method has been that of exchanging the hydrogen atoms in hydrocarbons with deuterium to yield products differing from the reactant molecules in isotopic composition only.

Exchange reactions can be characterized mechanistically in two ways by the number of deuterium atoms incorporated by the hydrocarbon molecule on each visit to the surface. In simple or stepwise exchange, only one hydrogen atom is replaced by deuterium before desorption of the adsorbate occurs, and the distribution of products in the initial stages of reaction should show a predominance of the monodeutero compound. Any species formed containing more than one deuterium atom
are a result of further similar sojourns to the catalyst. For this exchange mechanism to be observed, the adsorbed intermediate formed by dissociative loss of one hydrogen must have sufficient stability, while still on the surface, to prevent further C-H bond rupture and subsequent introduction of more deuterium. In multiple exchange, however, the adsorbed species is more reactive on the catalyst and more than one hydrogen by deuterium replacement takes place at a single visit, giving rise to initial product distributions with maxima at isotopic forms containing more than one deuterium atom. Depending on the nature of reactant and catalyst, it is also possible for both mechanisms to operate during the same exchange reaction.

Detailed illustrations of these concepts are found in the studies of Kemball (75-77) on the exchange of methane and ethane with an excess of deuterium, on evaporated metal films as catalysts. For the exchange of methane on nickel and tungsten films, the initial product distribution yielded substantial percentages of perdeuteromethane, CD₄, and the monodeutero form, CH₃D. By altering the reaction temperature and the methane to deuterium gas ratio, it was concluded from the variation in relative amounts of CD₄ and CH₃D that both stepwise and multiple exchange processes could take place on these metals. To form the monodeuterocompound, the methane molecule must chemisorb dissociatively as a methyl radical, which can then leave the surface by picking up a deuterium atom. The fully deuterated species requires a more complex sequence involving CX₃, CX₂ and probably CX radicals as adsorbed intermediates - 'X' denoting either a hydrogen or a deuterium atom; the greater reactivity of the methylene radical, CX₂, means that it can undergo several reversible dissociations to allow successive exchange of all the hydrogens with deuterium before desorption as CD₄.
The relative energy requirements for the various stages of the methane exchange mechanism are shown schematically in Figure 1.1, where $E_1$ is the energy barrier to formation of the adsorbed methyl radical and $E_2$ (larger than $E_1$) is that for the step in which the methylene radical is formed; interconversions between the $CX_2$ and $CX$ radicals will occur readily if the $E_2$ barrier is overcome.

![Figure 1.1](image_url)

FIG. 1.1. Energy diagram for the exchange of methane, where (g) and (a) denote gas phase or adsorbed species respectively.

The pattern observed for ethane was similar in that, on tungsten and molybdenum films, stepwise replacement was effected by an adsorbed ethyl radical, while on palladium and rhodium, interconversion between an adsorbed ethyl intermediate and an adsorbed ethylene species resulted in complete exchange of all six hydrogen atoms.

Comprehensive summaries of exchange reactions and their mechanisms are available in a number of excellent review articles (78-87).

Adsorbed Intermediates: Figure 1.2 illustrates the surface – adsorbate geometry of the various types of intermediate commonly found in the exchange reactions of alkanes. The nomenclature shown is dependent on the number and location of the
hydrogen atoms removed from the hydrocarbon on adsorption. The monoadsorbed species can be identified with stepwise processes, the $\alpha\ast$-diadsorbed with multiple exchange, in particular of methane, the $\alpha\beta$- with multiple replacement in the case of ethane and the longer chain homologues, and the $\alpha\gamma$- with multiple exchange of hydrocarbons containing a tertiary carbon atom. Evidence for the latter was indicated in the exchange of neopentane on tungsten and rhodium films$^{(88)}$.

\[ \text{MONOADSORBED} \]

\[ \alpha\ast \text{-DIADSORBED} \]

\[ \alpha\beta \text{-DIADSORBED} \]

\[ \alpha\gamma \text{-DIADSORBED} \]

\footnotesize{FIG. 1.2. Intermediates for exchange of hydrocarbons.}

Kemball$^{(87)}$ has discussed the relation between the stability of intermediates characteristic of a particular metal and the latter's ability to catalyse hydrocarbon reactions other than exchange. For example, the tendency of rhodium to catalyse multiple exchange reactions$^{(76)}$, some of them being self-poisoned at
higher temperatures (89), and its considerable activity at even greater temperatures towards hydrogenolysis (90) i.e. the breakdown of a hydrocarbon in the presence of hydrogen to form smaller molecules, can be ascribed to the variation in stability with temperature of the adsorbed species formed on the metal. Thus, the multiple exchange, self-poisoning and hydrogenolysis processes on rhodium may successively originate from a reversibly formed intermediate which, with increasing temperature,

\[
\begin{align*}
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surface area exposed to the gas phase; and in this respect, several different physical forms with varying surface areas have been employed such as metallic sponges, colloidal metals, skeletal metals (91-94) and metal powders (95). Although a larger surface area may enhance activity, any loss in surface purity even by trace contamination from materials involved in catalyst preparation may easily eliminate this advantage, and it is therefore often necessary to submit the metal surface to a lengthy period of thermal cleaning before catalytic use.

For high surface area and purity, industry has favoured the metal supported catalyst, manufactured, in general, by impregnating a support, such as silica or alumina, with a solution of the metal salt, evaporating to dryness and reducing to the metal at high temperature. These catalysts have been studied in exchange (96-98), hydrogenation (99-103), hydrogenolysis (104-107), isomerization (108-110) and aromatization reactions (111), the interpretation of results often being obscured by the need to distinguish the respective contributions of metal and support to the reaction mechanism (112).

Metal Films: High purity metal surfaces with lower surface area may also be derived from the evaporated film technique which has been widely applied to metals readily available in wire form since the initial developments of Beeck and his colleagues in 1941 (113), and has also been the source of all catalysts used in the present investigations. Their preparation basically involves a thin filament of the metal enclosed under vacuum in a glass vessel, the walls of which can be outgassed by a surrounding furnace while the wire itself is rid of dissolved species by resistance heating for an adequate length of time. The vessel can then be cooled and the current passing through the wire raised till metal atoms evaporate and condense as a metal film on the glass substrate.
Metal catalysts prepared in this manner have a porous structure, the total surface area presented to the gas phase being several times bigger than the observed geometric area, and are composed of large crystallites, sufficiently random in configuration to render the electrical conductivity of the film much less than that of the bulk metal\(^{113}\). The technique described does not normally lead to any preferred orientation of the crystal planes exposed on the surface; this latter effect can be achieved, however, by evaporation on to a carefully chosen substrate, and films with this property have been found to display catalytic behaviour\(^{114}\) characteristic of the oriented surface. Another feature of both random and oriented metal films is that they tend to be thermally unstable and undergo sintering with loss in surface area – and consequently catalytic activity – when heated to temperatures in excess of that used for deposition.

Catalytic scholars have traditionally sought a relationship between the activity of metal catalysts, their surface geometries and electronic properties. **Surface Geometry:** Effective interaction between reactant and catalyst may be expected if the stereochemistry of the adsorbate can be readily accommodated by the pattern of atoms constituting the solid surface, and there is considerable evidence to support this idea. The activation energies for \(\text{H}_2\) adsorption on various catalysts were found to be a function of the surface lattice spacing\(^{115,116}\), and the activity of the nickel (100) crystal planes towards ethylene hydrogenation was observed to be a factor of five greater than that of an unoriented nickel film\(^{113}\). The Balandin 'multiplet' theory of catalytic activity\(^{117-122}\), again based on the presence of precise atomic groupings, predicted that a metal such as iron with a body-centred cubic lattice should have difficulty in accommodating an adsorbed benzene structure in the hydrogenation of benzene to cyclohexane; experiments by
Emmett (123) with a powdered iron catalyst have verified its inactivity for this reaction. The role of stereochemistry in olefin hydrogenation mechanisms has been reviewed by Siegel (84) and Bond and Wells (124).

Two further considerations of this nature are the availability of catalytically active surface and the permanence of its geometry under different experimental conditions. Only a fraction of the total surface area present may be involved in promoting a particular process and this may be further reduced by 'poisoning' or thermal means. An instance of these effects was the preferentially inhibited replacement of ring hydrogens over their substituent group counterparts in the deuterium exchange of alkyl benzenes on nickel films (125), achieved by apparently destroying the highly active sites at 473K or by blocking them with presorbed carbon monoxide. Lastly, the concept of geometrically favoured catalysis has been somewhat complicated recently by increasing evidence from electron microscopy and low energy electron diffraction studies for the breakdown, rearrangement or generation of crystal planes on the surface as a result of considerable heating or chemisorption of gases (see Section 1.5.).

Electronic Properties: Assuming no stereochemical impediment prior to adsorption, the facility of reaction may then depend on the chemical i.e. electronic environment provided by the metal catalyst to the adsorbate. Early investigations (126) on these lines were based on the current advances in solid state theory, but a more precise approach was not evolved until Pauling (127) pointed out that the consistently higher activity of transition metals over other catalysts for most catalytic processes must be related to the vacant d-orbitals in their electronic structures. The correlation between the percentage d-bond character of a metal and its catalytic activity in the form of heats of adsorption (128), log of reaction rate (129) etc. has
been established for many systems (130,131), including the adsorption and hydrogenation of ethylene on films (128,129) and also reactions on alloys (132,133), a convenient way of varying the d-orbital content of essentially the same catalyst. The d-bond character tenet suffers from many weaknesses, not least of all its failure to rationalize the often widely diverging catalytic activities of different crystal faces belonging to the same metal and with the same d-orbital content, the variation in activity sometimes being more significant than that observed between two metals of markedly different d-bond character (134,135).

In criticizing the concept of an exactly defined electronic contribution to catalytic activity, Sachtler and his co-workers (136) have tried to shift emphasis to the energetics and thermodynamic aspects of the gas - solid interaction. They demonstrated clearly in their classical infra-red studies (137-140) of formic acid decomposition on metals that the concentration of adsorbed species, and hence the reaction rate and catalytic activity, was controlled by the heat of formation of the metal formate, the intermediate responsible for decomposition in each case; these arguments have in turn been discussed critically by Bond (141).

The conclusion one can draw from all the foregoing proposals is that the catalytic activity of a metal is probably due to a combination of several factors, geometric, electronic, thermodynamic etc., rather than a single cause, the predominant influence being determined by the nature of the system in question.

1.5. Research Techniques in Catalysis

Heterogeneous catalysis has consistently succeeded in keeping pace with, and making optimum use of, new research techniques, electronic, spectroscopic etc., which have evolved at regular intervals through the years as a result of theoretical
advances in physical chemistry.

**Surface Potentials:** One group of experimental methods applied to catalytic studies is that associated with the work function of a metal surface, the dipole moment of an adsorbate, and the interaction of these two effects to produce a surface potential when an adsorbed layer is formed. These phenomena have been the basis of several investigations by Roberts (142-144) and Tompkins (145) into the nature of catalyst - adsorbate bonding. Techniques for estimation of surface potentials, recently reviewed also by Tompkins (146), include photoelectric emission studies (147,148) and measurement of contact potential, the sign of which may alter with surface coverage (149) and with adsorption on different crystal faces (150,151). In the field emission microscope, first developed by Müller (152), electrons are emitted from the metal surface under test to form an image on a luminescent screen, characteristic of the various work functions of the exposed crystal planes; the emission current is sensitive to changes in surface potential, so the formation and surface mobility of adsorbed layers can be monitored with field emission patterns (153). In field ion microscopy (154-156), the electric fields present are strong enough to cause field desorption i.e. removal of adsorbed species from the surface which may then be identified by time-of-flight mass spectrometry.

**Flash Desorption:** A similar detection system is often employed in flash desorption (157), where evolution of adsorbed gas is produced by sudden heating of a metal filament to a sufficiently high temperature. The temperature dependence of desorption has yielded information on the kinetics of surface processes, and its tendency to occur in distinct stages, as with nitrogen on tungsten (158), has indicated the number, nature and strength of the available binding states between
adsorbate and surface. This method has also been one of those used to determine the sticking coefficient of a catalyst \(^{(159)}\), defined as the probability of an atom or molecule being adsorbed on a single encounter with the surface, and has been extensively investigated by several authors \((160-164)\).

**Magnetic Susceptibilities:** If the establishment of a bond between a surface atom and an adsorbed particle reduces or destroys any magnetic dipole associated with that atom, then the intensity of magnetisation of the substance as a whole is diminished. On this general basis, experiments involving changes in magnetic susceptibility have been carried out by workers such as Selwood \((165-167)\) and Stone \((168)\) to elucidate the nature of the bonds formed on adsorption.

We now move on to spectroscopy which, in all its guises, must today be considered the most formidable tool of catalytic research. Before hearkening back to the more traditional forms of the art, there follows a brief summary of those techniques which sprang to life soon after the advent of ultra-high vacuum technology, an essential means of obtaining and preserving clean metal surfaces.

**Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES):**

If a metal crystal is bombarded with a monochromatic beam of low-energy electrons, then the back-diffracted electrons which have been elastically scattered by the surface can give rise to a LEED pattern \((169)\). Alternatively, after electron impact, inner shell ionizations and radiationless electronic transitions within atoms of the metal, ejection of secondary electrons from the surface may result in an Auger spectrum \((170)\).

The particular usefulness of LEED for studying adsorption processes stems from the fact that adsorption usually takes place with some degree of order so that distinct diffraction patterns may emerge, allowing any new periodicity
parallel to the substrate surface to be easily established. For example, when oxygen was adsorbed on the (100) face of nickel\textsuperscript{(171)}, the unit mesh became twice the size of that characteristic of the nickel surface alone, suggesting a probable surface rearrangement with nickel atoms being replaced by oxygen in a regular manner. LEED experiments have also shown that metals such as silver may develop crystal planes not present originally, when heated to temperatures just below their melting points\textsuperscript{(172)}.

Auger spectroscopy is particularly suitable for the analysis of constituents on a solid surface or in the first few layers below the surface. An instance of its extreme sensitivity to surface impurities was the detection of caesium on a silicon (100) substrate at concentrations as low as 2% of a monolayer\textsuperscript{(173)}. The information provided by LEED and Auger spectra can often be complementary, so experimental arrangements are now generally designed to accommodate both techniques.

**Electron Spectroscopy for Chemical Analysis (ESCA):** The principle of ESCA (also called X-ray photoelectron spectroscopy) is that X-rays incident on a sample may cause the ejection of photoelectrons by primary or Auger processes, whose kinetic energy, and consequently binding energy in the solid, may be measured with high precision\textsuperscript{(174)}. Chemical shifts in these binding energies can reflect environmental changes in the surface layers of a solid upon adsorption, an effect observed for example with nitrogen - containing molecules adsorbed on zeolites\textsuperscript{(175)}. ESCA would therefore appear to be a promising method of characterizing catalytic systems.

**Molecular Beams:** Experiments involving the reactive scattering of incident molecular beams by different types of surface and the detailed examination of their resulting angle of scatter and energy distributions have begun, in very recent years, to augment our knowledge of the collision dynamics, reaction probabilities,
surface residence times, product selectivity, free radical formation and adsorption processes associated with gas-solid catalysis (176). Furthermore, the ability to define and measure at a fundamental level the elementary reaction steps constituting an overall catalytic change has been to some extent realised. Oxidation of ammonia (177) and hydrogenation of ethylene on platinum (178) are two systems which have been studied by this technique.

The more traditional spectroscopic methods, I.R., U.V. and E.S.R. have also been useful as direct sources of information on the nature of surface species, although interpretation has sometimes proved difficult.

Infrared and Ultraviolet Spectroscopy: I.R. studies in catalysis depend on the presence of adsorbed species with vibrations that are active in the infrared region of the spectrum; the appearance, absence or changes in intensity of the corresponding absorption bands can be followed closely as experimental conditions are varied. In examining the adsorption of ethylene on a nickel surface, Eischens (179,180), one of the pioneers in this field, deduced from the variations in position and intensity of the C-H bands the probable structure of the adsorbed intermediate. Recent catalytic sorties with the infrared include the delicate yet comprehensive experiments of Kokes and Dent (181-185) on ethylene hydrogenation, and also the elegant pursuit of a propylene disproportionation intermediate by Howe, Davidson and Whan (186). A limitation of this type of work — carried out less frequently on metals than on supported catalysts — is that an abundant but unreactive surface species may be easily identified, while an important catalytic intermediate may be present in too small a concentration to be detected.

Electronic transitions in adsorbed species have been observed by ultraviolet spectroscopy — a technique less widely applied than infrared. With this method,
Leftin and Hall (187) obtained the electronic spectra of \( \alpha \)-methylstyrene and 1,1-diphenylethylene adsorbed on a silica-alumina catalyst, and demonstrated the presence of carbonium ion intermediates.

**Electron Spin Resonance:** Paramagnetic surface entities with one or more unpaired electrons may be discernible by E.S.R. spectroscopy; these may be supported metal ions, surface defects, adsorbed complexes etc. Of particular interest to the catalytic chemist is the high sensitivity attainable for studying low concentrations of active sites and this may lead to information varying from a simple confirmation that an unknown paramagnetic species is present to a detailed description of the bonding and orientation of a surface intermediate. The investigations of Flockhart and co-workers (188-190) are typical of electron spin resonance work; for example, from the E.S.R. spectra of trinitrobenzene adsorbed on partially dehydrated aluminas, they attributed the generation of anion radicals to the availability of two types of reducing sites, the predominance of either being dependent on dehydration temperature.

**Tracer Methods and Mass Spectrometry:** As indicated earlier in this introduction (see Section 1.3.), tracer experiments, involving replacement of one isotope by another of the same element, have constituted a major avenue of research on the nature and properties of catalytic intermediates.

With isotopes such as \(^{14}\)C and tritium, a radioactivity counter is essential to the apparatus as a method of detection. Investigations with radioactive tracing include those on the mechanism of Fischer–Tropsch syntheses with \(^{14}\)C-labelled alcohols by Kummer and Emmett (191), and also the catalyst poisoning studies of Thompson and co-workers (192-198) using tritiated hydrogen and the mercury isotope \(^{203}\)Hg. Stable isotopes such as \(^{13}\)C and deuterium have been used more
extensively than their shorter-lived counterparts - predominantly for exchange reactions, but also in other types of catalytic work; for instance, the Anderson and Avery investigation into the isomerization mechanism of aliphatic hydrocarbons on platinum and palladium films\textsuperscript{(114)} included \textsuperscript{13}C tracer methods.

Deuterium incorporation in the exchange reactions of hydrocarbons has generally been monitored by mass spectrometry, the reactant and products for such a process being the same chemically, but differing in mass number according to their degree of isotopic substitution. The experimental arrangement for this technique has usually consisted of a reaction vessel coupled to a low resolution, high sensitivity mass spectrometer by means of a fine capillary leak, thus allowing continuous isotopic analysis of the reaction vessel contents during the exchange process\textsuperscript{(80)}. Mass spectrometry has therefore been a vital factor in the observation of deuterium substitution processes and consequently in the elucidation of catalytic mechanisms.

**Gas Chromatography:** The identification and quantitative estimation of catalytic reaction products may be achieved by chromatographic separation of each component from a sample of the reaction mixture and subsequent detection e.g. by flame ionization or thermal conductivity measurements. From the product distributions obtained in this way, it is possible to evaluate kinetic or thermodynamic parameters such as reaction rate or apparent activation energy - a typical illustration of this procedure again being found in the hydrogenolysis and isomerization studies of Anderson\textsuperscript{(114)}.

In concluding this section, it can be said that there are many more techniques not mentioned here which have also found a useful place in catalytic research; the final trio of those listed are, however, basic to the remainder of this thesis, which is devoted to the development and application of deuterium tracing with a
combined gas chromatograph - mass spectrometer apparatus.

1.6. The Present Study - Aspirations

The relevance of examining low temperature hydrocarbon exchange experiments, involving isotopic replacement only, to the industrially important higher temperature processes involving chemical changes to the reactant molecules such as breakdown or rearrangement of the carbon skeleton has been recently brought into question by increasing evidence (87) that the adsorbed species responsible for the low temperature exchange phenomena are not the same as those required for the higher temperature reactions. Broadly speaking, therefore, the purpose of this study was to examine the nature of these higher temperature intermediates, and also to deduce the reaction mechanisms of hydrocarbon decomposition or rearrangement processes dependent on them.

To achieve this aim by an extension of deuterium tracing techniques, it was fully realised that conducting experiments with more complex systems of this kind in the presence of deuterium would result in isotopic labelling of both reactant and products taking place simultaneously with the other catalytic processes under investigation. The problem, then, of analyzing such complicated reaction mixtures would inevitably be a formidable one, and almost certainly beyond the scope of the more traditional analytical methods (see Section 2.1.); it was decided therefore to develop an alternative technique for this purpose, involving the direct combination of gas chromatography and mass spectrometry.

The particular reactions chosen for examination in this manner were those of the lower molecular weight saturated hydrocarbons on evaporated metal films of platinum and iron.
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2.1. Introduction

The choice of experimental methods to be used in the work of this thesis was fashioned by the inherent analytical complexities of accurately estimating, at preferably limited extents of reaction, the isotopic contents of reactant and product components in a multi-hydrocarbon mixture. The standard techniques commonly employed in previous tracer studies were discarded in turn by the following arguments.

Exchange reactions of hydrocarbons have generally been investigated using a direct leak between the reaction vessel and a mass spectrometer \(^{(1)}\); this method would not be appropriate here as the potential precision in determining isotopic distributions for the lighter hydrocarbons would be considerably impaired by the presence of fragmentation contributions from those of higher carbon number, so analysis by mass spectrometry alone without prior separation of the compounds would be impracticable. It should also be said, perhaps, that although chromatographic separation of a small range of isotopic species has been achieved \(^{(2)}\), there was no G.C. column known to the author which could adequately resolve each member of the several groups of isotopic hydrocarbons formed in the reaction vessel; consequently, quantitative analysis by chromatography alone was equally impossible.

All the work on catalytic exchange reactions has shown convincingly that,
for optimum retrieval of information on intermediates and mechanisms, it is advantageous to obtain isotopic product distributions at low conversions. In these early stages of reaction, however, the small quantities of products present might be insufficient to permit use of the more established procedure\(^{(5,4)}\) of trapping out and collecting the individual hydrocarbons after chromatographic separation, followed by separate transfer of each fraction to a mass spectrometer. Furthermore this method, apart from being rather tedious and open to the hazards of poor trapping\(^{(5)}\), would also generally involve the complete removal of the reaction vessel contents in one sample, thus preventing further analyses being carried out, if desired, at later stages of the reaction.

On the basis of these foregoing considerations, the direct combination of gas chromatography for separation of the reactant and products and fast-scanning mass spectrometry for determination of the number and distribution of deuterium atoms present in each eluted component was chosen to meet the sensitivity requirements posed by the removal of several small samples at suitable points in the reaction from a labelled multi-hydrocarbon mixture.

A schematic representation of the complete experimental system is given in Figure 2.1., the basic units being the gas handling line, the reaction vessel, the gas chromatograph, the G.C.-M.S. interface, the spectrometer and mass spectra recording equipment. The greater operational intricacy of the combined G.C.-M.S. apparatus warranted careful selection of experiments to be studied by the technique. This was effected by using the gas chromatographic section only, with quantitative analysis provided by a flame ionization detector (see Figure 2.1.) for exploratory experiments involving the approximate measurement of kinetic parameters and general optimization of operating conditions for the subsequent
Figure 2.1. G.C.-M.S. APPARATUS
G.C.-M.S. runs; in some cases, G.C. analysis alone was used for more detailed kinetic studies (vide infra).

2.2. The Gas Handling Apparatus

A diagram of the gas handling vacuum line is shown in Figure 2.2. The line was constructed throughout of 'Pyrex' glass, all the ground glass joints and stopcocks being lubricated with low vapour pressure, Apiezon L high vacuum grease. Evacuation of this system to a pressure of $6.7 \times 10^{-4} \text{ Nm}^{-2}$ was attained by means of an electrically heated, Admiralty type mercury diffusion pump 'DPI', backed by a two stage 'Speedivac' rotary pump 'RPl', mercury contamination from the former being prevented by an adjacently placed liquid nitrogen cold trap 'CTl'. High vacuum pressure measurements were made with a McLeod gauge 'MG' of volume $3.12 \times 10^{-4} \text{ m}^3$, the calibration and operation of which have been described elsewhere\(^6\). Retention of a good vacuum was ensured by regular maintenance of the rotary pump, cleaning of the cold trap and avoidance of 'streaking' in the tap grease.

The gas handling apparatus provided facilities for purification and storage of hydrogen, deuterium and hydrocarbons in the glass bulbs 'GB' permanently attached to the line; any additional gases or liquid hydrocarbons required could be stored in detachable bulbs via the ground glass joints at 'DJ'. A diaphragm pressure gauge 'DG' calibrated in Torr ($= 133.3 \text{ Nm}^{-2}$) and connected to the mixing volume 'M' was used for measurements in the coarse vacuum range, as for example in the preparation of reaction mixtures.

**Volume Calibrations:** In preparing gas mixtures or calculating the number of molecules present in the reaction vessel it was useful to know the actual sizes
Figure 2.2. The Gas Line.
of the mixing volume 'M' and the reactor 'R'. These were obtained by successive expansions into the evacuated, uncalibrated sections of the line from a standard bulb of volume $5.27 \times 10^{-4} \text{ m}^3$ (calibrated with water at 298K), filled with a measured pressure of hydrogen and attached to the gas handling line at 'A4'. The reduced pressure value obtained on each expansion step was estimated with the diaphragm gauge 'DG' and Boyle's Law ($P_1 V_1 = P_2 V_2$) was applied in each case to calculate the unknown volume. The values obtained in this way at 298K were

\[
\text{Mixing Volume 'M' } = 1.547 \times 10^{-4} \text{ m}^3 \\
\text{and Reaction Volume 'R' } = 2.44 \times 10^{-4} \text{ m}^3,
\]

corresponding to an expansion factor of 0.382 between 'M' and 'R'. This factor determined the partial pressures of gases constituting the reaction mixture, and also allowed estimation of the actual number of molecules present in the reaction volume at any given temperature.

2.3. The Reaction Vessel and Sampling System

The 'Pyrex' glass reactor 'R' (see Figure 2.2.) consisted of a removable cylindrical vessel, approximately 35mm. in diameter and 0.13m. in length, and attached to the apparatus by means of a greased B24 ground glass joint which fitted into a water cooled jacket, thus allowing easy removal and replacement between experiments. A pair of glass-encased 2mm. tungsten rods were sealed through the top of the joint and carried internal mild steel connectors for holding the wires employed in evaporation of metal films. After dissolving the used metal catalyst (see Section 2.5.), the reaction vessel was thoroughly cleaned with chromic acid, washed out several times with distilled water and oven-dried in readiness for its next mounting on the apparatus.
The reactor could be outgassed to a pressure of 0.133 mN m⁻² with a mercury diffusion pump and rotary pump combination, 'DP2' and 'RP2', similar to that used for evacuation of the gas handling line, plus the assistance of external heating up to 723 K. In this case, mercury was excluded from the vessel by the liquid nitrogen trap 'CT2', and high vacuum pressure measurements were again carried out with the McLeod gauge 'MG' (see Figure 2.2).

Heat was supplied externally to the reactor by a close-fitting electric furnace, constructed from an iron tube about 55 mm in diameter and 0.2 m in length, wound evenly with resistance wire in the middle, but overwound at top and bottom to minimise temperature gradients. The furnace temperature was kept to within 0.5 K of the desired value by a Eurotherm proportional controller and chromel–alumel thermocouple; with maximum current flowing, the temperature of the furnace could be raised 50 K and stabilized within 6–7 minutes. The Eurotherm temperature scale was however found to be increasingly inaccurate the greater the temperature; to overcome this error, the true temperature was monitored with a digital voltmeter (D.V.M.), which was fed by a chromel–alumel thermocouple with its cold junction at 273 K. Table 2.1. gives the calibration points for determining the correct setting for any required furnace temperature. The D.V.M. temperatures were read directly from a chromel–alumel thermocouple calibration chart.

<table>
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<th>True Temperature (D.V.M.)</th>
<th>T/K</th>
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<td>321.5</td>
<td>369</td>
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| Required Eurotherm Setting | 323 | 373 | 423 | 473 | 523 | 573 | 623 | 673 | 723 |
Sampling: Removal of samples from the reactor at suitable stages in the course of a reaction was carried out by a three-way glass stopcock 'V1' and a Perkin-Elmer gas sampling valve 'G' fitted with a P.T.F.E. rotor (see Figures 2.1. and 2.2.). The valve was connected to one of two interchangeable stainless steel loops; these were of volume $5 \times 10^{-6} \text{ m}^3$ for G.C.-M.S. experiments and $2.5 \times 10^{-7} \text{ m}^3$ for those involving chromatography only, much smaller samples being required for that mode of analysis.

The steps involved in the sampling procedure were as follows:

1. Before taking a sample, the three-way stopcock and sampling valve (in fully clockwise position) were set such that the steel loop could be evacuated by the gas line pumping system.

2. On sampling, the three-way tap was turned clockwise through $120^\circ$ to link the reaction vessel and loop for a period of ten seconds.

3. The tap was then closed by turning it approximately $60^\circ$ anti-clockwise to a neutral position and at the same time, the sampling valve was rotated fully anti-clockwise to seal the loop from the gas line and link it to the carrier gas supply. It was kept in this position for about 1 minute to allow the contents of the loop to be flushed into the gas chromatograph column by the carrier gas.

4. Finally, both stopcock and valve were returned to their original positions to allow re-evacuation of the sampling loop in readiness for the next sample.

Calibrations at 298K showed that the steel loop used in G.C. experiments resulted in the removal of 2.4% of the reaction vessel contents on taking each sample; with the 20 times larger G.C.-M.S. loop at 298K, about 4.3% of the reacting material was withdrawn on each occasion. The values for sampling losses at actual reaction temperature could be calculated from the relationship
\[ \frac{P_1}{P_2} = \frac{T_1}{T_2} \]; in this way, it was possible to decide how many samples could be taken from the reaction vessel without seriously disturbing the reaction kinetics of the system under study. In general, a G.C.-M.S. experiment involved a much smaller number of samples than its 'G.C. only' counterpart, not solely from the standpoint of sample size, but also from the fact that G.C.-M.S. samples removed at later stages in a reaction were usually less informative than initial ones.

To prevent erratic variations in sample size, both the three-way stopcock and sampling valve were regularly checked for leaks or blockages; in this connection, it was sometimes found necessary to protect the three-way tap from heat-induced streaking or seizing by placing an aluminium heat-shield around the neck of the reaction vessel, just a few centimetres above the top of the furnace.

2.4. The Preparation of Reactants

Purification and storage of any of the gases used in this work was only attempted in the presence of a sufficiently good vacuum in the gas line as indicated by the McLeod Gauge 'MG' (Figure 2.2.). The source and purity (supplier's specification) of each reactant are listed in Table 2.2. Before admission of each

<table>
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<tr>
<th>Supplier</th>
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<tbody>
<tr>
<td>Cambrian Chemicals Ltd.</td>
<td>Deuterium, Hydrogen, Ethane, Isobutane</td>
<td>99.9%</td>
</tr>
<tr>
<td>Phillips Petroleum Co.</td>
<td>n-Butane, Propane</td>
<td>Research Grade</td>
</tr>
<tr>
<td>Chemical Standards Division, National Physical Laboratory</td>
<td>Neopentane</td>
<td>99.9%</td>
</tr>
<tr>
<td>Cambrian Chemicals Ltd.</td>
<td>Methane</td>
<td>99.9%</td>
</tr>
</tbody>
</table>
gas, the appropriate storage bulbs were repeatedly flamed under evacuation to remove any adsorbed impurities from the glass walls.

**Deuterium:** This was admitted to the crude deuterium storage bulb by means of the mercury bubbler 'MB' (Figure 2.2.) and was then purified by diffusion through an electrically heated palladium-silver alloy thimble 'PT'. Before collection of deuterium in the pure gas storage bulb, those sections of the gas line involved in the purification were flushed with deuterium, again to remove adsorbed impurities. The line was then isolated at 'A2' and 'A3' from the pumps, and the cold traps 'CT3' and 'CT4' were surrounded by liquid nitrogen; these traps performed the double function of preventing mercury vapour from reaching the hot thimble where it might cause leakage and rapid deterioration in performance and secondly of removing any remaining condensible impurities in the deuterium after diffusion through the thimble. The latter was heated by applying a voltage across the associated resistance heater (Figure 2.2.) such that diffusion of pure deuterium into the storage bulb occurred at a rate of approximately 2 kNm$^{-2}$ hr$^{-1}$. The technique described here for deuterium was also applicable to purification and storage of hydrogen.

**Hydrocarbons:** On admission to the gas line, either directly at 'D1' or via the mercury bubbler 'MB', each hydrocarbon was purified before being removed to one of the storage bulbs. This procedure involved thorough degassing of the hydrocarbon sample by a repeated cycle of freezing, pumping and thawing with the aid of the liquid nitrogen cooled traps 'CT3' and 'CT4'. On the final distillation step, only the middle third of the frozen hydrocarbon sample was used for storage purposes to ensure the highest purity possible, the other two thirds being released to the pumps. Methane, which has a sizeable vapour pressure even at
liquid nitrogen temperatures, could not be completely trapped down for distillation purposes; in this case, the hydrocarbon which was supplied in a state of ultra-high purity was extracted directly from the gas cylinder without further purification.

Reaction Mixtures: The standard reaction mixture employed in all but a few of the experiments in this work consisted of an 11.5:1 ratio of deuterium to hydrocarbon. The actual partial pressures used in the reactor 'R' were 427 kNm⁻² of hydrocarbon and 4.91 kNm⁻² of deuterium measured at 273K, and in a reaction volume of 2.44 x 10⁻⁴ m³, this mixture corresponded to values of 2.76 x 10¹⁹ and 3.17 x 10²⁰ molecules of hydrocarbon and deuterium, respectively. To achieve such reactant pressures in the reaction vessel, it was necessary to allow for the expansion factor between the mixing volume 'M' and the reactor 'R' (Section 2.2.), so the gas pressures required in the former were 1.07 kNm⁻² of hydrocarbon and 12.3 kNm⁻² of deuterium. In practice, the mixture was made by admitting the hydrocarbon component into the evacuated mixing volume first, the correct pressure being indicated by the diaphragm gauge 'DG' (Figure 2.2.). An adequate head of deuterium pressure was built up on the other side of the stopcock separating the mixing volume from the rest of the gas handling line; this tap was opened slightly till the desired total reactant pressure was reached on the diaphragm gauge and then closed, the excess of deuterium on the gas line side preventing any back diffusion of hydrocarbon from the mixing volume. Before expansion into the reactor at the start of a catalytic experiment, the gaseous reactants were generally kept in the mixing volume for at least 1 hour to obtain a completely homogeneous mixture. Lastly, in cases where an equimolar mixture of two or more hydrocarbons was necessary, it was possible to freeze down an equal pressure of each one individually from the mixing volume into a sample tube attached at 'A4' (Figure 2.2.)
and then re-expand the required fraction of this mixture back into the freshly evacuated mixing volume before adding the deuterium.

2.5. The Preparation of Metal Catalysts

The metal catalysts were prepared by the well-established technique (8,9) already described briefly in Section 1.4, and Table 2.3. gives details of the materials and mode of preparation for both platinum and iron films. Although it was possible to produce an iron film by direct evaporation from a filament of the metal, the platinum wire on its own showed a tendency to melt before its vapour pressure was sufficiently high for film deposition and consequently had to be supported on a tungsten filament (Tungsten Manufacturing Co. Ltd., pure grade); this was achieved by winding the platinum wire around one of tungsten (Table 2.3.), taking care to maintain an even distribution of the former throughout. The thickness of the supporting tungsten and its much higher vaporisation temperature

<table>
<thead>
<tr>
<th>Metal</th>
<th>Platinum</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Johnson Matthey</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Quality</td>
<td>Specpure grade</td>
<td>Specpure grade</td>
</tr>
<tr>
<td>Filament preparation</td>
<td>0.30m of 0.1mm diameter Pt wire wound on 0.15m of 0.3mm diameter W wire</td>
<td>0.15m of 0.4mm diameter Fe wire</td>
</tr>
<tr>
<td>Outgassing procedure</td>
<td>6.6A for 30min</td>
<td>2.5A for 30min (α→γ transition 3.0A)</td>
</tr>
<tr>
<td>Evaporation procedure for 10mg film</td>
<td>7.8A for 20min</td>
<td>3.6A for 8min</td>
</tr>
</tbody>
</table>
were such that evaporation of the support simultaneously with the platinum was extremely improbable and this supposition was vindicated by an unsuccessful attempt at forming even the lightest of films from a filament of the tungsten wire under the conditions of platinum film preparation.

With platinum, it was also possible to improve reproducibility of catalytic activity by throwing and discarding a light preliminary film from the tungsten supported platinum filament; this was carried out using the normal outgassing and evaporation currents for reduced periods (50% of standard) prior to the initial experimental procedures for reaction vessel and film preparation (vide infra). Such a technique was not employed with iron since the rate of evaporation from the latter was extremely sensitive to small changes in current and it could not be guaranteed either that the iron wire would not burn out during preparation of the second film or that the weight of catalyst so produced would be sufficiently reproducible. To increase the efficiency of outgassing in iron film preparation, the current was raised to 3.0A and then lowered to 2.5A again over a period of two minutes in the early stages of the outgassing process (Table 2.3.); these changes in current had the effect of inducing an \( \alpha \gamma \) phase transition in the iron filament and, consequently, facilitated removal of dissolved species such as hydrogen\(^{10}\) from the wire before evaporation.

The general catalyst preparation procedure was as follows. The filament (after throwing a preliminary film in the case of platinum) was weighed and then attached in the form of a loop to the tungsten rod connectors (Section 2.3.) such that it hung centrally inside the freshly cleaned reaction vessel which was subsequently placed in position around it (Figure 2.2.). The reactor enclosing the metal wire was then baked overnight at a pressure of \( 1.3 \times 10^{-4} \text{ Nm}^{-2} \) and
temperature of 723K. During the outgassing period, the reaction vessel was maintained at 723K and kept open to the pumps for evacuation of species desorbed from the metal filament. The furnace was then removed and the reactor cooled to 273K in an ice-water bath. The current was raised to the evaporation value and the film thrown for sufficient time to allow deposition of about 10mg of catalyst; during evaporation the filament resistance rose to an extent that the voltage applied to the wire had to be continually increased to maintain the correct throwing current. During the period of film deposition, the reactor was also closed off from the pumps since it was thought that the 'gettering' effects of the first few layers of evaporated metal atoms might be sufficient to significantly improve the vacuum present in the reaction vessel by removal of gaseous impurity, and hence give rise to a much cleaner catalytic surface. After preparation of the film, the wire was allowed to cool for about 3 minutes before admission of the reaction mixture. On completion of an experiment, the used filament was carefully removed and re-weighed to yield a precise measure of the catalyst weight. The metal film was dissolved from the walls of the reactor by addition of aqua regia.

When a metal catalyst is heated to temperatures above that employed for deposition, it may undergo sintering with a resultant loss in catalytically active surface area; for studies in which a sintered film was used as catalyst, the details of preparation have been quoted in the appropriate experimental section (see Chapters 4 and 5). No attempt was made to measure accurately the active surface area of either the platinum or iron films.

2.6. The Gas Chromatograph

Each gas sample withdrawn from the reaction vessel by the technique described
in Section 2.3. was flushed by the appropriate carrier gas into a Perkin-Elmer F11 gas chromatograph 'C' (Figure 2.1.) to enable separation of each hydrocarbon component in the sample mixture. In the G.C.-M.S. experiments, helium was used as carrier gas to allow efficient operation of the Biemann-Watson molecular separator (see Section 2.8.) while for G.C. analysis only, it was more economical to use nitrogen. The chromatograph employed a packed column, 8m in length and containing bis-2-methoxyethyladipate (13.5%) and di-2-ethylhexylsebacate (6.5%) on 60-80 mesh Chromosorb P. The column was maintained at room temperature inside the chromatograph oven and the carrier gas was fed at a pressure of 310 kNm⁻² and a flow rate of $0.67 \times 10^{-6} \text{ m}^3\text{s}^{-1}$; under these conditions, complete base-line separation of all the saturated hydrocarbons used in the present study was readily achieved, the approximate individual retention time for each paraffin being shown in Table 2.4.

**TABLE 2.4. GAS CHROMATOGRAPHIC RETENTION TIMES**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Isobutane</th>
<th>n-Butane</th>
<th>Neopentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention time/min</td>
<td>3.7</td>
<td>4.2</td>
<td>6.1</td>
<td>8.3</td>
<td>10.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The minimum interval between samples in a 'G.C. only' experiment was determined by the difference between the retention times (allowing for complete elution) of the first and last hydrocarbons to emerge from the column; in this way, it was possible to introduce a further sample to the chromatograph a few minutes before completion of the previous one. This procedure was not possible in a G.C.-M.S. run where the greater operational complexity of the mass spectrometer made maximum frequency sampling an impracticality.

The whole effluent from the column was either routed via the stainless steel
capillary 'J' (Figure 2.1.) to the molecular separator in the case of G.C.-M.S. studies or directly to the Perkin-Elmer flame-ionization detector 'F' (Figure 2.1.) when only chromatographic analysis was required. In the second of these, the detector flame was fed by hydrogen and air at pressures of 118 and 174 kNm\(^{-2}\), respectively, and the ionization current produced by combustion of each hydrocarbon was amplified and displayed in integrated peak form on a Servoscribe potentiometric recorder operated with a chart speed of 1 cm min\(^{-1}\) to facilitate product identification by means of retention time. The recorder was coupled in parallel with a Kent Chromalog 1 Digital Integrator which simultaneously provided a printed output of the hydrocarbon peak areas. Prior to each G.C. run, the ionization amplifier and recorder were 'zeroed' to give a steady base-line. With the standard reaction mixture pressures used, it was found that each hydrocarbon in any G.C. sample could be recorded on-scale with the attenuation range permanently set at a factor of 5 \times 10^2; hence, it was always possible between successive G.C. peaks to alter the integrator scale factor according to the anticipated size of the emergent hydrocarbon peak and at the same time correct any base-line drift, if necessary, by adjusting the zero control on the integrator. The integrated hydrocarbon peak intensities obtained by the above methods were analysed as detailed in Section 3.2.

In the combined G.C.-M.S. studies, the chromatographic column posed two difficulties. Even at room temperature, there was considerable elution of water from the column coupled with a smaller amount of bleed from the stationary phase, and both of these effects made permanent contributions to the background observed in the mass spectrometer. The possibility of water being introduced to the system via the helium carrier gas supply was eliminated by passing the latter through a
container of oven-dried molecular sieve for adsorption of any water impurity; furthermore, attempts to find an alternative column with less water content but approximately the same separation efficiency for the hydrocarbons under study were unsuccessful. The influence of mass spectrometer background on analysis of G.C.-M.S. data is discussed in Section 3.3.

Partial Separation of Deuterated Hydrocarbons: The second problem arose from the ability of the chromatographic column to partially separate different deuterated forms of the same paraffin; this meant that no single mass spectrometric scan taken during elution of the hydrocarbon could be considered as representative of its overall isotopic distribution. This phenomenon was illustrated by the G.C.-M.S. analysis of an equimolar mixture of propane-d\(_0\) and propane-d\(_8\). The peak intensities recorded at masses 44 and 52 in each scan taken after entrance of the propane mixture into the mass spectrometer were plotted against time as shown in Figure 2.3; it was clear that the 'light' and 'heavy' propanes were separated in retention time by about 10 seconds with the more deuterated propane appearing first. Hence, to obtain correct analyses of such mixtures of isotopic hydrocarbons, it was necessary to consider the contributions recorded in all of the mass spectral scans and the procedure devised to obviate this problem is described fully in Section 3.3.

2.7. The Mass Spectrometer

The mass spectrometer involved in the combined G.C.-N.S. experiments was an AEI MS20 'Rapide' - a single-focussing, \(\pi\)-radian deflection instrument with rapid magnetic scanning. A complete description of the MS20 and its operation may be found in the appropriate sections of the manufacturer's instruction manual\(^{(11)}\). The spectrometer source was kept under vacuum at a pressure of less than \(10^{-5}\) Nm\(^{-2}\).
Figure 2.3. Separation of Propane-$d_8$ and Propane-$d_0$
by means of a rotary pump, a water-cooled oil diffusion pump and a liquid nitrogen filled cold trap, the latter being topped up twice a day to maintain the high vacuum; to remove any accumulation either of material condensed just above the cold trap or of residues adsorbed on the various ion source components, the mass spectrometer was baked at 673K for a minimum of 24 hours per week. An indication of the pressure in the MS20 ion source was given by an AEI VC10 ionisation gauge (emission level set to 15 on calibration scale), the true source pressure value being a factor of ten greater than that observed on the meter due to the closer position of the ionisation head to the pumping system. Before the MS20 could be operational, it was necessary to check that the source connections plug and electrometer amplifier head were attached in place on the top flange of the spectrometer stack and secondly, with a view to maintaining adequate resolving power, that the poles of the variable electromagnet (500-9000 gauss) were correctly positioned around the ion source. Having energized the magnet, it was possible to switch on all the required sections of the MS20 electronics including the electron beam control, the electron multiplier, the galvanometer amplifiers, the ultraviolet chart recorder, the total ion trace recorder and the oscilloscope; however, in the absence of a magnetic radiation shield for the ionization gauge head, it was impossible to use the VC10 for pressure measurements while the magnet was in operation. A measure of the important ion source parameters such as filament current, electron voltage, trap current, ion repeller voltage etc. was available throughout operation of the spectrometer by merely choosing the appropriate dial position on a specially designed ion source monitor unit; in this way, it was possible to rapidly locate any electrical faults which developed inside the instrument and at the same time ensure that the latter was performing with
optimum efficiency.

The molecules in each sample entering the ion chamber were bombarded by a beam of electrons produced from a rhenium filament with a trap current rating of 50\(\mu\)A; the positive ions so formed were accelerated by a constant potential of 250V (for an m/e range of 1-400) and focussed on to the ion collector plate according to their different masses by varying the external magnetic field. The ionising energy of the electron beam was 20eV, this value being chosen to minimise formation of ions from residual helium in the source (ionization potential = 24eV) without incurring considerable losses in sensitivity, in particular, for detection of the smallest hydrocarbon molecule, methane (see Section 2.8.). With 20eV electrons, the production of fragment ions from each hydrocarbon was generally extensive and various techniques were employed to account for their contributions to the mass spectra recorded during a G.C.-N.S. experiment (see Section 3.3.).

The MS20 was also furnished with a total ion current monitor; this additional collector plate was positioned in front of the ion chamber to intercept approximately 1\% of the emergent total ion beam, and its output via an electrometer amplifier was represented simultaneously by the deflection on a total ion current meter and by a total ion intensity trace drawn on a Servoscribe recorder which was operated at the same chart speed as in experiments involving chromatographic analysis only (see Section 2.6.). The total ion intensity meter also served to indicate the pressure present in the ion source when the VC10 gauge was inoperative; the total ion trace, as illustrated in 'A' (Figure 2.1.), reflected the rise and fall in source pressure as each hydrocarbon passed into the spectrometer for analysis and was thus equivalent to the chromatogram produced by a flame-ionization detector (see Section 2.6.). When the total ion intensity began to increase from
its background value (total ion trace base-line) indicating the emergence of hydrocarbon from the ion chamber, the electromagnet was immediately switched into the repetitive scanning mode for the duration of that peak.

A series of hydrocarbon spectra were thereby produced, in each of which the magnet performed an exponential scan from high to low mass number over the mass range defined by preset upper and lower limits on the magnetic control unit; the principal feature of exponential scanning was that it provided an equal fraction of time for collection of ions at each mass number. Scanning was normally carried out at the fastest rate available of 1 second per decade of mass with an electromagnet reset time of approximately 1 second between successive scans. The maximum number of scans which could be recorded during elution of any hydrocarbon was therefore given by the expression

\[
\text{Number of scans} = \frac{\text{Peak elution time in seconds}}{\log_{10} \left( \frac{\text{High mass limit}}{\text{Low mass limit}} \right) + 1}
\]

hence, for a mass range of m/e 100 to m/e 10 and an elution period of 1 minute, it was possible to record a total of 30 spectra under standard scanning conditions, and this was the average number encountered per hydrocarbon in the G.C.-M.S. experiments of Chapters 4 and 5. A disadvantage of the MS20 ion source geometry, which becomes evident when recording spectra for a G.C. effluent, is that although helium passes on too low a radius to be intercepted by the total ion monitor when the magnetic field is suitable for focussing ions of mass number greater than 70 on to the peak ion collector, the same is not true at masses below about m/e 60, where helium collection by the monitor plate tends to markedly distort the resulting total ion trace; hence, it was not generally possible to produce a clean enough total ion chromatogram for quantitative measurements.
The individual ion currents produced at the collector for each m/e ratio present in the spectrum were fed via an electron multiplier 'E' (Figure 2.1.) operated at 3 kV and with a 1 kHz bandwidth for the faster scanning speeds, to a set of six SE galvanometer drive amplifiers. Each of the latter was capable of amplifying the incoming signal intensities to a different attenuation level and deflecting its associated galvanometer spot to produce a corresponding peak intensity trace on the SE3006 ultra-violet chart recorder, as illustrated in 'B' (Figure 2.1.). Although six attenuation factors of 1, 2, 5, 10, 50 and 100 were available, the size of the U.V. sensitive chart paper generally limited the number of interpretable traces to three, and so in normal practice, the ion peaks were simultaneously monitored at attenuation levels of 2, 10 and 100 only. The ultra-violet chart paper speed had to be matched with that of the magnetic scanning, so for 1 second scans, the U.V. paper was fed at a rate of 250 mm sec\(^{-1}\). During any G.C.-M.S. experiment, care was taken not to overexpose the spectra recorded on U.V. charts to strong sunlight, an effect which would seriously hazard the subsequent measurement of peak heights. As each spectrum was produced, it was also displayed on an oscilloscope screen, the sweep of the oscilloscope beam being triggered at the start of each magnetic scan; in this way, it was possible to make a rapid visual check on the results obtained by G.C.-M.S. analysis. The techniques used for detailed interpretation of the recorded MS20 spectra are fully described in Chapter 3.

Before commencing each combined G.C.-M.S. study, the spectrometer was carefully tested for optimum sensitivity. This was carried out by tuning the magnetic field to an easily identifiable peak such as m/e 18 (water background) and adjusting both the ion repeller voltage and deflector plate voltage finely
till the maximum galvanometer spot deflection was obtained for that peak; an ion
repeller voltage of approximately -1.8V was normally required for this purpose.
It was also necessary at less regular intervals to check the gain of the electron
multiplier, and this was achieved by setting the magnet current to give no peak
deflection on the U.V. recorder and then running out a short length of chart
paper at the fastest speed without actually scanning; for optimum multiplier
gain, small single ion peaks about 6mm in length were observable on the most
sensitive U.V. trace, but in the absence of such an effect, the multiplier supply
voltage had to be raised to restore the gain to its former level. Although the
sensitivity of the spectrometer varied from one hydrocarbon to another (see
Chapter 3), it was generally found to be such that identifiable spectra could be
obtained from a pressure of about 0.4 \( \text{Nm}^{-2} \) of hydrocarbon in the reaction vessel,
and that adequate isotopic distributions were calculable from product yields as
low as 0.3%. In the presence of helium flow, however, it was not possible to
achieve a resolving power of more than 300 (10% valley measurement), but this was
more than adequate for identification of the low molecular weight hydrocarbons
used in these investigations.

2.8. The G.C.-M.S. Interface

The interface between the gas chromatograph and mass spectrometer was an
all-glass Biemann-Watson molecular separator (12) operated at room temperature.
The separator, consisting of a glass frit through which the gas chromatographic
effluent passes, was mounted in a glass diffusion chamber which was evacuated by
a rotary pump; the size of the pores in the frit is such that passage of the
carrier gas should occur more easily than that of the larger hydrocarbon molecules
and in this way, a large proportion of the former should be pumped away while the sample reaching the mass spectrometer source should be enriched in hydrocarbon. To obtain the maximum differential in pumping rates, helium was used as carrier gas in the G.C.-M.S. experiments because of its very low molecular weight. The leak between the G.C. column and the separator was a 1 m length of 0.33 mm bore stainless steel capillary tubing 'J' (Figure 2.1.) and this was basically used to accommodate the reduction in pressure between the chromatograph and the mass spectrometer; before the start of a G.C.-M.S. experiment, the steel capillary was coupled to the column after adjusting the helium flow through the latter to the required level. When only chromatographic analysis was desired, the capillary was sealed off from the atmosphere by coupling it to a much smaller piece of tubing with a brazed end. Between the HS20 and the separator, the leak was a glass line and re-entrant, the latter being carefully sealed in position close to the spectrometer ion source by Gyrolok fittings.

The efficiency of helium removal to the pumps and transfer of hydrocarbon-enriched sample to the mass spectrometer was dependent on pressure conditions inside the glass diffusion chamber. To achieve the optimum operational ion source pressure of \(6.67 \times 10^{-3} \text{ Nm}^{-2}\), it was found necessary to insert a throttling valve 'T' (Figure 2.1.) in the form of a glass stopcock into the rotary pump line; in the absence of this valve, a source pressure of only \(1.5 \times 10^{-3} \text{ Nm}^{-2}\) was recorded on the VC10 gauge, indicating that the pumping was too efficient. On partially closing the stopcock, the pressure could be raised to the desired level, the disadvantage of this technique being that more helium as well as hydrocarbon was allowed to enter the spectrometer. Under these conditions, only an estimated 10% of the lower molecular weight paraffins was thought to be separated from the
carrier gas, the efficiency probably being greater than this value for the larger hydrocarbons. The marked dependence of separator efficiency on relative molecular weight was illustrated by the fact that significantly different responses were recorded for methane-$d_0$ and methane-$d_4$ due to preferential removal by the rotary pumps of the lighter of these molecules; this effect necessitated the use of different sensitivity factors for the various isotopic methanes (see Chapter 3), but was not generally observed for paraffins of greater carbon number where the percentage difference in mass between the light and heavy forms of the molecule was not so pronounced as for methane.

Tests carried out with larger molecules such as ethylbenzene and octane and various G.C. columns showed that hydrocarbon enrichment could be enhanced by operating the Biemann separator at higher temperatures, and a heating system was devised for this purpose. The best results were achieved by maintaining the separator and its connections at a slightly higher temperature than the chromatographic column and by keeping the capillary inlet 10 to 20 degrees higher than the separator itself with the glass line outlet and source re-entrant about 20 to 30 degrees lower. Care must also be taken to avoid creation of cold spots and use of thermolabile materials which may decompose during their passage through the system.

2.9. Experimental Procedure

For studies involving combined G.C.-M.S. analysis, a standard experimental procedure was developed with which it was hoped a high degree of operational efficiency would be maintained; the sequence of practical steps carried out in each experiment may be summarised as follows.
1. The reactor enclosing the metal filament was baked overnight under vacuum with the surrounding furnace at a temperature of 723K.

2. In cases where the MS20 had been baking, the band-heaters were switched off and the spectrometer allowed to cool for at least 2 hours before use.

3. The MS20 cold trap as well as those serving the gas line diffusion pumps were topped up with liquid nitrogen.

4. The pressures in the gas line and reaction vessel were measured using the McLeod gauge (sticking vacuum desirable), and the vacuum in the MS20 chamber was also checked with the VC10 ionisation gauge (better than $10^{-5}$ Nm$^{-2}$ preferred).

5. Helium was set to flow through the G.C. column at the required rate to allow the latter to stabilise (the helium was exhausted into the air at this stage).

6. If not already attached, the source connections plug and electrometer amplifier head were replaced on top of the spectrometer stack and the electromagnet was moved into position.

7. The reaction mixture was made on the gas line and allowed to stand in the mixing volume.

8. The column (with helium flowing) was then connected to the MS20 via the separator's capillary inlet and the throttling valve adjusted till a stable pressure of $\sim 7 \times 10^{-3}$ Nm$^{-2}$ was recorded on the VC10 gauge.

9. The ionization gauge was switched off and the magnet energised (remembering the magnet cooling water).

10. The electron beam control unit, the galvanometer amplifiers, the U.V. chart recorder, the total ion trace recorder and the oscilloscope were in turn switched on and rendered operational.

11. The MS20 filament was switched on and, as a consequence, the source monitor
box, the electron multiplier, and the total ion monitor also became operational.

12. The parameters such as electron ionising voltage, trap current, multiplier voltage etc. were each checked as being set to the desired level and the MS20 sensitivity was optimised by tuning the m/e 18 peak for maximum response.

13. Having adjusted the mass range, scanning speed and U.V. chart paper speed to their required values, the G.C.-M.S. apparatus was then ready to undertake analysis of samples.

14. The metal wire was outgassed for 30 minutes with the furnace at 723K; the latter was then removed and allowed to cool to the chosen reaction temperature whilst the reaction vessel was placed in an ice-bath for throwing of the metal film.

15. The reaction mixture was admitted to the catalyst at 273K as soon as possible after film deposition in order to minimise the possibility of surface contamination.

16. The furnace was then replaced round the reactor and the reaction allowed to proceed, samples being withdrawn at suitable time intervals with the gas sampling valve.

The experimental technique involved in chromatographic studies was not so intricate as that for the combined apparatus and can therefore be outlined by a smaller sequence of steps as follows.

1. The reactor and metal were prepared as in stage 1 above.

2. Having topped up the diffusion pump cold traps, the pressure was ascertained in both the gas handling and reaction vessel sections of the line with the McLeod gauge (sticking vacua preferred).

3. The pressures of hydrogen and air for the flame ionization detector and nitrogen as carrier gas were each set to the required value.

4. The ionization amplifier, integrator and chart recorder were all made
operational after igniting the detector flame; the amplifier and Servoscribe zero controls were adjusted to give a suitable base-line on the chromatogram and the G.C. apparatus was then ready to analyse gas samples.

5. The reaction mixture and film preparations were carried out as in stages 7 and 14 above; the reaction was then started and followed as in steps 14 to 16 above.
3.1. Introduction

This chapter describes the data-handling techniques which were applied to the results obtained by the experimental procedures of Chapter 2. Interpretation of chromatographic data was effected by methods similar to those reported by Anderson who has also studied hydrogenolysis reactions by chromatographic means \(^1\); the emphasis in the present work was placed on accurate detection of small quantities of product hydrocarbon, on the one hand, to enable detailed assessment of initial reaction behaviour and on the other, to establish evidence for such effects as loss of carbon to the catalyst (vide infra). The raw information supplied by G.C.-M.S. analysis was processed by methods based on those previously employed for exchange reactions as studied by the standard reaction vessel - capillary leak - mass spectrometer technique \(^2\); these procedures were re-designed to allow for the effects of chromatographic separation on each subsequent mass spectral scan and also for the practical difficulties entailed in reducing the large volume of data produced by one G.C.-M.S. experiment to a handful of detailed isotopic distributions. In view of the inherent irreproducibility of experimental parameters such as catalyst activity and reaction mixture composition, it was important to be able to assess the levels of precision obtainable with each of the analytical techniques and data handling methods. Most of the calculations were carried out on an IBM 370/155 computer with the
aid of programs written in FORTRAN IV, the details of which do not appear in this thesis because of their length but have been fully recorded elsewhere. In order to accommodate reaction systems other than those of the present investigation, each program was designed in a general rather than specific manner not only to allow continued use in the future but also to facilitate development of more sophisticated versions.

3.2. Gas Chromatographic Analysis of Hydrogenolysis Reactions

Gas chromatography is an efficient way of detecting small quantities of hydrocarbon material and will give precise quantitative analyses provided that accurate calibrations have been carried out for each hydrocarbon under study; the latter was ensured in this case by repeated calibration experiments which demonstrated the invariance of the sensitivity of each paraffin to the G.C. column and flame ionization detector over a substantial period of time. The relative sensitivity of the chromatograph to each hydrocarbon was calculated by measuring the relative hydrocarbon peak areas produced by each sample from a mixture of known pressures of hydrocarbons; Table 3.1. lists the sensitivity factors in terms of relative intensity count per molecule for the six hydrocarbons used in this work. It was found more informative, however, to express hydrogenolysis product distributions in terms of the percentage of the total carbon in the system associated with each product, so the factors applied in practice to the raw integrated peak intensities were in the form of relative carbon atom sensitivities for each hydrocarbon and these are also catalogued in the lower half of Table 3.1. If the flame ionization process were 100% efficient, then the integrator counts would exactly reflect the number of carbon atoms present in each component of the
TABLE 3.1. SENSITIVITY FACTORS FOR GAS CHROMATOGRAPHIC ANALYSIS

<table>
<thead>
<tr>
<th></th>
<th>C_5</th>
<th>C_4</th>
<th>C_3</th>
<th>C_2</th>
<th>C_1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Relative count per molecule</strong></td>
<td>4.416</td>
<td>3.846</td>
<td>3.566</td>
<td>2.908</td>
<td>1.947</td>
</tr>
<tr>
<td><strong>Relative count per carbon atom</strong></td>
<td>0.883</td>
<td>0.961</td>
<td>0.891</td>
<td>0.969</td>
<td>0.973</td>
</tr>
</tbody>
</table>

sample; however, taking the sensitivity for the methane carbon atom as unity, it was found that the efficiency of the G.C. detector fell with increasing carbon number and, in particular, for the branched chain hydrocarbons, isobutane and neopentane.

The product distribution for each G.C. sample was then evaluated by dividing each integrated peak area by the appropriate carbon sensitivity factor and normalising the corrected hydrocarbon intensities to a total of 100%; in this way, each product was determined in equivalent units of the reactant rather than as a percentage of the hydrocarbon molecules in the gas phase. For a reaction system where there is no predicted loss of hydrocarbon to the catalyst surface, a comparison between the calculated size of any particular sample withdrawn from the reaction vessel and the corresponding drop in total G.C. carbon count may provide a useful self-consistency check on the reliability of that analysis; conversely, a marked discrepancy between these two quantities may indicate a significant loss of material to the catalyst and consequently, severe poisoning of the reaction under investigation.

3.3. Combined G.C.-M.S. Analysis of Hydrogenolysis and Exchange Reactions

The large quantity of mass spectral data produced in each G.C.-M.S.
hydrogenolysis and exchange study was subjected to several stages of processing before it was possible to compute the isotopic contents of each hydrocarbon species present in the reaction mixture. For each mass spectrum recorded, the intensity of any peak was measured manually from the height of its most sensitive on-scale U.V. chart trace; as the scanning rate, mass range and chart recorder speed were kept the same throughout each G.C.-M.S. run, it was possible to plot a calibration curve for mass number against position in scan and then identify each mass peak present by its distance from an easily recognisable reference point such as m/e 18 (water background).

Simpson's Rule Integration: The need to measure the peak intensities in all of the spectra collected was brought about by the fact that, due to partial separation of deuterated paraffins by the gas chromatograph column, no single mass spectrometric scan could be representative of the overall isotopic distribution within any particular hydrocarbon in the sample (Section 2.6.). To determine the average isotopic spectrum for each eluted hydrocarbon, the following procedure was adopted; for each m/e value, the corresponding series of peak heights obtained from the set of scans recorded during elution of the hydrocarbon were integrated using Simpson's Rule\(^{(4)}\) to yield a total intensity value for that particular mass number. In practice, the individual peak intensities were first tabulated according to m/e value and scan number; since the scans were taken at equal intervals of time, it was valid to integrate the set of peak heights for each mass number according to the Simpson's Rule equation

\[
\text{Total Intensity} = \frac{h}{3} (y_1 + 4y_2 + 2y_3 \ldots + 4y_r + 2y_{r-1} \ldots + y_n) \quad 3.1
\]

where \(h\) is the constant interval in time between successive scans, \(y_r\) is the peak height in the \(r\)th scan \((r \text{ even})\) and \(n\) is the total number of scans recorded during
elution of the hydrocarbon. For easiest operation of the Simpson equation, it is necessary for \( n \) to be an odd number; in cases where this did not occur, it was possible to add on an extra dummy scan which was equivalent to the average background in the spectrometer (vide infra). The average isotopic spectrum was calculated by dividing the integrated intensity for each ion by the number of scans recorded, and the true isotopic composition of the hydrocarbon in terms of percentages of each isotopic species was then determined by applying the following series of corrections to this average spectrum.

**Background:** Contributions to each of the mass spectra collected were made by residual gases in the ion source such as air, water vapour and carbon monoxide from the filament and also, to a lesser extent, by hydrocarbon species from previous analyses which were adsorbed on the walls of the spectrometer inlet and ionization chamber. To allow for these effects, several background scans were recorded before and after each G.C.-M.S. sample and the peak heights present in these scans were averaged and subtracted from the integrated intensity values to which they contributed in the averaged hydrocarbon spectrum. With the G.C.-M.S. system, background was especially large at \( m/e \) 18 due to water elution from the chromatographic column. In most cases, the contribution at mass number 18 from water was much larger than that from any hydrocarbon ion e.g. \( \text{CD}_3^+ \) or \( \text{CH}_2\text{D}_2^+ \); as the \( m/e \) 18 peak was normally only measurable on the least sensitive U.V. chart trace, the intensity of the hydrocarbon fraction was difficult to estimate accurately. Consequently, isotopic analysis of deuterated methanes was less precise than that of any of the larger hydrocarbons; the seriousness of this error was considerably reduced, however, by the fact that most of the methane produced in the reactions of this work appeared to be in the form of \( \text{CD}_4 \), and there was no
mechanistic evidence to suggest formation of significant quantities of the m/e 18 product, CH$_2$D$_2$.

**Natural Isotopes:** Because of the natural occurrence of heavy isotopes $^{13}$C and deuterium, the mass spectra of hydrocarbons may exhibit peaks at mass numbers greater than that of the parent molecule due to their presence. In any catalytically produced distribution of isotopic hydrocarbons, it is necessary to take into account the contribution to these peaks from the $^{13}$C and D originally present in the hydrocarbon reactant. The isotopic abundances of heavy carbon and deuterium are 1.06% and 0.016%, respectively$^{(5)}$, so for the hydrocarbon molecule C$_n$H$_{m-r}$D$_r$, use can be made of the binomial expression

$$(0.98931 + 0.01069x)^n (0.99984 + 0.0016x)^m$$

3.2
to yield the expected intensity ratios of peaks containing natural isotopes relative to that of the parent hydrocarbon; on evaluating expression 3.2, the term in $x^0$ corresponds to the fraction of parent peak (mass number P), the term in $x^1$ to the (P+1) peak, the term in $x^2$ to the (P+2) peak, and so on. For a range of deuterated products, the values of these ratios will vary with the isotopic content of the molecule since, as the hydrogens are replaced by deuterium, the probability of the presence of naturally occurring deuterium decreases; hence, for any isotopic species C$_n$H$_{m-r}$D$_r$, the relative quantities of peaks containing heavy isotopes are obtained by substituting m-r for m in expression 3.2. The background corrected, 'Simpson-averaged' hydrocarbon spectrum was thus corrected for natural isotope by subtracting from the higher mass peaks the isotopic contributions due to peaks at lower masses; this was done on a systematic basis starting with the lowest mass number and working upwards to the higher masses using the corrected intensity at each mass to calculate the contribution to the
next highest masses. In practice, the isotope correction scheme was limited to allowance for single or double isotope occurrence in any of the products, since the probabilities of more than two natural isotope atoms being present in the one molecule are generally negligible.

**Fragmentation:** The final corrections to be applied to the background and isotope corrected mass spectral data are those for the formation of fragment ions from one isotopic hydrocarbon which may contribute to the peak intensities observed for other parent molecule ions of lower mass number\(^6\). Any correction scheme devised for this purpose will be dependent on the mass spectral fragmentation patterns of the hydrocarbons involved. To minimise fragmentation contributions, it is desirable to operate the mass spectrometer at a sufficiently low ionising voltage to reduce the formation of fragment ions without considerably impairing the sensitivity of the spectrometer to each hydrocarbon (see Section 2.7.); however, to produce adequate sensitivity towards methane, 20eV electrons were required for ionization and under these conditions, the measured cracking pattern for most of the hydrocarbons showed extensive fragmentation, as illustrated in Table 3.2. Insufficient parent ion was detectable for neopentane and isobutane so G.C.-M.S. analysis for these molecules was made in terms of the ions formed by loss of a methyl group i.e. \(\text{C}_4\text{H}_9^+\) and \(\text{C}_3\text{H}_7^+\), respectively. The methods for interpreting neopentane data are described more fully in Chapter 5.

The simplest approach to correcting for fragment ions is a purely statistical one which requires use of the light hydrocarbon (undeuterated) fragmentation pattern only; it is based on the assumptions that the formation of any fragment ion can be represented by a series of steps, each involving the loss of a single atom and that the loss of hydrogen or deuterium occurs on a statistical basis
TABLE 3.2. TYPICAL FRAGMENTATION PATTERNS USED IN G.C.-M.S. ANALYSIS

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Parent</th>
<th>-1X</th>
<th>-2X</th>
<th>-3X</th>
<th>-4X</th>
<th>-5X</th>
<th>-6X</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.2867</td>
<td>0.0073</td>
<td>0.0253</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>iso-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.4174</td>
<td>0.2607</td>
<td>0.0111</td>
<td>0.0741</td>
<td>0.0318</td>
<td>0.0168</td>
</tr>
<tr>
<td>neo-C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.0646</td>
<td>0.0081</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>1.0000</td>
<td>1.0705</td>
<td>0.1270</td>
<td>0.2129</td>
<td>0.0354</td>
<td>0.0707</td>
<td>0.0207</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;D&lt;sub&gt;8&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.7366</td>
<td>0.0761</td>
<td>0.1292</td>
<td>0.0240</td>
<td>0.0539</td>
<td>0.0138</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.5619</td>
<td>2.9823</td>
<td>0.4021</td>
<td>0.3093</td>
<td>0.0974</td>
<td>0.0075</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.4133</td>
<td>2.0162</td>
<td>0.1976</td>
<td>0.2435</td>
<td>0.0611</td>
<td>0.0052</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.6149</td>
<td>0.0375</td>
<td>0.0174</td>
<td>0.0058</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CD&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.0000</td>
<td>0.2519</td>
<td>0.0125</td>
<td>0.0099</td>
<td>0.0031</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> X = H or D as appropriate; <sup>b</sup> measured in terms of the propyl ion C<sub>3</sub>H<sub>7</sub><sup>+</sup>; <sup>c</sup> measured in terms of the isobutyl ion C<sub>4</sub>H<sub>9</sub><sup>+</sup>.

with equal probability of breaking a carbon-hydrogen or carbon-deuterium bond.

This extensively used method, the operation of which has been detailed elsewhere<sup>(7,8)</sup>, was employed in the present study for analysis of n-butane, isobutane and neopentane mass spectral data; it has been found to provide adequate fragmentation corrections in situations where the extent of fragmentation is not particularly large and where there is little indication of any difference in the rupture probabilities of carbon-hydrogen and carbon-deuterium bonds. In some cases the latter may not be true, with loss of deuterium being the more difficult process and in the presence of this effect, a better assessment of fragmentation may be made by utilising the cracking pattern of the fully deuterated hydrocarbon as well.
as that of the light molecule. For methane, ethane and propane, it was possible to prepare the heavy hydrocarbon to a high degree of purity by repeated exchange of the light molecule over a tungsten film\(^{(9)}\) and hence obtain its mass spectrum; Table 3.2. illustrates the considerable differences observed between the light and heavy hydrocarbon fragmentation patterns for these molecules. Fragmentation correction schemes employing the two cracking patterns include that devised by Gault and Kemball\(^{(9)}\) for analysis of isotopic propanes; alternatively, it is possible to use a procedure involving estimation of the fragmentation factors for intermediate species by linear interpolation between the light and heavy hydrocarbon spectra. The latter method has also been detailed previously\(^{(10)}\) and in the present investigation, it was found to be a satisfactory way of evaluating fragment ion contributions in the analysis of isotopic methanes.

For mixtures of deuterated ethanes and propanes, all of the above schemes were discovered to be inadequate and it was found necessary to devise a further empirical procedure for fragment ion correction which not only allowed for preferential dissociation of carbon-hydrogen bonds, but also for the possible additional dependence of each fragmentation process on the nature and numbers of the other bonds in the fragmenting parent molecule - an important secondary effect which had already been recognised by other workers studying the mass spectra of small isotopic hydrocarbons\(^{(6,11-13)}\); in other words, for isotopically labelled ethane and propane, conventional methods of fragment ion correction failed to take account of enhanced loss of hydrogen due to the deuterium content of the molecule and conversely, diminished loss of deuterium in the presence of carbon-hydrogen bonds.

The improved correction scheme may be explained as follows. Consider the
formation of the fragment ion $\text{C}_n\text{H}_{n-m-x}^+\text{D}^{+}$ by loss of $x$ hydrogen atoms and $y$ deuterium atoms from the hydrocarbon molecule $\text{C}_n\text{H}_{n-m}\text{D}^+$ containing $m$ deuterium atoms. Let $m_{x,y}^f$ be the intensity of the peak corresponding to this fragment ion relative to the height of the peak for the parent ion $\text{C}_n\text{H}_{n-m}^+$, assuming the former is observable, and let $m_{x,y}^w$ be the corresponding calculated fragmentation factor which will be required if direct observation of the fragment ion peak is impossible. Define factors $A$ and $B$, analogous to the $\Gamma$ and $\Pi$ factors originally proposed by Evans et al. (11), such that

$$A = \frac{\text{observed probability of losing an H atom from } \text{C}_n\text{H}_{n-1}\text{D}}{\text{statistical probability of losing an H atom from } \text{C}_n\text{H}_{n-1}^+}$$

$$B = \frac{\text{observed probability of losing a D atom from } \text{C}_n\text{HD}_{n-1}}{\text{statistical probability of losing a D atom from } \text{C}_n\text{HD}_{n-1}^+}$$

The empirical expression used for calculating a fragmentation factor then becomes

$$m_{x,y}^w = Z \left[ \frac{x_{o,x+y,0}^{f_{x+y,0}} + y_{o,x+y}^{f_{x+y}}}{x+y} \right] \left[ \frac{xA^m + yB^{N-m}}{x+y} \right]$$

where $Z$ is the a priori statistical factor i.e. the probability of any particular fragmentation process based on molecular composition only and ignoring the influence of the hydrocarbon cracking patterns. The first term in square brackets in equation 3.5 allows for the preferential dissociation of C-H compared with C-D bonds, and is equivalent to a linear interpolation between the relevant fragmentation factors measured for the light and heavy hydrocarbons. The second term in square brackets incorporates the principle (6) that the factors $A$ and $B$ have to be raised in geometrical fashion to powers corresponding to the number of D or H atoms, respectively, in the molecule and this term, like the first, also
includes a weighting according to the relative numbers of hydrogen and deuterium atoms lost in the particular dissociation process. In order to illustrate the use of equation 3.5, the correction factor for the fragment ion formed from the isotopic propane, \( \text{C}_3\text{H}_4\text{D}_4 \), by the loss of one H atom and one D atom is

\[
4_{l,1} = 2 \times \frac{4}{8} \times \frac{4}{7} \left[ \frac{0_{f_{2,0}} + 8_{f_{0,2}}}{2} \right] \left[ \frac{A^4 + B^4}{2} \right]
\]

It is important to note that the a priori factor considers the loss of each atom in the fragmentation process to be a separate event and thus incorporates the total number of possible fragmentation sequences which will yield the same net loss of particles.

Suitable values for A and B can be obtained from the mass spectra of appropriately labelled compounds or, more economically, by using an equilibrium mixture of isotopic hydrocarbons; the latter approach may again be illustrated by propane for which an equilibrated mixture of isotopic species can be prepared readily by exchange of \( \text{C}_3\text{H}_8 \) and \( \text{D}_2 \) over a tungsten film\(^9\). This method depends on an assumption that the equilibrium constants, \( K_{m+1} \), for the series of interconversion equilibria

\[
\text{C}_3\text{H}_{8-m}\text{D}_m + \text{C}_3\text{H}_{6-m}\text{D}_{m+2} \rightleftharpoons 2\text{C}_3\text{H}_{7-m}\text{D}_{m+1} \quad (0 < m < 6)
\]

(3.7)

correspond closely to the values which would be expected for a random distribution of the hydrogen and deuterium atoms available between the various isotopic species of the hydrocarbon\((2,14)\); consequently, it can be shown that each equilibrium constant is independent of the relative concentrations of hydrogen and deuterium and may be calculated solely from a ratio of binomial coefficients\((2)\). Let \( p_m \) be the intensity of the peak which corresponds to the mass of the molecule \( \text{C}_3\text{H}_{N-m}\text{D}_m \)
after allowing for background and naturally occurring isotopes and $p^*_m$ the value
after correction for the presence of fragment ions. In the case of propane, $A$ may
be obtained using the values of $p_6$, $p_7$ and $p_8$. No fragment ions can contribute to
$p_7$ and $p_8$ since the perdeuteropropane cannot lose a hydrogen atom; hence,

$$p'_7 = p_7 \quad \text{and} \quad p'_8 = p_8. \quad 3.8$$

The value of $f_{1,0}$ may be determined from the following pair of equations.

$$p'_6 = p_6 - p_8 \cdot 8_{0,1} - p_7 \cdot 7_{1,0}, \quad 3.9$$

and from the equilibrium considerations \( (2) \) mentioned above,

$$K_7 = \frac{(p'_7)^2}{p'_6 \cdot p'_8} = \frac{8^2}{1 \times 28}. \quad 3.10$$

in accordance with the definition of equation 3.3, $A$ may then be evaluated from
the relationship

$$A_7 = 7_{f_{1,0}} / \frac{1}{8} \cdot 0_{f_{1,0}}. \quad 3.11$$

Equations for $p'_5$ and $K_6$ analogous to those of 3.9 and 3.10 yield a value for
$7_{f_{0,1}}$ and hence $B$ from the equation

$$B = 7_{f_{0,1}} / \frac{7}{8} \cdot 8_{0,1}. \quad 3.12$$

The effects of correcting for fragmentation by various methods are shown in
Table 3.3. for an equilibrated mixture of isotopic propanes. The criterion used
to check the validity of this improved correction scheme was that the equilibrium
product distribution calculated from the experimental data should compare
favourably with a binomial distribution calculated on the basis of the
experimental mean deuterium content value, $M_D$, for the equilibrium mixture \(^{(2,14)}\).
The statistical method and the procedure used by Gault and Kemball \(^{(9)}\) are clearly
### TABLE 3.3. DISTRIBUTIONS OF EQUILIBRATED PROPANES

<table>
<thead>
<tr>
<th></th>
<th>I&lt;sup&gt;a&lt;/sup&gt; binomial</th>
<th>II&lt;sup&gt;b&lt;/sup&gt; binomial</th>
<th>III&lt;sup&gt;c&lt;/sup&gt; binomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>d&lt;sub&gt;0&lt;/sub&gt;</td>
<td>-0.2 0.0</td>
<td>-1.9 0.0</td>
<td>-0.6 0.0</td>
</tr>
<tr>
<td>d&lt;sub&gt;1&lt;/sub&gt;</td>
<td>-4.2 0.0</td>
<td>-3.3 0.0</td>
<td>0.2 0.0</td>
</tr>
<tr>
<td>d&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-1.6 0.1</td>
<td>1.6 0.1</td>
<td>0.2 0.1</td>
</tr>
<tr>
<td>d&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.2 0.5</td>
<td>0.0 0.9</td>
<td>0.9 0.9</td>
</tr>
<tr>
<td>d&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.0 3.1</td>
<td>1.3 4.7</td>
<td>4.3 4.3</td>
</tr>
<tr>
<td>d&lt;sub&gt;5&lt;/sub&gt;</td>
<td>9.6 11.5</td>
<td>16.3 14.8</td>
<td>13.8 14.2</td>
</tr>
<tr>
<td>d&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>32.5 29.4</td>
<td>28.8 29.1</td>
</tr>
<tr>
<td>d&lt;sub&gt;7&lt;/sub&gt;</td>
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<td>31.7 33.4</td>
<td>34.1 34.0</td>
</tr>
<tr>
<td>d&lt;sub&gt;8&lt;/sub&gt;</td>
<td>19.4 21.4</td>
<td>16.5 16.6</td>
<td>17.7 17.4</td>
</tr>
<tr>
<td>M&lt;sub&gt;D&lt;/sub&gt;</td>
<td>6.60 6.60</td>
<td>6.39 6.39</td>
<td>6.43 6.43</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fragmentation corrections using a statistical method; <sup>b</sup> using the method described by Gault and Kemball<sup>(9)</sup>; <sup>c</sup> using the present method; <sup>d</sup> binomial distribution with the appropriate average deuterium content, M<sub>D</sub>, is given for comparison with each set of data.

### TABLE 3.4. DISTRIBUTION OF EQUILIBRATED trans-BUT-2-ENES

<table>
<thead>
<tr>
<th></th>
<th>d&lt;sub&gt;0&lt;/sub&gt;</th>
<th>d&lt;sub&gt;1&lt;/sub&gt;</th>
<th>d&lt;sub&gt;2&lt;/sub&gt;</th>
<th>d&lt;sub&gt;3&lt;/sub&gt;</th>
<th>d&lt;sub&gt;4&lt;/sub&gt;</th>
<th>d&lt;sub&gt;5&lt;/sub&gt;</th>
<th>d&lt;sub&gt;6&lt;/sub&gt;</th>
<th>d&lt;sub&gt;7&lt;/sub&gt;</th>
<th>d&lt;sub&gt;8&lt;/sub&gt;</th>
<th>M&lt;sub&gt;D&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.09</td>
<td>6.59</td>
<td>17.78</td>
<td>26.76</td>
<td>25.16</td>
<td>15.19</td>
<td>5.69</td>
<td>1.38</td>
<td>0.35</td>
<td>3.456</td>
</tr>
<tr>
<td>Binomial</td>
<td>1.08</td>
<td>6.59</td>
<td>17.54</td>
<td>26.69</td>
<td>25.38</td>
<td>15.45</td>
<td>5.87</td>
<td>1.28</td>
<td>0.12</td>
<td>3.456</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fragmentation corrections made by means of eqn. 3.5.
unsatisfactory, giving some negative peaks, erratic changes in percentage with respect to deuterium content and consequently poor agreement with the calculated binomial distributions; however, the empirical method developed here is more satisfactory in all respects and was used throughout the present study for analysis of G.C.-M.S. data arising from deuterated ethanes and propanes. Typical values of the relative fragmentation of the heavy and light hydrocarbons were such that

\[
\frac{m_{f_0, i}}{o_{f_1, 0}} \approx 0.65, \quad \text{as shown in Table 3.1.} \tag{3.13}
\]

and A and B were generally found to be given by

\[ A \approx 1/B \approx 1.10 \tag{3.14} \]

The values in equations 3.13 and 3.14 may be used to estimate fragmentation in cases where calibration data for the perdeuterohydrocarbon and other labelled species are not available. Equation 3.5 can also be used to obtain fragment corrections for unsaturated hydrocarbons; for example, Table 3.4. shows the excellent agreement between observed and calculated isotopic compositions of the trans-but-2-enes prepared by reaction of light and heavy butenes over magnesium oxide at 425K and separated by gas chromatography.

For each of the techniques referred to in the preceding paragraphs, fragmentation corrections were made by a systematic process similar to that used in allowing for the presence of natural isotopes, but starting instead with the highest mass peak and working in order of decreasing mass by making corrections on the basis of each newly corrected peak intensity and taking into account all possible fragmentation processes; in this way, the fragment ion contributions from each peak were evaluated by multiplying the intensity for that particular peak by the relevant fragmentation factors and subtracting the products from the
appropriate peak intensities at lower mass numbers. On completing this sequence, the fragmentation corrected peak intensities for each isotopic product were summed and the amount of each species was expressed as a percentage of this total.

Comparison of Experimental and Binomial Isotopic Distributions: It was sometimes useful to compare the final distribution of deuterated hydrocarbons obtained by the above methods with a binomial product distribution calculated from the mean deuterium content of the experimental distribution, as in the case of the equilibrium data used to check the reliability of the amended fragmentation correction procedure. The usefulness of such a comparison arises from the fact that, if stepwise incorporation of deuterium takes place, then the distribution of isotopic species will remain binomial throughout the reaction till an equilibrium position is reached\(^{(16)}\); in this way, the existence or absence of favourable agreement between the two distributions may indicate the type of deuterium replacement mechanism prevailing during the reaction. The mean deuterium content of the isotopic products for each hydrocarbon was determined from the equation

$$M_D = \frac{\sum i \cdot D_i}{100}$$  \hspace{1cm} 3.15

where \(D_i\) is the percentage of the isotopic species containing \(i\) deuterium atoms, and \(0 \leq i \leq N\) where \(N\) is the number of replaceable hydrogen atoms in the hydrocarbon molecule. The binomial distribution (in percentages) may be evaluated by expanding the expression

$$100 \cdot (h + d)^N$$ \hspace{1cm} 3.16

where \(h\) and \(d\) are the probabilities of any hydrogen atom (in the generic sense) being an \(H\) or \(D\) atom, respectively. These probabilities are given by

$$d = \frac{M_D}{N} \quad \text{and} \quad h = 1 - d$$ \hspace{1cm} 3.17

Validity of Simpson's Rule Integration: Since the error in applying this form of
numerical integration is theoretically proportional to the fourth power of the separation constant \( h \) between contributing intensity values, it is clear that the accuracy of any isotopic distribution determined via this method will be fairly sensitive to the number of mass spectral scans recorded during elution of the hydrocarbon. Consequently, the error involved in calculating the average isotopic scan by integration was investigated by considering the data from two entirely separate G.C.-M.S. samples – the equimolar propane data which was illustrated in Figure 2.3. and an experimental distribution of isotopic butanes which was observed in a reaction of n-butane on platinum (see Chapter 4).

The problem is really one of determining the minimum number of individual scans which are required to provide a sufficiently accurate averaged scan. With the n-butane sample, 42 scans were recorded and Table 3.5 shows the isotopic analysis achieved using all of them. In order to arrive at an estimate of the variation in error with number of scans recorded, the analysis from 42 scans was assumed to be correct and the distribution was re-calculated for a smaller number of scans spaced at equal intervals throughout the sample. For example, there are three possible groups of 14 equally separated scans i.e. scan numbers 1, 4, 7 etc., 2, 5, 8 etc., and 3, 6, 9 etc. which may be extracted from the original set of 42, and the isotopic analyses obtained from these groups are also displayed in Table 3.5. The differences between each percentage value in these distributions and the corresponding one in the 42 scan analysis were used to measure the standard deviation of the errors produced by lowering the number of scans which contributed to the integration. Standard deviation \( (\sigma) \) is defined by

\[
\sigma^2 = \frac{\sum e^2 - \frac{1}{n} (\sum e)^2}{n-1}
\]
TABLE 3.5. COMPARISON OF CALCULATED ISOTOPIC DISTRIBUTIONS FOR n-BUTANE USING DIFFERENT NUMBERS OF SCANS

<table>
<thead>
<tr>
<th>Number of scans</th>
<th>Isotopic distribution / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>$d_0$ $d_1$ $d_2$ $d_3$ $d_4$ $d_5$ $d_6$ $d_7$ $d_8$ $d_9$ $d_{10}$</td>
</tr>
<tr>
<td>14</td>
<td>13.8 0.1 -0.5 0.1 1.4 3.7 8.2 17.2 25.7 20.7 9.1</td>
</tr>
<tr>
<td>14</td>
<td>13.6 0.3 -0.4 -0.1 2.0 3.3 7.5 17.7 27.2 19.3 9.1</td>
</tr>
<tr>
<td>14</td>
<td>13.8 0.1 -0.5 0.1 0.9 3.6 9.3 17.7 24.7 20.5 9.3</td>
</tr>
<tr>
<td>14</td>
<td>14.2 0.0 -0.5 0.5 1.0 4.2 8.5 17.1 24.7 21.0 8.8</td>
</tr>
</tbody>
</table>

where $\epsilon$ is the difference between each 14 scan % value and the correct answer from 42 scans, and $n$ is the total number of observations used in the calculation. In this case, the relevant parameters were $n = 33$, $\Sigma \epsilon = 0$ (since the total in each distribution is always 100%) and $\Sigma \epsilon^2 = 10.52$ and hence, the value found for $\sigma$ was 0.57. For a Gaussian error distribution, two standard deviations signify the range in value or 95% confidence interval within which the correct answer should lie 19 out of 20 times. Therefore, each value in the isotopic distributions calculated from 14 scans was thought to carry an error of $2 \times 0.57$ or ± 1.1%.

This procedure was repeated by selecting various numbers of scans from the original sets of 42 and 34 scans for the n-butane and propane samples, respectively and calculating the 95% confidence interval in each case. A plot of the latter against number of scans employed is shown in Figure 3.1. and from this graph, it was decided that an adequate scanning frequency for any G.C.-M.S. analysis was one which produced about 15 scans per hydrocarbon component where the associated 95% confidence level is approximately ± 1% (Figure 3.1.). In practice, the
alternative to limiting the number of scans recorded was to take as many scans as possible and then select an equally spaced fraction of them for use with Simpson's Rule, as illustrated above; by this procedure, the volume of data from each G.C.-M.S. experiment which required detailed processing could be considerably reduced.

Accuracy of Corrections to Mass Spectral Data: The fluctuations observed in percentage product values during the Simpson's Rule error analysis were assumed to be distributed in a Gaussian manner, independent of one another and independent of the size of the isotope percentage; none of these assumptions, however, may be strictly true because of the nature of the errors which may be introduced by the various corrections to the hydrocarbon peak intensities. For the background correction, it is assumed that there is at all times a linear superposition of the hydrocarbon and background peaks in each mass spectrum; at the ion chamber pressures used, it is probable that this was the case and that there was little suppression of background intensities on admission of the hydrocarbon sample. The natural isotope correction should not introduce a significant error to the final isotopic composition assuming that the tabulated isotope abundances are close to those observed experimentally.

The size of each error incurred in correcting for fragment ions is difficult to estimate precisely. In the absence of any alterations to the mass spectrometer source such as filament replacement during the period in which the G.C.-M.S. experiments of Chapters 4 and 5 were carried out, it was found on regular checking that the fragmentation patterns for the light hydrocarbons showed little variation from those quoted in Table 3.1; it was therefore assumed that the error induced by fluctuations in the mass spectrum of a hydrocarbon during any G.C.-M.S.
Figure 3.1. Error in Simpson's Rule Integration

Number of Scans
experiment would be an insignificant one for any set of scans. The assumption was also made that, in general, the sensitivity of the chromatograph - mass spectrometer combination to each isotopic form of the same hydrocarbon should be equal; although this was found to be apparently true for analysis of an equimolar mixture of propane-d\textsubscript{0} and propane-d\textsubscript{8} (Section 2.6.), it is possible that the assumption may be slightly less valid for the larger hydrocarbons where the range in mass number between the light and heavy forms of the molecule is greater. The major exception is that of methane for which measurable differences in sensitivity were recorded towards CH\textsubscript{4} and CD\textsubscript{4}, probably due to differential pumping in the Biemann molecular separator between these hydrocarbons of mass number close to that of the carrier gas helium; the sensitivities of the intermediate isotopic methanes were obtained by linear interpolation between the values for methane-d\textsubscript{0} and methane-d\textsubscript{4} (see Table 3.6.).

The precision of the fragmentation correction factors will be considerably dependent on the type of correction scheme used. In general, however, it can be said that the final percentage product values at the higher end of the mass range which are less complicated by fragment ion contributions should be more accurate than those for the species of lower deuterium content which are subject to a greater number of corrections. The reliability of the percentage isotopic distributions was generally assessed by a self-consistency check dependent on correction of peak intensities entirely composed of fragment ion contributions to values as close to zero as possible or alternatively, by comparison of experimental and binomial product distributions in cases where stepwise incorporation of deuterium was expected or where the data was drawn from a reaction which had reached equilibrium.
TABLE 3.6. SENSITIVITY FACTORS FOR THE G.C.-M.S. SYSTEM

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Sensitivity Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane-(d_0)</td>
<td>1.00</td>
</tr>
<tr>
<td>Methane-(d_4)</td>
<td>1.25</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.78</td>
</tr>
<tr>
<td>Propane</td>
<td>1.02</td>
</tr>
<tr>
<td>Isobutane (a)</td>
<td>9.36</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.57</td>
</tr>
<tr>
<td>Neopentane (a)</td>
<td>14.6</td>
</tr>
</tbody>
</table>

\(a\) For isobutane and neopentane the sensitivity for the parent ion is so small that the \(C_3H_7^+\) and \(C_4H_9^+\) ions were used, respectively.

Sensitivity Factors and Hydrocarbon Product Distributions: To obtain a quantitative analysis of the hydrocarbons in a G.C.-M.S. sample as well as their individual isotopic contents, the G.C.-M.S. apparatus was calibrated for its sensitivity to each paraffin by recording the spectra from known mixtures of light methane and the hydrocarbon in question. The observed parent ion intensity ratio was divided by the molar ratio of the two gases in the mixture to yield a sensitivity factor for that particular hydrocarbon relative to a value of unity for the light methane. Table 3.6. lists the sensitivity factors obtained in this way for each of the hydrocarbons used in the present study, including one for heavy methane as explained earlier; for isobutane and neopentane, the sensitivity factors were evaluated in terms of the \(C_4H_9^+\) and \(C_5H_7^+\) ions, respectively, due to the lack of parent ion. In measuring the distribution of paraffins in each G.C.-M.S. sample, the total ion count for each hydrocarbon was calculated by summing the corrected parent ion intensities for each of its isotopic components.
After division of each one by the appropriate sensitivity factor, these total ion intensities were themselves added and the quantity of each hydrocarbon was then expressed as a percentage of this new total. The accuracy of such a distribution was again largely dependent on that of the corrected mass spectral peak intensities; there was no evidence, however, to suggest any serious fluctuations of spectrometer sensitivity during the period over which the present work was carried out.

**Initial Distributions and Deuterium Dilution:** The importance of initial isotopic distributions with regard to obtaining mechanistic information has been stressed in much of the work on catalytic exchange reactions \(^2\); consequently, such distributions were a desirable objective in the G.C.-H.S. experiments of Chapters 4 and 5. A graphical technique which was useful in this connection consisted of plotting the selectivities for each isotopic species of the same hydrocarbon against the corresponding percentage conversion of the reaction from which they were produced; the selectivity of each isotopic component was defined as its fraction of the total quantity of hydrocarbon which had become deuterated. The selectivity curves were then extrapolated to zero conversion to obtain an accurate initial product distribution, and in this way it was possible to distinguish those products which were formed by consecutive reaction from those formed on one sojourn to the catalyst surface.

In any catalytic process involving hydrocarbons and deuterium, the latter becomes progressively diluted with hydrogen as the reaction proceeds. For example, in hydrogenolysis studies, this dilution effect may become considerable if the decomposition reaction is fast and a large conversion occurs in only a short period of reaction time; in such a situation, determination of an initial isotopic distribution for each hydrogenolysis product even with the first sample
withdrawn from the reaction vessel becomes a complicated problem due to the level of deuterium dilution in evidence. In cases where the extent of dilution is less than 40% of the way towards complete equilibration of the hydrogen-deuterium pool, it is still possible, however, to extract an informative isotopic distribution from the initial sample of data by applying the following treatment.

Assuming that the product hydrocarbons in the hydrogenolysis reaction mixture accumulate hydrogen or deuterium at random, then their resulting isotopic distributions will be binomial in nature and a function of the relative fractions of hydrogen and deuterium available in the system. For a product hydrocarbon with \( N \) replaceable hydrogen atoms, the isotopic distribution on desorption from a surface bearing relative proportions \( q \) and \( 1-q \) of deuterium and hydrogen, respectively, is given by

\[
F_i = \frac{N!}{i!(N-i)!} q^i (1-q)^{N-i} \quad (0 \leq i \leq N) \tag{3.19}
\]

where \( F_i \) is the fraction of hydrocarbon containing \( i \) deuterium atoms. If it is assumed that, in the short time before sampling, the hydrogenolysis products do not return to the surface to undergo exchange at an appreciable rate, then each of these hydrocarbons should retain the deuterium content which was required on their formation as a function of the isotopic dilution level at that point in time. As the hydrogenolysis reaction proceeds, the extent of dilution as designated by \( q \) will vary in value from \( q = 1 \) at zero conversion to \( q = q_f \) - the final dilution level present at the time of the first G.C.-M.S. sample. Hence, to obtain an average isotopic content, the distribution of equation 3.19 must be integrated over the extent of reaction with respect to the change in dilution level with conversion. The average isotopic distribution is given by
\[
D_i = \frac{N!}{i!(N-i)!} \int_{1}^{q_f} \frac{q^i (1-q)^{N-i}}{q_f} dq (0 \leq i \leq N) \tag{3.20}
\]

where \(D_i\) is the average fraction of isotopic hydrocarbon containing \(i\) deuterium atoms and \((1-q_f)\) is the factor required to normalize the distribution to a total of unity. Equation 3.20 cannot be completely accurate, however, inasmuch as it fails to take account of the overall consumption of hydrogen (in the generic sense) with increasing conversion or the mounting influence of dilution level \(q\) on the amount of hydrogenolysis observed over any small change in dilution \(dq\) at higher extents of reaction; these two discrepancies will tend to cancel one another and should be of less significance the greater the excess of deuterium employed. Tables of theoretical isotopic distributions may therefore be calculated for different numbers of replaceable hydrogens and a wide range of final dilution values using equation 3.20.

To utilise these theoretical tables, it is necessary for one of the hydrogenolysis products to exhibit an experimental isotopic distribution which clearly indicates the extent of dilution reached in the surface reaction. Consequently, in many of the hydrogenolysis processes where methane is produced, \(\text{CD}_4\) appears to be the initial product so the formation of \(\text{CD}_3\) in these cases will only occur by dilution of the deuterium excess. On this basis, it is possible to determine the final dilution level \(q_f\) at sample time by comparing the experimental ratio of methane-\(\text{d}_3\) and -\(\text{d}_4\) with the values displayed in the calculated tables for instances where \(N = 4\) and \(i = 3\) and 4. The final extent of dilution deduced from the methane analysis can then be used in correcting the isotopic distributions of the other hydrogenolysis products to obtain the amount of each species which would have been observed had there been no dilution present;
to do this, it is necessary to work through the distribution, starting with the
most deuterated species and correcting each percentage intensity for the effects
of dilution, the latter being indicated by the isotopic distributions which are
tabulated for the \( q \) value in question.

Although there was no opportunity to apply the above dilution correction
scheme in the G.C.-M.S. experiments performed here, the procedure was successfully
tested during a parallel G.C.-M.S. study of 1,1-dimethylcyclopropane
hydrogenolysis on metal films \(^{(17)}\) which was being carried out in the same
laboratory as that of the author.

3.4. The Kinetics of Hydrogenolysis and Exchange Reactions

Most of the analytical effort with respect to kinetic studies was directed
to measurement of reaction rate and, in particular, the rate of reaction
observable in the initial period of reaction; stress was laid on the latter in
order to enable rate comparisons between reactions of different kinetic order and
degree of reversibility and also to avoid the obscuring effects of sintering and
poisoning which were much more significant in later stages of reaction. The
evaluation of rates for isomerization processes on platinum films and also for
the retarded region of many of the reactions on that metal has been explained more
fully in Chapter 4.

Initial Reaction Rates: For the high temperature hydrogenolysis reactions
studied on platinum films by gas chromatography only, initial rates were
determined from product distribution versus time curves with the aid of numerical
methods; this procedure was necessary because of the settling down period of the
heating furnace and the subsequent uncertainty in assigning the origin of reaction
time. A least squares polynomial was fitted to the first three data points making up the initial portion of the plot for hydrocarbon reactant against time. It was then possible to derive the initial reaction rate in % min$^{-1}$ by calculating the gradient present at the new reaction time origin of the smoothed curve with the assistance of a Lagrangian numerical differentiation technique. The reliability of this method was tested by the measure of agreement displayed between the initial rate evaluated for disappearance of reactant and the sum of the initial rates determined by the same procedure for formation of each of the hydrogenolysis products. For the chromatographically analysed hydrogenolysis reactions on iron films which generally took place at temperatures about 150 to 200K lower than those on platinum, the initial reaction rates were measured graphically from the initial slope of the product distribution curve representing disappearance of reactant with time.

The concurrent exchange and hydrogenolysis reactions studied by the combined G.C.-M.S. apparatus were generally treated as first order processes with respect to assessment of reaction rates, although the latter were still quoted as initial values in % min$^{-1}$ for the sake of uniformity. Such a reaction system may be represented as a combined series-parallel network as shown in Figure 3.2, where the exchange process is assumed irreversible in the presence of a large excess of deuterium and the hydrogenolysis rates of the undeuterated and deuterated forms of the hydrocarbon are assumed to be the same.

```
Light Hydrocarbon → $k_D$ Exchanged Reactant → $k_H$ Hydrogenolysis Products
```

FIG. 3.2. Simultaneous exchange and hydrogenolysis network.
Assuming first order exchange and hydrogenolysis with rate constants $k_D$ and $k_H$, respectively, the network may be analysed as follows. Let $x$ be the total fraction of reactant used up in both processes, and $x_H$ and $x_D$ the fractional conversions of reactant via hydrogenolysis and exchange, respectively, at time $t$.

Hence, \[ \frac{dx}{dt} = (k_H + k_D)(1-x) \quad 3.21 \]

and \[ \frac{dx_D}{dt} = k_D(1-x) - k_H x_D \quad 3.22 \]

Integrating 3.21 with respect to time yields

\[ -\ln(1-x) = (k_H + k_D)t \]

so that \[ x = 1 - e^{-(k_H + k_D)t} \]

Substituting for $x$ in 3.22

\[ \frac{dx_D}{dt} + k_H x_D = -k_D e^{-(k_H + k_D)t} \]

Solving this first order differential equation gives

\[ x_D = e^{-k_D t} - e^{-(k_H + k_D)t} \quad 3.23 \]

From the original definitions

\[ x_H = x - x_D \]

so that \[ x_H = 1 - e^{-(k_H + k_D)t} - k_H t - e^{-(k_H + k_D)t} = 1 - e^{-k_H t} \]

and \[ -\ln(1-x_H) = k_H t \quad 3.24 \]

Eliminating $k_H$ between equations 3.23 and 3.24 gives

\[ x_D = (1-x_H)(1-e^{-k_D t}) \]

so that \[ -\ln\left(\frac{1-x_H-x_D}{1-x_H}\right) = k_D t \quad 3.25 \]
From the G.C.-I1.S. product distributions, values of $x_H$ and $x_D$ were calculated for each sample and the rate constants $k_H$ and $k_D$ were then determined from the initial gradients of the first order plots of $-\ln(1-x_H)$ and $-\ln\left(\frac{1-x_H-x_D}{1-x_H}\right)$, respectively, against time. The rate constants were converted to initial rates in $\% \text{ min}^{-1}$ by multiplying each value by 100 (the initial $\%$ of reactant).

**Arrhenius Parameters:** The initial rates of hydrogenolysis reactions studied by either of the analytical techniques were employed in the estimation of apparent activation energies ($E_a / \text{kJ mol}^{-1}$) by applying the Arrhenius equation

$$\ln r = \ln A - \frac{E_a}{R T}$$

where $r$ is the initial rate ($\% \text{ min}^{-1}$), $A$ is the pre-exponential or frequency factor in the same units, $R$ is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and $T$ is the absolute temperature in degrees Kelvin. Due to the presence of retardation effects, it was necessary in most cases to derive the activation energy value from the gradient of the linear, lower temperature section of the Arrhenius plot ($\ln r$ against $1/T$).

From the initial rates of hydrogenolysis and isomerization reactions on platinum, which gave rise to linear Arrhenius plots, it was also possible to calculate reliable values for the frequency factors; the latter were measured in units of molecules sec$^{-1}$ m$^{-2}$ by assuming an effective surface area for 10mg of platinum film (see Chapter 4).

**Errors:** The errors in graphically determined kinetic parameters (rates and activation energies) were generally estimated from the spread of points in the appropriate plots. It was found, however, that caution was necessary with the interpretation of graphical evidence, as it was sometimes found possible to draw two equally valid conclusions from different plots of the same experimental data; this effect is illustrated by some of the kinetic evidence from reactions on iron films (see Chapter 5).
CHAPTER 4

THE HYDROGENOLYSIS OF SATURATED HYDROCARBONS ON EVAPORATED PLATINUM FILMS

4.1. Introduction to Hydrogenolysis

The term hydrogenolysis refers, in general, to that class of catalytic reactions involving the rupture of chemical bonds in the presence of hydrogen. Examples of the types of bond in question include carbon-nitrogen, carbon-halogen and carbon-oxygen bonds; the present study is limited, however, to the hydrogenolysis of paraffinic carbon-carbon bonds over metal catalysts.

Ethane Hydrogenolysis: The most extensive kinetic and mechanistic investigations have been made for hydrogenolysis of ethane over the Group VIII transition metals and these have been recently reviewed by Sinfelt\(^{(1)}\). The most striking feature of the observed kinetics is the strong inverse dependence of reaction rate on hydrogen pressure; hence, the values of the exponent \( m \) in the simple power rate expression

\[
\text{Rate} = k p_{\text{C}_2\text{H}_6}^n p_{\text{H}_2}^m \quad (k = \text{rate constant})
\]

have been found to lie in the range \(-0.4\) to \(-2.5\) for all metals except iron and rhenium, where a positive reaction order with respect to hydrogen has been recorded. The ethane pressure dependence is generally close to first order implying that a low surface coverage of adsorbed \( \text{C}_2 \) species occurs on most of the metals. The Arrhenius parameters for ethane hydrogenolysis (derived from the equation \( k = A e^{-E/RT} \)) suggest that a compensation effect is operative, with the pre-exponential factor \( A \) tending to rise with increase in activation
energy $E$; a plot of $\log A$ against $E$, however, shows that two separate compensation lines may exist, one for the noble metals and a second for the remaining Group VIII members.

The various steps in the hydrogenolysis mechanism originally formulated by Taylor and his associates\(^{(2)}\) basically consist of dissociative adsorption of the hydrocarbon to form an unsaturated chemisorbed radical, followed by scission of the carbon–carbon bond and subsequent rehydrogenation of the adsorbed single carbon fragments from the surface to produce methane. The kinetics observed with most of the Group VIII metals indicate that an adsorption equilibrium is effectively established between ethane, hydrogen and the unsaturated surface species and that the rate-controlling hydrogenolysis step is probably dissociation of the carbon–carbon bond. The existence of an adsorption equilibrium also implies that the exchange of ethane with deuterium should occur readily in the absence of hydrogenolysis at sufficiently low temperatures, and this in fact is clearly the case for the noble metals of Group VIII. The rate inhibiting effects of hydrogen in ethane hydrogenolysis may result from an unfavourable change in the adsorption equilibrium position on increasing the hydrogen pressure, a lower concentration of reactive hydrocarbon intermediates being formed on the surface.

A wide range of ethane hydrogenolysis activities, amounting to seven or eight orders of magnitude, has been measured for the Group VIII metals and attempts have been made to correlate the respective activity values to properties of the metallic state\(^{(1)}\). Consequently, it has been found that the variation in activation energy and reaction orders with respect to ethane and hydrogen may be closely related to the precise position of the metal in the Periodic Table and that the catalytic activity towards hydrogenolysis may be a function of
electronic, geometric and thermodynamic factors such as the percentage
d-character of the metallic bond, the atomic spacings in the metal lattice and
the heat of adsorption of the hydrocarbon on the metal in question, respectively.

**Hydrogenolysis of Larger Hydrocarbons:** The additional feature of these reactions
is the possible variety in product distributions which may be obtained under
different experimental conditions and such information may be used to supplement
that deduced from the reaction kinetics concerning the nature of adsorbed
intermediates. With regard to reaction mechanism, the initial stages of
dissociative chemisorption and rupture of a carbon-carbon bond should occur as
with ethane, but the fragments so formed which contain 2 or more carbon atoms
now have the choice of desorbing from the surface via rehydrogenation or
undergoing further carbon-carbon bond splitting to yield even smaller surface
species. The extent to which each of these two parallel processes takes place
is then a function of the relative rates of desorption and carbon-carbon bond
dissociation for each of the adsorbed radicals; if desorption is faster, the
resultant hydrogenolysis product distribution may be characteristic of single
carbon-carbon bond scission per sojourn to the catalyst as, for example, in the
hydrogenolysis of n-butane on supported ruthenium\(^{(3)}\); when carbon-carbon bond
breaking has the higher rate, several bonds may be ruptured on each visit to the
surface and methane will be detected as the major initial hydrogenolysis product
often to proportions in excess of 90\% as recorded in hydrogenolysis reactions on
supported cobalt\(^{(4)}\). The tendency towards further breakdown of the initially
adsorbed fragment may also be enhanced by raising the temperature or reducing
the hydrogen pressure, both of which will lead to greater yields of the smaller
hydrogenolysis products.
The rates of hydrogenolysis of larger hydrocarbons generally increase with molecular size although there may be an even stronger inverse rate dependence on hydrogen pressure than observed for ethane, because of the greater number of carbon-hydrogen bonds which may be broken during the initial dehydrogenative chemisorption of the hydrocarbon\(^{(5)}\). The order of reaction with respect to hydrocarbon is dependent on the strength of reactant adsorption on the metal concerned. It is likely that the reactive intermediates responsible for the hydrogenolysis process are strongly adsorbed, multiply bonded species of the types shown in Figure 1.3, so in cases where adsorption is largely irreversible, the hydrocarbon order may be clearly less than unity\(^{(4)}\) and a significant degree of poisoning may also be detected due to the blocking of active surface sites by irreversibly bound hydrocarbon residues\(^{(6)}\).

4.2. Catalysis on Platinum

Considerable research has gone into the diversity of reactions which platinum has the ability to catalyze; as well as investigations into the hydrogenolytic splitting of carbon-halogen\(^{(7)}\), carbon-oxygen\(^{(8)}\) and carbon-nitrogen bonds\(^{(9)}\), the published literature includes details of the exchange reactions of amines and ethers with deuterium\(^{(10,11)}\) and also of hydrogenation studies\(^{(12)}\). The reactions most closely related to the present work on platinum are those involving either deuterium exchange or hydrogenolysis and isomerization of saturated hydrocarbons.

*Exchange:* For the smaller paraffins including ethane and methane, exchange on platinum films proceeds readily at temperatures in the range 280K to 480K\(^{(13,14)}\); the initial product distribution in each case consists mainly of the perdeutero-
hydrocarbon indicating that platinum tends to promote extensive multiple exchange with stepwise replacement of hydrogen occurring to a much lesser extent. It is clear therefore that adsorption of hydrocarbons on platinum at lower temperatures is completely reversible, and that the rapid interconversion of alkyl radicals with both \( \alpha \alpha \) - and \( \alpha \beta \) -diadsorbed species, which was found in the case of rhodium \(^{15}\), is also the predominant exchange mechanism on platinum. Evidence for poisoning of exchange at higher temperatures has been obtained by Jaggers\(^{14}\) who showed that presorption of saturated hydrocarbons for one hour at temperatures in excess of 473K considerably reduces the rate of a subsequent neopentane exchange reaction.

With a quaternary carbon atom present, the exchange reaction of neopentane might be expected to produce evidence for \( \alpha \gamma \) adsorbed intermediates, but, at the moderate temperatures required to propagate this reaction, there is little indication of multiple exchange involving more than a single methyl group per residence on the catalyst\(^{16}\). However, exchange of neopentane beyond the quaternary carbon does occur to a slight extent at higher temperatures\(^{14}\) and further evidence for the formation of \( \alpha \gamma \) species on platinum has also been found in exchange reactions of substituted cyclopentanes containing gem-dimethyl groups\(^{17}\). The role of such intermediates in exchange processes at moderately high temperatures provides an interesting correlation with the behaviour observed in other hydrocarbon reactions on platinum.

**Hydrogenolysis and Isomerization:** The hydrogenolysis of various alkanes on platinum films has been investigated by Anderson and co-workers\(^{18-21}\). Temperatures in excess of 523K were generally required for reaction and the initial distributions of reaction products indicated that hydrogenolysis on
platinum tends to occur with rupture of a single carbon-carbon bond per visit to the surface \(^{(20)}\). The reactivity of the butanes and neopentane was much higher than that of ethane, and this was attributed to the less favourable formation of an \(\alpha_\beta\)-diadsorbed intermediate for hydrogenolysis of the latter. As neopentane, which cannot be adsorbed in the \(\alpha_\beta\) mode, had a similar activity to the C\(_4\) molecules, it was concluded that an \(\alpha_\gamma\) adsorbed species must be involved in hydrogenolysis of the larger hydrocarbons. A major finding by these investigators was the ability of platinum to catalyse skeletal isomerization of hydrocarbons concurrently with the hydrogenolysis process. Since the activation energies for rearrangement and decomposition were found to be equal, it was proposed that the \(\alpha_\gamma\) intermediate is common to both reactions, and from evidence obtained using \(^{13}\)C tracer techniques, it was shown that the isomerization mechanism is intramolecular and does not involve recombination of surface fragments \(^{(21)}\). In the case of isobutane, the selectivity for isomerization relative to that for hydrogenolysis is enhanced by the presence of surfaces, such as the (111) planes of platinum, which facilitate the formation of intermediates attached to the catalyst at three different carbon atoms.

Gault and his associates \(^{(22-24)}\) have also studied hydrogenolysis, isomerization and other related reactions such as dehydrocyclization or ring enlargement on various platinum catalysts. They found, for example, a strong negative dependence on hydrogen pressure in the hydrogenolysis of methylcyclobutane on platinum films \(^{(22)}\), and in their experiments on the hydrogenolysis of methylcyclopentane to various hexane isomers, the initial product distribution was the same as that detected in the isomerization of n-hexane, 2-methylpentane and 3-methylpentane over a supported platinum catalyst, indicating clearly the involvement of a
common cyclic intermediate in the mechanisms for these reactions$^{(23,24)}$.

4.3. The Present Study

The preceding paragraphs illustrate the extent to which the hydrogenolysis and isomerization reactions of saturated hydrocarbons have been examined on platinum surfaces. It is interesting to note, however, the frequency with which detailed experimental investigations on platinum have been limited to the initial stages of reaction; Anderson and Baker$^{(18)}$, for instance, have tended to quote experimental results for reaction conversions of less than 10% and this trend has been followed by other workers in the field. There is a possibility, therefore, that further useful information about the behaviour of paraffins on platinum films in the presence of excess hydrogen may be gathered by examining the kinetics of such reactions at more extensive conversions where the effects of possible competition for surface sites between reactant and products may become important. Existing evidence of relevance to this proposal includes the retardation in rate or self-poisoning observed in reactions of neopentane on platinum$^{(20)}$ and also the increase in poisoning with reduction in hydrogen to hydrocarbon ratio which, in the case of some hydrocarbons, is accompanied by detection of significant quantities of the appropriate olefins$^{(20)}$.

As the hydrogenolysis of hydrocarbons on platinum films is already a relatively well-documented subject, there may not be much in the way of new mechanistic information to be gained by carrying out reactions in the presence of deuterium and applying combined gas chromatographic and mass spectrometric analysis; it was thought, however, that such a choice of system might provide an alternative means of substantiating some of the existing theories concerning
hydrogenolysis on platinum and at the same time permit testing and development of the experimental technique and the data handling methods. It was also realised, nevertheless, that the ability of platinum to cause rapid extensive exchange and consequently isotopic equilibration at lower temperatures might be a serious obstacle to detailed interpretation of G.C.-M.S. data collected from higher temperature reactions involving isotopic labelling.

4.4. Experimental

The analyses of reactions on platinum involved either gas chromatography only or the combined techniques of chromatography and mass spectrometry, and were carried out under standard operating conditions with the apparatus detailed in Chapter 2.

Materials: The reactant gases and the tungsten and platinum wires used in catalyst preparation were provided by the manufacturers specified previously; the methods employed for storage and purification of gaseous materials and production of the platinum films were those also described earlier (see Chapter 2, Sections 4 and 5).

Procedure: The standard experimental procedures defined in Chapter 2 were suitable for most of the platinum reactions, minor amendments being introduced where required. Each platinum film weighed from 10 to 15mg and had an approximately constant geometric surface area of 0.015m². In the experiment involving a presintered catalyst, the freshly prepared platinum surface was heated in vacuo for 1 hour at a temperature just above that chosen for reaction, before cooling to 273K for admission of the reactants. In cases where consecutive reactions were studied on the same film, removal of the used reaction
mixture and insertion of a fresh one were both carried out at ice temperature, thus preventing preferential desorption of deuterium and subsequent cracking of the remaining hydrocarbon on the surface which might arise from evacuation at high temperature. A standard 11.5:1 excess of deuterium to hydrocarbon was employed in each experiment except run 15, where the same ratio of hydrogen ($H_2$) to hydrocarbon was used, and run 18, in which a 1:1 mixture of isobutane and ethane accompanied the normal deuterium pressure. Before carrying out any catalytic experiments, a blank run was performed in the absence of a metal film by heating a mixture of deuterium plus all the hydrocarbon reactants to be studied to a high temperature in the glass reaction vessel; no exchange, decomposition or rearrangement of the hydrocarbons was detected from the subsequent G.C.-M.S. analyses indicating that the walls of the reactor and the attached tungsten rods were devoid of measurable catalytic activity.

**Analytical** The procedures described in Chapter 3 were generally employed for assessment of product distributions and kinetic parameters, but additional methods were required for evaluation of reaction rates (see Section 4.5.). Chromatographic analyses were made in terms of the total gas phase carbon present in the reactor and this allowed estimation of any material lost to the catalyst during reaction taking into account removal of hydrocarbon by sampling. In the chromatographic studies of n-butane hydrogenolysis and isomerization, the total retention time for base-line separation of the five hydrocarbons including isobutane was such that samples could comfortably be removed from the reactor every 15 minutes if necessary; with such a sampling frequency, however, timing of the first sample in high temperature reactions was fairly critical with regard to measurement of initial reaction rate (vide infra).
Mass spectral data from the G.C.-M.S. studies were corrected for background, naturally occurring isotopes and for fragmentation of the molecules within the spectrometer ion source. The fragmentation corrections were largely based on hydrocarbon cracking patterns measured with 20eV electrons - the electron energy necessary for sufficient spectrometer sensitivity towards methane. It was found, however, that a statistical fragmentation scheme based on random detachment of either a hydrogen or deuterium atom was particularly inadequate for accurate analysis of mixtures of isotopic propanes or ethanes; the methods devised to negotiate this problem have been detailed in Chapter 3. Lastly, the variation in isotopic distribution per mass spectral scan, which is caused by partial separation of the deuterated hydrocarbons in the gas chromatograph, was allowed for by summing the intensities at each mass number in a series of scans according to Simpson's Rule.

4.5. Results

The hydrocarbons chosen for study were ethane, propane, isobutane, n-butane and neopentane and reactions of each of these molecules on platinum were followed to a considerable degree of conversion with a view to observing any possible influence of product formation on the course of the reaction. The general effects of the latter are summarized in Figure 4.1, which illustrates the comparative behaviour of ethane, propane, n-butane and isobutane hydrogenolysis reactions on platinum at 633K. In terms of the overall rate of disappearance of reactant, the n-butane and isobutane reactions were found to decelerate markedly with time while that of propane remained constant, exhibiting the character of a zero order process; with ethane, however, the rate of reaction appeared to
**FIGURE 4.1. HYDROGENOLYSIS OF HYDROCARBONS**

ON PLATINUM AT 633 K
accelerate with time. Neopentane (not shown in Figure 4.1.) also behaved similarly to the butanes but with a sharper decline in rate as the reaction proceeded.

With regard to interpretation of reaction kinetics, it is clear from Figure 4.1. that, for any particular experiment, it was possible to extract two distinct rates representative of the kinetic behaviour at 'initial' and 'subsequent' stages of reaction. In order that these initial and subsequent rates should be truly comparable, the latter were extrapolated to zero time (100% reactant) and expressed in the same manner as initial rates in the form of % min$^{-1}$. In this way, subsequent rates for ethane and propane experiments were extrapolated from the zero order portion of their concentration versus time curves; on the other hand, the reactions of the butanes exhibited approximately first order behaviour at the later stages of reaction and, for convenience, the subsequent rates for these reactants were obtained by extrapolation from the relevant section of their first order kinetic plots.

The inherent analytical inaccuracy during the first few minutes of a high temperature reaction, due principally to the difficulty in stipulating precisely the origin with respect to reaction time, necessitated the use of numerical methods for accurate estimation of initial rates. The experimental points from the chromatographic analyses were first fitted to a smooth curve from which the corresponding initial rate was calculated by numerical differentiation$^{(25)}$. The appropriate reaction rates for each system studied are quoted in Table 4.1.

Where activation energies are quoted, these were determined using the Arrhenius equation in the normal way, and frequency factors were evaluated in units of molecules s$^{-1}$ m$^{-2}$ by assuming an effective surface area of 3 x 10$^{-2}$ m$^2$. 
<table>
<thead>
<tr>
<th>Run number</th>
<th>Reactant  \textsuperscript{g}</th>
<th>T/K</th>
<th>Hydrogenolysis \textsuperscript{h}</th>
<th>Isomerization \textsuperscript{h}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial Rate (r_1)</td>
<td>Subsequent Rate (r_2)</td>
</tr>
<tr>
<td>1</td>
<td>Ethane</td>
<td>603</td>
<td>0.017</td>
<td>0.058</td>
</tr>
<tr>
<td>2</td>
<td>Ethane</td>
<td>633</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>3\textsuperscript{a}</td>
<td>Ethane</td>
<td>633</td>
<td>0.11</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>Propane</td>
<td>633</td>
<td>0.40</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>n-Butane</td>
<td>553</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>6</td>
<td>n-Butane</td>
<td>573</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>n-Butane</td>
<td>603</td>
<td>0.25</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>n-Butane</td>
<td>633</td>
<td>0.59</td>
<td>0.20</td>
</tr>
<tr>
<td>9</td>
<td>n-Butane</td>
<td>663</td>
<td>1.39</td>
<td>0.29</td>
</tr>
<tr>
<td>10</td>
<td>n-Butane</td>
<td>683</td>
<td>2.09</td>
<td>0.36</td>
</tr>
<tr>
<td>11\textsuperscript{b}</td>
<td>n-Butane</td>
<td>683</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>12\textsuperscript{b}</td>
<td>n-Butane</td>
<td>683</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>13\textsuperscript{b}</td>
<td>n-Butane</td>
<td>683</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>14\textsuperscript{c}</td>
<td>n-Butane</td>
<td>663</td>
<td>1.29</td>
<td>0.23</td>
</tr>
<tr>
<td>15\textsuperscript{d}</td>
<td>n-Butane</td>
<td>553</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>16</td>
<td>iso-Butane</td>
<td>633</td>
<td>0.54</td>
<td>0.17</td>
</tr>
<tr>
<td>17\textsuperscript{e}</td>
<td>iso-Butane</td>
<td>633</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>18\textsuperscript{f}</td>
<td>iso-Butane</td>
<td>633</td>
<td>0.22</td>
<td>0.08</td>
</tr>
<tr>
<td>19</td>
<td>neo-Pentane</td>
<td>633</td>
<td>2.50</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction on same film as experiment 2; \textsuperscript{b}reaction on same film as experiment 10; \textsuperscript{c}reaction on presintered film; \textsuperscript{d}reaction in the presence of hydrogen\(\text{H}_2\); \textsuperscript{e}reaction on same film as experiment 16; \textsuperscript{f}reaction of 1:1 mixture of isobutane and ethane; \textsuperscript{g}all reactions carried out with an 11.5:1 ratio of \text{D}_2:hydrocarbon unless otherwise stated; \textsuperscript{h}all rates measured in \(\% \text{ min}^{-1}\).
of platinum for each experiment. This value for active surface area was obtained by combining the observed geometric area for each catalyst (see Section 4.4.) together with a roughness factor of 2 for a platinum film; the validity of such an approximation lies in the facts that film weights and geometric areas tended to show little variation in magnitude and, at the high reaction temperatures used, sintering cut to quickly reduce the film area to a constant value of the order specified (18).

**Chromatographic Studies**

(a) Ethene: The hydrogenolysis reactions of ethane on platinum (Table 4.1. runs 1-3) were each characterised by an induction period during which hydrogenolysis to methane occurred slowly. Subsequently, as illustrated in Figure 4.1, the reaction followed zero order kinetics with respect to ethane but at an increased rate of reaction. For a second experiment on the same platinum film, the induction period was reduced to approximately half that of a first experiment and the hydrogenolysis process quickly accelerated to a subsequent rate comparable to that for the first reaction.

The Arrhenius equations obeyed by initial and subsequent ethane hydrogenolysis were

\[ r_1(\text{ethane}) = 10^{34.6} \exp \left(-222 \times 10^3/RT\right) \]

and

\[ r_2(\text{ethane}) = 10^{28.7} \exp \left(-148 \times 10^3/RT\right) \]

respectively, with rates expressed in molecules s\(^{-1}\) m\(^{-2}\) and activation energies in k J mol\(^{-1}\). The estimated error in these kinetic parameters is ± 4 k J mol\(^{-1}\) in the activation energy and a factor of two in the frequency factor.

(b) Propane: A typical hydrogenolysis reaction of propane on platinum at 633K is shown in Figure 4.1. and the rates determined from this experiment are quoted
in Table 4.1, run 4. The disappearance of propane was faster than that of ethane at the same temperature and obeyed approximately zero order kinetics throughout the reaction, the subsequent rate listed in Table 4.1. being representative of all but the first few minutes of reaction up to at least 75% conversion.

If propane hydrogenolysis involves only the fission of a single carbon-carbon bond then a product distribution of 66.7% ethane and 33.3% methane would be expected in terms of the carbon contents of the molecules. The observed initial distribution was 63.4% ethane and 36.6% methane indicating that a small fraction of the propane molecules hydrogenolysed completely to methane on a single visit to the catalyst.

(c) n-Butane: As detailed in Table 4.1, the reaction of n-butane on platinum was studied in the temperature range 553K to 683K and the reactivity of the C\textsubscript{4} molecule was observed to be greater than that of the smaller paraffins. As expected\cite{20}, hydrogenolysis to species of lower carbon number was found to be accompanied by reversible isomerization of the reactant to isobutane, formation of the latter being thermodynamically more favourable at the lower reaction temperatures. A typical reaction at 683K, showing clearly the pattern of products and the slowing of reaction with time, is demonstrated in Figure 4.2, and the initial distribution of products for this reaction and for a second reaction on the same film at the same temperature is given in Table 4.2.

Considering hydrogenolysis alone, the ratio of propane: ethane: methane in the product distribution was not 3:2:1 which would be expected on the basis of equally probable single carbon-carbon bond breakage at either the central or terminal positions in the hydrogenolysis step. However, the relative amounts of hydrogenolysis products were found not to vary significantly with the reaction
Figure 4.2. Reaction of n-Butane on Platinum at 683K
temperature. The overall rate of disappearance of n-butane normally followed first order kinetics but at high temperatures the fall off in rate with time was initially greater than that expected on the basis of first order behaviour. This point is illustrated in Figure 4.3, which contrasts the first order rate plots for n-butane reactions at 553 and 683K.

Initial and subsequent rates for isomerization and hydrogenolysis were calculated by assuming that interconversion of n-butane and isobutane was possible and that either of these molecules could be irreversibly hydrogenolysed to species containing less than four carbon atoms. To examine the isomerization equilibrium alone, it was possible to disregard the hydrogenolysis reaction by normalizing the total \( C_4 \) entities present at each experimental point to a total of 100%. The equation used to evaluate the information from the reversible first order isomerization was

\[
\ln \left( \frac{x-x_e}{1-x_e} \right) = \ln \left( \frac{100-x_e}{1-x_e} \right) - (k_f \cdot k_r)t
\]

where \( x \) is the percentage of reactant at time \( t \), \( x_e \) is the percentage of reactant at equilibrium, \( k_f \) is the rate constant for the reaction by which isobutane is formed from n-butane, and \( k_r \) is the rate constant for the reverse reaction (see Chapter 3). As may be seen from Figure 4.4, this equation accurately accounted for the isomerization of n-butane at 553 and 683K using thermodynamic equilibrium values of \( x_e \) of 50.7% and 58.9% respectively. Subsequent rates for hydrogenolysis and isomerization were estimated from first order plots of the types shown in Figures 4.3 and 4.4, while all initial rates were determined using numerical methods as described earlier.

It is apparent from Table 4.1, experiments 5-10, that the divergence between initial and subsequent rates increased with temperature for both hydrogenolysis
Figure 4.3. First order plots for reactions of n-butane on platinum.
Figure 4.4. First Order Reversible Plots for Isomerization Reactions on Platinum
and isomerization. The ratio of initial to subsequent rates was observed to be similar for both hydrogenolysis and isomerization indicating that both processes were being poisoned to comparable extents.

The Arrhenius equations obeyed by initial hydrogenolysis and isomerization were

\[ r_1(\text{n-butane}) = 10^{24.5} \exp \left( -91.1 \times 10^3 / RT \right) \]

and

\[ r_3(\text{n-butane}) = 10^{24.2} \exp \left( -90.3 \times 10^3 / RT \right) \]

respectively.

The parameters for each process were thus equal within experimental error.

Further evidence for the poisoning of the reactions of n-butane was obtained by carrying out four consecutive experiments on the same platinum film at 683K. The initial and subsequent rates quoted in Table 4.1, runs 10-13, indicate that the rate of poisoning for both hydrogenolysis and isomerization was less in second and later reactions than in the first. Table 4.2 shows that no significant change was observed in the initial product distribution in terms of the ratio of hydrogenolysis to isomerization, implying no preferential inhibition of either of these reactions. Formation of C4 olefins, not detected during a first experiment on a platinum catalyst at any temperature, was found to occur during second and subsequent reactions at 683K. The quantity of olefin formed rose to a maximum of approximately 1.5% of the total product in the early stages of each further reaction and then declined slowly with time.

An attempt to recover any carbon lost to the catalyst was made by heating a used platinum film immediately after the reaction in the presence of a fresh quantity of deuterium, but no significant quantity of methane was detected. This observation agreed with the fact that the measured decrease in size between
### Table 4.2. Product Distributions

<table>
<thead>
<tr>
<th>Run number</th>
<th>Reactant</th>
<th>T/K</th>
<th>Product / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>n-butane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>683</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt; 17 iso-C&lt;sub&gt;4&lt;/sub&gt; 32 C&lt;sub&gt;3&lt;/sub&gt; 32 C&lt;sub&gt;2&lt;/sub&gt; 19 iso-C&lt;sub&gt;5&lt;/sub&gt; - n-C&lt;sub&gt;5&lt;/sub&gt; -</td>
</tr>
<tr>
<td>11</td>
<td>n-butane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>683</td>
<td>- 17 iso-C&lt;sub&gt;4&lt;/sub&gt; 35 C&lt;sub&gt;3&lt;/sub&gt; 27 C&lt;sub&gt;2&lt;/sub&gt; 21 iso-C&lt;sub&gt;5&lt;/sub&gt; - n-C&lt;sub&gt;5&lt;/sub&gt; -</td>
</tr>
<tr>
<td>16</td>
<td>iso-butane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>633</td>
<td>73 - 16 C&lt;sub&gt;3&lt;/sub&gt; 4 C&lt;sub&gt;2&lt;/sub&gt; 6 iso-C&lt;sub&gt;5&lt;/sub&gt; -</td>
</tr>
<tr>
<td>17</td>
<td>iso-butane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>633</td>
<td>73 - 17 C&lt;sub&gt;3&lt;/sub&gt; 5 C&lt;sub&gt;2&lt;/sub&gt; 5 iso-C&lt;sub&gt;5&lt;/sub&gt; -</td>
</tr>
<tr>
<td>19</td>
<td>neo-pentane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>633</td>
<td>7 16 C&lt;sub&gt;3&lt;/sub&gt; 12 C&lt;sub&gt;2&lt;/sub&gt; 9 C&lt;sub&gt;1&lt;/sub&gt; 8 iso-C&lt;sub&gt;5&lt;/sub&gt; 42 n-C&lt;sub&gt;5&lt;/sub&gt; 6</td>
</tr>
</tbody>
</table>

<sup>a</sup> First reaction on fresh Pt film; <sup>b</sup> second reaction on same Pt film; <sup>c</sup> all product distributions, in terms of carbon content, are initial except for neo-pentane which is at 20% conversion.

### Table 4.3. Isotopic Contents of Products from First and Second Reactions of n-Butane on Platinum at 63.3K

<table>
<thead>
<tr>
<th>Composition/%</th>
<th>M&lt;sub&gt;D&lt;/sub&gt;</th>
<th>Isotopic Content / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d&lt;sub&gt;1&lt;/sub&gt; d&lt;sub&gt;2&lt;/sub&gt; d&lt;sub&gt;3&lt;/sub&gt; d&lt;sub&gt;4&lt;/sub&gt; d&lt;sub&gt;5&lt;/sub&gt; d&lt;sub&gt;6&lt;/sub&gt; d&lt;sub&gt;7&lt;/sub&gt; d&lt;sub&gt;8&lt;/sub&gt; d&lt;sub&gt;9&lt;/sub&gt; d&lt;sub&gt;10&lt;/sub&gt;</td>
</tr>
<tr>
<td>n-butane</td>
<td>79</td>
<td>7.9</td>
</tr>
<tr>
<td>n-butane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>7.9</td>
</tr>
<tr>
<td>propane</td>
<td>3</td>
<td>6.5</td>
</tr>
<tr>
<td>propane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>iso-butane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>ethane</td>
<td>3.5</td>
<td>4.7</td>
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<tr>
<td>methane</td>
<td>1.5</td>
<td>3.2</td>
</tr>
<tr>
<td>n-butane&lt;sup&gt;e&lt;/sup&gt;</td>
<td>26</td>
<td>7.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Binomial distribution; <sup>b</sup> insufficient material for accurate analysis; <sup>c</sup> sample taken after 5 min of reaction; <sup>d</sup> sample taken after 15 min of reaction; <sup>e</sup> isomerization and hydrogenolysis totalled %; <sup>f</sup> M<sub>D</sub> is the mean deuterium content.
successive samples withdrawn from the reaction vessel was approximately equal to that expected on the basis of the percentage of reaction vessel contents removed per sample by the chosen sampling loop (see Section 2.3.).

The possibility that progressive sintering of the catalyst was the cause of the deceleration in rate observed was investigated by carrying out a reaction of n-butane with deuterium at 663K on a platinum film previously sintered for 1 hour in vacuo at 673K. Reaction rates quoted in Table 4.1, runs 9 and 14, for experiments at 663K on unsintered and sintered films, respectively, were found to be comparable, the distinct slowing of reaction also being observed on the sintered catalyst.

Finally, to confirm that reactions in the presence of deuterium, which was used merely for convenience in the chromatographic studies, did not differ from those in the presence of hydrogen, an experiment was conducted at 553K involving n-butane and hydrogen. Runs 5 and 15 listed in Table 4.1. illustrate that there is no significant difference between reactions performed with hydrogen and those with deuterium.

(d) Isobutane: Data from reactions of isobutane on platinum at 633K were treated in the same manner as those for n-butane. Estimation of subsequent rates for isomerization was more difficult than with n-butane because poisoning was more extensive as indicated in Figure 4.4. Values for the initial and subsequent rates of hydrogenolysis and isomerization for a reaction of isobutane are given in Table 4.1, run 16, and they demonstrate the similarity in reactivity between the two C4 reactants. Run 17 in the same table, where the subsequent rates do not differ from the initial rates by as much as was the case for run 16, shows again that a lesser rate of poisoning was observed for a second reaction on the
same platinum film.

As would be expected thermodynamically, the initial product distribution for a reaction of isobutane, which is catalogued in Table 4.2, showed a much greater proportion of isomerization than was observed with n-butane; since rupture of a single carbon-carbon bond in isobutane can only yield methane and propane, the small percentage of ethane produced initially must be attributable either to dissociation of more than one carbon-carbon bond per residence on the catalyst or hydrogenolysis of some of the n-butane molecules formed by isomerization. This product distribution did not vary significantly between first and second experiments on the same film, again indicating no preferential poisoning of either hydrogenolysis or isomerization.

The influence on the course of a reaction of competition for the surface from product molecules was directly tested by carrying out an isobutane experiment in the presence of an equal pressure of ethane, the latter being only a very minor product of isobutane hydrogenolysis; a comparison of reactions 18 and 16 in Table 4.1. shows that the reaction rates with ethane present were only about half those obtained with isobutane alone.

(e) Neopentane: Neopentane was found to undergo hydrogenolysis readily on platinum at 633K. The reaction proceeded initially with a rapid rate of conversion but subsequently poisoned more quickly than that of any of the other hydrocarbons investigated; rates for such a neopentane study are quoted in Table 4.1, run 19. Since the immediate products of the neopentane reaction tended to rapidly undergo further processes, an initial distribution was difficult to determine; however, a typical product distribution measured at 20% conversion from an experiment with neopentane as reactant at 633K is given in Table 4.2, and shows that
isomerization was the predominant mode of reaction, isopentane being the major initial product.

Gas Chromatograph - Mass Spectrometer Studies: The combined G.C.-M.S. technique was applied to the reaction of n-butane with deuterium on platinum at 683K and the results are detailed in Table 4.3. The exchange of n-butane with deuterium was extremely rapid in relation to hydrogenolysis or isomerization, and extensive incorporation of deuterium into each of the hydrogenolysis products was also observed. The isotopic distribution of the exchanged n-butane was found to be in good agreement with a binomial distribution calculated from the value of the mean deuterium content which was 7.9 for the reaction in Table 4.3.

The isotopic compositions of the hydrogenolysis products, propane being quoted as an example in Table 4.3, also corresponded closely to binomial distributions of the available hydrogen-deuterium pool. Furthermore, it was notable that the fractional deuterium content or percentage of exchanged hydrogen present in the n-butane reactant and propane product molecules had similar values of 79 and 82% respectively.

For a second reaction at 683K on the same platinum film, accurate isotopic analysis in the initial stages of the reaction was only possible for n-butane because of the small extents of isomerization and hydrogenolysis. The rate of exchange in a second reaction was less than that of a first reaction by a factor comparable to that for the reduction in rates of isomerization and hydrogenolysis. The isotopic composition of the exchanged n-butane in a second reaction was not binomial but displayed maxima at species having one or ten deuterium atoms.
4.6. Discussion

The differences in the reaction characteristics of the various hydrocarbons investigated are obvious from Figure 4.1, where the kinetic behaviour is illustrated. The rate of the reaction of ethane is seen to increase with time in contrast to those of n-butane, isobutane and neopentane where retardation was observed; the reaction of propane, however, appeared to maintain an almost constant rate throughout the course of an experiment. These striking differences in behaviour between the various hydrocarbons, which become most evident at extensive conversions, serve to indicate the nature of the processes which may take place on the platinum catalyst as the composition of the surface phase changes with time.

Figure 4.1. illustrates clearly the retardation in rate observed for reactions of n-butane and isobutane. This type of poisoning of the reactions was found to be greatest for neopentane and to occur more with isobutane than with n-butane. In the case of n-butane, the rate decreased with time in a manner corresponding approximately to that of a process obeying first order kinetics, an observation which was fully utilised in the evaluation of rates for that reactant.

The exact nature of the apparent poisoning of the n-butane, isobutane and neopentane reactions is difficult to elucidate precisely, but several conclusions can be drawn from the experimental evidence provided. The results from experiment 14 in Table 4.1. imply that a progressive sintering of the platinum catalyst would not in itself give rise to the degree of slowing down observed in these hydrogenolysis reactions; indeed, at the high reaction temperatures employed, it is probable that the major part of any effects due to sintering would occur fairly rapidly in the short period required to raise the reactor and
its contents to a steady reaction temperature and that further reduction in the active surface area of platinum by sintering might be considerably limited during reaction by the presence of the adsorbed gases \(^{(26)}\). The data obtained from run 18 (Table 4.1) also suggests that competition for the surface between the reactant and a product molecule such as ethane only slightly reduces the rate of reaction, and cannot be nominated as the principal source of reaction poisoning.

The greater divergence between initial and subsequent rates for the reaction of n-butane on platinum at higher temperatures indicates that the concentration of species responsible for the poisoning of the reaction must increase with temperature. The suggestion that build-up of irreversibly adsorbed species may be responsible for the poisoning is further stressed by the continued decrease in rates for consecutive n-butane experiments on the same platinum film, as shown in Table 4.1, runs 10-13; the fall in the rate of poisoning with each successive reaction merely reflects the progressively lower fraction of unpoisoned surface available to the reactants.

From their detailed consideration of ionic rearrangements and stabilities of intermediates, Anderson and Avery \(^{(21)}\) have postulated that species exhibiting partial carbonium ion character may play an important role in hydrogenolysis and isomerization reactions on platinum; similarly, Matsumoto et al. \(^{(27)}\) have also interpreted the hydrogenolysis and skeletal isomerization of saturated C\(_6\) hydrocarbons on platinum by carbonium ion mechanisms. In particular, for neopentane and the butanes, Anderson established that the isomerization process should be favoured by partial electron transfer from the adsorbed hydrocarbon residue to the metal, and taking into account the hyperconjugative effects of free methyl groups, this led to a predicted order for isomerization activity of
neopentane > isobutane > n-butane

which, in fact, agreed with the experimental data obtained. Thus, it is particularly interesting that the results presented here clearly demonstrate the same trend for isomerization activity and rate of poisoning; it is also significant that poisoning is only severe for the molecules neopentane and isobutane, both of which may readily give rise to stable tertiary carbonium ions, and also for n-butane where formation of such ions may occur to a significant extent as a consequence of isomerization to isobutane. It may be tentatively proposed, therefore, that there is a direct relation between the involvement of carbonium-type intermediates and the observed degree of retardation in the reactions of these molecules and this is corroborated by the fact that the reactions of propane and ethane do not suffer extensive poisoning, presumably because of the inability of these reactants to form reasonably stable carbonium ions.

The formation of carbonium ions per se should not, however, be a sufficient criterion for the poisoning of reactions on platinum since, as indicated already, species of carbonium ion character are likely to be important intermediates in the hydrogenolysis and isomerization mechanisms(21). What is more probable is that species of carbonium ion nature may participate in side reactions that lead to products which are capable of blocking catalytically active sites. Hence, the formation of C₄ olefins, which was observed in the initial stages of a n-butane reaction at 633K on a previously used film, may be assisted by the presence of carbonium type fragments on the surface. Although gas phase thermodynamic calculations for the equilibrium

\[ 1 - C_4H_{10} \rightarrow n-C_4H_8 + H_2 \]
at 683K predict an olefin concentration of approximately 4% under the standard experimental conditions, it is likely that equilibrium with respect to formation of intermediates which might desorb as olefin may be rapidly reached on a platinum surface and that subsequent conversion of such species to other products may preclude detection of gas phase olefin, in particular during a first experiment on a platinum film where there is a large excess of deuterium present. In the later stages of such a reaction, the ratio of deuterium to hydrocarbon on the surface may be reduced by consumption of deuterium in the formation of hydrogenolysis products, and there is considerable evidence to suggest that such an effect may allow the propagation of side reactions such as dimerization or disproportionation which may be aided by the presence of carbonium type species.

Csicsery\(^{(28)}\), for instance, has shown that alkanes may be converted to aromatic dimers on platinum by a mechanism involving cyclization, which requires the formation of two carbon-carbon bonds, followed by dehydrogenation to the closed ring product. A typical example of this process was the dimerization of isobutane to p-xylene

\[
2 \text{iso-C}_4H_{10} \rightarrow \text{p-C}_6H_4(CH_3)_2 + 5 \text{H}_2
\]

which apart from the aromatic product also yielded a wide range of others from fragmentation, isomerization and dehydrogenation reactions including a small proportion of butenes, the concentration of which rose to a maximum at quite low reactant residence times; Csicsery has pointed out that this behaviour is consistent with the olefin being a precursor to dimerization which, in turn, implies a mechanism of the type already proposed for ring closure reactions\(^{(29)}\) and, hence, the possible involvement of carbonium ions. Further interesting evidence of poisoning on platinum surfaces has come from Sachtler and
co-workers who found that repeated isomerization and hydrogenolysis reactions of n-butane in the temperature range 623K to 673K produced a drop in the total activity of the catalyst by a factor of 20 with respect to initial rate; once the platinum was deactivated in this way for cracking, disproportionation of the C\textsubscript{4} reactant to pentane and propane was also observed, together with formation of small quantities of but-1-ene and but-2-ene.

The conclusion to be drawn from a comparison between these examples and the present study is that, in situations such as the later stages of a first reaction or the start of a second reaction on the same platinum film in both of which the proportion of surface hydrogen (in the generic sense) may be considerably reduced, inhibitory reactions which may benefit mechanistically from the presence of carbonium-like fragments can proceed with formation of dehydrogenation products or molecules larger than the reactant; experimental detection of these incidental products will depend on desorption conditions and in this connection only small amounts of butenes were observed at the start of a reaction on a used film after insertion of the fresh reaction mixture. While species of carbon number greater than the reactant were not detected presumably because of irreversible attachment to the catalyst, it must also be said that the gas chromatography system was not primarily geared for identification of such molecules. In general, the poisoning of the n-butane, isobutane and neopentane reactions on platinum may be tentatively attributed to the blocking of active sites by the formation of irreversibly adsorbed carbonaceous products from the types of side reaction described.

The hydrogenolysis of propane, as may be seen from Figure 4.1, followed zero order behaviour during the course of reaction. Mechanisms depending on carbonium ions are much less likely with propane and thus poisoning by larger molecules
formed from processes other than hydrogenolysis would not be anticipated. The non-preferential inhibition of hydrogenolysis or isomerization reactions on platinum, either during a first or subsequent reaction on the same catalyst, suggests that the poisoning occurs generally over the catalyst surface and not on sites peculiar to any particular process. The normal exchange reaction of butane was also observed to be poisoned to a similar extent.

Ethane hydrogenolysis on platinum behaves in a manner contrary to that normally observed for reactions on metal films in that an acceleration in rate is observed before the reaction assumes zero order kinetics. The presently reported results cannot be easily reconciled with the reaction mechanism proposed by Cimino et al.\(^{(2)}\) which has been used to explain the observations made in previous investigations of this reaction on platinum\(^{(18,31)}\). The initial step in that mechanism is the dissociative chemisorption of ethane to form adsorbed \(\text{C}_2\text{H}_5\) which then dehydrogenates further to yield the surface species \(\text{C}_2\text{H}_x\) \((x<5)\); the latter then undergoes carbon-carbon bond scission to form monocarbon fragments which are subsequently hydrogenated and desorbed as methane. This sequence of reaction steps has been found to satisfy the experimental data already obtained on platinum in that ethane exchange with deuterium\(^{(13)}\) tends to occur readily at low temperatures and the hydrogenolysis reaction normally takes place at higher temperatures with rupture of the ethane carbon-carbon bond as the rate controlling process\(^{(20)}\); in none of these earlier ethane hydrogenolysis studies was the removal of methane from the surface considered to have any rate-determining effects. Bearing this in mind, an attempt can be made to explain the irregular behaviour found in the present work. Since the literature evidence generally suggests that breaking of the carbon-carbon bond in ethane appears to require a
high energy of activation \(^{(20,31)}\), the fact that the subsequent rate of ethane hydrogenolysis at 633K (Table 4.1, run 2) is comparable to that of the other hydrocarbons merely emphasises the slow nature of ethane carbon-carbon bond dissociation and the likelihood of it being the rate-determining step, not only throughout reactions at lower temperatures but also after the induction period in higher temperature experiments. Evidence from deuterium exchange reactions\(^{(14)}\) is that the adsorption and desorption of methane on platinum is generally slower than that of the other hydrocarbons; therefore the induction period prior to faster zero-order decomposition may represent conditions on the platinum surface under which the rate of ethane hydrogenolysis is limited in part by the rate of methane desorption. In such circumstances, it is probable that the initial concentration of single carbon fragments on the catalyst is very low; gradually the \(C_1\) units will accumulate on the surface until the rate of their desorption as methane increases to a value which equals the rate of carbon-carbon bond rupture, and the latter once more becomes the rate controlling process.

These suggestions are corroborated by the considerably shorter induction period before attainment of the more rapid subsequent rate which was displayed in a second experiment on a platinum film already extensively covered with \(C_1\) residues from a previous reaction (Table 4.1, runs 2 and 3). The importance of the balance on the surface between adsorbed reactant and product species with regard to the general course of the hydrogenolysis reaction is further reflected in the initial and subsequent activation energies for ethane hydrogenolysis on platinum. While the initial activation energy, 222 kJ mol\(^{-1}\), was found to be similar to the values of 226 and 239 kJ mol\(^{-1}\) reported for ethane hydrogenolysis on platinum films\(^{(20)}\) and silica supported platinum\(^{(31)}\), respectively, the
activation energy for the subsequent reaction, 145k J mol\(^{-1}\), was much lower indicating that the activation energy depended markedly on the extent and composition of the material adsorbed on the surface.

The product distributions from the reactions on platinum films indicate that, to a large extent, only one carbon-carbon bond is broken per visit of the reactant molecule to the surface and also that splitting of different carbon-carbon bonds is non-selective. For example, the hydrogenolysis reaction of propane yielded ethane and methane in approximately equal amounts, and the product distributions for n-butane hydrogenolysis showed no significant variation with temperature, implying similar activation energies for the breaking of terminal and central carbon-carbon bonds. These properties have been commonly observed on platinum\(^{(27)}\) and are in marked contrast to the situation with hydrogenolysis of alkanes on nickel catalysts where there is highly selective attack on the terminal carbon-carbon bonds\(^{(32)}\), and with cobalt\(^{(27)}\) where multiple dissociation of carbon-carbon bonds is favoured per residence of the reactant on the catalyst surface.

The present observations made on the initial stages of the n-butane, isobutane and neopentane reactions, including detection of skeletal isomerization in each of these cases, correspond closely to those reported elsewhere\(^{(18,19,33)}\). In particular, the results obtained for the initial behaviour of n-butane reactions on platinum agree with those of Anderson and Avery\(^{(20)}\) in all respects except their initial rate values which were distinctly higher than those measured here; it is difficult to account for this discrepancy, particularly in the light of experiment 15, Table 4.1. from which it may be concluded that the possibility of kinetic isotope effects being introduced by the use of deuterium instead of hydrogen in these reactions is a negligible one. The similar activation energies
estimated for hydrogenolysis and isomerization again lend support to the concept of a common mechanism for the two processes; it must also be realised, however, that there is always the possibility that activation energies are rendered suspect because of more extensive poisoning at higher temperatures and it is significant to note in this respect that the results quoted in Table 4.1. for the subsequent isomerization of n-butane would clearly indicate a 'turning over' of the Arrhenius plot with the reaction rate decreasing as the temperature is raised.

The n-butane experiments performed using the gas chromatograph - mass spectrometer combination clearly demonstrate the extremely rapid exchange which may take place at high temperatures on a platinum surface concurrently with the hydrogenolysis and isomerization processes; they also indicate the extent to which dissociative adsorption of n-butane under these conditions is rapid and readily reversible. The exchange of n-butane on platinum is so extensive that there is a tendency for any molecule which exchanges to become almost equilibrated with the deuterium-hydrogen gas mixture. On the basis of the pressures of reactants used in the standard reaction mixture, a random distribution of hydrogen and deuterium atoms between the 'hydrogen' and exchanged 'hydrocarbon' (both in the generic sense) should yield a theoretical mean deuterium content value of 7.4; the experimental value of 7.9 in Table 4.3. corresponds closely to the latter and shows that there is an isotope effect in the expected direction, the deuterium slightly preferring to remain in the 'hydrocarbon' as in previous exchange studies.

Because of the extensive and rapid exchange of the n-butane reactant, the products of hydrogenolysis might also be expected to contain equilibrium
concentrations of deuterium. That this is the case is illustrated in Table 4.3, where the propane which was derived from the n-butane hydrogenolysis process had a deuterium content such that 82% of the 'hydrogen' atoms in the molecule were deuterium; this figure was again in good agreement with the value of 79% mentioned for n-butane. The major disadvantage incurred by the rapid equilibration of the hydrogen-deuterium pool in the platinum reaction systems was that the G.C.-M.S. experiments could not contribute any additional information about the mechanisms of the hydrogenolysis and isomerization processes and their essential surface intermediates.

Lastly, the maxima displayed at species containing either one or ten deuterium atoms in the isotopic distribution for exchange of n-butane in a second and much slower reaction on the same platinum film are indicative of the type of distribution which recent investigations have shown to be characteristic for exchange reactions on platinum (14).
BIBLIOGRAPHY

5.1. Introduction to Catalysis on Iron

In comparison with metals such as platinum or nickel, the catalytic activity of iron films has not aroused the same level of research interest. Although iron is an abundant element, its intrinsic impurity level in the metallic state can make it a difficult catalyst to characterise; furthermore, its willingness to strongly adsorb gaseous impurities as well as the reactant species and its inherent chemical reactivity as illustrated, for example, by carbide formation both tend to diminish reproducibility of catalytic activity and catalyst longevity.

Adsorption: Detailed studies have been made of hydrogen chemisorption on iron by different techniques\(^1,2\), the main conclusions being that dissociative adsorption occurs readily at room temperature, the strength of adsorption being such that subsequent liberation of hydrogen from the surface requires an activation energy of about 80 kJ mol\(^{-1}\). The adsorption of saturated hydrocarbons on iron films was investigated by Trapnell\(^3\); no appreciable chemisorption of methane or ethane was detected below 340K. Similar observations were made later by Wright et al.\(^4\); adsorption of methane occurred on iron at \(\sim 440K\) producing surface species \(\text{CH}_n\) with an average composition at equilibrium equivalent to a value of \(n = 2\).

Chemisorption of ethane was significant at 350K, indicating a lower activation energy for adsorption of the larger hydrocarbon. Uptake of carbon into the bulk of the metal, which was observed during decomposition of methylamine on iron\(^5\)
at typical methane adsorption temperatures, was also thought to account for the unexpectedly slow additional adsorption of methane on iron during the liberation of hydrogen formed by the initial uptake of hydrocarbon.

**Exchange:** Iron films have been found to exhibit no catalytic activity for low temperature exchange of saturated hydrocarbons with deuterium; previous investigations into the exchange of methane and ethane with deuterium \(^{(6,7)}\) revealed no reaction at temperatures up to 693K and 643K, respectively; low temperature exchange of larger saturated hydrocarbons on iron has also not been reported in the literature.

**Hydrogenolysis:** Various hydrocarbons and types of iron catalyst have been involved in studies of this kind. Anderson and Kembali \(^{(7)}\) showed that ethane underwent hydrogenolysis on iron films in the presence of deuterium at temperatures in the range 583K to 638K, yielding perdeuteromethane, CD\(_4\), as the major product; they postulated that desorption of the deuterated product from the surface could not take place before rupture of the carbon-carbon bond. As part of their detailed kinetic assessment of ethane hydrogenolysis, Cimino et al. \(^{(8)}\) employed iron catalysts of varying alkalinity, and saw that the reaction order with respect to hydrogen was dependent on the alkali content. The same reaction was again probed by Sinfelt \(^{(9)}\) on silica-supported iron over the temperature range 512K to 649K. In contrast to all the other Group VIII transition metals apart from rhenium, iron displayed a positive rather than an inverse dependence on hydrogen pressure for the rate of ethane hydrogenolysis; this observation was thought to be related to the lack of low temperature exchange of ethane found on the same metal.

The Japanese school has recently focussed more attention on the hydrogenolysis
of larger aliphatic hydrocarbons on iron. The reactions of n-pentane\(^{10}\) and the hexane isomers\(^{11}\) on silica-supported iron yielded similar results; in both cases, the products consisted of at least 90\% methane, indicating that desorption of surface residues was much slower than the rupture of carbon-carbon bonds. n-Pentane reacted at high temperatures (643K to 673K) with an activation energy of 96 kJ mol\(^{-1}\) and reaction orders with respect to hydrocarbon and hydrogen of 0.5 and -0.6, respectively. The lowish activation energy and reaction order for the n-pentane both pointed to the presence of strongly adsorbed hydrocarbon, as did the product distributions which were similar to those found on nickel at low partial pressures of hydrogen\(^{10}\). The hexane isomers exhibited comparable hydrogenolysis behaviour but at generally lower temperatures (~523K). Also in these studies, a linear correlation between the activities for ethane and n-pentane hydrogenolysis was observed for several of the Group VIII transition metals including iron\(^{10}\), while the activity of the latter for hydrogenolysis of hexanes\(^{11}\) was found to be comparable with that of cobalt and nickel, the other so-called 'non-noble' transition metals of Group VIII. No isomerization of the C\(_5\) and C\(_6\) hydrocarbons occurred, and this agreed with the experiments of Boudart\(^{12}\) which revealed no isomerization of neopentane on iron.

Lastly, hydrogenolysis on iron films of alicyclic hydrocarbons such as cyclopropane and methylcyclopropane has been examined by Anderson and Avery\(^{13}\). To obtain more detailed mechanistic information, the reactions were carried out in the presence of deuterium; the products consisted of deuterocyclopropanes which indicated stepwise exchange of the reactant and also perdeutero-hydrocarbons \(C_3D_8\), \(C_2D_6\) and \(CD_4\) from the hydrogenolysis reaction, such an extent of deuterium incorporation again suggesting slow desorption of surface fragments.
5.2. The Present Study

The relatively slight number of earlier ventures into catalysis on iron metal films might in itself be sufficient reason to warrant further research into the topic, but the problems posed by the existing literature would seem in any case to deserve renewed attention. For example, the inability of iron to propagate low temperature hydrocarbon exchange or the various factors which determine the 'depth' of hydrogenolysis have not yet been adequately explained, nor has there been a concerted study of the reactions of a series of homologous hydrocarbons to determine a general pattern of behaviour for iron relative to other metals.

The reactions of methane, ethane, propane, n-butane and neopentane on iron in the presence of deuterium were therefore chosen for investigation. As intermediates adsorbed to the surface at more than one carbon atom are thought to occur widely in hydrogenolysis processes \(^{(14,15)}\), molecular geometry becomes an important consideration in choosing reactants; hence, while propane and n-butane may be multi-adsorbed in both the \(\alpha\beta\) and \(\alpha\gamma\) modes, ethane may only do so in the \(\alpha\beta\) form, and neopentane, with its quaternary carbon atom, is restricted to the \(\alpha\gamma\) mode of two-carbon adsorption.

The hydrogenolysis reactions of hydrocarbons on platinum reported in Chapter 4 failed to realise the full potential of combined G.C.-M.S. analysis. Rapid reversible adsorption of the reactants meant that exchange with deuterium was so much faster than hydrogenolysis that the isotopic composition of the hydrogenolysis products was more a function of the deuterium content of the reactant than of any incorporation process occurring as a consequence of the hydrogenolysis mechanism; interpretation of reaction intermediates and mechanisms using G.C.-M.S. was therefore not readily achieved for the platinum system. The
available evidence in the literature suggests that iron is a poor catalyst for the exchange of saturated hydrocarbons; thus, iron might be a more suitable catalyst for G.C.-M.S. experiments, excessive exchange not being a likely complicating factor in examining the isotopic distributions associated with reactant and products.

Lastly, the transition metals of Group VIII appear to fall broadly into two groups with regard to catalytic properties, as, for example, in the hydrogenolysis of ethane\(^{(15)}\). As iron, unlike platinum, does not belong to the group of 'noble' metals, the results obtained here on iron films were expected to provide an interesting contrast to those already recorded with platinum in Chapter 4.

3.3. Experimental

Three different analytical techniques were employed for the reactions on iron. The majority of experiments involved either gas chromatography only or combined chromatography and mass spectrometry, and were carried out under standard operating conditions with the apparatus already described in detail in Chapter 2. The remaining runs, including all those for exchange of methane, required mass spectrometry only and were performed with a separate system consisting of an A.R.I. MS10 mass spectrometer coupled to a reaction vessel and gas handling line through a fine glass capillary leak; the principles of operation for this arrangement have been well-documented elsewhere\(^{(16)}\).

Materials: The gaseous reactants and the iron wire for film preparation were supplied by the sources previously listed; storage and purification of gases and production of the iron catalysts were also effected by the methods stated earlier (see Chapter 2, Sections 4 and 5).
Procedure: The standard experimental technique catalogued in Chapter 2 was utilised for most of the reactions on iron, slight variations being applied where necessary. In experiments where a presintered surface was required, the newly prepared iron film was heated in vacuo at the chosen sintering temperature for 30 minutes before re-cooling to 273K for admission of the reaction mixture. As with the platinum studies, consecutive reactions on the same film were carried out by cooling the reactor to 273K in an ice-water bath at an appropriate stage in the first experiment and evacuating at this temperature for about 5 minutes before admitting fresh reactants. Removal of the first reaction mixture by pumping at much higher temperatures was avoided, since preferential desorption of deuterium under these conditions probably leaves irreversibly adsorbed hydrocarbon residues on the surface, which can undergo further cracking to smaller fragments thus causing more serious poisoning of the catalyst before commencing a second reaction.

All experiments were performed with a standard 11.5:1 excess of deuterium to hydrocarbon except run 33 (vide infra), in which equal pressures of three hydrocarbons were reacted simultaneously with deuterium, the ratio of deuterium to hydrocarbon on this occasion being only 3.8:1. In any run involving chromatography, the frequency of sampling from the reactor was governed by the total retention time of the reactant and product hydrocarbons, as well as the apparent rate of reaction. In the MS10 experiments, the capillary leak allowed, if necessary, almost continuous analysis of the reaction vessel contents, each spectrometer scan requiring about 2 minutes for completion.

Analyses: In general, product distributions and kinetic parameters were determined using the procedures specified in Chapter 3. All chromatographic
analyses were made in terms of the total carbon in the reaction system; consequently, by allowing for material losses due to sampling, it was also possible to estimate approximately any loss of carbon to the iron catalyst during the experiment. In the G.C.-M.S. studies on iron, partial separation of deuterated paraffins in the chromatograph once again meant that no single mass spectrometric scan was representative of the overall isotopic distribution; the latter was obtained by a Simpson's Rule integration of the peak heights at each m/e value in a series of scans taken at equal intervals of time during elution of a hydrocarbon, as described before in Chapter 3.

In correcting the raw isotopic distributions from either mass spectrometer, allowance was made firstly for background, which was especially large at m/e 18 in the case of G.C.-M.S. experiments due to water elution from the chromatographic column, and secondly for naturally occurring isotopes, deuterium and $^{13}$C. Ionizing electrons at 20 eV were required by both spectrometers to produce adequate sensitivity for methane; the cracking patterns for each hydrocarbon recorded at this electron energy formed the basis of fragmentation corrections which were finally applied to the background and isotope corrected data. The various empirical schemes for assessment of fragmentation contributions were fully discussed in Chapter 3. No parent ion was detected for neopentane, so analysis was made in terms of the $(C\bar{X})_3\bar{C}^+$ ions ($\bar{X}$ representing H or D) which were formed by loss of a methyl group.

With the G.C.-M.S. apparatus, variations in sensitivity of the spectrometer and molecular separator to each hydrocarbon, including different responses for 'light' and 'heavy' methane, were measured by calibrating with standard mixtures; the relative quantity of any hydrocarbon in a sample could then be calculated
using the appropriate sensitivity factor (tabulated in Chapter 3).

5.4. Results

The reactions of saturated hydrocarbons on iron films in the presence of deuterium were studied under varied conditions of temperature, reaction mixture composition and film preparation. As reproducibility of catalytic activity (measured in terms of reaction rate) was not as readily attainable for iron as for platinum films, several of the experiments attempted proved to be rather inconclusive; the results reported in this chapter are those that were found to contribute to the general patterns of behaviour observed.

As with platinum, reactions were usually followed to a considerable degree of conversion to demonstrate the influence of product formation on the reaction kinetics, and several experiments were undertaken to investigate more closely the effects of hydrocarbon poisoning and film sintering on catalytic activity. Tables 5.1. and 5.2. include the reaction temperatures and reaction rates measured for each system studied and the experimental technique employed in each experiment. All reaction rates, whether for exchange or hydrogenolysis are quoted as initial rates in % min⁻¹, and were obtained by extrapolating to zero time either the relevant product distribution v. time curves or the corresponding first order rate plots.

Apparent activation energies for the hydrogenolysis of each hydrocarbon and also for the exchange of methane were determined from the Arrhenius plots of Figure 5.1. and are listed in Table 5.3; no particular importance was attached to the detailed evaluation of frequency factors, it being difficult to assume a constant effective surface area of iron for each experiment, as was possible in the case of platinum.
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</table>

<sup>a</sup> All reactions carried out with an 11.5:1 ratio of $\text{H}_2$:hydrocarbon; <sup>b</sup> reaction on film presintered at 513°K; <sup>c</sup> reaction on same film as experiment 8; <sup>d</sup> reaction on film presintered at 453°K; <sup>e</sup> reaction on same film as experiment 16; <sup>f</sup> reaction on same film as experiment 7; <sup>g</sup> reaction on same film as experiment 3; <sup>h</sup> all rates measured in $\% \text{ min}^{-1}$. 
TABLE 5.2. INITIAL RATES FOR REACTIONS OF METHANE, PROPANE AND NEO-PENTANE

<table>
<thead>
<tr>
<th>Run number</th>
<th>Reactant\textsuperscript{a}</th>
<th>T/K</th>
<th>Initial Rates\textsuperscript{b}</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrogenolysis ( r_1 )</td>
<td>Exchange ( r_2 )</td>
</tr>
<tr>
<td>20</td>
<td>Propane</td>
<td>429</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>Propane</td>
<td>453</td>
<td>0.043</td>
<td>0.021</td>
</tr>
<tr>
<td>22</td>
<td>Propane</td>
<td>469</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>Propane</td>
<td>493</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>Propane</td>
<td>493</td>
<td>0.35</td>
<td>0.19</td>
</tr>
<tr>
<td>25</td>
<td>Propane</td>
<td>493</td>
<td>0.32</td>
<td>0.10</td>
</tr>
<tr>
<td>26</td>
<td>Propane</td>
<td>554</td>
<td>1.67</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>Propane</td>
<td>602</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>28</td>
<td>neo-Pentane</td>
<td>446</td>
<td>0.012</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>neo-Pentane</td>
<td>486</td>
<td>0.44</td>
<td>0.88</td>
</tr>
<tr>
<td>30</td>
<td>Methane</td>
<td>385</td>
<td>-</td>
<td>0.008</td>
</tr>
<tr>
<td>31</td>
<td>Methane</td>
<td>456</td>
<td>-</td>
<td>0.065</td>
</tr>
<tr>
<td>32</td>
<td>Methane</td>
<td>523</td>
<td>-</td>
<td>0.08</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All reactions carried out with an 11.5:1 ratio of D\textsubscript{2}:hydrocarbon; \textsuperscript{b}all rates measured in \% min\textsuperscript{-1}.

TABLE 5.3. ARRHENIUS DATA\textsuperscript{b}

<table>
<thead>
<tr>
<th>Reactant\textsuperscript{a}</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>n-Butane</th>
<th>neo-Pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy ( E_a ) /k J mol\textsuperscript{-1}</td>
<td>43</td>
<td>133</td>
<td>152</td>
<td>154</td>
<td>160</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All values, except that for methane, refer to hydrogenolysis only and were calculated using the initial rates of Tables 5.1. and 5.2; \textsuperscript{b}the average error in estimation of these parameters was ± 8\%.
Reactions of Ethane: Experiments using gas chromatographic analysis only (runs 1, 2 and 7) were carried out in the temperature range 483K to 543K and served to illustrate the general course of the ethane hydrogenolysis reaction; methane was the only hydrogenolysis product observed. The dependence of reaction rate on ethane pressure was not clear as the reactions appeared graphically to satisfy both zero order and first order kinetics up to considerable degrees of conversion. The initial rates of hydrogenolysis (Table 5.1. runs 1, 2 and 7) were converted to Arrhenius data (Figure 5.1.) and an activation energy of 133 kJ mol\(^{-1}\) for ethane hydrogenolysis was determined from the low temperature section of the plot. At higher temperatures, the Arrhenius curve exhibited a 'turning over' effect indicating a retardation in rate with increasing temperature.

An exploratory experiment (run 3) involving continuous analysis by mass spectrometry alone was carried out to establish whether ethane underwent exchange with deuterium as well as hydrogenolysis in the temperature range of interest. While slow hydrogenolysis to methane was first observed at 423K, significant exchange of the reactant was not readily detectable till the temperature reached 513K, where the major exchange product was found to be perdeuteroethane, \(\text{C}_2\text{D}_6\).

At all temperatures in the range 423K to 513K, isotopic analysis of the methane formed yielded \(\text{CD}_4\) as the major hydrogenolysis product. The reaction was followed for a considerable time at 513K, and Table 5.4. shows the relative extents of hydrogenolysis and exchange with time, and the isotopic contents of both ethane and methane for reaction at that temperature. (The first set of data in Table 5.4. also includes the amount of reaction already recorded at lower temperatures).

Figure 5.2. illustrates the respective progress of ethane hydrogenolysis
Figure 5.1. Arrhenius Plots
TABLE 5.4. REACTION OF ETHANE/D$_2$ ON Fe AT 513K (H.S.)

| Time t/min | Hydrogenolysis / % | Exchange / % | Isotopic Species / %
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CHD$_3$ CD$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_2$HD$_5$ C$_2$D$_6$</td>
</tr>
<tr>
<td>10</td>
<td>13.0</td>
<td>1.1</td>
<td>11.5 88.5</td>
</tr>
<tr>
<td>20</td>
<td>15.9</td>
<td>1.5</td>
<td>13.5 86.5</td>
</tr>
<tr>
<td>30</td>
<td>18.0</td>
<td>1.8</td>
<td>15.0 85.0</td>
</tr>
<tr>
<td>50</td>
<td>21.4</td>
<td>2.5</td>
<td>17.5 82.5</td>
</tr>
<tr>
<td>70</td>
<td>26.3</td>
<td>3.1</td>
<td>19.7 80.3</td>
</tr>
<tr>
<td>90</td>
<td>26.9</td>
<td>3.5</td>
<td>22.3 77.7</td>
</tr>
<tr>
<td>105</td>
<td>33.8</td>
<td>3.6</td>
<td>19.7 80.3</td>
</tr>
<tr>
<td>120</td>
<td>35.8</td>
<td>3.8</td>
<td>20.6 79.4</td>
</tr>
</tbody>
</table>

*a* No methane-d$_2$ was detected but may have been obscured by H$_2$O background;

*b* the quantities of isotopic ethanes d$_1$-d$_4$ did not total more than 3% and were not significant considering the error in estimating isotopic ethanes from mass spectral data;  

*c* the fractional deuterium content was equal for methane and ethane throughout the reaction, varying from 0.97 to 0.95 over 2 hours.

---

TABLE 5.5. REACTION OF ETHANE/D$_2$ ON Fe AT 513K (G.C.-M.S.)

| Time t/min | Hydrogenolysis / % | Exchange / % | Isotopic Species / %
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CHD$_3$ CD$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_2$HD$_5$ C$_2$D$_6$</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>0.24</td>
<td>- 100</td>
</tr>
<tr>
<td>6</td>
<td>2.6</td>
<td>0.60</td>
<td>- 100</td>
</tr>
<tr>
<td>20</td>
<td>3.5</td>
<td>1.3</td>
<td>- 100</td>
</tr>
<tr>
<td>40</td>
<td>6.9</td>
<td>2.3</td>
<td>3.2 96.8</td>
</tr>
<tr>
<td>60</td>
<td>9.1</td>
<td>3.9</td>
<td>7.4 92.6</td>
</tr>
<tr>
<td>90</td>
<td>15.2</td>
<td>4.3</td>
<td>8.9 91.1</td>
</tr>
</tbody>
</table>

*d* No exchanged ethane was detected with less than 5 deuterium atoms.
FIGURE 5.2. REACTIONS OF ETHANE ON IRON AT 513 K
and exchange processes for reaction at 513K (run 3), using the data of Table 5.4. As there was a large excess of deuterium present, the system could be represented by a combined series-parallel network (see Chapter 3) where the exchange reaction was assumed irreversible and the rates of hydrogenolysis of deuterated and undeuterated ethane assumed equal as shown.

\[
\begin{align*}
\text{C}_2\text{H}_6 & \xrightarrow{k_D} \text{C}_2\text{X}_6 \\
\text{K}_H & \xrightarrow{2CX_4} \text{K}_H
\end{align*}
\]

\((X = \text{H or D})\)

First order plots for this network (Figure 5.3.) yielded rate constants \(k_D\) and \(k_H\) for exchange and hydrogenolysis of ethane, with values of \(4.06 \times 10^{-4}\) min\(^{-1}\) and \(2.88 \times 10^{-3}\) min\(^{-1}\), respectively i.e. hydrogenolysis 7 times faster than exchange.

Both processes appeared to follow first order behaviour with respect to ethane throughout the reaction although approximately zero order hydrogenolysis was indicated in Figure 5.2. The initial hydrogenolysis rate quoted in Table 5.1. for run 3 was lower than expected in comparison with those from the chromatographic experiments, but this may have been due to measuring the rate as an initial value at more than 10% conversion.

The variations in isotopic content of methane and ethane with increasing conversion is illustrated in Figure 5.4. Extrapolation to zero conversion of the selectivity curves showed that methane-\(d_4\) was the only initial hydrogenolysis product and similarly ethane-\(d_6\) for exchange. Formation of methane-\(d_3\) and ethane-\(d_5\) increased as the proportion of deuterium in the hydrogen-deuterium pool available for exchange decreased. No other isotopic species of reactant or product were detected in sufficient quantity not to be obscured by the inherent errors of fragmentation corrections for ethane, or background correction for water at m/e 18 in the case of methane. The fractional contents of deuterium in
Figure 5.3. First Order Plots for Ethane Reactions on Iron at 513K.
Figure 5.4: Reactions of Ethane on Iron at 513K

% Exchange; ○ and □

% Hydrogenolysis; ○ and □

○ Methane-d4
○ Ethane-d6
● Methane-d3
□ Ethane-d5

Isotopic Contents
reactant and product were found to be equal throughout the reaction; for example, after 2 hours at 513K, the 'hydrogen' in both methane and ethane was 95% deuterium.

The combined G.C.-M.S. technique was employed in two further experiments with ethane at 513K (Table 5.1. runs 4 and 5). These experiments served to verify the results obtained from prior studies without providing any essentially different information. The sampling times for runs 4 and 5 were chosen to give complementary data and the overall pattern of the exchange and hydrogenolysis reactions is catalogued in Table 5.5. The initial rates calculated for hydrogenolysis were on average a factor of 5 greater than those for exchange (Table 5.1. runs 4 and 5) and the only initial products of hydrogenolysis and exchange were clearly again CD₄ and C₂D₆, respectively. The fractional deuterium contents were again the same for both reactant and product throughout both experiments.

Reactions of n-Butane: The hydrogenolysis of n-butane was studied by chromatography in the temperature range 443K to 483K (Table 5.1. runs 10-12, 15 and 16) and the low temperature section of the Arrhenius plot derived from the initial rates of these reactions provided an activation energy value for hydrogenolysis of 184 kJ mol⁻¹ (Figure 5.1.). The rates at higher temperatures caused a 'turning over' effect in the Arrhenius curve which suggested increasing retardation of reaction with increase in temperature. Methane constituted about 90% of the observed reaction products, while the intermediate hydrocarbons ethane and, to a lesser extent, propane were also detected. The variation of hydrogenolysis product distribution with temperature at 10% conversion is demonstrated in Table 5.6; at the higher reaction temperatures, more extensive breakdown to methane occurred and the ratio of ethane to propane was also seen to increase.

The general characteristics of n-butane hydrogenolysis are illustrated in
TABLE 5.6. VARIATION OF HYDROGENOLYSIS PRODUCT DISTRIBUTION WITH TEMPERATURE

<table>
<thead>
<tr>
<th>Reactant</th>
<th>T/K</th>
<th>Methane / %</th>
<th>Ethane / %</th>
<th>Propane / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>443</td>
<td>88</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>n-Butane</td>
<td>458</td>
<td>90</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>n-Butane</td>
<td>473</td>
<td>93</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>n-Butane</td>
<td>483</td>
<td>95</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

*a All product distributions are in terms of the total carbon in the system and correspond to 10% conversion.

TABLE 5.7. REACTION OF n-BUTANE/D₂ ON Fe AT 458K (G.C.-M.S.)

<table>
<thead>
<tr>
<th>Time t/min</th>
<th>Exchange / %</th>
<th>Hydrogenolysis / %</th>
<th>Methane / %</th>
<th>Ethane / %</th>
<th>Propane / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>9.7</td>
<td>10.0</td>
<td>9.0</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>35</td>
<td>14.3</td>
<td>14.5</td>
<td>13.2</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>60</td>
<td>17.7</td>
<td>17.4</td>
<td>16.1</td>
<td>1.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotopic Content / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane  / d₃ d₄</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td>60</td>
</tr>
</tbody>
</table>
Figure 5.5. Reactions of n-Butane on Iron at 443 K and 473 K
Figures 5.5. and 5.6. for reactions followed chromatographically at 443K and 473K (runs 10 and 15). The reaction proceeded at a much slower rate at 443K and the disappearance of n-butane apparently conformed to both zero and first order kinetics at these comparatively low conversions. At 473K, the hydrogenolysis rate decreased markedly with time from an initial value of 1.46 % min\(^{-1}\) to one which was even lower than the 0.12 % min\(^{-1}\) recorded throughout the experiment at 443K (see Figure 5.5.); the curvature of the corresponding first order plot (Figure 5.6.) suggested that the reaction at this higher temperature was either a 'poisoned' first order process or one of true reaction order with respect to the reactant of between zero and unity.

Evidence that n-butane underwent exchange with deuterium simultaneously with hydrogenolysis was first provided in the form of a pronounced shoulder on the G.C. peak for n-butane due to partial resolution of isotopic hydrocarbons by the chromatographic column; this effect was observed in all the G.C. runs and the position of the peak shoulder was found to alter with increasing conversion according to the varying exchange distribution. Confirmation of the concurrent exchange process was acquired in a G.C.-M.S. study with n-butane as reactant carried out at 458K (Table 5.1. run 14). One difficulty encountered in this run was a considerable overshoot in temperature which occurred for a few minutes just after removal of the first sample; in terms of the data obtained, this event may have contributed significantly to an enhanced retardation of reaction, and thus may partly explain, for example, the marked curvature of the plots shown in Figure 5.7.

Three samples were analyzed during the experiment and Table 5.7. details the relative extents of hydrogenolysis and exchange, the ratio of the hydrogenolysis
Figure 5.6. First Order Plots

Reactions of n-Butane on Iron at 443K and 473K
Figure 5.7. Exchange and Hydrogenolysis of n-Butane on Iron at 458K.
products formed, and the isotopic contents of reactant and products calculated in each case. At 458K, the hydrogenolysis and exchange conversions appeared to increase at comparable rates; this was substantiated by the initial rates (Table 5.1, run 14) evaluated for the two processes from the initial slope of the appropriate first order rate plot (Figure 5.7), the latter again being generated by a combined series-parallel network of the form

\[ nC_4H_{10} \xrightarrow{k_D} nC_4X_{10} \]

\[ k_H \]

\[ C_4X, C_2X_6, C_3X_8 \]

\[ (X = H \text{ or } D) \]

As indicated already, these plots also exhibited a pronounced curvature similar to that found for the reaction at 473K (Figure 5.6), and it was interesting to note that this effect was approximately equivalent for both hydrogenolysis and exchange.

The relative yields of each hydrogenolysis product followed the pattern set by the G.C. experiments, but the small quantities of propane produced made isotopic analysis of that hydrocarbon difficult. By extrapolating the selectivities for each isotopic component to zero conversion (Figure 5.8), it was established that the perdeuterohydrocarbons \( CD_4 \), \( C_2D_6 \) and \( C_3D_8 \) were the only initial hydrogenolysis products. For exchange of the reactant, extrapolation to zero conversion revealed two initial species - \( n\)-butane-\( d_1 \) and \( n\)-butane-\( d_{10} \) - in the approximate ratio of 1:4 (Figure 5.9); the other products observed during reaction were attributed either to successive exchange steps or dilution of the deuterium excess by hydrogen. Throughout the experiment, the fractional deuterium contents of the hydrogenolysis products were equal within analytical error and although the overall values for exchanged \( n\)-butane were about 20% lower, the percentage deuterium in the multiply exchanged species remained close to that
Figure 5.8. Isotopic Contents of n-Butane Hydrogenolysis Products from reaction at 458 K.
Figure 5.9. Isotopic content of exchanged n-butane at 458 K.
calculated for methane and ethane.

Reactions of Propane: In an exploratory study involving only chromatography, trace quantities of hydrogenolysis product were first detected at about 423K; at 458K, formation of methane was more rapid and was accompanied by a small but measurable yield of ethane. On raising the temperature to 623K, 90% conversion was quickly achieved. An activation energy of 152 kJ mol\(^{-1}\) for propane hydrogenolysis was determined from the initial rates of further chromatographic experiments (Table 5.2, runs 20, 22, 23, 26 and 27) - in particular, those performed at lower temperature (see Figure 5.1); a turning over of the Arrhenius plot was again produced by the rates from reactions studied at higher temperatures. The G.C. analysis of a propane hydrogenolysis reaction carried out at 493K (run 23) is illustrated in Figure 5.10. The product was almost exclusively methane, the yield of ethane at no time constituting more than 0.5% of the total carbon in the system, and the rate of reaction appeared to decrease slowly with time.

An independent mass spectral investigation (run 21) revealed that exchange and hydrogenolysis of propane occurred simultaneously at 453K, with exchange proceeding approximately 2 times slower than hydrogenolysis. The relative extents of the two processes with increasing time and the variation in isotopic contents of methane and ethane are collected in Table 5.8. The analyses for extent of reaction and isotopic content of the hydrocarbons were much more erratic than those of Table 5.4. for the ethane/D\(_2\) systems, but this may probably be accounted for by the low conversions and small quantities present in this case, as well as fluctuating sensitivity in the MS10 spectrometer. The initial exchange product was clearly perdeuteropropane, with C\(_3\)H\(_7\)D appearing later due to isotopic dilution; the distributions also suggested somewhat indecisively that formation of C\(_3\)H\(_7\)D by
Figure 5.10. Hydrogenolysis of propane on iron at 493K
TABLE 5.8. REACTIONS OF PROPANE/D₂ ON Fe AT 453K (H.S.)

<table>
<thead>
<tr>
<th>Time t/min</th>
<th>Hydrogenolysis/%</th>
<th>Exchange/%</th>
<th>CH₂D₂</th>
<th>CHD₃</th>
<th>CD₄</th>
<th>C₃DH₇</th>
<th>C₃H₂D₆</th>
<th>C₃HD₇</th>
<th>C₃D₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>0.2</td>
<td>0.0</td>
<td>17.0</td>
<td>83.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>0.8</td>
<td>0.3</td>
<td>0.0</td>
<td>13.6</td>
<td>86.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>1.1</td>
<td>0.5</td>
<td>0.0</td>
<td>13.4</td>
<td>86.6</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>35</td>
<td>1.6</td>
<td>0.8</td>
<td>0.0</td>
<td>10.7</td>
<td>89.3</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
<td>87.5</td>
</tr>
<tr>
<td>83</td>
<td>2.6</td>
<td>1.7</td>
<td>0.0</td>
<td>12.4</td>
<td>87.6</td>
<td>6</td>
<td>6</td>
<td>12</td>
<td>76</td>
</tr>
<tr>
<td>98</td>
<td>2.6</td>
<td>1.6</td>
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<td>11.7</td>
<td>88.3</td>
<td>-</td>
<td>6</td>
<td>12.5</td>
<td>81</td>
</tr>
<tr>
<td>227</td>
<td>3.2</td>
<td>3.9</td>
<td>4.0</td>
<td>16.1</td>
<td>79.9</td>
<td>5</td>
<td>-</td>
<td>12.5</td>
<td>82.5</td>
</tr>
<tr>
<td>236</td>
<td>3.3</td>
<td>3.1</td>
<td>0.0</td>
<td>14.4</td>
<td>85.6</td>
<td>6</td>
<td>-</td>
<td>12.5</td>
<td>81</td>
</tr>
<tr>
<td>245</td>
<td>3.8</td>
<td>4.3</td>
<td>0.9</td>
<td>13.9</td>
<td>85.2</td>
<td>27</td>
<td>-</td>
<td>11</td>
<td>62</td>
</tr>
</tbody>
</table>

aFractional deuterium contents of methane and propane were approximately the same throughout reaction.

TABLE 5.9. REACTIONS OF PROPANE/D₂ ON Fe AT 493K (G.C.-H.S.)

<table>
<thead>
<tr>
<th>Time t/min</th>
<th>Hydrogenolysis/%</th>
<th>Exchange/%</th>
<th>CHD₃</th>
<th>CD₄</th>
<th>C₃DH₇</th>
<th>C₃H₂D₆</th>
<th>C₃HD₇</th>
<th>C₃D₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>5.3</td>
<td>2.8</td>
<td>-</td>
<td>100</td>
<td>10</td>
<td>-</td>
<td>26.7</td>
<td>63.3</td>
</tr>
<tr>
<td>20</td>
<td>6.3</td>
<td>1.9</td>
<td>1.8</td>
<td>98.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>45</td>
<td>12.8</td>
<td>4.2</td>
<td>9.7</td>
<td>90.4</td>
<td>-</td>
<td>-</td>
<td>18.7</td>
<td>81.3</td>
</tr>
<tr>
<td>90(run24)</td>
<td>28.5</td>
<td>7.2</td>
<td>12.4</td>
<td>87.6</td>
<td>8.9</td>
<td>-</td>
<td>25.8</td>
<td>65.3</td>
</tr>
<tr>
<td>90(run25)</td>
<td>21.1</td>
<td>6.8</td>
<td>24.3</td>
<td>75.7</td>
<td>-</td>
<td>8.1</td>
<td>26.8</td>
<td>65.1</td>
</tr>
<tr>
<td>180</td>
<td>37.9</td>
<td>9.0</td>
<td>30.7</td>
<td>69.3</td>
<td>-</td>
<td>17.2</td>
<td>31.7</td>
<td>51.1</td>
</tr>
</tbody>
</table>
exchange of a single hydrogen atom was also taking place. Extrapolations of the deuterated methanes to zero conversion were not straightforward, but qualitatively it seemed that CD$_4$ and CD$_3$H were both produced initially.

A clearer picture was derived from two G.C.-H.S. experiments (Table 5.2, runs 24 and 25) which were conducted under the same conditions, the second of these not only providing a check on the results of the first, but adding more data for other stages in the reaction. Both runs were studied at 493K, their respective outputs being merged to produce Table 5.9; for graphical purposes the two sets of data for samples taken after 90 minutes were averaged. Initial rates of exchange and hydrogenolysis evaluated for both experiments are quoted in Table 5.1. and show adequate agreement between these two studies, and also with the corresponding G.C. run. The course of reaction with respect to hydrogenolysis and exchange is illustrated in Figure 5.11, hydrogenolysis being the dominant process. The first order rate plots of Figure 5.12. were derived from a combined series-parallel network as shown below, and allowed calculation of rate constants $k_H$ and $k_D$, as before.

\[
\begin{align*}
\text{C}_3\text{H}_8 & \xrightarrow{k_D} \text{C}_3\text{D}_8 \\
\text{C}_4\text{H}_2 & \xrightarrow{k_H} \text{C}_4\text{D}_2 \\
\end{align*}
\]

\(X = \text{H or D}\)

It was found that both modes of reaction appeared to follow first order kinetics with only a slight decline in rate at higher conversions; the ratio of rate constants, $k_H/k_D$, was approximately 3.

Table 5.9. includes the variations in isotopic distribution for propane and methane, but not for ethane where there was insufficient hydrocarbon for detailed isotopic analysis. Extrapolations to zero conversion revealed that the perdeutero-
Figure 5.11. Exchange and Hydrogenolysis of Propane on Iron at 493K
Figure 5.12. First Order Plots
Exchange and Hydrogenolysis of Propane on Iron at 493K
Species CD$_4$ and C$_3$D$_8$ were the initial hydrogenolysis and exchange products, respectively, the less deuterated forms methane-d$_3$, propane-d$_7$ and -d$_6$ again emerging as a result of deuterium pool dilution. Further evidence was provided for the formation of C$_3$H$_7$D, although there was no quantitative trend observed in successive samples. The percentages of deuterium in the 'hydrogen' of reactant and product remained equal within experimental error throughout the two studies; a value of 92%, for example, being present in both methane and propane after 180 minutes.

**Reactions of Neopentane:** Exploratory chromatographic experiments revealed that hydrogenolysis of neopentane on iron was slow but observable at 417K and an activation energy of 160 ± 10 kJ mol$^{-1}$ was estimated from initial rates at conversions of less than 10% over the temperature range 446K to 485K, e.g. Table 5.2, run 28. The product was almost exclusively methane ($\sim$99%) along with small quantities of isobutane and traces of ethane and propane. Higher temperatures favoured more extensive cracking with the amount of methane formed increasing from 99.0% at 486K to 99.8% at 506K.

Simultaneous exchange and hydrogenolysis was detected using the combined techniques; at 486K (Table 5.2, run 29), the exchange of neopentane was faster than hydrogenolysis by a factor of 2.0 and some poisoning of the reaction was observed with increasing time (Figure 5.13) causing a deviation from first order behaviour. The deuterium content of the exchanged neopentanes was measured in terms of the (C$_X$)$_3$C$^+$ ions (X representing H or D) which were formed by loss of a methyl group. This loss occurs on a random basis since it has been shown by Langer and Johnson (17) that neopentane terminally labelled with one C$^{13}$ produces isobutyl fragments which are 76% labelled. These authors also proved that with
Figure 5.13.
EXCHANGE AND HYDROGENOLYSIS
OF NEOPENTANE ON IRON AT 486K.
70 eV electrons, the methyl ions detected consisted almost entirely of those lost individually from the original neopentane molecules and not from more extensive dissociation processes.

In the present study, isobutyl-d$_0$, -d$_1$ and -d$_3$ ions were observed at low exchange conversions, but no d$_2$ ions were formed. From the foregoing statements, the only deuterated neopentanes that can yield -d$_3$ ions without -d$_2$ also being formed are (CH$_2$D)$_4$C and (CH$_3$)$_3$(CD$_3$)C. To confirm these possibilities, the relative amounts of methyl ions CH$_3^+$ and CH$_2$D$^+$ present in the spectra were measured and it was established that (CH$_3$)$_3$(CD$_3$)C was the only multiply exchanged neopentane responsible for the isobutyl-d$_3$ ions. The -d$_1$ ions were directly attributable to monodeuterated neopentane. Percentage isotopic distributions for the neopentanes were calculated from the measured distribution of deuterated isobutyl ions; the probabilities of formation of the various C$_4$H$_9^+$ ions by random loss of methyl groups were derived assuming that neopentane-d$_1$ and neopentane-d$_3$ with the deuteriums bonded to one carbon atom were the only initial exchange products and that the other species observed at higher conversions (neopentane-d$_2$, -d$_4$, -d$_5$, -d$_6$) resulted from multiple occurrences of the initial exchange processes. These probabilities were then used to calculate the neopentane isotopic distribution beginning with the most deuterated isobutyl ion and working towards the less deuterated forms (see Chapter 3).

The selectivity of each isotopic neopentane was plotted against the percentage of exchanged neopentane as illustrated in Figure 5.14. Extrapolation to zero deuteration showed that neopentane-d$_1$ and neopentane-d$_3$ were indeed the only primary products. At higher conversions, further exchange products were formed due to successive deuteration steps and also progressive dilution of the
Figure 5.14.
DISTRIBUTION OF DEUTERATED NEOPENTANES
FORMED ON IRON AT 4.86K.
hydrogen-deuterium pool. The neopentane-d$_1$ was produced 1.5 times faster than the d$_3$ species, the initial distribution being 60% d$_1$ and 40% d$_3$.

The methane formed from hydrogenolysis again contained a preponderance of highly deuterated species; extrapolation to zero conversion revealed that perdeuteromethane was the only initial product and that the yield of less deuterated species with increasing conversion was again a consequence of deuterium dilution. The isobutane isotopic distributions were difficult to measure accurately because of the small quantities involved, but at 17% hydrogenolysis the fully deuterated form, isobutane-d$_{10}$, was predominant (60%).

Reactions of Methane: In contrast to previous findings$^6$, the exchange of methane on iron films was observed by continuous mass spectrometric analysis at temperatures in the range 385K to 523K, the rates of reaction in all cases being distinctly slow. An activation energy for exchange of only 43 k J mol$^{-1}$ was derived from the initial rates of reactions at 385K, 456K and 523K (Table 5.2, runs 30-32) which were carried out on the same iron film; once again, however, the Arrhenius plot exhibited a steady curvature, the rates at higher temperatures falling short of their expected values (Figure 5.1). This apparent poisoning effect was corroborated by the first order plots for reactions at 456K and 523K (Figure 5.15.) which also displayed marked deviations from linearity; it was interesting to note that the rate after 60 minutes at the higher temperature had fallen to a value of 5 x 10^-3 % min$^{-1}$, which was below that measured at the same point in the lower temperature reaction (6 x 10^-3 % min$^{-1}$). The initial product distribution for exchange consisted entirely of perdeuteromethane, CD$_4$, and trace quantities only of CHD$_3$ were detected at higher conversions.

Competing Reactants: The use of combined G.C.-M.S. techniques may also provide
Figure 5.15. First order plots for exchange of methane on iron.
an opportunity to make a comparative study of the behaviour of several hydrocarbons on a catalyst in a single experiment. This concept was demonstrated in run 33 which involved the simultaneous reactions of n-butane, propane and ethane on iron at 513K. The choice of a relatively high reaction temperature, at which all three hydrocarbons were known from earlier work to react readily, also meant that the product, consisting almost exclusively of methane, would not tend to obscure analyses of the reacting species. The reaction mixture for this experiment consisted of equal pressures of each alkane and an overall deuterium to hydrocarbon excess of only 3.8:1. The iron film used in this run was heavier than usual, weighing approximately 16mg; for purposes of comparison, the measured hydrogenolysis rates were corrected proportionately to the equivalent values for 10mg. of iron, in doing so assuming a linear relationship between reaction rate and film weight.

Table 5.10. illustrates the distribution of carbon in the system at progressive stages in the reaction. Allowing for losses due to sampling, the G.C. analyses which in this case were evaluated from total ion intensities revealed that carbon was being taken up by the catalyst throughout the experiment. The degree of apparent carbon loss was considerable and after 20 minutes was clearly greater than the yield of methane from hydrogenolysis. The relative rates of disappearance of the three reactants were in the expected order of

\[ n\text{-butane} > \text{propane} > \text{ethane}. \]

The extent of hydrogenolysis with time was determined separately for each hydrocarbon as shown in Figure 5.16; while the propane and n-butane decompositions appeared to follow first order kinetics but with a marked deceleration at higher conversions, the ethane reaction again displayed an apparent zero order dependence.
### TABLE 5.10. COMPETING REACTIONS OF n-BUTANE/PROPANE/ETHANE ON Fe AT 513K (G.C.-M.S.)

<table>
<thead>
<tr>
<th>Time ( t/\text{min} )</th>
<th>Hydrocarbon / % ( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-Butane</td>
</tr>
<tr>
<td>0</td>
<td>45.4</td>
</tr>
<tr>
<td>3</td>
<td>38.5</td>
</tr>
<tr>
<td>23</td>
<td>2.7</td>
</tr>
<tr>
<td>53</td>
<td>-</td>
</tr>
</tbody>
</table>

\( a \) Distributions calculated in terms of the total amount of carbon in the system; \( b \) evaluated by comparing the total carbon in each gas phase sample.

### TABLE 5.11. VARIATION IN HYDROGENOLYSIS RATES WITH DEUTERIUM PRESSURE

<table>
<thead>
<tr>
<th>Deuterium:Hydrocarbon Pressure Ratio</th>
<th>Initial Rates ( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/K</td>
</tr>
<tr>
<td>11.5:1</td>
<td>513</td>
</tr>
<tr>
<td>3.8:1 (run 33)</td>
<td>513</td>
</tr>
</tbody>
</table>

\( a \) Rates quoted in \% \( \text{min}^{-1} \); \( b \) estimated from Figure 5.1.

### TABLE 5.12. ISOTOPIC CONTENTS OF COMPETING REACTANTS ON Fe AT 513K

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Isotopic Content / % ( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d_1 )</td>
</tr>
<tr>
<td>n-Butane</td>
<td>13</td>
</tr>
<tr>
<td>Propane</td>
<td>2</td>
</tr>
<tr>
<td>Ethane</td>
<td>-</td>
</tr>
<tr>
<td>Methane</td>
<td>8</td>
</tr>
<tr>
<td>Methane ( b )</td>
<td>6</td>
</tr>
</tbody>
</table>

\( a \) Sample taken after 10 minutes of reaction; \( b \) binomial distribution with mean deuterium content \( M_D = 3.0. \)
Figure 5.16. Competing reactions of ethane, propane and n-butane on iron at 513K.
on hydrocarbon pressure. The hydrogenolysis rates which were calculated from the initial slopes of these curves are compared in Table 5.11, with those obtained for hydrogenolysis of the single reactant at the same temperature. This comparison in effect describes the variation in hydrogenolysis rates with deuterium pressure; for a 3-fold reduction in deuterium excess, the initial rates of propane and n-butane hydrogenolysis increased approximately by a factor of 2 while that of ethane was essentially unchanged.

The mass spectral analyses for each reactant indicated that exchange again took place concurrently with hydrogenolysis and Table 5.12, details the isotopic compositions of each hydrocarbon after 10 minutes of reaction. The degree of isotopic dilution observed reflected the smaller deuterium to hydrocarbon ratio and initial rates of exchange were consequently difficult to estimate. The distribution of deuterium in the hydrogenolysis product compared favourably with a binomial spread based on a mean deuterium content of 3.0 per methane molecule. Similar levels of dilution were present in the exchanged species, their fractional deuterium contents again falling close to the 75% mark; in spite of this, there was nothing in the exchange patterns to suggest that the initial products were not as before - n-butane-d₄ and -d₁₀, propane-d₈ with small amounts of -d₁, and ethene-d₆. The isotopic distributions obtained from later samples only served to indicate more extensive dilution of the deuterium available for exchange.

Poisoning Studies: Evidence for catalyst poisoning by deposition of irreversibly adsorbed carbon residues or formation of carbide was first obtained experimentally from several of the high temperature G.C. runs where a marked retardation in reaction rate had been observed at higher conversions, but in the absence of any significant analytical discrepancy in the carbon balance. For example, at the
close of run 15, by pumping away the reaction mixture at 273K and then heating the
used film to high temperatures in a fresh supply of deuterium, it was possible to
retrieve a small amount of carbon from the catalyst in the form of methane. A
much larger quantity was evolved from the iron film used in the competing reactants
study, throughout which carbon loss had been readily detected from the G.C. analyses.

Further poisoning experiments involving consecutive reactions on the same
iron film were carried out with combinations of ethane and n-butane as reactants,
their initial hydrogenolysis rates being catalogued in Table 5.1. A reduction in
rate by a factor of 7.5 was observed for consecutive ethane reactions at 543K
(Table 5.1. runs 8 and 9) while for two n-butane reactions on the same catalyst at
483K (Table 5.1. runs 16 and 17), the corresponding ratio was only 1.3. In
contrast, by following an ethane study at 543K with a n-butane reaction at 483K
(Table 5.1. runs 7 and 18), the hydrogenolysis rate for the latter was 8.6 times
lower than that recorded for the second of the two n-butane reactions also at 483K
(Table 5.1. run 17). It was also interesting to observe that the n-butane reaction
poisoned by the original ethane run exhibited a noticeable acceleration in rate
after an initially slower period. A similar G.C.-M.S. investigation with both
reactions at 513K (Table 5.1. runs 3 and 19) yielded initial rates for n-butane
hydrogenolysis and exchange which were respectively factors of 6.1 and 21.7 lower
than those measured in the G.C.-M.S. study at the much lower temperature of 458K
(Table 5.1. run 14). Thus, in all cases, the effect of carrying out the first
hydrogenolysis reaction on the iron catalyst was to considerably reduce its
activity for any subsequent reactions.

Reactions on Sintered Films: The apparent 'poisoning' of reactions, in
particular at higher temperatures, made it necessary to gauge the possible effects
of loss in catalytic activity due to sintering of the iron catalysts. The contribution of the latter at temperatures down to 453K was indicated in two experiments on films presintered at reaction temperature; the hydrogenolysis of ethane at 513K (Table 5.1, run 6) was found to proceed about 10 times slower than the corresponding reaction with an unsintered film (Table 5.1, run 4) and similarly with n-butane at 453K (Table 5.1, runs 12 and 13), a reduction in hydrogenolysis rate by a factor of 3 was also recorded.

5.5 Discussion

The results obtained clearly indicate the relative activity patterns of the various hydrocarbons for each process occurring on the iron catalyst, and from such information, which has been summarised qualitatively in Table 5.13, it is possible to assess the probable sequence of events on the surface governing each mode of reaction observed.

Adsorption: The absence of low temperature exchange with deuterium for each of the reactants studied on iron confirms the findings of earlier work (6,7). Since adsorption of saturated hydrocarbons on iron is known to occur readily at these lower temperatures (4), it can be concluded that desorption of these molecules from an iron surface is not a rapid process. The lack of such exchange also implies that the weakly and reversibly adsorbed intermediates of the kind normally associated with exchange reaction mechanisms (18) are only metastable at lower temperatures on iron with respect to more strongly adsorbed and more highly dissociated species; furthermore, the fact that more extensive dehydrogenation of the adsorbed molecules is energetically more favourable at low temperatures than desorption from the surface clearly illustrates the apparent willingness of iron
### Table 5.13. Patterns of Hydrocarbon Reactivity on Iron Films

<table>
<thead>
<tr>
<th>Process</th>
<th>Order of Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange (overall)</td>
<td>n-butane &gt; neopentane &gt; propane &gt; ethane &gt; methane</td>
</tr>
<tr>
<td>Stepwise Exchange</td>
<td>neopentane &gt; n-butane &gt; propane &gt; ethane &gt; methane</td>
</tr>
<tr>
<td>Multiple Exchange</td>
<td>n-butane &gt; neopentane &gt; propane &gt; ethane &gt; methane</td>
</tr>
<tr>
<td>Exchange: Hydrogenolysis</td>
<td>neopentane &gt; n-butane &gt; propane &gt; ethane</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>n-butane &gt; neopentane &gt; propane &gt; ethane</td>
</tr>
<tr>
<td>Formation of Intermediate</td>
<td>n-butane &gt; neopentane &gt; propane</td>
</tr>
<tr>
<td>Hydrogenolysis Products</td>
<td></td>
</tr>
</tbody>
</table>

To form multiple bonds with hydrocarbon fragments.

The irreversibility of adsorption at low temperatures suggests that the process is strongly exothermic and involves fairly large heats of adsorption. The values of the latter might be expected to decrease with increasing molecular size as was found previously with the activation energies for adsorption of methane and ethane on iron (4) which reflected the greater energy required to dissociate a carbon-hydrogen bond in the smaller molecule; such a trend was also indicated by the order of high temperature exchange activity displayed by the series of hydrocarbons studied here (see Table 5.13.). As hydrogen itself may also be strongly adsorbed on iron (1,2), a further consequence of strong hydrocarbon adsorption is that there may be significant competition for surface sites between deuterium and hydrocarbon, which may in turn greatly influence reaction kinetics; for example, if the deuterium surface coverage is reduced as the temperature increases (19,20), then the number of sites on the iron catalyst responsible for
dissociative adsorption of hydrocarbon will be larger. This effect will be returned to later with reference to hydrogenolysis studies.

**Exchange:** For the hydrocarbons other than methane, exchange on iron was only detectable at higher temperatures and was found in each case to proceed concurrently with hydrogenolysis. The fact that exchange only takes place if hydrocarbon decomposition has commenced means that when the temperature is high enough to rupture the carbon-carbon bonds of those strongly adsorbed intermediates which have hitherto blocked the low temperature exchange process, it is then that the subsequent desorption of hydrogenolysis product molecules releases sites on the iron catalyst for further adsorption of reactant; at these higher reaction temperatures, the energy situation is less unfavourable to stable formation and subsequent desorption of weakly adsorbed intermediates which, if formed, may be rehydrogenated by addition of deuterium atoms before returning to the gas phase as exchange products. Although the exchange of methane cannot be influenced by the occurrence of hydrogenolysis, the extremely slow rates of reaction also point to the presence of strongly adsorbed C₁ species on the iron surface.

In the exchange of ethane, propane and n-butane on iron films, the perdeuterocompound was the major product detected in each case, indicating that the exchange process for these reactants must involve intermediates adsorbed at more than one carbon atom. Such a degree of multiple exchange can be accounted for by the slow desorption of hydrocarbons from iron, insofar as the majority of those adsorbed species formed from the reactant which are not broken down via hydrogenolysis to lower homologues still remain on the surface for sufficient time to allow complete replacement of the hydrogen atoms in the molecule by deuterium before desorption. The mechanism for this mode of reaction presumably
corresponds to that proposed by Kemball for the multiple exchange of these hydrocarbons on other transition metals \(7,18,21\); this means that the fully deuterated product is formed as a result of interconversions between two or more types of relatively weakly adsorbed species exhibiting different states of hydrogenation, as for example in the reaction step

\[
\text{alkyl (monoadsorbed)} \rightleftharpoons \text{alkene (diadsorbed)}.
\]

Of the straight chain hydrocarbons studied, stepwise exchange was most in evidence with n-butane (Table 5.13.) indicating that, for a weakly held monoadsorbed intermediate such as \(n-C_4H_{10}\)ads, desorption from the catalyst with incorporation of a single deuterium atom only may be an alternative to further dehydrogenation followed by multiple exchange or hydrogenolysis.

In contrast, the exchange reactions of neopentane and methane on iron films only involve intermediates which are adsorbed at a single carbon atom. Exchange of methane on iron was exclusively multiple, \(CD_4\) being the sole initial product. This observation corresponds to a multiple exchange mechanism similar to that reported by Kemball for methane exchange \(18,22\), in this case the energy barriers to subsequent formation of the more strongly adsorbed \(CH_2\) and \(CH\) intermediates being much lower than that for the initial carbon-hydrogen bond dissociation required for adsorption (see Section 1.3. and Figure 1.1.); once again, desorption of \(C_1\) species is so slow that their lifetime on the iron surface is always long enough to permit alternation between intermediates and, consequently, complete replacement of hydrogen atoms by deuterium.

The exchange of neopentane on iron yielded two primary products, neopentane-d_1 and neopentane-d_2, providing evidence for stepwise and multiple exchange, respectively. Incorporation of only one deuterium atom per visit to
the catalyst indicates that neopentane, like n-butane, also displays a considerable tendency to form reversibly adsorbed alkyl species on iron. Unlike the straight chain hydrocarbons, multiple exchange of neopentane is limited to replacement of the hydrogens on one methyl group only, the mechanism again being similar to that described previously for methane exchange\(^{(18,22)}\). The absence of neopentane-\(d_2\) as an initial product suggests that the intermediate for multiple exchange is either diadsorbed to the iron surface at one carbon atom with the remaining hydrogen exchanging rapidly by interconversion before desorption, or that the intermediate is triadsorbed. None of the primary exchange products contained more than three deuterium atoms; hence, there is no evidence for multiple exchange of neopentane involving an \(\alpha\gamma\) -diadsorbed species as was found for reaction on rhodium, where the fully deuterated neopentane-\(d_{12}\) was observed as an initial product\(^{(23)}\).

The patterns of exchange behaviour on iron exhibited by the five hydrocarbon reactants can be summarised in terms of the relative ease of adsorption and desorption for each hydrocarbon and the types of exchange intermediates derived from them. Table 5.13. shows that the overall activity towards exchange generally increases with molecular size, except that neopentane appears to be less reactive than n-butane. Considering the constituent processes separately, the same sequence is found for multiple exchange; in the stepwise mode, however, the relative positions of neopentane and n-butane are reversed and the trend of greater reactivity with increase in carbon number is carried through to the C\(_5\) molecule.

Although activation energies were not measured for exchange, the order of overall reactivity is almost certainly controlled by the ease of hydrocarbon
adsorption and desorption. It is probable that adsorption on iron is governed to a considerable extent by the energy involved in breaking a carbon-hydrogen bond to form an alkyl species\(^{(4)}\); on the other hand, desorption of any weakly adsorbed intermediates as exchange products is likely to depend on their stability towards further dehydrogenation and formation of more strongly adsorbed species. A clear illustration of these two effects is given by the slow initial rates recorded for exchange of methane; these can be partly attributed not only to the higher dissociation energy required for rupture of the more stable tetrahedral bond in methane, which makes adsorption more difficult, but also to the tendency of the methyl species so formed to undergo further rapid loss of hydrogen, thus yielding a C\(_1\) fragment which is much more difficult to desorb from the iron surface. The irreversible nature of these residues may also be a contributory factor to the poisoning of methane exchange which was observed at each of the chosen reaction temperatures (vide infra). The relative activities of ethane, propane and n-butane towards exchange can be accounted for by similar arguments.

The overall exchange behaviour of neopentane was found to be similar to that of propane and this may be tentatively explained, in the first instance, by a simple stereochemical approximation. Neopentane may equally be described as 2,2-dimethylpropane, which in turn can be thought of as propane itself by assuming stereochemical equivalence between the two substituted methyl groups and the secondary hydrogen atoms of propane. If adsorption to form an alkyl intermediate generally occurs by removal of one of the hydrogen atoms on a terminal propyl carbon, then it might be expected that the ease of adsorption for propane and neopentane should be comparable at the same temperature, the greater stability of the adsorbed neopentyl species possibly being attributable to the
fact that it cannot undergo further rapid dehydrogenation to form an α-β-diadsorbed species, as is the case with propane. This leads directly to a less speculative explanation for the position of neopentane in the exchange activity sequence, which involves general consideration of the types of intermediates which are formed during exchange reactions on iron.

\[\text{C}_2\text{H}_6(g) \rightarrow \text{CH}_3\]

\[\text{S} \quad \text{S} \quad \text{S} \quad \text{MONOADSORBED} \quad \alpha\beta^-\text{DIADSORBED}\]

Hydrogenolysis Intermediates

\[\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{C} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{S} \quad \text{S}
\end{array} \quad \xrightarrow{+} \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{C} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{S} \quad \text{S}
\end{array} \quad \text{MONOADSORBED} \quad \alpha\beta^-\text{DIADSORBED} \quad \alpha\alpha\alpha^-\text{TRIADSORBED}

\]

FIG. 5.17. Intermediates for exchange processes on iron.

It is clear from the relative extents of multiple and stepwise exchange within the group ethane, propane and n-butane, that α-β-diadsorbed intermediates are more stable than the monoadsorbed alkyl forms at those higher temperatures where exchange becomes observable. The importance of αβ-adsorption with respect to exchange behaviour is underlined by the fact that neopentane, with its quaternary carbon atom, cannot form such a species and tends to undergo multiple
exchange less readily by formation of \( \alpha \alpha \alpha \) -diadsorbed or \( \alpha \omega \omega \) -triadsorbed species; the latter are obviously less reversibly adsorbed than the neopentyl intermediate and consequently neopentane is the only reactant for which stepwise exchange predominates. At the other end of the scale, methane also requires multiply bonded intermediates for the exchange process, but these are much more strongly adsorbed and more stable relative to the methyl species. The neopentane results show that adsorption in the \( \alpha \gamma \) -mode does not contribute to exchange activity; in the absence of \( \alpha \beta \) -adsorption, however, such species, when formed, may be short-lived precursors to the more strongly adsorbed intermediates required for neopentane hydrogenolysis. Figure 5.17 summarises the types of adsorption involved in exchange processes on iron with particular reference to ethane and neopentane.

**Hydrogenolysis**: As indicated in Table 5.13, the order of hydrogenolysis reactivity is clearly the same as that deduced for exchange. For the straight chain hydrocarbons, hydrogenolysis reaction rates recorded at the same temperature were found to increase with the size of the molecule (see Table 5.11); the reactivity of neopentane did not follow this trend and was again much closer to that of propane than \( n \)-butane.

The principal features of the hydrogenolysis results may also be accounted for by the slow desorption of hydrocarbons from iron. The major product of hydrogenolysis in each case was perdeuteromethane. This observation suggests that when the reaction temperature is high enough to rupture the carbon-carbon bonds of the irreversibly adsorbed intermediates present on the surface, degradation of the reactant is extensive and the intermediate hydrogenolysis fragments corresponding to lower homologues are very much slower to desorb
relative to further scission of carbon-carbon bonds; in this way, the formation of intermediate reaction products is limited and most of the molecules which undergo hydrogenolysis end up as $C_1$ species, the lifetime of the latter on the iron surface also being long enough to permit complete deuteration, before desorption as $CD_4$.

Table 5.6. shows that, with increasing temperature, the extent of hydrogenolysis becomes more severe producing an even greater yield of methane but smaller amounts of the larger products; this trend indicates that for any particular hydrocarbon the activation energy for rupture of a carbon-carbon bond must be higher than that for desorption. It is interesting to note from Table 5.6. that the ratio of ethane to propane formed from n-butane also increases with temperature; at first sight, it might be concluded that the activation energy for carbon-carbon bond dissociation must increase with molecular size, but apart from the fact that the reverse is generally true for hydrogenolysis of hydrocarbons on metals$^{(15,24)}$, it is probable that adsorption of the hydrogenolysis intermediates formed from any of the reactants studied is sufficiently irreversible to minimise differences in the carbon-carbon bond strengths; this will be particularly true if scission tends to occur adjacent to a carbon atom which is multiply bonded to the iron surface. It is therefore more likely that the increasing ethane to propane product ratio from n-butane occurs because the gap between activation energy values for carbon-carbon bond rupture and desorption increases with molecular size. The minor hydrogenolysis products were also shown to be fully deuterated on extrapolation to zero conversion, and their fractional deuterium contents at higher conversions matched those of methane and the multiple exchange products, all of which were formed from slowly desorbed species; the agreement between deuterium contents implies that the latter are purely a function of the hydrogen-
deuterium pool available on the iron catalyst at any stage in the reaction, desorption of each hydrocarbon being slow enough to permit equilibration.

The 'depth' of hydrogenolysis, or extent to which degradation of the reactant occurs, will depend on the nature of the surface fragments formed by each successive carbon-carbon bond rupture. Although direct information concerning these reactive intermediates is largely precluded by the predominance of perdeutero-compounds as hydrogenolysis products, it is still possible to make several indirect and somewhat tentative deductions about their nature from the available experimental data. Firstly, if adsorption of those species which can undergo hydrogenolysis is assumed to be almost completely irreversible, then propagation of carbon-carbon bond rupture to an extent where the original reactant molecules are reduced to an equivalent number of C\textsubscript{1} residues will only occur if each multi-carbon fragment formed as a result of any dissociation step remains or becomes irreversibly adsorbed on the iron catalyst. Alternatively, such an assumption also implies that desorption of intermediate hydrogenolysis products is only possible if a more weakly adsorbed species of the kind already identified with exchange processes on iron is either left on the surface or formed by hydrogenation after the breaking of a carbon-carbon bond. A typical example of these effects might be the hydrogenolysis of a C\textsubscript{4} intermediate which is bonded to the surface in such a way that splitting of the central carbon-carbon bond yields two C\textsubscript{2} fragments — one of them adsorbed sufficiently strongly to incur further degradation to methane, and the other bound weakly enough to allow eventual return to the gas phase as perdeuteroethane. It therefore follows that surface-adsorbate geometry must also be an important factor in deciding the fate of an irreversibly adsorbed species.

The work of Anderson and Baker on metal-catalysed hydrogenolysis of
paraffins suggests that the reaction generally proceeds via intermediates attached to the surface at two carbon atoms. For neopentane with its quaternary carbon atom, such a theory necessitates the formation of an \( \alpha \gamma \) type of species, and since the latter do not apparently participate in exchange of neopentane on iron, it can be concluded that when adsorption of neopentane occurs in the \( \alpha \gamma \) mode, then it is completely irreversible and leads directly to scission of carbon-carbon bonds. It is probable that an \( \alpha \gamma \) -diadsorbed species with two carbon atoms only singly bonded to the iron surface is not in itself the reactive hydrogenolysis intermediate, but instead may be one of the likely precursors to more extensively dehydrogenated and irreversibly adsorbed forms such as \( \alpha \gamma \) -triadsorbed and \( \alpha \gamma \gamma \gamma \) -tetra-adsorbed neopentane.

The importance of \( \alpha \gamma \) -adsorption in hydrogenolysis on iron as portrayed by the neopentane results is offset by the fact that the latter is significantly less active towards hydrogenolysis than n-butane (Table 5.13); indeed, consideration of initial reaction rates at comparable temperatures (see Tables 5.1. and 5.2.) reveals a difference in hydrogenolysis activity which is at least a factor of two greater than the corresponding value for exchange. It is also interesting to note from Table 5.13, that neopentane exhibits the highest ratio of exchange to hydrogenolysis activity. The major conclusion to be drawn from these observations is that although formation of \( \alpha \gamma \) species must certainly be possible for n-butane, it is likely that the extra hydrogenolysis activity of the latter is partly due to the more favourable formation of various types of irreversibly adsorbed \( \alpha \) intermediates; furthermore, the greater difficulty in forming \( \alpha \gamma \) species causes exchange to predominate in the case of neopentane. Since the hydrogenolysis activity of ethane, propane and n-butane increases by approximately the same
factor with increase in chain length (Figure 5.1.), and as ethane cannot form an $\alpha\gamma$ intermediate, it would appear that $\alpha\beta$-adsorption is preferred for the straight-chain reactants; for example, the species giving rise to hydrogenolysis of ethane on iron are probably multiply bonded and irreversibly adsorbed forms such as $\alpha\beta$-triadsorbed or $\alpha\beta\beta$-tetra-adsorbed ethane with intermediates of similar geometry and bonding being responsible for the decomposition of propane and n-butane. Figure 5.18 summarises the types of adsorbed species essential to hydrogenolysis on iron.

**FIG. 5.18.** Intermediates for hydrogenolysis processes on iron.

The apparent preference shown by metallic iron towards $\alpha\beta$ adsorption of hydrocarbons in both exchange and hydrogenolysis processes is in contrast to the important role of $\alpha\gamma$ intermediates in hydrogenolysis and isomerization reactions on platinum, as is clearly demonstrated in the work of Anderson (24). The variation in behaviour between these metals may be partly due to a geometrical
factor. For a molecule such as propane, calculations involving recognised bond angles and standard carbon-carbon bond lengths reveal that the difference in the distances between two carbon atoms bonded in the $\alpha_\beta$ and $\alpha_\gamma$ positions is approximately 1Å; it is, therefore, interesting to note that the longer of the two metal-metal bond lengths in the body cubic-centred iron lattice is 1.02Å shorter than the corresponding distance in the face cubic-centred platinum structure, indicating that the latter may be more suited geometrically to $\alpha_\gamma$ adsorption.

It is probable that the rate-determining step in hydrogenolysis of hydrocarbons on iron is the desorption of methane from the surface. The predominance of methane in the product distributions shows that all the carbon-carbon bonds tend to break before desorption of the C$_1$ residues occurs and this observation is underlined by the fact that the activation energy for dissociation of a carbon-carbon bond in any surface fragment is higher than that for desorption. There is further evidence to suggest that rupture of carbon-carbon bonds is not rate-controlling; firstly, if it were the slow step, one might expect exchange of the reactant to be observable at lower temperatures than those for hydrogenolysis and, secondly, although the hydrogenolysis of n-butane proceeds at a much faster rate than that of ethane at the same temperature, it must still involve the decomposition of an ethane intermediate to yield methane. Having chosen methane desorption as the rate-determining process, it is necessary to explain the observed order of hydrogenolysis reactivity. Considering only the straight-chain hydrocarbons where the rate increases with molecular size, a tentative explanation may be one concerning the different extents of surface coverage by C$_1$ species formed from each reactant; to amplify this suggestion, it is useful to make a
quantitative estimate of the 'virtual' pressures of methane to be expected in each of these hydrogenolysis reactions.

The concept of a 'virtual' pressure was introduced by Tempkin and Fyzhev\textsuperscript{(27)} to account for the observed kinetics of the catalytic decomposition of ammonia, in which the slow step was assumed to be desorption of the product nitrogen. In a more recent review by Kemball\textsuperscript{(28)}, the use of this concept was generally advocated for situations where some but not all of the molecules in the gas phase are equilibrated with the surface and, in particular, for cases where the final desorption - for instance, of methane - tends to control the overall process. Taking hydrogenolysis of ethane on iron as an example, the various equilibria which may be established in the system are described in Figure 5.19. The diagram demonstrates the possibility of a 'real' adsorption equilibrium (heavy arrows) between surface species and gas-phase reactants, and, in doing so, implies that chemisorption of ethane and carbon-carbon bond rupture are both reversible reaction steps; in practice, on an iron surface, however, a much greater degree of irreversibility exists in both cases, and, in particular, there is certainly no evidence to suggest recombination of C\textsubscript{1} residues on the catalyst.

The circumstances on iron may be compared with those found by Guczi for ethane on nickel\textsuperscript{(29)} where the assumption of an adsorption equilibrium appears to
break down at higher temperatures and the rate of exchange of ethane with deuterium becomes small relative to that of hydrogenolysis. The ethane hydrogenolysis kinetic scheme originally proposed by Cimino et al. (8) has recently been extended by Sinfelt (30) to include situations in which adsorption equilibria are not established. In the reaction sequence defined by Sinfelt (Figure 5.20.), such a situation will arise if steps (1) and (2) become irreversible, and evidence of such behaviour has been obtained from hydrogenolysis of ethane on cobalt (15, 31) where chemisorption of the reactant appeared to be

\[
\begin{align*}
{\text{C}_2\text{H}_6} & \rightleftharpoons {\text{C}_2\text{H}_5}\text{(ads)} + {\text{H}}\text{(ads)} \quad (1) \\
{\text{C}_2\text{H}_5}\text{(ads)} + {\text{H}}\text{(ads)} & \rightleftharpoons {\text{C}_2\text{H}_x}\text{(ads)} + a{\text{H}}_2 \quad (2) \text{ where } a = \frac{6 - x}{2} \\
{\text{C}_2\text{H}_x}\text{(ads)} & \rightarrow 2{\text{C}_1}\text{(ads)} \quad (3) \\
{\text{C}_1}\text{(ads)} & \xrightarrow{\text{H}_2} \text{CH}_4 \quad (4)
\end{align*}
\]

FIG. 5.20. Mechanism for ethane hydrogenolysis (8, 30).

completely irreversible. Under such conditions, the kinetics may be solved by a steady-state treatment in which the net rate of ethane adsorption is assumed equivalent to the rate of disappearance of C₂ species by carbon-carbon bond rupture (31). The general conclusion to be drawn from these considerations is that, if non-equilibrium adsorption occurs and rupture of the ethane carbon-carbon bond is rate-controlling, as is the case for most of the Group VIII transition metals (15), then an effective overall balance may still be maintained between the gas-phase reactants and adsorbed C₂ species on the surface.

The preceding arguments may be applied to ethane hydrogenolysis on iron
where steps (1), (2) and (3) in Figure 5.20. are largely irreversible; the rate-determining stage is step (4) involving desorption of methane, so that, in this case, in spite of the non-equilibrium chemisorption an overall balance may still be established between gas-phase ethane and deuterium and the various single carbon species formed on the catalyst. The 'virtual' pressure of methane may be defined as that pressure which would be required in the gas phase to maintain equilibrium with the concentration of C\(_1\) fragments present on the surface and at the same time satisfy a gas phase equilibrium with the reactants (dotted arrows Figure 5.19.). The actual pressure of methane in the gas phase at any point in the reaction is likely to be substantially below the virtual pressure value; this is equivalent to saying that the quantity of chemisorbed methane formed from any particular pressure of hydrocarbon during hydrogenolysis is much greater than the amount which would be adsorbed from the same pressure of methane under the same reaction conditions, and this is substantiated by the low methane exchange rates recorded. The foregoing justifications for introducing virtual pressures may be similarly employed for the other hydrocarbon reactants.

The dependence of hydrogenolysis rate on methane desorption and consequently on the surface concentration of C\(_1\) fragments means that the order of hydrogenolysis activity may be a function of the virtual pressure of methane produced by each reactant. The extent to which this is true is demonstrated by Table 5.14. which provides values of the latter for methane-forming reactions at 500K; these were determined by using standard equilibrium constants\(^{(32)}\) to calculate the pressure of methane in equilibrium with the standard reaction mixture pressures of hydrocarbon and deuterium. As expected for the three straight-chain hydrocarbons, the trend in methane virtual pressure emulates that of hydrogenolysis activity,
TABLE 5.14. VIRTUAL PRESSURES OF METHANE AT 500K \(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\log_{10} K_p)</th>
<th>(p_{CH_4}^* /) atmos</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_6 + \text{H}_2 \rightleftharpoons 2\text{CH}_4)</td>
<td>7.3651</td>
<td>69</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8 + 2\text{H}_2 \rightleftharpoons 3\text{CH}_4)</td>
<td>13.8792</td>
<td>907</td>
</tr>
<tr>
<td>n-(\text{C}<em>4\text{H}</em>{10} + 3\text{H}_2 \rightleftharpoons 4\text{CH}_4)</td>
<td>20.0645</td>
<td>2729</td>
</tr>
<tr>
<td>neo-(\text{C}<em>5\text{H}</em>{12} + 4\text{H}_2 \rightleftharpoons 5\text{CH}_4)</td>
<td>26.7045</td>
<td>6573</td>
</tr>
</tbody>
</table>

\(^a\) \(K_p\) is the equilibrium constant; \(p^*\) is the virtual pressure.

confirming the choice of methane desorption as the rate-controlling process on iron.

The use of virtual pressure measurements, however, gives rise to two further problems. Firstly, the temperature variation of enthalpy\(^{(32)}\) in methane-forming reactions is such that \(p_{CH_4}^*\) should be larger at lower temperatures; hence, if the virtual pressures of methane were compared at temperatures where the hydrogenolysis rate for each reactant is the same, it would be revealed, for example, that

\[
p_{CH_4}^* (\text{n-butane, 453K}) \gg p_{CH_4}^* (\text{propane, 493K}) \gg p_{CH_4}^* (\text{ethane, 513K}).
\]

The question then arises as to why such a large \(p_{CH_4}^*\) is required for reaction of n-butane at a rate which may be equalled for ethane hydrogenolysis at a higher temperature, but with a very much smaller \(p_{CH_4}^*\) value. The second problem lies in the fact that the hydrogenolysis activity of neopentane on iron is less than that of n-butane yet it yields a much higher virtual pressure of methane than the \(\text{C}_4\) paraffin. These anomalies may be tentatively accounted for by reconsidering those factors which control the surface coverages and desorption rates of adsorbed \(\text{C}_1\)
species and deuterium, all of which contribute to the rate-determining hydrogenolysis process; by way of illustration, special reference is made to the behaviour exhibited in n-butane and ethane hydrogenolysis reactions on iron at 453K and 513K, respectively.

The relation between the quoted virtual pressures (Table 5.14.) and the true surface coverage by single carbon species under reaction conditions may be gauged in the first instance from the data for methane exchange on iron; for example, the very low methane exchange conversion observed in the 453K temperature region suggests that the associated concentration of C₁ fragments may be rather small.

It is clear, therefore, that under the prevailing circumstances, the methane equilibrium, \( \text{CH}_4 \rightarrow \text{C}_1 (\text{ads}) \), considerably favours the gas phase and that a high virtual pressure value from, for example, n-butane hydrogenolysis at 453K may still only be indicative of a moderate surface coverage by single carbon intermediates. If, as would seem likely, the heat of adsorption of methane is fairly large, then as the methane equilibrium shifts away from the gas phase at higher temperatures, a more extensive concentration of C₁ residues may be maintained on the iron surface by a lower virtual pressure of methane - a situation which might be relevant to the hydrogenolysis of ethane at 513K. In general, it can be deduced that the degree to which the virtual pressure reflects the actual coverage by C₁ species will depend on the position of the methane equilibrium at the reaction temperature in question.

At temperatures in the region of 453K, it is likely that the surface coverage by reactant hydrocarbon and, hence, adsorbed C₁ residues is much lower than that of deuterium; at higher temperatures, however, the latter may compete less strongly for surface sites and the relative coverage by hydrocarbon may greatly
increase. These conclusions are largely drawn from the apparent reaction orders with respect to hydrocarbon and deuterium which are suggested by the kinetic rate plots and also the study involving competing reactants (Table 5.11.). Although the graphical evidence is not completely consistent, it would appear in particular for the larger molecules, propane, n-butane and neopentane, that the hydrogenolysis rate dependence on hydrocarbon pressure is almost first order at lower temperatures (e.g. Figure 5.6.); the apparent deviations from first order behaviour observed for propane and n-butane at higher reaction temperatures may indicate a fall in the hydrocarbon pressure exponents to values of less than unity (Figure 5.16.).Less information is available for ethane at lower temperatures, but an approximately zero order dependence is clearly evident at 513K (Figure 5.3.) implying that there may be a temperature-dependent gradation in hydrocarbon reaction order and, consequently, in strength of adsorption within the group of hydrocarbons studied.

The results contained in Table 5.11. refer to parallel reactions at 513K and indicate that there is a negative order dependence on deuterium pressure for n-butane and propane hydrogenolysis reactions while that for ethane is again closer to zero. If the deuterium surface coverage decreases with increasing temperature, then it is probable at lower temperatures that the reaction orders with respect to deuterium are more negative and that inhibition of the hydrogenolysis rate by deuterium is correspondingly more significant; evidence of similar behaviour has also been reported by Gucci(29) for hydrogenolysis of ethane on nickel, where methane formation eventually becomes independent of hydrogen pressure at higher temperatures. In general, the hydrocarbon and deuterium pressure exponents recorded in the present investigation compare favourably with
the values of 0.6 and 0.5, respectively, for ethane hydrogenolysis\(^{(15)}\) and 0.5 and -0.6, respectively, for n-pentane hydrogenolysis\(^{(10)}\) which were determined in earlier studies on supported iron catalysts.

An important consequence of extensive surface coverage is that the phenomena of surface heterogeneity and repulsive interactions between species in the adsorbed layer may cause the heats of adsorption of any of the molecules involved to fall sharply as the amount of adsorbed material on the catalyst increases\(^{(33)}\). Since observations of this kind have already been made in relation to chemisorption of hydrogen on iron surfaces\(^{(2,34)}\), it may be useful to extend this concept to hydrogenolysis of hydrocarbons on iron, and in particular to the rate-controlling step. Hence, if the surface coverage increases during hydrogenolysis to an extent where the heat of adsorption of methane begins to fall, then desorption of adsorbed C\(_1\) species may occur more easily than would be expected on the basis of a straightforward Arrhenius rate prediction for that process.

The foregoing arguments may now be summarised with reference to the two chosen examples. For hydrogenolysis of n-butane at 453K, it is likely that in spite of the high virtual pressure value suggested in Table 5.14, the surface coverage by reactant and consequently by adsorbed single carbon intermediates will be low relative to that of deuterium; the surface concentration of the latter is sufficient to inhibit the hydrogenolysis rate at this temperature but at the same time maintain complete replacement of all the hydrogen atoms in the reaction product. For ethane hydrogenolysis at 513K, the adsorption of reactant is much stronger and the coverage by C\(_1\) fragments relative to that of deuterium may be greater; the extent of surface coverage at this higher temperature may be sufficient to cause a fall in the heat of adsorption of methane and, consequently,
an increase in the ease of desorption; the lower deuterium concentration will be less inhibiting with respect to hydrogenolysis rate but will still be sufficient to permit production of the fully deuterated product. Thus, all of these factors may contribute to an ethane hydrogenolysis rate which belies the low methane virtual pressure value indicated in Table 5.14. The problem arising from the anomalous hydrogenolysis activity of neopentane may simply hinge on the relative surface coverages by reactant and deuterium under the reaction conditions employed; it is probable that the inability of neopentane to form an αβ intermediate results in a much lower concentration of strongly adsorbed reactant and hence of C₂ species than is intimated by the virtual pressure value.

The important point to realise from the preceding discussion is that, although the virtual pressures of methane may in relative magnitude correctly predict to a considerable extent the order of increasing hydrogenolysis reactivity, it is, in fact, the effective surface coverage and desorption rate of the single carbon fragments together with the relative concentration of adsorbed deuterium which collectively govern the hydrogenolysis rate observed. Lastly, it is also significant that the relative sizes of the hydrogenolysis activation energies quoted in Table 5.3 follow the same trend as the hydrogenolysis activities, even though the values listed may be partly invalidated by the 'turning over' effects present in the Arrhonius plots of Figure 5.1. From this trend, it may be concluded that the variation in the rate of the hydrogenolysis slow step with temperature may also be a function of the temperature dependent relative surface coverages of hydrocarbon and deuterium; hence, n-butane which produces four C₂ residues per adsorbed reactant molecule may exhibit the sharpest change in relative coverages with rise in temperature. Furthermore, it is also interesting
to note in this respect that the methane virtual pressure value for n-butane hydrogenolysis varies more widely with temperature than that of the other straight-chain paraffins.

Poisoning on Iron Films: The apparent losses in catalytic activity, which were mainly observed at higher conversions and reaction temperatures, can be largely attributed to three causes - gradual poisoning by irreversibly adsorbed hydrocarbon, formation of iron carbide and progressive sintering of the iron films. It is difficult, however, to distinguish the individual contributions from any of these three sources to any particular loss in reaction rate, so that the primary evidence for reaction poisoning which includes the curving of Arrhenius plots (Figure 5.1.) as well as marked retardation in some of the kinetic rate plots (e.g. Figure 5.7.) can only be explained in general rather than specific terms. In all the instances where poisoning is indicated there is no suggestion of selectivity or preferential inhibition of either the exchange or the hydrogenolysis process.

The experiments carried out on presintered iron films show that sintering may cause some loss in catalytic activity in any reaction performed at temperatures down to 453K and, as expected\(^1\), that the effect may become more extensive with increasing temperature (Table 5.1. runs 6 and 13). It is known, however, that sintering of a metal film may be considerably inhibited by the presence of adsorbed gases\(^3\); hence, if the actual decrease in activity observed under experimental conditions depends on the extent of surface coverage established during the reaction, the consequences of sintering may be less significant than predicted.

The division between blocking of active sites by irreversibly adsorbed hydrocarbon and actual formation of carbide may be a fine one with respect to
experimental detection; it is not easy therefore to establish whether the retrieval of small amounts of carbon in the form of methane at the close of experiments which displayed a marked deceleration at higher conversions was due to decomposition of carbide or rehydrogenation of carbonaceous residues. Positive evidence for hydrocarbon poisoning on iron films was provided by the results from consecutive reactions carried out on the same catalyst. The extent to which the first reaction on an iron surface impairs the catalytic activity for any subsequent processes is dependent on the reaction temperature and the strength of hydrocarbon adsorption; consequently, ethane tends to progressively poison an iron film to a greater degree than n-butane (cf. Table 5.1. runs 7-9, 16-18) and the blocking of active sites is more pronounced at higher temperatures where the surface coverage by deuterium may be much lower, thus allowing extensively dehydrogenated fragments to become permanently bound to the catalyst surface. Furthermore, the acceleration observed after the initial stages of run 18 implies that the ethane residues deposited on the iron film during the preceding reaction (run 7) may be partly removed by hydrogenation with fresh deuterium from the second reaction mixture, thus freeing more surface sites for the inherently faster n-butane reaction.

Carbide formation in an iron-catalysed hydrocarbon reaction is not an unrecognised phenomenon (5, 36) and may be a distinct possibility particularly in a case such as that of the competing reactants study (run 33) where the deuterium to hydrocarbon pressure ratio was only 3.8:1 and a considerable quantity of carbon was apparently lost to the catalyst. In energetic terms, if the rate of desorption of single carbon species in a hydrogenolysis reaction is sufficiently slow, then the thermodynamic potential of the species (C)ads may be large enough to permit incorporation of carbon into the bulk of the iron catalyst from the
The temperature variation of equilibrium constant $K_p$ has been catalogued (36) for the reaction

$$C_2H_6 + 4Fe \rightleftharpoons 2Fe_2C + 3H_2$$

and this data may be utilised to determine a value of 541K for the temperature at which carbide formation from ethane in a standard hydrogenolysis reaction mixture becomes feasible. Fe$_2$C or 'Hagg' carbide, however, is known to be less stable than Fe$_3$C (cementite) at temperatures below 573K (36), so the calculated value of 541K may be in excess of that actually required to sustain carbide formation. A second factor which may enhance the carbide yield is that the ratio of deuterium to hydrocarbon on the surface may be considerably less than that in the gas phase at higher temperatures; hence, the corresponding lower limit of temperature required for carbide production from, for example, a 3.8:1 deuterium to hydrocarbon mixture drops to a value of 494K. In general, it can be concluded that the conditions under which the hydrogenolysis and exchange reactions were carried out were sufficiently suitable to support some form of uptake of carbon by the iron catalysts.

Finally, the poisoning of methane exchange on iron (Table 5.2. runs 30-32) is difficult to characterise precisely in terms of the preceding evidence. Although sintering of the iron film might contribute to the apparent loss in activity at 456K and 523K, it would not be expected to be significant at a reaction temperature as low as 385K; the latter should also be true for carbide formation which, in thermodynamic terms, will be less feasible from methane than the larger hydrocarbons. The surface coverages and desorption rates of methane in hydrogenolysis reactions imply that the very slow rates of exchange are probably associated with really small coverages of strongly adsorbed methane.
species and such a situation might well arise if chemisorption of methane is difficult and is accompanied by a large heat of adsorption. Consequently, if surface heterogeneity is important on an iron film, it may be postulated that a proportion of the more active sites involved in methane chemisorption at 385K could become blocked by extensively dehydrogenated single carbon residues, thus giving rise to a falling off in rate. At the higher temperatures required for greater surface concentrations of adsorbed C<sub>1</sub> species, it would appear that sintering, carbide formation and hydrocarbon poisoning of active sites may all be sizable effects, and this will preclude observation of methane exchange on iron at an appreciable reaction rate.
BIBLIOGRAPHY

6.1. Hydrogenolysis and Exchange Reactions on Group VIII Transition Metals

Although the transition metals of Group VIII in the Periodic Table are collectively noted for their catalytic properties, there is substantial evidence in the literature to suggest that differences in their individual behaviour with reference to several aspects of catalysis are somewhat allied to whether the metal in question falls under the description of 'noble' or 'non-noble' metal. Since platinum and iron, respectively, are to a large extent representative of these two categories, the results of Chapters 4 and 5 may be best reviewed by directly comparing the main features of exchange and hydrogenolysis processes carried out on these metals and, at the same time, assessing their relevance to the general patterns of behaviour observed in metal-catalysed reactions.

Reactive Intermediates and Temperature Effects: One of the objects of the present study was to consider further the relation between the adsorbed intermediates responsible for hydrocarbon exchange reactions and the species required for those catalytic processes involving breakdown or skeletal rearrangement of the hydrocarbon molecules which generally take place at higher temperatures. Kemball\(^{(1)}\) has emphasised the unlikelihood of the same intermediates functioning under the same conditions in all of these types of reaction; for example, if an adsorbed species is to be effective in an exchange medium, it must be stable to changes such as carbon-carbon bond rupture, otherwise its role as an exchange
intermediate will cease. A more likely possibility is that the intermediate which participates in exchange may alter in stability as the temperature is increased and consequently lead to species suitable for other reactions such as hydrogenolysis or isomerization. Hence, before summarizing the variations in reaction characteristics between one metal and another, it may be useful to reconsider the sequence of changes which take place with respect to the mode of interaction between hydrocarbon and metal as the temperature of the system is raised.

The temperature range of catalytic interest has been divided by Kemball (1) into three regions labelled A, B and C, the designations of which have been recently revised and extended (2) as follows. At the lower end of the temperature scale, exchange of alkanes other than methane is generally observed, indicating that, in region A, dissociation of carbon-hydrogen bonds in molecules larger than methane is readily reversible; the extent of dehydrogenation of the reacting hydrocarbon is therefore limited and the exchange intermediates so formed tend to be weakly adsorbed species which are completely stable to fission of carbon-carbon bonds. The stronger tetrahedral bond in methane is probably responsible for its lack of exchange activity in this region compared with the larger homologues in the series. The upper limit of region A may be indicated by the temperature required for exchange of ethane which is normally less reactive than the other linear or branched chain hydrocarbons (3). At temperatures below those of region A, hydrocarbon adsorption will be entirely physical in nature and any catalytic processes involving rupture of chemical bonds will consequently be precluded.

The second temperature region B corresponds to that range over which the
weakly held intermediates characteristic of the low temperature reactions gradually lose their stability and are converted to more strongly adsorbed species which may accumulate on the catalyst surface to cause progressive poisoning of the exchange process as the temperature rises. It is also likely that irreversible dissociative adsorption of methane takes place in region B, with or without the evolution of hydrogen, and the fact that the latter often accompanies the adsorption of hydrocarbons on metals at these temperatures implies that the irreversibly adsorbed intermediates thus formed are much more extensively dehydrogenated species than those of region A.

When the temperature is raised further into region C, exchange of methane with deuterium becomes detectable; furthermore, the exchange of larger hydrocarbons, which was inhibited in region B, recommences in this range and proceeds concurrently with other reactions such as hydrogenolysis or isomerization. These observations suggest that conditions may be reached under which the strongly adsorbed multi-carbon species of region B can undergo decomposition or rearrangement of their carbon skeletons; the products formed from such processes may escape from the metal surface to the gas phase leaving vacant sites for both weak and strong adsorption of further hydrocarbon molecules, which in turn may lead to simultaneous exchange and hydrogenolysis of the reactant, respectively. In catalytic terms, the division between regions C and B may be a rather nebulous one since in the latter there is no overall reaction detectable. This means that, if desorption of product molecules is the rate-determining stage in a hydrogenolysis process, then scission of carbon-carbon bonds may also take place at region B temperatures; the surface may therefore be covered with species containing fewer carbon atoms than the reactant until the apparent onset of region C and detection of
hydrogenolysis by desorption of these fragments. Conversely, if rupture of carbon-carbon bonds is the slow step, as is most frequently the case on metals, the species on the surface at region B temperatures will contain the same number of carbon atoms as the reacting hydrocarbon. There is currently no reason to suggest that there is an upper limit to region C, although unequivocal interpretation of catalytic behaviour at temperatures greater than 973K may be obscured by effects such as carbide formation, extensive sintering and reorientation of the metal's crystalline structure.

The temperature regions for any system will depend on the metal and the nature of the reacting hydrocarbon; however, there appears to be no distinguishable trends for the noble or non-noble members of Group VIII. For a metal such as nickel\(^{2}\), the three zones for low temperature exchange, poisoning of the latter and finally simultaneous exchange and hydrogenolysis tend to be clearly distinguishable. For platinum, the boundaries between the temperature regions are less distinct. Data from the exchange of larger hydrocarbons suggests that region A begins at about 280K; exchange of methane, however, which should occur in region C has been recorded at temperatures down to 450K\(^{5}\), as has the exchange of ethane\(^{6}\) which usually signifies the upper end of region A, so the middle region B is difficult to recognise on this basis. Alternatively, the inhibitory effects of presorbing saturated hydrocarbons on platinum prior to a neopentane exchange reaction\(^{5}\) appear to indicate that region B has a lower limit of about 378K. Region C on platinum commences at approximately 480K and is typified by the results of Chapter 4 for the concurrent exchange and hydrogenolysis of \(\text{n-butane}\) which both proceed at temperatures in excess of 523K.

In contrast to most other metals including platinum, iron exhibits zero
activity for low temperature exchange of hydrocarbons because of its ability to form irreversibly adsorbed species at temperatures which would normally be typical of region A. Consequently, the lower boundary of region 5 extends down to temperatures at which formation of the reversibly adsorbed intermediates required for exchange would be so slow as to make detection impossible; region A, as defined, is therefore absent in the case of iron. The exchange process, however, does accompany hydrogenolysis in region C at temperatures greater than 420K and this effect was illustrated in the reactions of saturated hydrocarbons with deuterium on iron as detailed in Chapter 5.

Exchange: Comparison of the rates of exchange in temperature region C shows that hydrocarbon exchange reactions on platinum are extremely fast relative to the rates measured for hydrogenolysis and isomerization on that metal, while on iron the deuterium exchange rates are comparable to those for the hydrogenolysis process; thus, platinum is a much better exchange catalyst than iron. This contrast merely reflects the fact that irreversible adsorption is much more extensive on iron, reactant molecules being less likely to leave the latter surface with their carbon skeletons unaltered than with platinum on which reversibly adsorbed species are more readily formed at lower temperatures. The exchange patterns commonly observed for saturated hydrocarbons on the majority of metal film catalysts display characteristics typical of either of two mechanisms, one indicative of simple stepwise incorporation of deuterium and the other involving multiple interchange between mono-adsorbed alkyl and di-adsorbed alkene-type species. The maxima found at the singly deuterated and perdeutero forms in the isotopic product distribution from exchange of n-butane on platinum imply that both exchange mechanisms may occur on that metal, multiple replacement
of hydrogen being the predominant process. Similarly on iron, the extent to which the stepwise reaction takes place tends to increase with hydrocarbon size, but in all cases except neopentane, multiple exchange remains the major process. It is interesting to note that most of the Group VIII metals readily propagate a multiple exchange mechanism and this perhaps emphasises the general ability of these metals to accommodate weakly held $\alpha\beta$-diadsorbed species as intermediates for exchange reactions. The evidence from exchange of neopentane, which cannot adsorb in the $\alpha\beta$ fashion due to its quaternary carbon atom, suggests that $\alpha\gamma$ intermediates are not important in metal-catalysed exchange mechanisms; on platinum and iron, for example, multiple exchange of this molecule is generally limited to the hydrogens on a single methyl group indicating that replacement probably proceeds by interconversion between $\alpha-$ and $\alpha\gamma$-diadsorbed species as postulated for methane exchange.

Hydrogenolysis and Isomerization: The ability of the Group VIII transition metals to catalyse hydrogenolysis of hydrocarbons has been extensively investigated in recent years and the results obtained have consistently shown the extent to which the nature of the hydrogenolysis process as revealed by the distribution of reaction products is dependent on the metal involved. The two extremes of the wide range of behaviour observed consist, on the one hand, of the dissociation of a single carbon-carbon bond per residence on the catalyst as found here on platinum films and, on the other, of complete fragmentation of the adsorbed reactant molecule to yield methane only as recorded in the hydrogenolysis reactions on iron films (Chapter 5).

The tendency to promote exclusive formation of methane is characteristic of hydrogenolysis reactions on the non-noble metals and Kikuchi has demonstrated
how the proportion of methane produced from n-pentane increases with reaction temperature on supported iron, cobalt and nickel catalysts; such an effect indicates that an increase in temperature favours decomposition of an adsorbed fragment over desorption and the hydrogenolysis reaction moves further in the direction of multiple cracking rather than stepwise carbon-carbon bond rupture. Extensive breakdown to methane implies that there is little differentiation between the reactivity of various types of carbon-carbon bonds on these metals; although this appears to be true in the case of iron, nickel tends to selectively attack the terminal carbon-carbon bond in alkanes and methane is produced by successive demethylation of the hydrocarbon chain, as illustrated in the hydrogenolysis of several hexane isomers \(^{(11)}\). Amongst the noble metals of Group VIII, specificity of the same kind has been exhibited by palladium and rhodium in n-heptane hydrogenolysis \(^{(12)}\); platinum and iridium, however, generally display non-selective rupture of a single carbon-carbon bond per reactant molecule and consequently the much broader distribution of hydrogenolysis products from these two metals may be simply expressed in terms of the relative probabilities for dissociation of different types of carbon-carbon bond \(^{(13)}\).

The overall trend for the noble metals is one of limited fragmentation of the hydrocarbon skeleton and much lower yields of methane than those obtained from the non-noble members of Group VIII. It is also interesting to note that the behavioural division observed in hydrogenolysis of paraffins is also apparent in other types of reaction; for example, the hydrogenation of cyclopropane to propane occurs cleanly on the noble metals platinum, palladium, rhodium and iridium, but is also accompanied by decomposition to methane and ethane on the non-noble nickel and cobalt \(^{(14)}\).
Another major contrast between non-noble and noble catalysts is the exclusive activity of several of the latter for skeletal isomerization of hydrocarbons concurrently with the hydrogenolysis reaction; in terms of selectivity relative to hydrogenolysis, platinum is by far the most active metal for rearrangement processes with palladium and iridium also displaying appreciable isomerization activity \( (13, 15) \). Typical studies including those of the present work on isomerization of the butanes and neopentane on platinum films clearly indicate that the proportion of parent hydrocarbon reacting to isomeric rather than hydrogenolytic products is considerably smaller for a hydrocarbon with an unbranched as opposed to a branched chain containing an isostructural unit. With larger reactant molecules – for instance, the hexanes – platinum may also catalyze related reactions \( (16, 17) \) such as dehydrocyclization and dimerization, the products from which may in turn contribute to inhibition of the normal isomerization and hydrogenolysis processes. In the present investigation, it was found that conditions existed on both iron and platinum under which the rate of hydrogenolysis could be markedly affected by poisoning. In comparing the likely causes of such poisoning, the formation of irreversibly adsorbed by-products from side reactions on platinum provides an interesting contrast to the greater ability of the non-noble metal to form a stable carbide from irreversibly adsorbed reactant; the common factor with these effects, however, is that they are both enhanced by a reduced partial pressure of hydrogen.

The isotopic compositions of hydrogenolysis products from reactions carried out in the presence of deuterium may also be compared. The deuterium distributions in the products of \( n \)-butane hydrogenolysis on platinum were binomial in nature and reflected the rapid and extensive exchange of the reactant
with deuterium; on iron, perdeuteromethane and, to much lesser extents, $C_2D_6$ and $C_3D_8$ were the products of the corresponding n-butane reaction. The significant contrast here is that deuterium incorporation is extensive on platinum by virtue of the latter's tendency to readily form weakly and reversibly adsorbed intermediates for exchange, while on iron the products become heavily deuterated because of slow desorption of much more strongly held species. The respective roles of weakly and strongly adsorbed intermediates in exchange and hydrogenolysis reactions on platinum and iron are summarized in Figures 6.1 and 6.2; in both diagrams, the probable sequence of steps involved in each of these processes is clearly indicated.

The general evidence available on reaction mechanisms leads to the conclusion that metal-catalysed hydrogenolysis requires adsorbed intermediates which are extensively dehydrogenated and are bonded to the surface at more than one carbon atom (18). For ethane hydrogenolysis on any of the Group VIII metals including iron and platinum, this criterion will be simply met by a mechanism involving an $\alpha\beta$-adsorbed species. On platinum, the pattern of activation energies evaluated for reactions of the butanes, neopentane (13) and neohexane (11) points to a common $\alpha\gamma$-adsorbed intermediate for both hydrogenolysis and isomerization on that metal; Anderson and Avery have further established that the $\alpha\gamma$ species formed on platinum from hydrocarbons larger than ethane may be precursors to a bridged intermediate of partial carbonium ion character, which will undergo dissociation or skeletal rearrangement depending on whether attack by hydrogen does or does not take place, respectively, during its lifetime on the surface (19). The considerable importance of $\alpha\gamma$ adsorption in the hydrogenolysis mechanism on platinum is again in contrast to the general behaviour of the non-noble metals;
FIG. 6.1. Sequence of Reaction Steps for Hydrogenolysis and Exchange on Platinum.

FIG. 6.2. Sequence of Reaction Steps for Hydrogenolysis and Exchange on Iron.

Note: In the above figures, (va) and (sa) represent weakly and strongly adsorbed species, respectively.
for instance, in the present work on iron, hydrogenolysis rates were found to increase with molecular size except in the case of neopentane which was slower in rate than the n-butane reaction, thus indicating the preference displayed by iron towards fragmentation of \( \alpha \beta \) adsorbed intermediates. The hydrogenolysis of neopentane on platinum and iron is, in fact, a good example of how the same reaction may vary mechanistically from one metal to another. On the noble metal, the tendency is for a single carbon-carbon bond to be broken in the bridged \( \alpha \gamma \) species, the fragments so formed being sufficiently weakly held to permit desorption as isobutane and methane; on the other hand, the initial rupture of a carbon-carbon bond in the neopentane \( \alpha \gamma \) intermediate formed on iron yields surface residues which may in turn be strongly enough adsorbed to allow further extensive degradation to methane, probably via the preferred \( \alpha \beta \) adsorption mode. With nickel, however, it is interesting to note that \( \alpha \beta \) and \( \alpha \gamma \) adsorption are competitive rather than consecutive in action and this is illustrated by the similar extents of carbon-carbon bond rupture within the ethyl and neopentyl groups during hydrogenolysis of neohexane (11) on that catalyst.

In a reaction system as relatively complicated as hydrogenolysis on metals, the identification of a rate-determining step may be difficult. For reactions on platinum involving \( \alpha \gamma \) species, the available evidence points to formation of the bridged intermediate described by Anderson and Avery as the step which is rate-controlling (19). On most of the Group VIII metals, where the hydrogenolysis mechanism may be more dependent on \( \alpha \beta \) adsorption, the reaction rate is thought to be determined by the step involving carbon-carbon bond dissociation and this theory is reinforced by the fact that in the majority of these cases, exchange of the hydrocarbon takes place independently of hydrogenolysis at much lower temperatures (9). As indicated in Chapter 5, iron appears to be at least one
exception to this trend, and it would seem probable on this metal where low
temperature hydrocarbon exchange is not observed that the reaction rates are
controlled by product desorption; evidence to support both carbon-carbon bond
rupture and desorption of products as the slow step has been reported for
hydrogenolysis on nickel \(^{18,20}\).

Studies on the kinetics of hydrocarbon hydrogenolysis processes on Group VIII
metals – in particular those of ethane – have also revealed distinct patterns
of behaviour. For ethane hydrogenolysis on each member of Group VIII except iron,
Sinfelt \(^9\) has reported a negative reaction order with respect to hydrogen pressure
indicating that an increase in the latter causes an unfavourable shift in the
adsorption equilibrium and, consequently, a lower concentration of reactive
hydrocarbon intermediates on the surface; similarly, the dependence of reaction
rate on ethane pressure was generally found to be close to first order implying
the presence of reversible adsorption and comparatively low surface coverages by
hydrocarbon species. With larger reactant molecules, the inverse dependence on
hydrogen pressure tends to become even stronger. The behaviour on iron catalysts
is different in that competition for the surface between hydrogen and irreversibly
adsorbed hydrocarbon radicals becomes significant and this is reflected in
hydrocarbon pressure exponents of much less than unity for ethane and n-pentane
hydrogenolysis reactions on supported iron \(^9,10\); the corresponding hydrogen
reaction orders of 0.5 and \(-0.6\), respectively, are much less negative than those
for the other metals and agree with the apparent zero order value obtained in the
present investigation of ethane hydrogenolysis on iron films. There is no sharp
division in behaviour between the noble and non-noble metals, however, with regard
to reaction orders since, although the hydrogen exponent for ethane hydrogenolysis
on cobalt has been observed to vary between -1 and zero and is thus not too remote from the iron value, the corresponding order on nickel catalysts is less than -2 and, hence, is typical of that recorded on the noble metals\(^{(9)}\).

The relative hydrogenolysis activity of each of the Group VIII metals - measured in terms of reaction rate at a specific temperature - is generally not characteristic of the type of metal in question; for example, although platinum appeared to be 10,000 times less active for ethane hydrogenolysis at 473K than iron, the latter was, in turn, less active than the noble metal, osmium, at the same temperature by a similar factor\(^{(9)}\). Sinfelt also observed that the enormous decrease in catalytic activity for ethane hydrogenolysis amongst the noble metals was also accompanied by a large increase in apparent activation energy, the values measured for osmium and platinum being 146 and 226\(\text{kJ mol}^{-1}\), respectively; for the noble metals, therefore, it seems that the wide variation in activity may be primarily associated with the changes in activation energy. The order of activity for ethane hydrogenolysis amongst the non-noble metals was seen to be nickel > cobalt > iron and, in this case, there was a marked compensation effect between pre-exponential factor and activation energy suggesting that the differences in rate detected on these catalysts are not entirely a function of the latter but are also influenced by other factors.

In this connection, attempts have also been made to correlate the catalytic activity of Group VIII metals with their electronic and geometric properties. With regard to the first of these possibilities, extensive use has been made of Pauling's valence bond theory of metals\(^{(21)}\); for catalytic purposes the most relevant aspect of this theory is the 'percentage d-character' of the metallic
bond, a quantity devised by Pauling to represent the degree of participation of electronic d orbitals in the bonding between atoms in a metal lattice and consequently the strength of metal-metal bonds. The catalytic postulate is that the latter may directly influence the strength of bonds formed during chemisorption on metal surfaces, and, in this way, heats of adsorption and, in turn, catalytic activities might then be related to the percentage d-character for each metal. A plot of ethane hydrogenolysis activity against percentage d-character for all the Group VIII metals\(^9\) resulted in not one but two separate curves corresponding to different correlations for the noble and non-noble members, respectively. With each of these categories, the curves showed that an increase in strength of binding of the reactive \(\text{C}_2\) intermediate, estimated in terms of percentage d-character, was broadly associated with an increase in hydrogenolysis activity. The absence of a single relationship between catalytic activity and percentage d-character covering the Group VIII metals collectively also indicates the presence of another activity-determining factor; this is clearly illustrated by the fact that iron has a lower percentage d-character than platinum yet displays much higher hydrogenolysis activity, stronger hydrocarbon adsorption and lower reaction orders with respect to the reactant hydrocarbon.

The present investigation has yielded some indications of the possible influence of geometrical properties on catalytic activity. The mechanistic importance of \(\alpha\gamma\) adsorption in hydrogenolysis on platinum but not on iron may be associated with the fact that the longer of the two metal-metal bond lengths in the face cubic-centred platinum lattice is approximately 1 Å greater than the corresponding distance in the body cubic-centred iron structure. As a similar difference in length applies to pairs of carbon atoms bonded in the \(\alpha\beta\) and \(\alpha\gamma\) positions, respectively, it is likely that \(\alpha\gamma\) adsorption is geometrically more
feasible on platinum; conversely, $\alpha\beta$ adsorbed intermediates should be stereochemically more favourable on an iron surface and similar arguments should be applicable to the other non-noble metals, cobalt and nickel, which have the same crystalline structure as iron and also catalyse hydrogenolysis processes via $\alpha\beta$ adsorption. There is also evidence for geometric considerations in relation to isomerization activity on platinum. Apart from its ability to accommodate $\alpha\gamma$ adsorbed isomerization intermediates, it has been found that the selectivity for rearrangement of isobutane is considerably enhanced on a (111) platinum surface$^{(13)}$; to explain this observation, an intermediate involving three carbon atoms bonded to the surface has been tentatively proposed, in keeping with the presence of triplets of equally spaced metal atoms in the (111) face to which an adsorbed isohydrocarbon may be readily fitted. It is also interesting that the body cubic-centred non-noble metals, which are inactive for isomerization, are not thought to expose (111) planes to the gas phase to the same extent as face cubic-centred metals when they are in the form of low temperature polycrystalline films$^{(22)}$.

In conclusion, it suffices to say from the preceding paragraphs that the catalytic activities of the Group VIII transition metals cannot be wholly ascribed to any particular property or effect; although many parallels and contrasts may be drawn between different categories of metal catalyst or catalytic behaviour, it is clear that a combination of several factors, be they electronic or geometric, kinetic or thermodynamic, controls the overall activities of each of the metals and, in particular, of iron and platinum.

6.2. C.C.-M.S. and Future Studies

In spite of the title of this thesis, it will have been readily gathered
from the results of Chapters 4 and 5 that the combined G.C.-M.S. technique was only employed in a minor fraction of the experiments actually carried out, although, at the same time, it must also be said that a considerable proportion of the effort involved in this work was devoted to development of the apparatus, the experimental procedures and the data handling methods for G.C.-M.S. analysis. The major practical restrictions to more extensive application of the technique in its present form were the expense of recording several hundred mass spectra per run on U.V.-sensitive chart paper and the time required for detailed processing of such a large volume of data from a single experiment. The exact choice of suitable G.C.-M.S. studies and the optimum operating conditions for their execution was therefore limited to that made on the basis of information gathered from a number of exploratory reactions involving gas chromatographic analysis only which themselves served as useful sources of data for estimation of kinetic parameters.

An obvious development which would overcome the difficulties mentioned above and, in particular, the tedious manual measurement of literally thousands of mass spectral peak intensities, is the coupling of the G.C.-M.S. apparatus to an on-line mini-computer which has facilities for digitizing the mass spectrometer signal output, storing the resultant mass spectra and subsequently processing them by the standard methods to obtain the required isotopic distributions. Apart from leading the six-inch ruler to redundancy, on-line data capture might also provide future researchers with 'real-time' bulk retrieval of quantitative catalytic information. Experimentally, however, such a development would almost certainly entail usage of a direct inlet system to the spectrometer to permit insertion of a reference hydrocarbon prior to each G.C.-M.S. study as an aid to the computerized assignment of a mass number to each recorded peak in the mass spectra.
There are two principal types of catalytic experiment to which the G.C.-M.S. analysis technique readily lends itself. The first of these includes systems where a single hydrocarbon reactant participates in more than one process in the presence of deuterium and an example of this was the hydrogenolysis, isomerization and exchange of n-butane with deuterium at high temperatures on platinum, as reported in Chapter 4. The second possibility covers situations where there may be several hydrocarbons competing simultaneously for the catalyst surface, each of them taking part in one or more processes and an instance of this type of experiment was the concurrent hydrogenolysis and exchange of ethane, propane and n-butene with deuterium on an iron film, as reported in Chapter 5. Systems of the latter kind cannot be easily studied unless there exists a temperature at which the range in rates of the competing reactions is not wide enough to make isotopic analysis of the faster ones an impracticality. The interpretation of product distributions may also be difficult in such a system if two or more of the reaction processes yield the same products or, alternatively, if any of the products formed also happens to be one of the hydrocarbon reactants present; this problem will not arise, however, in circumstances where each competing reactant only undergoes exchange with deuterium, since the latter does not involve any rearrangement or breakdown of the carbon skeleton.

The extent to which any G.C.-M.S. experiment satiates the need for information on reaction mechanisms and surface intermediates depends to a considerable degree on the various rates of deuterium labelling processes. This may be clearly illustrated by considering the behaviour observed in simultaneous exchange and hydrogenolysis reactions on platinum and iron. The isotopic content of each hydrogenolysis product will be determined by three modes of deuterium incorporation
exchange of the reactant molecule before it undergoes hydrogenolysis, addition of two deuterium atoms per carbon-carbon bond rupture to yield a saturated product and replacement of hydrogen in the adsorbed hydrogenolysis intermediates. While the first of these three processes occurs much more rapidly than the others on platinum, it is the last of the trio which predominates on iron; the net effect in both cases is that little information can be gained on the nature of the reactive species responsible for hydrogenolysis since with both of these metals, the hydrogenolysis products tend to be extensively deuterated before they reach the gas phase. It is clear, therefore, that systems in which either weak reversible adsorption allows rapid exchange of the reactant or slow product desorption permits extensive surface accumulation of deuterium are not the most suitable for combined G.C.-M.S. analysis; such a conclusion may be generally applicable to exchange and hydrogenolysis of saturated hydrocarbons on metals, the exceptions to the rule being reactions such as those of neopentane on iron where the structure of the molecule exerts a strong influence on the patterns of behaviour observed and useful mechanistic deductions can still be made from the G.C.-M.S. data.

In terms of future research, however, it might be more interesting to shift attention to the study of competing reactions, such as exchange and hydrogenation, on metal oxide catalysts, since the latter tend to favour ionic mechanisms and modes of adsorption which do not vary so widely in strength as with metal film catalysts.
2. J.C. Kempling and D.A. Whan, to be published.
APPENDIX
The effects of correcting for fragmentation by various methods are shown in table 4 for an equilibrated mixture of propanes. The statistical method and the method used by Gault and Kemball \(^{16}\) are unsatisfactory, giving some negative peaks, erratic changes in percentage with respect to deuterium content and consequently poor agreement with the calculated binomial distributions. The empirical method described here is more satisfactory in all respects.

**Table 4.—Distributions of equilibrated propanes**

<table>
<thead>
<tr>
<th></th>
<th>I (^a)</th>
<th>II (^b)</th>
<th>III (^c)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>binomial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d_0)</td>
<td>-0.2</td>
<td>0.0</td>
<td>-1.9</td>
<td>0.0</td>
</tr>
<tr>
<td>(d_1)</td>
<td>-4.2</td>
<td>0.0</td>
<td>-3.3</td>
<td>0.0</td>
</tr>
<tr>
<td>(d_2)</td>
<td>-1.6</td>
<td>0.1</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>(d_3)</td>
<td>2.2</td>
<td>0.5</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>(d_4)</td>
<td>0.0</td>
<td>3.1</td>
<td>1.3</td>
<td>4.7</td>
</tr>
<tr>
<td>(d_5)</td>
<td>9.6</td>
<td>11.5</td>
<td>16.3</td>
<td>14.8</td>
</tr>
<tr>
<td>(d_6)</td>
<td>31.4</td>
<td>27.1</td>
<td>32.5</td>
<td>29.4</td>
</tr>
<tr>
<td>(d_7)</td>
<td>37.4</td>
<td>36.4</td>
<td>31.7</td>
<td>33.4</td>
</tr>
<tr>
<td>(d_8)</td>
<td>19.4</td>
<td>21.4</td>
<td>16.5</td>
<td>16.6</td>
</tr>
<tr>
<td>(M_D)</td>
<td>6.60</td>
<td>6.60</td>
<td>6.39</td>
<td>6.39</td>
</tr>
</tbody>
</table>

\(^a\) fragmentation corrections using a statistical method; \(^b\) using the method described by Gault and Kemball \(^{16}\); \(^c\) using the present method; \(^d\) binomial distribution with the appropriate average deuterium content, \(M_D\), is given for comparison with each set of data.

Typical values of the relative fragmentation of the heavy and light hydrocarbons were

\[
m f_{0,1}/ f_{0,0} \approx 0.65, \tag{10}\]

and \(A\) and \(B\) were given by

\[
A \approx 1/B \approx 1.10. \tag{11}\]

The values in eqn (10) and (11) may be used to estimate fragmentation in cases where calibration data for the perdeutero-hydrocarbon and other labelled species are not available.

**Table 5.—Distribution of equilibrated trans-but-2-enes**

<table>
<thead>
<tr>
<th></th>
<th>(d_0)</th>
<th>(d_1)</th>
<th>(d_2)</th>
<th>(d_3)</th>
<th>(d_4)</th>
<th>(d_5)</th>
<th>(d_7)</th>
<th>(d_8)</th>
<th>(M_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>expt.(^a)</td>
<td>1.09</td>
<td>6.59</td>
<td>17.78</td>
<td>26.76</td>
<td>25.16</td>
<td>15.19</td>
<td>5.69</td>
<td>1.38</td>
<td>0.35</td>
</tr>
<tr>
<td>binomial</td>
<td>1.08</td>
<td>6.59</td>
<td>17.54</td>
<td>26.69</td>
<td>25.38</td>
<td>15.45</td>
<td>5.87</td>
<td>1.28</td>
<td>0.12</td>
</tr>
</tbody>
</table>

\(^a\) fragmentation corrections made by means of eqn (3).

Eqn (3) can also be used to obtain fragment corrections for unsaturated hydrocarbons. Table 5 shows the excellent agreement between observed and calculated isotopic compositions of the trans-but-2-enes prepared by reaction of light and heavy butenes over magnesium oxide \(^{22}\) at 425 K and separated by gas chromatography.
Consider the formation of the fragment ion $C_nH_{m-x}D_{i+y}$ from the hydrocarbon molecule $C_nH_{N-m}D_m$. Let $mW_{x,y}$ be the observed height of the peak corresponding to this fragment ion relative to the height of the peak for the parent ion $C_nH_{N-m}D_m^+$. Let $mW_{x,y}$ be the corresponding calculated fragmentation factor for cases where direct observation is difficult. Define factors $A$ and $B$, analogous to the $\Gamma$ and $\Pi$ factors originally proposed by Evans et al., such that

$$A = \frac{\text{observed probability of losing an H atom from } C_nH_{N-1}D}{\text{statistical probability of losing an H atom from } C_nH_{N-1}D'}$$

(1)

and

$$B = \frac{\text{observed probability of losing a D atom from } C_nHD_{N-1}}{\text{statistical probability of losing a D atom from } C_nHD_{N-1}}.$$  

(2)

Then the empirical expression used for calculating a fragmentation factor is

$$mW_{x,y} = Z \left[ \frac{x^{0f_{x,y}+y}Nf_{0,x+y}}{x+y} \right] x^{A^{m+y}B^{N-m}}$$

(3)

where $Z$ is the a priori statistical factor i.e. the probability of any particular fragmentation process based on molecular composition only. The first term in square brackets in eqn (3) allows for the preferential dissociation of C—H compared with C—D bonds. The second term in square brackets incorporates the principle that the factors $A$ and $B$ have to be raised to powers corresponding to the number of D or H atoms respectively in the molecule. In order to illustrate the use of eqn (3), the correction factor for the fragment ion formed from the isotopic propane, $C_3H_4D_4$, by the loss of one H atom and one D atom is

$$A = 2 \times \frac{f_2.0 + 8f_{0.2}}{2} \frac{A^4 + B^4}{2}.$$  

(4)

Estimates of $A$ and $B$ can be obtained from the mass spectra of appropriately labelled compounds or, more economically, by using an equilibrated mixture of isotopic hydrocarbons. We shall illustrate this approach for propane for which an equilibrated mixture of isotopic species can be prepared readily by exchange of $C_3H_8$ and $D_2$ over a tungsten film. The method depends on an assumption that the equilibrium constants, $K_{m+1}$, for the interconversion equilibria

$$C_3H_{8-m}D_m + C_3H_{6-m}D_{m+2} \rightleftharpoons 2C_3H_{7-m}D_{m+1},$$

(5)

correspond closely to values expected for a random distribution of the hydrogen and deuterium atoms between the various isotopic species of the hydrocarbon. Let $p_m$ be the height of the peak in the mass spectrometer corresponding to the mass of the molecule $C_3H_{N-m}D_m$ after allowing for naturally occurring isotopes and $p'_m$ the value after correction for the presence of fragment ions.

$A$ is obtained from $p_6$, $p_7$ and $p_8$. No fragment ions contribute to $p_7$ and $p_8$ so that

$$p'_7 = p_7 \quad \text{and} \quad p'_8 = p_8.$$  

(6)

The value of $\gamma f_{1,0}$ is obtained from the following pair of equations.

$$p'_6 = p_6 - p_8 \times \gamma f_{0,1} - p_7 \times \gamma f_{1,0},$$  

(7)

and

$$K_7 = \frac{p'_6 \times p'_8}{p_6 \times p_8} = \frac{g^2}{1 \times 28^2}.$$  

(8)

Then $A$ is evaluated from the relationship

$$\gamma = \frac{\gamma f_{z,0} / \gamma f_{1,0}}{\gamma f_{z,0} / \gamma f_{0,0} = B}.$$  

(9)

Use of $p_6$ in equations analogous to (5) and (7) gives a value of $\gamma f_{0,1}$ and hence $B$ from eqn (5).
adsorption of butane is rapid and readily reversible. This is in marked contrast to reactions on iron. The exchange of n-butane on platinum is so extensive that there is a tendency for any molecule which exchanges to become almost equilibrated with the deuterium–hydrogen gas mixture. A random distribution of hydrogen and deuterium atoms between the "hydrogen" and exchanged "hydrocarbon" would give \( M = 7.4 \); the experimental value of 7.9 in table 3 shows that there is an isotope effect in the direction expected.

Because of the extensive and rapid exchange of n-butane the products of hydrogenolysis would also be expected to have equilibrium concentrations of deuterium. That this is the case is illustrated in table 3 where the propane, for example, produced from the reaction of n-butane had a deuterium content indicating that 82% of the "hydrogen" atoms in the molecule were deuterium which is in good agreement with the figure of 79% mentioned for n-butane. Because of the rapid equilibration of the "hydrogen" in the system the g.c.–m.s. experiments could not contribute information about the mechanism of the hydrogenolysis process.

The authors acknowledge a grant from the S.R.C. for the purchase of the apparatus used in this work. R. S. D. thanks the British Petroleum Co. Ltd., for a studentship.

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APPENDIX

Corrections to allow for the formation of fragment ions are important in the determination of the composition of isotopically labelled hydrocarbons from the observed mass spectra. The use of a statistical approach assuming equally probable loss of hydrogen or deuterium atoms is satisfactory only if the extent of fragmentation is small and the amount of exchange is limited. When the mass spectrum of the fully deuterated hydrocarbon is available, a better assessment of fragmentation may be made by allowing for the greater chance of rupture of C—H than C—D bonds, as for example, in the type of scheme devised by Gault and Kemball.

A further improvement can be achieved by allowing for the dependence of fragmentation of a C—H or C—D bond on the nature of the other bonds in the molecule. We have devised an empirical method of calculating fragmentation corrections incorporating statistical factors, the preferential rupture of C—H compared with C—D bonds and the influence of other bonds.
Ethane hydrogenolysis behaves in a manner contrary to that normally observed for reactions on metal films in that an acceleration in rate is observed before the reaction assumes zero order behaviour. The presently reported results cannot be easily reconciled with the reaction mechanism proposed by Cimino et al.\textsuperscript{12} used to explain the observations made in previous investigations of this reaction on platinum.\textsuperscript{1,13} We attempt to explain this phenomenon in the following way. Breaking of the carbon-carbon bond in ethane appears to require a high energy of activation yet the rate of hydrogenolysis of ethane at 633 K is comparable to that of other hydrocarbons. Because of this, the rupture of the carbon-carbon bond will clearly be slow and is thus likely to be rate determining at lower temperatures. Evidence from exchange reactions is that the adsorption and desorption of methane is slower than that of other hydrocarbons, therefore there may be conditions under which ethane hydrogenolysis is limited in part by the rate of desorption of methane. Under such conditions $C_1$ units will accumulate on the surface until the rate of their desorption as $CH_4$ equals the rate of the rupture of carbon-carbon bonds.

This suggestion is corroborated by the considerably shorter induction period displayed by a second reaction on a platinum film already extensively covered with $C_1$ residues from a first reaction before the faster subsequent rate is again attained (table 1, runs 2 and 3). The importance of the balance on the surface between adsorbed reactant and product species with regard to the general course of the hydrogenolysis reaction is further reflected in the initial and subsequent activation energies for ethane hydrogenolysis. While the initial activation energy, 222 kJ mol\textsuperscript{-1}, was found to be similar to the values of 226 and 239 kJ mol\textsuperscript{-1} reported for ethane hydrogenolysis on platinum films\textsuperscript{4} and silica supported platinum,\textsuperscript{13} respectively, the activation energy for the subsequent reaction, 148 kJ mol\textsuperscript{-1}, was much lower indicating that the activation energy depended markedly on the extent and composition of the material adsorbed on the surface.

The product distributions from the reactions on platinum films indicate that, to a large extent, only one carbon–carbon bond is broken per visit of the reactant molecule to the surface. For example the reaction of propane yielded ethane and methane in approximately equal amounts.

Reactions of n-butane, isobutane and neopentane included skeletal isomerization of the reactant as had been observed previously.\textsuperscript{1,2,6} Our results for the initial stages of the n-butane reaction are slower than those reported by Anderson and Avery\textsuperscript{4} but agree with theirs in all other respects. The similar activation energies for hydrogenolysis and isomerization support the concept of a common mechanism for the two reactions. Similarly, the observations on the initial behaviour of the reactions of isobutane and neopentane on platinum correspond to those reported elsewhere. The non-preferential inhibition of hydrogenolysis or isomerization reactions on platinum, either during a first or subsequent reaction on the same catalyst, suggests that the poisoning occurs generally over the catalyst surface and not on sites peculiar to any particular process. The normal exchange reaction of butane was also observed to be poisoned to a similar extent.

There is always the possibility that activation energies are rendered suspect because of more extensive poisoning at higher temperatures and it is significant to note that the results quoted in table 1 for the subsequent isomerization of n-butane would indicate a "turning over" of the Arrhenius plot with the reaction rate decreasing as the temperature is raised.

The experiments performed using the gas chromatograph–mass spectrometer combination show clearly the extremely rapid exchange which takes place on the platinum surface and which indicates that, under these conditions, dissociative
DISCUSSION

The differences in the characteristics of the reactions of the various hydrocarbons investigated are obvious from fig. 1 where the kinetic behaviour is illustrated. The rate of the reaction of ethane is seen to increase with time in contrast to those of n-butane, isobutane and neopentane where retardation was observed. The reaction of propane appeared to maintain an almost constant rate throughout the course of an experiment. These differences in behaviour between the various hydrocarbons are striking.

Fig. 1 illustrates clearly the retardation in rate observed for reactions of n-butane and isobutane. This type of poisoning of the reactions was found to be greatest for neopentane and more with iso- and with n-butane. In the case of n-butane the rate decreased with time in a manner corresponding approximately to a process conforming to first order kinetics and this observation has been used to evaluate rates for this reactant.

The exact nature of the apparent poisoning of the n-butane, isobutane and neopentane reactions is difficult to elucidate precisely, but several conclusions can be drawn from the experimental evidence provided. The results from experiment 14 in table 1 imply that a progressive sintering of the catalyst would not give rise to the degree of slowing down observed, while those of experiment 18 illustrate that competition between reactant and product ethane only slightly reduces the rate of reaction. The greater divergence between initial and subsequent rates for the reaction of n-butane at higher temperatures suggests that the concentration of species responsible for the poisoning of the reaction increases with temperature. That build up of irreversibly adsorbed species may be responsible for the poisoning is further stressed by the continued fall in rates for consecutive n-butane experiments on the same platinum film shown in table 1, runs 10-13.

It has been suggested by Anderson and Avery \(^5\) that species exhibiting partial carbonium ion character may be intermediates in reactions on platinum. Similarly Matsumoto et al.\(^7\) have interpreted the hydrogenolysis and skeletal isomerization of saturated hydrocarbons on platinum by carbonium ion mechanisms. It is interesting that our results show that poisoning is only severe for the molecules neopentane and isobutane which may give tertiary carbonium ion formation or for n-butane where such ion formation may be significant via isomerization to isobutane. Presumably the reactions of propane and ethane do not suffer extensive poisoning because of their inability to form reasonably stable carbonium ions.

The formation of carbonium ions per se is not a sufficient criterion for the poisoning of the reactions since species of carbonium ion character are likely to be important intermediates for hydrogenolysis and isomerization.\(^5\) What is significant is that species of carbonium ion nature may dimerize or polymerize olefinic material thus blocking catalytically active sites. The formation of \(\text{C}_4\) olefins in the initial stages of a reaction of n-butane on a previously used film may be assisted by carbonium type fragments on the surface. Gas phase thermodynamic calculations for the equilibrium

\[
\text{n-C}_4\text{H}_{10} \rightleftharpoons \text{n-C}_4\text{H}_8 + \text{H}_2
\]

at 683 K predict an olefin concentration of approximately 4 % under our experimental conditions.

The reaction of propane, as may be seen from fig. 1, followed zero order behaviour during the course of a reaction. Mechanisms depending on carbonium ions are less likely with propane and thus no poisoning by larger molecules formed as side products would be anticipated.
An experiment with added ethane was carried out to see if this influenced the course of a reaction. A comparison of reactions 18 and 16 in table 1 shows that rates in the presence of ethane were about half those of isobutane alone.

**NEOPENTANE.**—Neopentane was found to undergo hydrogenolysis readily at 633 K, the reaction poisoning more rapidly than that of any other hydrocarbon investigated. Rates for a neopentane reaction are quoted in table 1, run 19. Because the products of the reaction of neopentane underwent further reaction, an initial distribution was difficult to determine. A typical product distribution for a reaction of neopentane at 633 K at 20 % conversion is given in table 2.

**GAS CHROMATOGRAPH—MASS SPECTROMETER STUDIES**

The combined g.c.-m.s. technique was applied to the reaction of n-butane with deuterium at 683 K and the results are quoted in table 3. The exchange of n-butane with deuterium was extremely rapid in relation to hydrogenolysis or isomerization. Extensive incorporation of deuterium was also observed into each of the hydrogenolysis products. The isotopic distribution of the exchanged n-butane was found to be in good agreement with a binomial distribution calculated from the value of the mean deuterium content which was 7.9 for the reaction in table 3.

### Table 3.—Isotopic Contents of Products from First and Second Reactions of n-Butane on Platinum at 683 K

| Composition | Mean Deuterium Content | Isotopic Content/|  |
|-------------|------------------------|-----------------|
|             |                        | d₁ | d₂ | d₃ | d₄ | d₅ | d₆ | d₇ | d₈ | d₉ | d₁₀ |
| n-butane    | 79                     | 0.1 | 0.0 | 0.1 | 1.5 | 4.3 | 9.6 | 20.0 | 29.7 | 24.1 | 10.7 |
| n-butane    | 7.9                    | 0.0 | 0.0 | 0.1 | 0.8 | 3.4 | 10.3 | 21.8 | 30.0 | 24.5 | 9.0  |
| propane     | 3                      | 6.5 | 0.0 | 0.0 | 2.0 | 3.4 | 8.2 | 28.6 | 38.7 | 19.1 | —    |
| propane     | 6.5                    | 0.0 | 0.1 | 0.6 | 3.3 | 12.1 | 27.6 | 35.9 | 20.4 | —    | —    |
| isobutane   | 1b                     | —   | —   | —   | —   | —   | —   | —   | —   | —    | —    |
| ethane      | 3.5                    | 4.7 | 1.0 | 2.0 | 9.0 | 25.0 | 38.0 | 25.0 | —    | —    | —    |
| methane     | 1.5                    | 3.2 | 2.0 | 20.0 | 39.0 | 39.0 | —   | —   | —   | —    | —    |

For a second reaction on the platinum film, accurate isotopic analysis in the initial stages of the reaction was only possible for n-butane because of the small amount of isomerization and hydrogenolysis. The rate of exchange in a second reaction was less than that of a first reaction by a factor comparable to that for the reduction in rates of isomerization and hydrogenolysis. The isotopic composition of the exchanged n-butane in a second reaction was not binomial but displayed maxima at species having one or two deuterium atoms. Similar distributions of products have been observed for the exchange of n-butane with deuterium over platinum at lower temperatures.
and subsequent rates increased with temperature for both hydrogenolysis and isomerization. The ratio of initial to subsequent rates was observed to be similar for both hydrogenolysis and isomerization indicating that both processes were being poisoned to comparable extents.

The Arrhenius equations obeyed by initial hydrogenolysis and isomerization were

\[ r_1(\text{n-butane}) = 10^{24.5} \exp \left(-91.1 \times 10^3 / RT \right) \]

and

\[ r_3(\text{n-butane}) = 10^{24.2} \exp \left(-90.3 \times 10^3 / RT \right) \]

respectively.

The parameters for each process are equal within experimental error.

Further evidence for the poisoning of the reactions of n-butane was obtained by carrying out four consecutive experiments on the same platinum film at 683 K. The initial and subsequent rates, quoted in table 1, runs 10-13, indicated that the rate of poisoning for both hydrogenolysis and isomerization was less in second and later reactions than in the first. Table 2 shows that no significant change was observed in the initial product distribution in terms of the ratio of hydrogenolysis to isomerization, implying no preferential inhibition of either of these reactions. Formation of C\textsubscript{4} olefins, not detected during a first experiment on a catalyst at any temperature, was found to occur during second and subsequent reactions at 683 K. The quantity of olefin formed rose to a maximum of \( \sim 1.5 \% \) of the total product in the early stages of each further reaction and then declined slowly with time.

An attempt to recover any carbon lost to the catalyst was made by heating a used film immediately after the reaction in the presence of a fresh quantity of deuterium. No significant quantity of methane was detected. This observation agreed with the fact that the decrease in size between successive samples withdrawn from the reaction vessel could be attributed to loss due to sampling.

The possibility that progressive sintering of the catalyst was the cause of the deceleration in rate observed was investigated by carrying out a reaction of n-butane with deuterium at 663 K on a platinum film previously sintered for 1 h in vacuum at 673 K. Reaction rates, quoted in table 1, runs 9 and 14, for experiments at 663 K on unsintered and sintered films respectively, were found to be comparable, the distinct slowing of reaction also being observed on the sintered catalyst.

Finally, to confirm that reactions in the presence of deuterium, used merely for convenience, did not differ from those in the presence of hydrogen an experiment was conducted at 553 K involving n-butane and hydrogen. Runs 5 and 15 as quoted in table 1 illustrate that there is no significant difference between reactions conducted with hydrogen and those with deuterium.

**ISOBUTANE.—**Data from reactions of isobutane on platinum at 633 K were treated in the same manner as those for n-butane. Estimation of subsequent rates for isomerization was more difficult than with n-butane as poisoning was more extensive as can be seen from fig. 4. Values for the initial and subsequent rates of hydrogenolysis and isomerization for a reaction of isobutane are given in table 1, run 16. Run 17 in the same table, where the subsequent rates do not differ from the initial rates by as much as was the case for run 16, shows that less poisoning was observed for a second reaction on the same platinum film.

The initial product distribution for a reaction of isobutane, as illustrated in table 2, showed a much greater proportion of isomerization than was observed with n-butane. This product distribution did not vary significantly between first and second experiments on the same film, again indicating no preferential poisoning of either hydrogenolysis or isomerization.
this reaction and for a second reaction on the same film is given in table 2. Considering hydrogenolysis alone, the ratio of propane : ethane : methane is not 3 : 2 : 1 which would be expected on the basis of equally probable single carbon–carbon bond breakage in the hydrogenolysis step.

The relative amounts of hydrogenolysis products were found not to vary significantly with the reaction temperature. The overall rate of disappearance of n-butane normally followed first order kinetics but at high temperatures the fall off in rate with time was initially greater than that expected on the basis of first order behaviour. This point is illustrated in fig. 3 which contrasts the first order rate plots for n-butane reactions at 553 and 683 K.

Initial and subsequent rates for isomerization and hydrogenolysis were calculated by assuming that interconversion of n-butane and isobutane was possible and that either of these molecules could be irreversibly hydrogenolyzed to species containing less than four carbon atoms. To examine the isomerization equilibrium alone it was possible to disregard the hydrogenolysis reaction by normalizing the total C₄ entities present at each experimental point to 100 %. The equation used to evaluate the information from the reversible first order isomerization was

\[ \ln \left( x - x_e \right) = \ln \left( 100 - x_e \right) - \left( k_f + k_r \right) t \]

where \( x \) is the percentage of reactant at time \( t \), \( x_e \) is the percentage of reactant at equilibrium, \( k_f \) is the rate constant for the reaction by which isobutane is formed from n-butane and \( k_r \) is the rate constant for the reverse reaction. As may be seen from fig. 4, this equation accurately accounted for the isomerization of n-butane at 553 and 683 K using thermodynamic equilibrium values of \( x_e \) of 50.7 and 58.9 % respectively.

![Fig. 4.—First order reversible kinetic plots for the isomerization of n-butane at 553 and 683 K and isobutane isomerization at 633 K on platinum: □, n-butane at 553 K; ×, isobutane at 633 K; ○, n-butane at 683 K.](image)

Subsequent rates for hydrogenolysis and isomerization were estimated from first order plots of the types shown in fig. 3 and 4, while all initial rates were determined using numerical methods as described earlier.

It is apparent from table 1, experiments 5–10, that the divergence between initial
HYDROGENOLYSIS OF HYDROCARBONS ON Pt FILMS

Fig. 2.—Reaction of n-butane in the presence of deuterium on a platinum film at 683 K: ×, methane; O, ethane; ●, propane; □, isobutane; □, n-butane.

TABLE 2.—PRODUCT DISTRIBUTIONS

<table>
<thead>
<tr>
<th>run number</th>
<th>reactant</th>
<th>T/K</th>
<th>n-C₄</th>
<th>iso-C₄</th>
<th>C₃</th>
<th>C₂</th>
<th>C₁</th>
<th>iso-C₅</th>
<th>n-C₅</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>n-butane (first)</td>
<td>683</td>
<td>—</td>
<td>17</td>
<td>32</td>
<td>32</td>
<td>19</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>n-butane (second)</td>
<td>683</td>
<td>—</td>
<td>17</td>
<td>35</td>
<td>27</td>
<td>21</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>isobutane (first)</td>
<td>633</td>
<td>73</td>
<td>—</td>
<td>16</td>
<td>4</td>
<td>6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>isobutane (second)</td>
<td>633</td>
<td>73</td>
<td>—</td>
<td>17</td>
<td>5</td>
<td>5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>19</td>
<td>neopentane (first)</td>
<td>633</td>
<td>7</td>
<td>16</td>
<td>12</td>
<td>9</td>
<td>8</td>
<td>42</td>
<td>6</td>
</tr>
</tbody>
</table>

* All product distributions, in terms of carbon content, are initial except for neopentane which is at 20% conversion.

Fig. 3.—First order plots for reactions of n-butane on platinum at: □, 553 K; O, 683 K. A, first order region.
time curves. The reactions of the butanes exhibited approximately first order behaviour at later stages of reaction and, for convenience, the subsequent rates for these reactants were obtained by extrapolation of first order kinetic plots.

The inherent analytical inaccuracy during the first few minutes of reaction, in particular at higher temperatures, necessitated the use of numerical methods for accurate estimation of initial rates. The experimental points from the chromatographic analyses were first fitted to a smooth curve from which the initial rate was calculated by numerical differentiation.

Where activation energies are quoted these were determined using the Arrhenius equation and frequency factors were evaluated in units of molecules s\(^{-1}\) m\(^{-2}\) by assuming an effective surface area of 3 \times 10^{-2} \text{ m}^2 of platinum for each experiment. This area assumes a roughness factor of 2 for a platinum film. This assumption was made because film weights and geometric areas showed little variation and, at the high reaction temperatures used, sintering would quickly reduce the film area to a constant value of this order.\textsuperscript{1}

The appropriate reaction rates for each system studied are quoted in table 1.

**CHROMATOGRAPHIC STUDIES**

**ETHANE.**—The reactions of ethane, runs 1-3 in table 1, were each characterized by an induction period during which hydrogenolysis to methane occurred slowly. Subsequently, as is illustrated in fig. 1, the reaction followed zero order kinetics with respect to ethane at an increased rate. For a second experiment on the same platinum film the induction period was reduced to approximately half that of a first experiment and the hydrogenolysis quickly accelerated to a subsequent rate comparable to that for the first reaction.

The Arrhenius equations obeyed by initial and subsequent ethane hydrogenolysis, expressed as molecule s\(^{-1}\) m\(^{-2}\), were

\[
r_1(\text{ethane}) = 10^{34.6} \exp\left(-222 \times 10^3/RT\right)
\]

and

\[
r_2(\text{ethane}) = 10^{28.7} \exp\left(-148 \times 10^3/RT\right)
\]

respectively, with activation energies in kJ mol\(^{-1}\). The estimated errors in the kinetic parameters are \(\pm 4 \text{ kJ mol}^{-1}\) in the activation energy and a factor of two in the frequency factor.

**PROPANE.**—A typical reaction of propane at 633 K is shown in fig. 1, and the rates determined from this experiment are quoted in table 1, run 4. Propane obeyed approximately zero order kinetics and the subsequent rate quoted in the table was representative of all but the first few minutes of reaction up to at least 75% conversion.

If propane hydrogenolysis involves only the fission of a single carbon–carbon bond then we would expect a product distribution of 66.7% ethane and 33.3% methane, in terms of the carbon contents of the molecules. The observed initial distribution was 63.4% ethane and 36.6% methane indicating that a small fraction of the propane molecules hydrogenolyzed completely to methane in a single visit to the catalyst.

**n-BUTANE.**—As detailed in table 1, the reaction of n-butane was studied in the temperature range 553-583 K. Hydrogenolysis to species of lower carbon number was found to be accompanied by reversible isomerization of the reactant to isobutane. A typical reaction at 583 K, showing clearly the pattern of products and the slowing of reaction with time, is illustrated in fig. 2. The initial distribution of products for
It is apparent from fig. 1 that, for any particular experiment, it was possible to extract two distinct rates representative of the kinetic behaviour at "initial" and "subsequent" stages of reaction. In order that these initial and subsequent rates should be truly comparable, the latter were extrapolated to zero time and expressed in the form of \( \% \text{ min}^{-1} \). In this way subsequent rates for ethane and propane experiments were extrapolated from the zero order portion of their concentration against time.

![Fig. 1.—Reactions of ethane, propane, isobutane and n-butane in the presence of deuterium on platinum films at 633 K: O, ethane; O, propane; □, isobutane; □, n-butane.](image)

<table>
<thead>
<tr>
<th>Table 1.—Reaction rates</th>
</tr>
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<tbody>
<tr>
<td>run number</td>
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<td>1</td>
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<td>17</td>
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<tr>
<td>18</td>
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<tr>
<td>19</td>
</tr>
</tbody>
</table>

\( a \) Reaction on same film as experiment 2; \( b \) reaction on same film as experiment 10; \( c \) reaction on a presintered film; \( d \) reaction in the presence of hydrogen (\( \text{H}_2 \)); \( e \) reaction on same film as experiment 16; \( f \) reaction of 1:1 mixture of isobutane and ethane; \( \theta \) all reactions were carried out with an 11.5:1 ratio of \( \text{D}_2 : \) hydrocarbon unless otherwise stated.
EXPERIMENTAL MATERIALS

Methane, ethane, isobutane and deuterium (99.5 %) were supplied by Cambrian Chemicals, Ltd. Propane and n-butane were obtained from Phillips Petroleum Co. and were of research grade. High purity neopentane (99.9 %) was supplied by the Chemical Standards Division of the N.P.L. All gases were purified either by distillation from liquid nitrogen traps, in the case of hydrocarbons, or diffusion through a heated palladium-silver alloy thimble in the case of deuterium or hydrogen.

For the preparation of the evaporated film catalysts the tungsten was pure grade, supplied by the Tungsten Manufacturing Co. Ltd., and the platinum was Specpure quality supplied by Johnson, Matthey and Co., Ltd.

APPARATUS AND PROCEDURE

The apparatus used for this work was identical to that described previously. Essentially, this consisted of a static reaction system of volume $2.44 \times 10^{-4}$ m$^3$ coupled via a gas sampling valve to a Perkin-Elmer type F11 gas chromatograph. The normal reaction mixture consisted of 427 N m$^{-2}$ of hydrocarbon and 4.91 kN m$^{-2}$ of deuterium measured at 273 K corresponding to $2.76 \times 10^{19}$ molecules of hydrocarbon in the reaction vessel and a deuterium : hydrocarbon ratio of $11.5 : 1$.

Platinum films were prepared by evaporation from 0.3 m of 0.1 mm diameter platinum wire supported by 0.15 m of 0.3 mm diameter tungsten wire. Each film weighed about 10 mg and had a geometric surface area of approximately 0.015 m$^2$.

By means of the evacuated Perkin-Elmer gas sampling valve quantities of material, amounting to $\sim 2.5 \%$ of the contents of the reaction vessel, could be withdrawn and analyzed on an 8 m column of bis-2-methoxyethyl adipate (13.5 %) and di-2-ethylhexyl sebacate (6.5 %) on 60-80 mesh Chromosorb P operated at room temperature. For experiments involving only gas chromatography the carrier gas was nitrogen and for those involving gas chromatography and mass spectrometry it was helium. The output from the chromatograph column could be fed either to a flame ionization detector or through a sintered glass molecular separator to an A.E.I. MS 20 Rapide mass spectrometer.

For experiments involving only chromatography, the integrated areas of peaks produced by the flame ionization detector were used to calculate product distributions at different extents of reaction. Results are expressed in terms of the carbon present in the system. Mass spectral data from the g.c.-m.s. studies were corrected for background, naturally occurring isotopes and for fragmentation of the molecules within the ion source of the mass spectrometer. Details of the fragmentation corrections are given in the Appendix to this paper, as it was found that a statistical fragmentation scheme based on random loss of either a hydrogen or deuterium atom was inadequate for accurate analysis of mixtures of isotopic propanes or ethanes.

To allow for partial separation of the isotopic hydrocarbons in the gas chromatographic column, summation of the intensities for each mass number was carried out using Simpson's rule.

RESULTS

Each reaction was followed to a considerable degree of conversion to allow observation of any possible influence of product formation on the course of the reaction. Fig. 1 illustrates the comparative behaviour of ethane, propane, n-butane and isobutane on platinum at 633 K. In terms of the overall rate of disappearance of reactant, the n-butane and iso-butane reactions were found to decelerate markedly with time while that of propane remained constant exhibiting the character of a zero-order process. With ethane, however, the rate of reaction accelerated with time. Neopentane behaved similarly to the butanes but with a sharper decline in rate as the reaction proceeded.
The reactions of ethane, propane, n-butane, isobutane and neopentane have been examined in the presence of deuterium on platinum films. Details of the products of exchange, hydrogenolysis and, where possible, isomerization are reported. The kinetic behaviour of the hydrogenolysis reaction showed a trend in that reactions of ethane were acceleratory, those of propane maintained a constant rate and those of molecules with four or more carbon atoms decelerated with time. The retardation in rates was much more marked with branched chain than with linear hydrocarbons.

The results are discussed in terms of the nature of the adsorbed species accumulating on the surface, species possessing some carbonium ion character being likely precursors to the material responsible for the observed poisoning. Little additional mechanistic information was obtained from an analysis of the deuterium contents of the various molecules as exchange was fast compared to hydrogenolysis or isomerization, leading to rapid isotopic equilibration.

A fragmentation correction scheme taking into account the influence of molecular composition on bond rupture has also been developed for analysis of the mass spectral data.

The ability of platinum to catalyze the hydrogenolysis of saturated hydrocarbons is well known and has been the subject of several investigations. In particular, significant contributions to the understanding of the hydrogenolysis and isomerization of n-butane on platinum have been made by Anderson and Avery although they, in common with other workers in this field, have limited their study to the initial stages of reaction. For example, Anderson and Baker quoted experimental results for less than 10 % of reaction.

We believe that useful information about the behaviour of alkanes on platinum in the presence of hydrogen may be obtained by examining the kinetics of such reactions at more extensive conversions when the effects of possible competition for surface sites between reactant and products may be important. Such competition is one of several possible causes of the retardation in rate or self-poisoning observed in reactions of neopentane on platinum. It is also indicated that poisoning increases as the ratio of hydrogen to hydrocarbon is reduced and, with some hydrocarbons, significant quantities of the appropriate olefins have been detected.

The recently developed technique of using a combination of gas chromatography coupled with high speed mass spectrometry to monitor the simultaneous labelling of reactant and products with deuterium has been shown to provide interesting information about the reactions of hydrocarbons on iron catalysts. It was hoped that this system could similarly be of use for reactions on platinum, although it was realized that the ability of platinum to cause rapid extensive exchange at low temperatures, resulting in isotopic equilibration, might be a serious limitation.
The application of a combined gas chromatograph–mass spectrometer to study the deuterolysis of neopentane over iron films

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(Received 26 November 1971)

INTRODUCTION

Exchange reactions of hydrocarbons have generally been investigated using a direct leak between the reaction vessel and the mass spectrometer (Kemball 1951). This technique is inadequate for more complex catalytic systems involving multi-hydrocarbon mixtures because fragmentation of the larger hydrocarbons interferes with the observation of the smaller hydrocarbons. Some reactions have been studied by trapping each component after gas-chromatographic separation and subsequent individual analysis (Anderson & Avery 1966, 1967). However, this method is very tedious and open to the hazards of poor trapping (Biemann 1962). Also, because very large samples are required, only one sample can be taken per reaction mixture and initial product distributions are difficult to obtain.

The alternative is a direct analysis of the hydrocarbons after gas-chromatographic separation by a fast-scanning mass spectrometer. In this way, smaller samples are required and these can be taken intermittently as the reaction progresses. This paper describes the development of the technique specifically with reference to reactions involving hydrocarbons and deuterium.

Because iron is relatively poor as an exchange catalyst for straight-chain para-fins (Dowie, Gray, Whan & Kemball 1971), excessive exchange will be less of a complicating factor in examining hydrogenolysis intermediates. Over some transition metals, such as platinum, the exchange reaction is so fast with respect to hydrogenolysis that the hydrocarbons are quickly equilibrated with the hydrogen-deuterium pool and the intermediate species are difficult to interpret (Dowie,
Kemball & Whan 1972). Neopentane is an interesting reactant because the quaternary carbon atom allows only the $\alpha\gamma$ mode of two-carbon adsorption. The $\alpha\gamma$-exchange mechanism has previously been shown to be slow (Kemball 1954). The hydrogenolysis of paraffins is usually thought to occur through an intermediate adsorbed to the surface at more than one carbon (Anderson & Baker 1963; Sinfelt 1969).

**EXPERIMENTAL**

**Apparatus**

Reactions were carried out in a static system (figure 1) using conventional vacuum techniques for the preparation of reaction mixtures. The reactor ($2.44 \times 10^{-4} \text{ m}^3$) was connected to a Perkin-Elmer gas sampling valve through a stopcock so that the stainless steel sample loop ($5 \times 10^{-6} \text{ m}^3$) could be evacuated between samples.

![Diagram](image)

Figure 1. Combined gas chromatograph–mass spectrometer; H, hydrocarbon source; D, deuterium source; M, mixing volume; V, vacuum line; R, reactor; W, three-way valve; G, gas-sampling valve; He, helium carrier gas; C, chromatographic column; F, flame ionization detector; J, capillary tubing; S, Biemann-Watson separator; T, throttling valve; P, rotary pump; MS, mass spectrometer; E, electron multiplier; A, total ion signal; B, mass-spectrometric scan.

Separation of the hydrocarbons was provided by a Perkin-Elmer F11 gas chromatograph fitted with an 8 m column of bis-2-methoxyethyladipate (13.5%) and di-2-ethylhexylsebacate (6.5%) on 60/80 mesh chromosorb P. The column was maintained at room temperature and helium carrier gas was fed at a pressure of $310 \text{ kPa}$ and a flow rate of $0.37 \times 10^{-6} \text{ m}^3 \text{s}^{-1}$. The effluent from the column could either be routed to a flame ionization detector for normal gas-chromatographic analysis or to the mass spectrometer. A 1 m length of capillary stainless steel tubing was employed to reduce the pressure between the gas chromatograph and the mass spectrometer. The interface between the chromatograph and the mass spectrometer...
A combined g.c.–m.s. technique for studying catalysis

was an all-glass Biemann–Watson molecular separator (Watson & Biemann 1964) operated at room temperature. The removal of helium from the chromatographic effluent was accomplished by a rotary pump and the efficiency of transfer of the hydrocarbon-enriched sample to the spectrometer was controlled by a throttling valve in the rotary pump line; optimum operational pressure in the ion source was 6.67 mPa. Under the experimental conditions, less than 10 % of the low molecular mass hydrocarbons was transferred to the ion source. An A.E.I., M.S. 20 ‘Rapide’ mass spectrometer, a single-focusing π-radian-deflexion instrument was used with magnetic scanning. The acceleration potential was 250 V and ionizing electrons at 20 eV were used to give good sensitivity but without ionization of helium (ionization potential 24 eV). A collector to measure total ion current was positioned to intercept about 15 % of the ion beam and thus provide a trace of the components entering the spectrometer. The fastest mass spectrometer scan speed was 1 s per decade of mass with a reset time of 1 s, allowing about 20 to 40 scans per component between preset upper and lower mass limits. These signals were amplified using an electron multiplier and recorded at three different attenuation levels on photographic paper using an ultraviolet recorder.

**Materials**

Neopentane of 99.9 % purity was supplied by the Chemical Standards Division, National Physical Laboratory. Deuterium (99.5 %) and any other hydrocarbons (99 %) used for calibration purposes were supplied by Cambrian Chemicals. Deuterium was further purified by diffusion through a heated palladium/silver alloy thimble. The iron wire, from which the films were prepared, was Johnson Matthey ‘Specpure’ grade with total impurities of less than 15 parts/10⁶.

**Procedure**

The reaction vessel was baked overnight at 1.5 x 10⁻⁴ Pa and 720 K. The iron films were prepared by evaporation from 0.15 m of 0.4 mm diameter wire. Outgassing was at 2.5 A for 30 min with an increased current (to 3.0 A) for a short time to facilitate an αγ phase transition and increase the efficiency of outgassing (Porter & Tompkins 1953). The films were thrown at 3.6 A for 8 min.

An 11.5:1 ratio of deuterium to neopentane was admitted to the reaction vessel at 5.34 kPa and 273 K and the vessel was then heated by an electric furnace to the required temperature. Initial experiments to determine good operating conditions were carried out using only chromatography. Subsequent experiments with the mass spectrometer were done at temperatures yielding approximately 20 % hydrogenolysis per hour. Samples were taken intermittently and scanning was from m/e = 100 to m/e = 10.

In correcting the spectra, allowance was made for background, which was especially large at m/e = 18 due to water elution from the chromatographic column, for naturally occurring deuterium and ‘heavy’ carbon, and also for fragmentation. No parent ion was detected for neopentane so analysis was made in terms of
(CX₃)₃C⁺ ions (X representing H or D) which result from the loss of methyl groups. Because the formation of C₄X₃⁺ and C₄X⁺ ions was less than 10%, fragmentation corrections were applied using the measured fragmentation pattern for ‘light’ neopentane. Ionizing electrons at 20 eV were required to produce adequate sensitivity of the methane and under these conditions the fragmentation was substantial (61% formation of CX⁺ from methane. The fragmentation patterns for both methane-d₀ and methane-d₄ were measured and the fragmentations for intermediate species were linearly interpolated. Statistical loss of hydrogen or deuterium according to the isotopic distribution was assumed.

**RESULTS**

**Development of the technique**

Because there is a variation in the sensitivity of the mass spectrometer and the molecular separator to different paraffins, calibrations were made with standard hydrocarbon mixtures. A difference in the responses to methane-d₀ and methane-d₄ was also observed. However, no change in the sensitivity was detected with propane-d₀ and propane-d₈ and the hydrocarbons other than methane were calibrated using the ‘light’ isotope. Sensitivity factors relative to a methane-d₀ value of unity are listed in table 1. The sensitivity factors for the intermediate methane isotopes were linearly interpolated.

**TABLE 1. SENSITIVITY FACTORS† FOR THE GAS CHROMATOGRAPH—MASS SPECTROMETER SYSTEM**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Sensitivity Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane-d₀</td>
<td>1.00</td>
</tr>
<tr>
<td>methane-d₄</td>
<td>1.25</td>
</tr>
<tr>
<td>ethane</td>
<td>0.78</td>
</tr>
<tr>
<td>propane</td>
<td>1.02</td>
</tr>
<tr>
<td>isobutane†</td>
<td>9.36</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.57</td>
</tr>
<tr>
<td>neopentane†</td>
<td>14.6</td>
</tr>
</tbody>
</table>

† Dimensionless molar quantity = \( \frac{\text{signal intensity}}{\text{sensitivity factor}} \).

‡ For isobutane and neopentane the sensitivity for the parent ion is so small that the C₄H⁺ and C₄H₃⁺ ions were used.

The overall sensitivity of the technique was such that identifiable mass spectra were obtained from 0.4 Pa of propane in the reaction vessel. Isotopic distributions could be determined for a product yield of about 0.3%.

Due to the partial separation of deuterated paraffins in the chromatograph, no single mass-spectrometric scan is representative of the overall isotopic distribution. Examination of an equimolar propane-d₀/propane-d₈ mixture shows that ‘light’ and ‘heavy’ propane are separated by about 10 s with the more deuterated propane appearing earlier (figure 2). To determine the average isotopic distribution, a
number of mass-spectrometric analyses were taken at equal intervals of time as each component emerged from the chromatograph. The peak heights at each m/e value were integrated over the series of scans using Simpson's rule, thereby producing an average value for each ion. The error involved in this procedure was investigated using two samples: the equimolar propane data (figure 2) and an experimental distribution from a reaction of n-butane with deuterium over platinum (table 2).

![Figure 2. Separation of propane-$d_8$ and propane-$d_0$ on the chromatographic column; $\bigcirc$, propane-$d_0$; $\bigcirc$, propane-$d_8$; ---, total signal.](image)

**TABLE 2. COMPARISON OF CALCULATED ISOTOPIC DISTRIBUTIONS FOR n-BUTANE USING DIFFERENT NUMBERS OF SCANS**

<table>
<thead>
<tr>
<th>number of scans</th>
<th>$d_0$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$d_4$</th>
<th>$d_5$</th>
<th>$d_6$</th>
<th>$d_7$</th>
<th>$d_8$</th>
<th>$d_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>13.8</td>
<td>0.1</td>
<td>-0.5</td>
<td>0.1</td>
<td>1.4</td>
<td>3.7</td>
<td>8.2</td>
<td>17.2</td>
<td>25.7</td>
<td>20.7</td>
</tr>
<tr>
<td>14</td>
<td>13.6</td>
<td>0.3</td>
<td>-0.4</td>
<td>-0.1</td>
<td>2.0</td>
<td>3.3</td>
<td>7.5</td>
<td>17.7</td>
<td>27.2</td>
<td>19.3</td>
</tr>
<tr>
<td>14</td>
<td>13.8</td>
<td>0.1</td>
<td>-0.5</td>
<td>0.1</td>
<td>0.9</td>
<td>3.6</td>
<td>9.3</td>
<td>17.7</td>
<td>24.7</td>
<td>20.5</td>
</tr>
<tr>
<td>14</td>
<td>14.2</td>
<td>0.0</td>
<td>-0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>4.2</td>
<td>8.5</td>
<td>17.1</td>
<td>24.7</td>
<td>21.0</td>
</tr>
</tbody>
</table>

The isotopic distributions calculated using all of the mass-spectrometric scans available (34 for propane and 42 for n-butane) were assumed correct and for isotopic distributions calculated from smaller numbers of scans chosen at equal intervals, the variances of the errors were determined. The 95% confidence intervals for the percentage isotopic distributions were estimated by taking twice the standard deviations (figure 3). A comparison of the n-butane distributions calculated from 42 and 14 scans is shown in table 2. In the following experiments, the scanning frequency was set so that about 15 scans were produced per component.
The hydrogenolysis reaction to methane was slow but observable at 417 K and an activation energy of $160 \pm 10 \text{kJ mol}^{-1}$ was estimated from initial rates (conversions less than 10%) over the temperature range 446 to 486 K. Methane was the most extensive product (\sim 99%) along with small quantities of isobutane and traces of ethane and propane. Higher temperatures favoured more extensive cracking with the amount of methane formed increasing from 99.0% at 486 K to 99.8% at 506 K.

At 486 K, the exchange of neopentane occurred 2.0 times more quickly than hydrogenolysis (figure 4) and there was some 'poisoning' of the reaction with increasing time. The initial rate of hydrogenolysis was $1.4 \times 10^{-10} \text{mol mg}^{-1}\text{s}^{-1}$.

The deuterium content of the exchanged neopentanes was measured in terms of the $(\text{CX}_3)_3\text{C}^+$ ion (X representing H or D) which results from the loss of a methyl group. This loss occurs on a random basis; neopentane terminally labelled with one $^{13}$C produced $\text{C}_4\text{H}_{10}^+$ fragments which are 76% labelled (Langer & Johnson 1957). At low conversions isobutyl-$d_0$, $-d_1$ and $-d_3$ ions were detected. The only deuterated neopentanes which can yield $-d_3$ ions without $-d_2$ also being formed are $(\text{CH}_2\text{D})_2\text{C}$ and $(\text{CH}_3)_3(\text{CD}_3)\text{C}$. Operating with ionizing electrons of 70 eV, methyl ions are observed to about 5% the level of isobutyl ions and according to Johnson & Langer (1957), they are derived almost exclusively from methyl groups lost by the original molecule. Measurements of the relative amounts of $\text{CH}_3^+$ and $\text{CH}_2\text{D}^+$ ions formed showed that $(\text{CH}_3)_3(\text{CD}_3)\text{C}$ was the multiply exchanged neopentane present. The percentage isotopic distributions of the neopentanes were calculated from the measured distribution of the deuterated isobutyl ions (figure 5). The probabilities of formation of the various $\text{C}_2\text{X}_4^+$ ions by random loss of methyls were derived assuming that neopentane-$d_1$ and neopentane-$d_3$ with the deuteriums residing on one carbon atom were the initial species and the other products (neopentane-$d_2$, $-d_4$, $-d_5$, $-d_6$) resulted from multiple occurrences of these processes. The probabilities were used to calculate the neopentane isotopic distribution beginning with the most deuterated species and working towards the less deuterated species.

Selectivity has been defined as the number of moles of a particular isotopic species formed divided by the total moles of deuterated neopentanes formed and this is
plotted against the percentage of neopentane containing deuterium (figure 5). Extrapolation to zero deuteration shows that neopentane-$d_1$ and neopentane-$d_3$ are the only primary products. At higher conversions, the other deuterated species are formed due to consecutive deuteration steps and dilution of the hydrogen–deuterium pool. Neopentane-$d_1$ is formed at a rate 1.5 times that of neopentane-$d_3$, with the initial products being 60% $-d_1$ and 40% $-d_3$. No deuterated neopentanes were observed which would suggest an $\alpha\gamma$-adsorbed intermediate for exchange.

**Figure 4.** The exchange and hydrogenolysis of neopentane over an iron film (14.3 mg) at 486 K; □, exchange; ○, hydrogenolysis.

**Figure 5.** Distribution of the deuterated neopentanes formed; ○, neopentane-$d_1$; ○, $-d_2$; ○, $-d_3$; □, $-d_4$; □, $-d_5$; □, $-d_6$. 

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The methane formed from hydrogenolysis contained a preponderance of highly deuterated species (figure 6). Extrapolation to zero conversion shows that methane-$d_4$ is the major primary product and that the formation of less deuterated species with increasing conversion is due to dilution of the hydrogen–deuterium pool. The isobutane product also contains mostly deuterium with isobutane-$d_{10}$ being 60% of the product at 17% hydrogenolysis. The isotopic distributions of the isobutane were difficult to determine because of the small quantities formed.

\[ \text{DISCUSSION} \]

The reaction system can be represented by a combined series–parallel network where the exchange reaction has been assumed irreversible due to the large excess of deuterium present.

\[
\text{neopentane}-d_0 \xrightarrow{k_p} \text{deuterated neopentanes} \xrightarrow{k_H} \text{hydrogenolysis products}
\]

The rate of hydrogenolysis of undeuterated and deuterated neopentane have been assumed equal. For first-order reactions (Kembell 1954; Sinfelt 1969), this network can be solved to yield

\[
-ln[1-x_H] = k_H t, \quad (1)
\]

\[
-ln\left[\frac{1-x_H-x_D}{1-x_H}\right] = k_D t, \quad (2)
\]

where $x_D$ and $x_H$ are the fractional conversions for exchange and hydrogenolysis, $t$ is time, and the rate constants are as shown in the reaction scheme. At low conversions the data show a linear relation (figure 4) but at higher conversions there is considerable reduction in the rate. Both the exchange and the hydrogenolysis reactions are affected to an equal extent indicating that the ‘poisoning’ mechanism
is not selective with respect to reaction type. Much of the decrease in rate may be due to sintering of the film (Porter & Tomkins 1953).

The exchange of neopentane on iron films involves adsorption via only one carbon. The two primary exchange products result from a stepwise exchange mechanism replacing one hydrogen per reaction and a multiple exchange mechanism similar to that reported for methane exchange (Kemball 1971) which replaces all of the hydrogens on one methyl group. The absence of neopentane-\(d_2\) suggests that the multiple-exchange intermediate is either diadsorbed to the surface at one carbon with the remaining hydrogen exchanging very rapidly relative to desorption or the intermediate is triadsorbed. There is no evidence for \(\alpha\gamma\) exchange of neopentane on iron such as has been reported for rhodium where perdeutero-neopentane was observed as an initial product (Kemball 1954).

Hydrogenolysis of paraffins on metals is generally thought to occur through a species adsorbed to the surface at two carbon atoms (Anderson & Baker 1963). With neopentane only \(\alpha\gamma\) species can be formed due to the quaternary carbon atom. The absence of \(\alpha\gamma\)-exchanged products shows that the \(\alpha\gamma\) adsorption of neopentane on iron must be irreversible and leads directly to carbon–carbon bond rupture. Once hydrogenolysis begins, the degradation of the neopentane is extensive indicating that the adsorbed i-C\(_4\), C\(_3\), and C\(_2\) fragments desorb slowly relative to further carbon–carbon bond rupture. In this way, no substantial quantities of isobutane, propane or ethane are observed. With increasing temperature, the cracking reaction becomes more severe, i.e. a greater percentage of methane is formed, because the activation energy for carbon–carbon bond rupture is greater than that for desorption.

For \(n\text{-}\)butane, propane and ethane over iron the exchange and hydrogenolysis rates are comparable (Dowie et al. 1971), suggesting that there is an adsorbed intermediate which has nearly equal probability of desorbing to form an exchanged species or reacting further by rupture of a carbon–carbon bond. However, the adsorbed i-C\(_4\), C\(_3\), and C\(_2\) fragments from neopentane hydrogenolysis are much more likely to crack further than desorb. Therefore, different intermediates are involved in the hydrogenolysis and exchange reactions with the hydrogenolysis intermediate being much more irreversibly adsorbed.

The hydrogenolysis products are all completely exchanged. Exchange may occur by an \(\alpha\beta\) mechanism for each of the products except methane; this type of exchange is very rapid compared to desorption of the hydrogenolysis fragments.

The irreversible adsorption of the neopentane intermediate for hydrogenolysis is in agreement with the kinetic evidence for ethane hydrogenolysis (Sinfelt 1969) and for \(n\text{-}\)pentane hydrogenolysis (Kikuchi, Tsurumi & Morita 1971) on supported iron catalysts. The kinetic orders for these reactions with respect to the hydrocarbon and hydrogen suggest that the hydrocarbon is less reversibly adsorbed over iron than on the other transition metals.

The combined chromatograph–mass spectrometer technique can be applied to a wide range of catalytic reactions in which one atomic species is replaced by its
isotope to elucidate the mechanism. The technique is easy to apply but has the
disadvantage that the analysis of the data is complex and tedious. The present
system is to be connected to a computer employing anologue-to-digital conversion
to overcome this problem.

We thank the Science Research Council for a grant for the purchase of equipment,
British Petroleum Ltd for a studentship (to R. S. D.) and Nato for a postdoctorate
fellowship (to J. C. K.).

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Hydrogenolysis of Hydrocarbons on Iron Catalysts

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Reprinted from

Chemical Communications 1971

The Chemical Society, Burlington House, London W1V OBN
Hydrogenolysis of Hydrocarbons on Iron Catalysts

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Summary The use of a combined g.i.c.-mass spectrometry technique shows that the hydrogenolysis† of ethane, propane, or butane in the presence of deuterium on iron films gives CD₄ as the main product and that the reactions are accompanied by exchange of the hydrocarbons producing mainly the perdeuterio-compounds.

Experiments on reactions of alkenes with deuterium have provided useful information about the types of adsorbed intermediates formed on metal catalysts in reactions at low or moderate temperatures. At higher temperatures, different adsorbed species may be involved and may be studied by the isomerization or hydrogenolysis of saturated hydrocarbons in the presence of deuterium and by determination of the isotopic composition of reactant and products at low conversions. This can be accomplished by the combination of separation by g.i.c. and of fast-scan mass spectrometry to determine the isotopic composition of each substance as it emerges from the chromatographic column. The potentialities of this technique, which has not previously been used in catalytic studies, may be evaluated from our results for ethane, propane, and butane on iron films.

Reactions were carried out in a static system (2.44 × 10⁻⁵ m³) with hydrocarbon (at 400 Nm⁻²) over evaporated iron films (ca. 10 mg) and a ratio of D₂ to hydrocarbon of 12:1. Samples of the gas were withdrawn and passed into a gas chromatograph linked through a molecular separator directly to a mass spectrometer (A.E.I. M.S. 20 'Rapide'). A mass spectrum could be obtained in less than 1 s and normally ca. 30–40 spectra were recorded for each peak. Several scans were needed to obtain adequate analyses of the isotopic content of each hydrocarbon because partial separation of the exchange hydrocarbons occurred in the chromatograph, the heavier molecules being eluted faster than the lighter ones.

The order of reactivity is clearly butane > propane > ethane (see Table 1) and the ratio of exchange to hydrogenolysis increases with the size of the molecule. The results with butane are characteristic (see Table 2). The major product of hydrogenolysis was methane and only small amounts of propane and ethane were formed; in each

† Hydrogenolysis is used in a generic sense and implies here carbon-carbon fission by either hydrogen or deuterium.
case, the perdeuterio-compound was by far the most abundant isotopic species. The major product of the

TABLE 1

<table>
<thead>
<tr>
<th>Reactant</th>
<th>T/K</th>
<th>t/min</th>
<th>% Reaction</th>
<th>hydro-</th>
<th>exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>504</td>
<td>20</td>
<td>3.6</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>481</td>
<td>15</td>
<td>5.3</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>~461</td>
<td>10</td>
<td>9.3</td>
<td>10.6</td>
<td></td>
</tr>
</tbody>
</table>

exchange reaction was perdeuteriobutane. Propane and ethane behaved similarly; no hydrogenolysis products other than CD₂ were observed. Exchange gave the deuteriated propanes C₅D₇ (70%) and C₃HD₇ (30%) and the only exchanged ethane detected was C₅D₀.

We conclude that desorption of the hydrocarbons from an iron surface is not rapid which accounts for the three principal features of the results. First, the perdeuterio-compound is the main product of exchange because any adsorbed species formed from the reactant and not broken down to lower homologues remains on the surface for a sufficient time for complete replacement of hydrogen by deuterium to take place. The multiple exchange presumably occurs by alternation between two or more types of adsorbed species of different states of hydrogenation, e.g. alkyl ≈ alkene. Secondly, species which undergo scission of the carbon–carbon bond mostly end up as C₂ species leading to methane as the main product of hydrogenolysis. Desorption of intermediate products occurs only to a very small extent with butane and is not observed with propane. Thirdly, the lifetime of the Cⱼ species on the surface is long enough to give CDⱼ as the main product. Since all the products from exchange and hydrogenolysis are predominantly perdeuterio-compounds no deductions about the reactive intermediates can be made from the product distributions.

The desorption of methane, being slow, may be the rate-determining reaction but it is not easy to explain why the hydrogenolysis of ethane and propane takes place more slowly than that of butane. A tentative explanation may be the different coverage of the surface by Cⱼ species in each case. A quantitative study of the virtual pressures of methane to be expected in each reaction might amplify this suggestion.

The predominance of methane as the major product of the hydrogenolysis of butane is greater with iron than with nickel or rhodium. The present evidence for exchange with hydrogenolysis conflicts with a brief report made some years ago of the absence of such exchange with ethane on iron films.

Preliminary experiments with other metals indicate that reversible dissociative adsorption, detectable by exchange techniques, may commonly occur simultaneously with hydrogenolysis.

The technique provides a rapid and sensitive method of following complex processes in heterogeneous catalysis; kinetic data can be obtained readily by analysis of a succession of samples. The high sensitivity is shown by the results for propane in Table 2; the partial pressure of this compound was 0.4 N m⁻² in 5 cm² and it would have been difficult to estimate and analyse such a small quantity by conventional trapping and subsequent introduction into a mass spectrometer.

The apparatus was purchased through an S.R.C. grant and one of us (R.S.D.) holds a BP Research Studentship.

\( (Received, May 18th, 1971; Cons. 803.) \)