Hydrocarbon Reactions on Platinum-Iridium Bimetallic Catalysts

by

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ABSTRACT

Despite the industrial importance of the second generation supported bimetallic catalysts, little attention has been given to the nature of the reactions on their surfaces and why these catalysts are so suitable for catalytic cracking. The work contained in this thesis set out to investigate the platinum-iridium series. A set of bimetallic catalysts supported on γ-alumina were made whose metal contents were about 0.5% by weight and which investigation by hydrogen chemisorption showed the metal dispersions to be high i.e. nearly all metal atoms were present as surface atoms. Temperature programmed reduction suggested that the most stable point in the bimetallic series to be at the 1:1 atomic ratio.

Hydrogen-deuterium exchange was carried out with methane and cyclopentane. Both molecules showed platinum to be a better catalyst for exchange than iridium but there was little difference in rate across the bimetallic catalysts. Initial product distributions (I.P.D.) showed stepwise exchange to be the dominant process for the methane reaction. For cyclopentane, repeated αβ diadsorption was the major reaction on platinum. With increasing iridium content, this process decreased in importance and αα diadsorption became more dominant.

The reactions of ethane, propane, butane, n-pentane and cyclopentane with hydrogen were carried out on the catalyst series. Iridium was a better hydrogenolysis catalyst for all molecules. Central bond scission was the dominant process for all catalysts although iridium rich catalysts showed a greater tendency for multiple bond scission. Comparison with the rate of methane exchange showed carbon-carbon bond rupture to be the rate-determining step for all catalysts. Product desorption only became significant on iridium itself. Rates of hydrogenolysis do not show an additive effect for the bimetallic catalysts and the trend in rate may be due to an ensemble effect.
FOREWORD

This thesis describes work undertaken personally in the Chemistry Department of the University of Edinburgh and in the laboratories of Petrochemicals Division of Imperial Chemical Industries Ltd. from October 1978 to October 1980.

Many people have helped me in the course of these studies. I am particularly indebted to my academic supervisors, Professor C. Kemball and Dr. D.A. Whan for their direction and encouragement and to my industrial contacts, Dr. R.J. Sampson and Dr. M.A. Day for their helpful discussion and genial hospitality. Special thanks to the Science Research Council and Petrochemicals Division of ICI for the provision of an SRC-CASE award and to ICI for laboratory facilities and materials.

I would also like to thank other members of the catalytic group, especially Ian Haining for help and advice concerning apparatus and Ronnie Brown for his technical expertise (not to mention coffee). Finally thanks to John Broom of the Chemistry Department for his glassblowing finesse and Marie Manson who deciphered my impossible handwriting and typed this thesis so well.

In the course of this work I attended the following seminars and lecture courses:

2) Detergency and the design of surface active agents. Dr. W.O. Cooper (Nov. 1979)


4) Zeolites. Dr. B.M. Love

5) Catalysis and chemical productivity. Staff of Petrochemicals Division I.C.I. (March 1979)

6) Scottish Universities Catalysis Meeting. (March 1979)

7) Aspects of industrial and inorganic chemistry. - Dr. H.L. Roberts I.C.I. (March 1980)
To my parents
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1.1 Historical Background

Chemical studies of catalytic processes have increased in range and depth over the last one hundred and fifty years. A catalyst is most often defined as "a substance which increases the rate at which a reaction approaches equilibrium without being consumed in the process". Life itself depends on specific catalytic processes and man has used catalysis from the production of the socially accepted narcotic ethanol in pleasantly tasting forms to the manufacture of ether by the action of sulphuric acid on alcohol by the alchemists.

Modern scientific study of catalysis started when Berzelius\(^{1}\) in 1836 reviewed a group of results by other workers\(^{2-7}\). He ignored rates of formation of products and only considered the new species formed by the addition of the catalyst. His conclusion was that the role of the "catalyst" was to produce a favourable chemical environment for reaction. Van't Hoff\(^{8}\) defined the catalyst's role similarly; that it increased the concentration of reactants at the reaction site.

Ostwald\(^{9,10}\) was the first to consider reaction rate as a measure of catalyst activity and that the position of equilibrium did not change. He defined a catalyst as "any substance which alters the velocity of a chemical reaction without affecting the end products of reaction". An important implication here is that a catalyst can only effect a reaction already
thermodynamically feasible. Sabatier\(^{11,12}\) drew attention to the fact that one compound could undergo different reactions on different catalysts; for example the decomposition of ethanol to ethylene and water on alumina, or to acetaldehyde and hydrogen on copper, all at 573 K. Sabatier also showed how catalyst activity could be impaired by impurities in the reactants or catalyst contamination by the products of reaction. Many forms of catalyst 'selectivity' and catalyst 'poisoning' are recognised today.

The most recent and definitive review of the catalyst's role has been made by Hinshelwood\(^{13}\). He states that a catalyst provides an alternative and faster reaction pathway which consists of chemical reaction between catalyst and reactant to give intermediates which rearrange to yield the products, and regenerate the catalyst. It follows that to fully understand the catalyst's function, it is necessary to know the nature and stability of the intermediates formed, the reaction in which they are produced and subsequently the reactions undergone to give the products. The formation and reaction of intermediates is common to all catalysed reactions but there are many possible kinetic mechanisms which make a universal theory of catalysis impossible. Catalytic reactions are therefore subdivided into three main categories, the mechanism in each being alike in kind if not in detail. These are, heterogeneous catalysis where reactant and catalyst are in different phases, homogeneous catalysis where both are in the same phase and enzyme catalysis which controls
most biological processes. This thesis is concerned exclusively with the first category, and in this case reactions between gaseous reactants on a solid catalyst.

1.2 Adsorption Processes

For a heterogeneous catalytic reaction to occur one or more of the reactants must be adsorbed on the surface of the catalyst for a sufficient length of time for reaction to occur. Catalytic reactions are governed by the amount and strength of adsorption of the absorbate reactant on the solid surface. Experimental studies of adsorption phenomena have established two ways that a molecule can be held on a catalyst surface. These types of adsorption are described as physical adsorption and chemical adsorption (chemisorption).

**Physical adsorption**

In this mode of adsorption the adsorbate molecules or atoms are held to the surface by Van der Waals forces. These are the attractions between temporary dipole moments caused by the arrangement of nuclei and electrons within molecules or atoms. The bonding energy, the enthalpy of physical adsorption, is comparable to the corresponding heat of condensation of the gas adsorbate, about 5-20 kJ mol\(^{-1}\). The enthalpy of physical adsorption is now due to the weak forces involved. Rates of adsorption and desorption are fast due to the processes having a low activation energy, as long as the surface sites are readily accessible. A slow rate of physical adsorption often shows slow diffusion in porous substances.
Multilayer physical adsorption may be found, especially at temperatures near the boiling point of the gas.

As physical adsorption involves such weak forces it is not usually important for catalytic reactions, but weakly adsorbed molecules may become chemisorbed with or without molecular dissociation. Physical adsorption is useful for measuring a catalyst's surface properties by the adsorption of gas under different conditions. The most important of these is the measurement of surface area of a catalyst by the method of Brunauer, Emmett and Teller (14).

Chemisorption

This type of adsorption is the result of chemical bonds between adsorbed reactant and the solid surface of the catalyst, similar to those occurring in chemical compounds. Adsorption of the molecule causes a rearrangement of electrons between adsorbate and adsorbent. Much stronger forces are involved than in physical adsorption and chemisorption is an essential part of a heterogeneous catalytic reaction.

For a spontaneous process the Gibbs free energy, $\Delta G$, is negative and from the equation:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} 1.1

it follows that enthalpy, $\Delta H$, is also negative as the entropy change, $\Delta S$, must always be negative for adsorption creates a higher degree of order. Since $\Delta H$ is negative the process is exothermic and the heat of adsorption is
usually between 80-800 kJ mol\(^{-1}\). Chemisorption can only form a monolayer over the available area. Rates of adsorption are generally very fast with small activation energies but there are some activated processes, e.g. the adsorption of nitrogen on iron\(^{(15)}\).

Langmuir\(^{(16,17)}\) was the first to quantify the adsorption process. Assuming that there are a fixed number of surface sites that accommodate one adsorbed molecule each and which all have the same heat of adsorption, the equation

\[
\theta = \frac{ap}{1 + ap} \tag{1.2}
\]

can be derived where \(\theta\) is the fraction of surface covered by adsorbed species, \(p\) the pressure of the gas and \(a\) is a constant related to the heat of adsorption. This equation does not take into account interaction between adsorbed species. Due to surface heterogeneity, heat of adsorption is not uniform over the total surface, and this is not taken into account in equation 1.1.

The Brunauer, Emmett and Teller isotherm\(^{(14)}\) makes similar assumptions as the Langmuir equation but allows for multilayer adsorption. The equation derived for this isotherm is of the form:-

\[
\frac{P}{V(P_0-P)} = \frac{1}{VmC} + \frac{(C-1)}{VmC} \cdot \frac{P}{P_0} \tag{1.3}
\]

where \(V\) is the volume of gas adsorbed, \(Vm\) the value of adsorbate corresponding to a monolayer coverage, \(P\) the
partial gas pressure, $P_0$ the saturated vapour pressure and $C$ is a constant. The value of a monolayer can be calculated by plotting $P/V(P_0-P)$ versus $P/P_0$ for a series of pressures and hence the surface area can be calculated if the area of one adsorbed molecule is known. This method measures total surface area but does not give information on the activities of the surface sites. Adsorption isotherms have also been derived by Freundlich (18) and Tempkin (19).

1.3 The Mechanism of Heterogeneous Catalysis

Chemisorption of one or more of the reactants is essential to a heterogeneous catalytic reaction. Two mechanisms have been generally accepted to explain reaction at the catalyst surface, these being the Langmuir-Hinshelwood (20,21) and the Eley-Rideal (22,23).

The mechanism of Langmuir and Hinshelwood relates the overall catalytic rate to interactions between chemisorbed species in adjacent sites on the catalyst surface, adsorption and desorption processes being in equilibrium. A saturated hydrocarbon reacting with deuterium would have the following reaction scheme:

$$C_nH_{2n+2} + D \rightarrow H \cdash C_nH_{2n+1} \cdash D \rightarrow H + C_nH_{2n+1}D$$

where the dashed lines denote physical adsorption and the continuous lines chemisorption. Surface metal atoms are represented by $M$. 
The Eley-Rideal mechanism proposes that interaction occurs between a chemisorbed species and a molecule in either the gas phase or physically adsorbed on the surface. The reaction scheme for the hydrocarbon-deuterium reaction above would be:

\[
\begin{align*}
C_{n}H_{2n+2} + D-D & \rightarrow C_{n}H_{2n+1}^{+} + D \\
M & \quad M & \quad M & \quad M
\end{align*}
\]

There is no evidence to suggest that one of these mechanisms operates exclusively but the Eley-Rideal mechanism appears to be a good description of low temperature reactions. At higher temperatures where adsorption and desorption are rapid the Langmuir-Hinselwood is more applicable.

The exact mechanism of the surface reaction is difficult to determine as overall reaction kinetics do not tell much of the type and amounts of surface species present. Spectroscopic techniques such as infra-red, ultra-violet, laser raman and high resolution nuclear magnetic resonance give direct information on the nature of a surface species but the exact nature of the intermediates is open to speculation. Indirect experimental methods with tracer elements and hydrogen-deuterium exchange give useful information on the types of bonds between hydrocarbons and metal surfaces and about the relative stabilities of different types of intermediate.

A heterogeneous catalytic reaction can be considered in five stages:-
1) The diffusion of reactants to the catalyst surface.
2) Adsorption of reactants on the surface.
3) Chemical reaction on the surface.
4) Desorption of products from the surface.
5) Diffusion of products away from the surface.

If one is much slower than the rest then this will be the rate determining step of the overall reaction. In the static system, steps (1) and (5) are usually fast while steps (2), (3) and (4) are activated processes. Adsorption is relatively fast compared to reaction and desorption of products and it is these latter two processes which jointly or singly constitute the rate determining step in heterogeneous catalysis.

The energy diagram for a unimolecular reaction, A→B is shown in figure 1.1 with the five elementary steps indicated. The energy barriers to reaction are shown in the presence of a catalyst and with no catalyst present. From this it can be seen that the catalytic reaction is faster than the thermal at the same temperature, and thus the catalytic reaction will be able to produce a given rate at a lower temperature than the thermal reaction.

1.4 Activity of Metal Catalysts

The activity and selectivity of a metallic catalyst (metal or alloy) for a catalytic reaction, are attributed to one or both of the following effects.

1) The electronic structure of metal atoms in the solid. In the case of group VIII metals the role of the d-electrons and their orbitals
is of crucial importance. This is called the "electronic factor".

2) Reaction requires an ensemble of several metal atoms as one or more of the reactants are bound either to tops of several atoms or adsorbed in the "valley" among several surface atoms of the same kind. This is called the "geometric factor". It appears that when bonds such as C=C, C-OH and C=O are taken an ensemble of several metal atoms is required but C-H may be split by isolated active sites or atoms\(^{(28,29,30)}\).

(1) and (2) appear to be responsible for heat of adsorption and adsorption made of hydrocarbons respectively.

**Electronic factor**

The high catalytic activity of group VIII metals can be directly attributed to the d-electron characteristics as recently reviewed by Ponec\(^{(28)}\). The binding by d-electrons not only applies to the metallic bond in the bulk metal but to the metal to carbon chemisorption bond at the surface. This contribution from d-orbitals is low in the group Ia to IIa metals and hence the gaseous molecules are weakly adsorbed or not adsorbed at all. The group III to VI metals have a very high contribution to binding from the d-electrons and the surface becomes covered by a firmly adsorbed layer which prevents further reaction. The catalyst surface is thus poisoned. The transition metals of group VIII have an optimum contribution from the d-electrons for adsorption, one that allows reaction and
product desorption to be facile reactions. Hence the transition metals are catalytically more active than the non-transition metals.

The catalytic activities within group VIII can be correlated with percentage $d$-character, of the metallic bond, as first introduced by Pauling$^{(29)}$. This is illustrated in figure 1.2. The pattern of percentage $d$-character to hydrogenolysis activity is similar from one metal to another in a long period or transition series. However Sinfelt$^{(30)}$ found the metals in the first transition series (iron, cobalt and nickel) show activities comparable to metals with higher $d$-character in the second and third transition series. Therefore correlation between activity and $d$-character is not by itself adequate for describing activities of transition metals.

Dowden$^{(31-33)}$ related catalytic activity to the number of $d$-holes (unoccupied energy levels of high $d$-character) and a highly occupied state at the Fermi level, $E_F$. Later work by Trapnell$^{(34)}$ and Ponec$^{(35,36)}$ failed to find a direct connection between electronic structure ($d$-holes, electric conductivity, work function or $d$-character) and catalytic properties.

**Geometric factor**

Adsorption sites on catalyst surfaces do not all have the same energy of adsorption and so some sites are more active than others for certain catalytic reactions. The surface is thus said to be heterogeneous and the catalyst activity is determined by the arrangement of these active sites on the surface.
Koňbožeř (37) in 1938 and later Dowden (38) in 1972 related the size of these surface atom "ensembles" to catalytic activity. Balandin (39), also considered number and size of "ensembles" important. These groups or "multiplets" had to be of such a size as to fit the reactant molecules. In this way certain areas of catalyst surface are more active than others and the overall activity is related to the number and distribution of these multiplets. Selectivity of catalysts is heavily dependent on the formation of suitable types of sites.

Ensemble effects are generally regarded to be responsible for the reactions of alloy catalysts. Alloys of nickel and copper have very small changes in electronic structure as the atom percentage copper content is increased, however, selectivity changes markedly, see figure 1.3. Alloying decreases the hydrogenolysis reaction as this requires ensembles of several nickel atoms which decrease in number as the percentage copper increases. Large ensembles are required to break a carbon to carbon bond as at least two multiple carbon to metal bonds are involved. The activity of C-H bonds changes only slightly on alloying as this reaction requires a smaller size of nickel ensemble.

The alloy of an active group VIII metal to an inactive group Ib decreases hydrogenolysis activity. This is generally considered as 'dilution' of the active group VIII in the ensembles by the inactive group Ib, and leads to a much greater activity for "non-destructive" reactions such as isomerization and cyclisation. The literature gives several examples of these 'geometrical'
effects on alloying\(^\text{40-44}\). Activity and selectivity of metals and alloys are heavily dependent on the type and/or number of certain ensembles.

**Surface Composition of Bimetallic Catalysts**

Catalytic activity depends only on the outer atomic layer of the metal particles and this can differ quite markedly from the bulk metal composition. A surface creates a positive contribution to the free energy of the system due to the decreased coordination of surface atoms. The system tries to minimise this by increasing the concentration of these atoms with the lowest surface free energy, i.e. the lowest heat of atomisation, at the surface. This results in a 'surface enrichment' of one constituent of the alloy with respect to the other.

This situation where a layer rich in the volatile component surrounds a core composed mainly of the less volatile metal has been described as the "cherry model" by Sachtler\(^\text{45}\). This is illustrated in figure 1.4, and results in a series of alloy catalysts over which the surface composition remains reasonably constant. When the alloy is surrounded by reactant gases, the component to which these gases has the highest heat of chemisorption will migrate to the surface to form as many chemisorption bonds as possible. This may cancel or enhance the effect due to different heats of atomisation.

Surface enrichment effects are not thought to be of any significance where the particles are very small.
1.5 Petroleum Reforming Catalysts

The petroleum refining industry is a major user of heterogeneous catalysts and the energy crisis has speeded the search for more efficient and economical catalysts and processes. 'Reforming' means changing the molecular structure of napthas to raise the octane number and eliminate 'knock' i.e. irregular ignition in an internal combustion engine. Octane number is rated on a scale starting at zero for n-heptane (i.e. very prone to 'knocking') to 100 for iso-octane, increasing through the normal paraffins, branched hydrocarbons, napthenes and cycloparaffins to aromatics. The octane number of straight run napthas is too low for gasoline, so the chemical composition has to be changed by reforming.

The first process used was thermal reforming but this gave low yields of aromatics. Catalytic reforming has developed rapidly from the 1930's up to the present day. In the period 1960 to 1974 the catalytic reforming capacity of the world rose from 2.8 to 7 million barrels per day. Since the 1950's group VIII metals have been used as reforming catalysts supported on an acidic alumino-silicate such as γ alumina. The support assists in the formation and stabilisation of large specific areas of active species and economises in the use of costly metals. They are not inert and must be regarded as a separate catalytically active phase.

The first group VIII was platinum on halogenated γ alumina in the U.O.P. 'platforming' process. Despite the potential of alloys to effect catalyst activity and
selectivity, economic pressures were not sufficient to develop bimetallic catalysts until the end of the last decade. The platinum reforming catalysts were replaced by bimetallic catalysts especially the platinum-rhenium pair (Rheniforming). This first generation of bimetallic reforming catalysts increased catalyst stability and enabled operating pressures to be decreased. A second generation of bimetallic catalysts has emerged including platinum-iridium, platinum-germanium and development of multimetallic catalysts e.g. platinum-rhenium, germanium, cobalt on chlorided γ alumina has emerged. These give further gains in selectivity with improving stability further at low pressures
References

Chapter 1

8) Van't Hoff, "Physico-chemical Studies" I, 216, (1898).
10) W. Ostwald, Phys. Z., 3, 313, (1902).
31) D.A. Dowden, Research, 1, 239, (1948).
Figure 11: The Energy Path diagram for a unimolecular reaction.

1- Diffusion of reactants to the surface.
2- Chemisorption of reactants on the surface.
3- Chemical reaction on the surface.
4- Desorption of products.
5- Diffusion of products away from the surface.
Figure 1.2 Catalytic activities of metals for ethane hydrogenolysis.

Taken from Catal. Rev. 2, 156 (1974)
Figure 1.3  Activity and Selectivity in n-hexane reactions on Ni./Cu alloy catalyts.

S- selectivity for non destructive reactions. (%).
M- depth of hydrogenolysis.

From Progress in Surface and Membrane Science 13,1,(1979).
Figure 1.4  The 'Cherry' model for the surface composition of an alloy. From J.C. Rasser, Ph.D. Thesis, Delft University.
CHAPTER 2
APPARATUS AND EXPERIMENTAL

2.1 Preparation of Catalysts

All catalysts were prepared in the laboratories of Petrochemicals Division, Imperial Chemical Industries Ltd. The aim of the catalyst preparation was to obtain a platinum and an iridium monometallic catalyst and a series of bimetallic catalyst of the metal contents as shown in Table 2.1.

<table>
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<th>Table 2.1 Proposed Catalyst Compositions</th>
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<td>metal Pt</td>
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<td>100 80 60 50 40 20 0</td>
</tr>
<tr>
<td>metal Ir</td>
</tr>
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<td>0 20 40 50 60 80 100</td>
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The total metal content was to be 0.5% by weight and the support was to be γ-alumina. No halogens were to be present on these catalysts.

As an added precaution all metal solutions were to be made and used on the same day, to prevent differences in concentrations or ageing of the solutions.

Preparation of Condea Granules

To 50 g of Condea Pural ALC 169 was added 7.5 ml of 10% acetic acid and 7.5 ml of distilled water and mixed thoroughly. The mix was transferred to a mortar and pestle, ground until homogeneous, divided into 10 g lots and pressed into 3 cm pellets under a force of 55,152 kPa. These pellets were crushed into granules between 1000-425 μm in size as determined by a pair of
granule sieves. The dust left was remade into 3 cm pellets and the process repeated. Three lots of 50 g condea were used to give about 130 g of support.

The support was calcinated in 50 g batches in an oven whose temperature was raised 50 K every 30 minutes until a temperature of 878 K was reached. Air was then passed over the condea at a rate of 20 l hr\(^{-1}\) for 84 hours. Analysis of the resulting alumina showed carbon content to be only 0.03% by weight.

**Impregnation of the Support**

Solutions of bis(acetylacetaneto)platinum II and tris(acetyl acetanato)iridium III were prepared in benzene and the relevant amounts of these were added to 10 g samples of the condea support to produce the planned catalysts.

The liquid levels were made up to 25 ml with benzene and allowed to soak overnight. All solution preparations and catalyst impregnation was carried out on the same day. After 16 hours soaking the catalysts were transferred to a drybox with a nitrogen purge. The excess benzene was decanted into a beaker and the catalysts placed in silver foil trays, and then transferred directly to an oven where they were heated to 393 K over an hour and kept at this temperature for three hours. After cooling the catalysts were returned to the drybox and placed in weighed jars.

**Calcination**

All seven catalysts were placed in porcelain dishes and placed in an oven where the temperature was
raised by 50 K every 30 minutes until 753 K was reached, under a continuous air purge. The catalysts were then held at 753 K for two hours.

Catalyst Reduction

The catalysts were placed in a porcelain boat and, while purging with nitrogen, the temperature was increased at a rate of 50 K every 15 minutes up to 693 K at which temperature the catalyst was left under nitrogen for one and a half hours. After this time, the nitrogen was replaced by hydrogen and the catalyst reduced for three hours. The average rate of hydrogen flow was 3.8 l hr⁻¹.

The completed catalysts were analysed by neutron activation and the metal contents are listed in Table 2.2.

<table>
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2.2 The Gas-Handling Apparatus

Two separate vacuum lines were used for this project, line 1 which was connected via a capillary leak to an MS10 mass spectrometer and line 2 which was connected to a gas chromatograph, a Perkin Elmer F33. Diagrams of lines 1 and 2 are displayed on figures 2.1 and 2.2. Both lines were similar in design, differing only in the position of
the various bulbs, taps and sockets.

As it had been found necessary to dismantle and clean both vacuum lines at the beginning of the project, it was possible to fit 'greaseless' taps made by Springharn Ltd. Details of these high vacuum stopcocks can be found in the makers catalogue\(^{(1)}\). These prevented adsorption of the hydrocarbon by the grease. Apart from this both lines were constructed of 'Pyrex' glass and all ground glass joints and stopcocks lubricated with Apiezon 'L' vacuum grease.

Each gas line was evacuated by two Edwards ED50 'Speedivac' rotary pumps and two electrically heated mercury diffusion pumps. These attained a pressure of 133000 Pa. Mercury contamination was prevented by the liquid nitrogen cold traps. The maintenance of the high vacuum was achieved by periodic inspection and cleaning of cold traps and greased joints. Diaphragm pressure gauges, which were calibrated in torr, were used for gas pressure readings such as in preparations of reaction mixtures. The high vacuum pressure could be determined by a McLeod gauge.

Hydrogen and deuterium were purified by diffusing through a palladium thimble and the resulting gas, after passing through a liquid nitrogen cold trap, stored in a bulb permanently attached to the line. The other reactant gases were introduced via the ground glass sockets from detachable bulbs and cylinders. After double distillation from liquid nitrogen, these were stored in the other bulbs.

2.3 Volume Calibration

Volume calibrations involved a bulb of known value \( V_1 \) (determined by distilled water) containing a known pressure...
of helium gas $V_1$, which was expanded into the evacuated section of the vacuum lines $V_2$ and resulted in a lower pressure $P_2$. The unknown volume was calibrated using Boyle's law ($P_1V_1 = P_2V_2$). The volumes at 298 K were:

Line 1, mass spectrometer apparatus

- mixing volume = $10.30 \times 10^{-4}$ m$^3$
- reaction vessel volume = $2.60 \times 10^{-4}$ m$^3$

Line 2, gas chromatograph apparatus

- mixing volume = $6.36 \times 10^{-4}$ m$^3$
- reaction vessel volume = $1.83 \times 10^{-4}$ m$^3$

knowing the partial pressures of the gases the number of molecules in the reaction vessel could now be calculated.

### 2.4 Reaction Vessel, Chromatographic Sample Loop and Capillary Leak

The reaction vessel used for all experiments is illustrated in figure 2.3. This was constructed for the project from silica glass to which was attached a 'pyrex Rotoflow' tap via a graded glass seal. The catalyst was placed on the quartz sinter. This arrangement allowed a through flow of $H_2$ for catalyst reduction and reactant gases. The probe of the thermometer was placed in the sheath which rested on the catalyst. Between reactions the vessel was washed in chromic acid and distilled water and dried in an oven. The reaction vessel was completely detachable from the line to which it was attached via the B24 ground glass socket lubricated with Apiezon 'L' grease.
Heating the vessel and catalyst on both lines was carried out using an electrical furnace consisting of a close-fitting silica tube of about 0.05 m in diameter around which was wound a resistance wire. Temperature control was achieved by a chromel alumel thermocouple probe attached to a 'Eurotherm' proportional controller. The actual temperature of the catalyst was measured by a second chromel-alumel probe in the vessel socket. This was attached to a Comark digital thermometer. The temperature was steady to ±1 K during a reaction.

On line 2 the reaction vessel was connected via two three-way taps to a Perkin-Elmer stainless steel sampling valve. This was in turn connected to a Perkin-Elmer F33 gas chromatograph fitted with a flame ionisation detector. The sample size was about 7% of the reaction mixture.

On line 1 the reaction vessel was connected to a fine capillary leak made from 'pyrex' glass. This allowed about 2% per hour of the reaction mixture into the spectrometer, enough for analysis without seriously altering the gas pressures in the reaction vessel.

2.5 The Gas Chromatograph and Mass Spectrometer

The gas chromatograph was fitted with a 4 m column of bis-2-methoxyethylaplidate (13.5%) and di-2-ethylhexyl-sebecate (6.5%) on Chromosorb P. This was operated at room temperature with nitrogen (207 kPa) as the carrier gas. The hydrocarbon analysis was done by the use of a flame ionisation detector, the signals from which were fed in parallel to a 'Servoscribe' potentiometric pen recorder.
and a Hewlett Packard 3373 B electronic integrator which gave an integrated area for each peak.

The mass spectrometer was a general purpose AEI MS10 which is fully described in the makers manual\(^{(2)}\). This can be described as a high sensitivity, low resolution spectrometer which can detect a difference in mass of one mass unit, which is sufficient for hydrogen-deuterium exchange.

An electromagnet allowed the mass range 1-400 to be scanned. The scan time could be chosen from six speeds varying from 100 to 5000 seconds. The slowest scan time was generally chosen which meant the time taken to scan from m/e 12 to 20 would be about two minutes.

The vacuum inside the mass spectrometer was produced by an oil diffusion pump and an AEI 'Metrovac' type GDR1 rotary pump. Background pressure was measured by an AEI 'Metrovac' VC3 ionisation gauge positioned between diffusion pump and the source. Typical operating pressures were 53 \(\mu\)Pa on 'ready' and 1060 \(\mu\)Pa when scanning spectra. The mass spectrometer was baked out between experiments, by three band heaters.

2.6 The Pretreatment of Catalysts

A catalyst sample of 50 mg was weighed accurately and placed in the clean, dry reaction vessel and attached to the vacuum line. This was evacuated until a 'sticking' vacuum as determined by the McLeod gauge was obtained. The catalyst was then purged with hydrogen which had been passed through liquid nitrogen for thirty minutes at room temperature. After this time the temperature was raised over three hours to 773 K and the
catalyst reduced for sixteen hours under the continuous flow of hydrogen.

After reduction the catalyst was cooled to 573 K, then degassed to a sticking vacuum and finally set to the temperature required for reaction. This procedure was the same for all experiments.

2.7 The Pretreatment of Reactants and Experimental Procedure

The source and level of purity of reagents used for reaction, sensitivity factors and reduction of catalysts are given in Table 2.3. A sticking vacuum as indicated on the McLeod gauge was obtained at all times prior to admission of gases into the lines. The relevant parts of the lines were flushed with the gas involved to remove any adsorbed impurities.

Purification of hydrogen and deuterium were carried out by passing the gas through electrically heated palladium-silver alloy thimble. The gases were then passed through a liquid nitrogen cold trap at 78 K which removed any condensible impurities. The hydrocarbons were purified by distillation which was done by repeatedly freezing, pumping and then thawing the gas. Only the middle third of the sample was retained on the final distillation; the high and low boiling point fraction were pumped away. Methane has a vapour pressure at 78 K so extra care was taken in purifying this reagent, only about the middle sixth was used for reaction. The use of ultra high purity methane should have greatly reduced the possibility of impurity.
Reaction mixtures were prepared in the mixing volume section of the line by admitting the pressure of hydrocarbon, as measured by the diaphragm gauge and then making up to the total pressure with deuterium by opening the stopcock to the deuterium bulb slightly. The excess pressure of deuterium (about 30 to 50 times that of hydrocarbon) prevented any back diffusion. When two hydrocarbons were required, the first could be frozen down in a sample tube before adding the second. The gases were allowed to mix for at least 20 minutes before a reaction was started.

For all experiments the hydrocarbon to hydrogen/deuterium ratio was 1:10. The pressures used were 0.80 kPa of hydrocarbon and 8.0 kPa of hydrogen/deuterium. This gave $4.6 \times 10^{19}$ molecules of hydrocarbon in the reaction vessel for exchange experiments and $3.0 \times 10^{19}$ molecules for hydrogenolysis experiments.
References

Chapter 2

1) 'Interkey' and 'Interflow' Glassware.
   G. Springham and Co. Ltd.

2) Instruction manual, mass spectrometer type MS10.
   Associated Electrical Industries Ltd.,
   Instrumentation Division.
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Source</th>
<th>Purity</th>
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<td>Hydrogen</td>
<td>British Oxygen Co.</td>
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<tr>
<td>Deuterium</td>
<td>Matheson Company Ltd.</td>
<td>99%</td>
</tr>
<tr>
<td>Methane</td>
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<td>Ethane</td>
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<td>99%</td>
</tr>
<tr>
<td>Propane</td>
<td>Philip '66'</td>
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</tr>
<tr>
<td></td>
<td>Philips Petroleum Co. Ltd.</td>
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<tr>
<td>Butane</td>
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<td>n-Pentane</td>
<td>Dept. of Scientific and Industrial Research</td>
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</tr>
<tr>
<td></td>
<td>Laboratory, Teddington</td>
<td></td>
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<tr>
<td>Cyclopentane</td>
<td>B.D.H. Chemicals Ltd.</td>
<td>99.9%</td>
</tr>
</tbody>
</table>
Figure 2.1 Gas handling apparatus for mass spectrometer

- greaseless socket
- cold finger
- MIXING BULB
- cold finger
- Bl4 sockets
- Diaphragm gauge
- greased taps
- greaseless taps

A - purified gases
B - palladium diffusion thimble

To pump
Gas handling line for gas chromatograph

Figure 2.2

cold fingers

socket

3-way tap

capillary tubing

socket

Cold finger

McLeod Gauge

To pump

cold finger

To pump

A - purified gases

B - diaphragm gauge
Figure 2.3 The reaction vessel

A  'pyrex' TF2/13 rotoflow tap
B  graded glass seal
C  catalyst sinter
D  thermocouple pocket
E  B24 ground glass silica cone
CHAPTER 3

ANALYSIS OF EXPERIMENTAL DATA

3.1 Analysis of Mass Spectral Data

The exchange reactions produced spectra which consisted of a number of peaks of varying intensity, corresponding to the species of different mass. A run at one temperature produced a number of these spectra taken at definite time intervals. The peak heights were measured and converted to a common sensitivity. For each mass the heights were plotted against time, taking into account the time difference between each peak in one spectrum. A smooth curve was then drawn through the points of each mass to correct for any fluctuations in sensitivity. Peak heights at certain time intervals were read of these graphs and this data was then subjected to three sets of corrections.

1) Correction for background interference.

2) Correction for naturally occurring heavy isotopes of the elements present.

3) Correction for molecular fragmentation which occurs in the source of the spectrometer.

Background Correction

The peak heights for the various background species were measured immediately before letting in the reactant gases and after evacuation when the experiment was terminated. These were substracted from the experimentally obtained peak heights during reaction.
Isotope and fragmentation calculations were carried out using an ICL 4/75 computer. The program used had already been written and is described at length elsewhere\(^1\). A copy of the program, written in Fortran, is included in Appendix 1.

**Correction for Naturally Occurring Isotopes**

A hydrocarbon molecule containing only carbon and hydrogen has stable isotopes of \(^{13}\)C and \(^2\)H(D) in the abundances 1.069% and 0.016% respectively\(^2\). For the hydrocarbon \(C_nH_m\) the binomial expression:-

\[
(A_{12} + A_{13} X)^n \quad (A_{1H} + A_{2H} X)^m
\]

where \(A\) is the abundance of the isotope denoted by the subscript can be used to find the ratio of peaks containing natural isotopes to that of the parent hydrocarbon. Substituting the relevant numbers this becomes:-

\[
(0.98931 + 0.01069X)^n \quad (0.99984 + 0.00016X)^m
\]

and expansion of this binomial expression gives terms in \(X\) as follows;

\(x^0\) denoting the probability of the parent peak (P)
\(x^1\) denoting the probability of the (P+1) peak
\(x^2\) denoting the probability of the (P+2) peak etc.
With increasingly deuterated species, \( C_{n}H_{m-r}^{D_{r}} \), the contribution due to naturally occurring deuterium will be reduced. This can be expressed by replacing \( m \) in equations 3.1 and 3.2 by \( (m-r) \). The correction is carried out from low masses working up to high mass values due to the greater abundance of the low mass isotopes of carbon and hydrogen. The corrected peak heights are used for the calculation of the next highest mass.

Correction for Molecular Fragmentation

Molecules in the source collide with the electron beam and can:-

a) lose an electron to give the parent ion
b) lose one or more hydrogen atoms to give \((P-1), (P-2), \ldots, (P-X)\) peaks in the spectrum
c) break carbon-carbon bonds leading to fragmentation of the molecule.

Some of the electrons have enough energy to carry out the last process which gives rise to peaks in the spectra at lower mass numbers than the parent molecule \(^{(3)}\). The extent of fragmentation is directly proportional to the energy of the ionising electrons, the electron beam voltage. However, sensitivity also decreases with electron voltage so a balance had to be maintained between peak heights and parent to fragment peak ratio. This was determined by experiment and for all molecules used in the MS10 an electron voltage of 20 eV \((32 \times 10^{-16} \text{ kJ})\) was found to be an adequate compromise.

For exchange of hydrocarbons with deuterium only
those fragments resulting from hydrogen and/or deuterium are of importance. The fragmentation factor of the light hydrocarbon, $f_1$, is defined as

$$f_1 = \frac{C_{nH_m-i}}{C_{nH_m}}$$

3.3

i.e. the ratio of the peak heights of fragment and parent ion after correction for background and naturally occurring isotope. This can be determined from the mass spectrum of the reactant hydrocarbon. The fragmentation factor, $f_1'$, that of the fully deuterated molecule can be calculated by multiplying the relevant peak heights in $f_1$ by 0.65, this being the average ratio of heavy to light fragmentation factors (4).

Knowing the fragmentation factors $f_1$ and $f_1'$ and assuming that C-H bonds are broken more readily than C-D, a statistical scheme (5) can be used to correct for fragmentation. Quantitative descriptions of the different probabilities for the loss of hydrogen or deuterium atoms from a molecule is given by the $\Gamma$ and $\Pi$ factors first defined by Evans et al (6).

$$\Gamma = \frac{\text{observed prob. of losing an H from } C_{nH_{n-1}D}}{\text{statistical prob. of losing an H from } C_{nH_{n-1}D}}$$

3.4

$$\Pi = \frac{\text{observed prob. of losing a D from } C_{nHD_{n-1}}}{\text{statistical prob. of losing a D from } C_{nHD_{n-1}}}$$

3.5

An improvement on the statistical method is an empirical scheme where the dependence of fragmentation of
C-H and C-D bond is related to the nature of the other bonds in the molecule \(^{(4)}\). The method of Dowie et al \(^{(4)}\) was used in the computer program. The values for \(f_i/f_i' = 0.65\), \(\Pi = 0.91\), \(\Gamma = 1.1\) \(^{(3)}\) were found to be adequate to describe the fragmentation of the molecules studied at an electron beam voltage of 20 eV.

Fragmentation corrections were made from the highest mass peak working down the mass range, calculations being made with the corrected peak heights. The contributions from fragmentation was found by multiplying the fragment factor and the magnitude of the higher mass peak, then subtracting this from the lower mass peak height.

After the appropriate corrections, each isotope was expressed as a percentage. This gave the results in the form of isotopic distributions at times throughout the experiment. The mean number of deuterium atoms entering 100 hydrocarbon molecules can be defined as \(\phi\) where

\[
\phi = \sum id_i
\]

\(d_i\) is the percentage of hydrocarbon with \(i\) deuterium atoms. \(\phi\) was also calculated and tabulated against time.

3.2 Exchange Reactions

The treatment of exchange reactions has been well defined by Kemball \(^{7-10}\). Only the appropriate equations and definitions are repeated here.

The course of an exchange reaction can be followed by the mean deuterium content of the hydrocarbon. If \(x_i\)
is the percentage of hydrocarbon with \( i \) deuterium atoms at time \( t \) then parameter \( \phi \) is defined as in equation 3.5.

\[
\phi = x_1 + 2x_2 + 3x_3 + \ldots \ldots mx_m
\]

the mean deuterium content of 100 molecules is then given by \( \phi/m \). If all the hydrogen atoms in the molecule are equally likely to exchange the reaction can be described by:

\[
\frac{d\phi}{dt} = k_\phi (1-\frac{\phi}{\phi_\infty})
\]

\( k_\phi \) is a rate constant equivalent to the number of deuterium atoms entering 100 hydrocarbon molecules in unit time. \( \phi_\infty \) is the equilibrium value of \( \phi \) found either by experiment or by calculation knowing the probability of a deuterium atom entering the hydrocarbon molecule.

If equation 3.7 is integrated it gives the empirical first order equation:

\[
-log_{10}(\phi_\infty - \phi) = \frac{-k_\phi t}{2.303 \phi_\infty} - log_{10}(\phi_\infty - \phi_o)
\]

where \( \phi_o \) is the initial value of \( \phi \). A plot of \( ln(\phi_\infty - \phi) \) versus time will have a slope of \(-k_\phi/\phi_\infty\) and hence the rate constant can be simply found.

Further understanding of the nature of an exchange reaction may be obtained by determining a second rate constant \( k_o \), representing the initial rate of disappearance of the light hydrocarbon, \( C_nH_m \) in terms of percentage loss per unit time. A similar empirical first order equation to that for \( \phi \), in equation 3.8, can be derived.
\[-\log_{10}(x_0-x) = \frac{k_0 t}{2.303 (100-x_0)} = -\log_{10}(100-x_\infty) \] 3.9

where \(x_0\) represents the percentage of \(C_nH_m\) at time \(t\); \(100\) and \(x_\infty\) are initial and final percentages of the light hydrocarbon.

The ratio of the two rate constants is represented by \(M\) where:

\[ M = \frac{k_\phi}{k_0} \] 3.10

and represents the mean number of hydrogen atoms exchanged with deuterium in each molecule of the hydrocarbon.

It is now possible to distinguish between two types of reaction:

1) Simple or stepwise exchange. Only a single hydrogen atom is replaced by a deuterium on one adsorption of the molecule to the catalyst's surface. Isotopic species containing two or more deuteriums are formed by successive reactions. This reaction is recognised by two criteria:
   a) The value of \(M\) is unity.
   b) The only initial product is the monodeutero species \(C_nH_{m-1}D\).

2) Multiple exchange reactions. Where more than one deuterium atom is introduced into the hydrocarbon molecule on one interaction with the catalyst. This class of reaction is recognised by:
   a) The value of \(M\) is greater than unity, and gives the average number of
deuterium atoms exchanged into each molecule of hydrocarbon on one visit to the catalyst's surface.

b) The initial products will contain species having more than one deuterium atom.

3.3 **Analysis of Gas Chromatographic Data**

Gas chromatography can be used to detect small quantities of hydrocarbons provided the sensitivity of each paraffin to the column and flame ionisation detector is accurately measured. This was done by taking similar pressures of the reactant and product gases, passing each through the gas chromatograph and determining the mean peak area for each hydrocarbon over several samples. The area obtained for the methane peak was taken as unity and the other gases quoted as a multiple of the methane area. Typical examples of sensitivity factors obtained are shown in Table 3.1.

The integrator values for the peak areas were divided by the relevant sensitivity factors and the values used to express the amount of each hydrocarbon as a percentage of molecules present in the gas phase. The initial product distributions were calculated in terms of molecule per cent as this best allows for the formation of low hydrocarbons by multiple bond rupture.

\[ \text{e.g. } nC_4 \rightarrow 4C_1 \]

1 molecule \quad 4 molecules

hence to have an accurate representation of the initial product distribution, the percentages must be calculated in terms of molecules.
To obtain an accurate rate of reaction, i.e. loss of the reactant hydrocarbon, the amount of hydrocarbon must be expressed as a percentage of total carbon in the system. The error resulting from a rate calculated in molecules per cent becomes obvious in a simple example; if 50% of 100 n-butane molecules reacted via a central bond scission to give 100 molecules of ethane, the total number of molecules in the system would now be 150 and to calculate the amount of butane left in the system it would appear that 50/150 i.e. only a third of the butane was left in the system and 2/3 had reacted. This is clearly not true and a calculation carried out in carbon per cent would give a total of 100 molecules and the factor reacted = 50/100 i.e. 50% reacted. Expressing rate in carbon per cent eliminates the error arising from small fragments.

The course of the reaction was followed by plotting the constituent percentages with time. For butane and n-pentane, disappearance of the reactant hydrocarbon followed apparent first order kinetics.

\[
\log_{10} (a-x) = \log_{10} a - \frac{kt}{2.303}
\]

where \((a-x)\) is the concentration of the reactant at time \(t\) and \(k\) is the first order rate constant in per cent per minute. The initial rate constant \(k\) was obtained from the slope of a plot of \(\log_{10} (a-x)\) against time. In the case of cyclopentane the plot of percentage against time gave a good straight line and the reaction appeared to follow zero order kinetics. The rate constant was found by the slope of the \((a-x)\) against time plot.
For all reactions the initial rates of the products were calculated by taking the tangent to the initial slope of percentage species against time plots. The relative magnitudes of these initial rates of formation gave the initial product distributions.

3.4 Rate Calculations

Rates of reaction for exchange and hydrogenolysis reactions obtained from the experimental observations were in per cent per minute per 50 mg catalyst sample as described previously. There were converted to turnover frequencies, \( Z \), as shown in equation 3.12.

\[
Z = \frac{\text{Rate} \times \text{no. of molecules gas in reaction vessel} \times 20}{\text{Weight of catalyst sample} \times \text{no. of atoms on catalyst surface per gram} \times 60} \times 10
\]

Hence rates in terms of molecules reacted per second per surface metal atom were obtained.
References

Chapter 3


TABLE 3.1

Sensitivity Factors

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Iso Butane</th>
<th>N Butane</th>
<th>Iso Pentane</th>
<th>N Pentane</th>
<th>Cyclo Pentane</th>
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<td>Sensitivity Factor</td>
<td>1.00</td>
<td>1.93</td>
<td>2.92</td>
<td>4.20</td>
<td>3.97</td>
<td>5.20</td>
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Both the hydrogen adsorption measurements and the temperature programmed reduction spectra were carried out in the laboratories of Petrochemicals Division, Imperial Chemical Industries Ltd.

4.1 Metal Area Determinations

Low temperature physical adsorption such as that used for Brunauer, Emmett and Teller isotherm\(^{(1)}\), cannot distinguish between metal and uncovered support surfaces. The surface area of the metal is often a small fraction of the total catalyst surface area and a selective method is required in which the gas is adsorbed on the metal but not on the carrier. This means chemisorption must be employed at temperatures higher than those at which physical adsorption can occur\(^{(2,3,4)}\). For most group VIII metals dispersed on silica or alumina \(\text{H}_2\) or CO adsorption at room temperature is found to be satisfactory\(^{(5,6)}\). Saturation coverage of the metal is attained at very low equilibrium pressures, so the isotherms are flat over the range of pressures of the isotherms, usually 3.78 to 75.66 kPa. The saturation (monolayer) value for the amount of adsorbed gas can be determined by extrapolation of the isotherm to zero pressure. The linear part of the isotherm corresponds to the weakly bound fraction of the total chemisorbed gas, extrapolation of this to zero pressure gives an estimate of the strongly bound fraction since this is obtained at pressures much lower than the measured isotherm\(^{(7)}\).
Another method to determine the amount of strongly bound hydrogen is to evacuate the catalyst at room temperature and then measure a second isotherm. The amount of strongly bound hydrogen is found by subtracting the second isotherm from the first. The monolayer coverage found by this 'subtraction' method is usually about 75% of that found by 'extrapolation' \(^{(8)}\), used by Sinfelt.

When hydrogen is chemisorbed on group VIII metals, it is generally believed that the molecule dissociates into atoms on chemisorption \(^{(7),(8)}\) and that each hydrogen atom is bound to one metal atom only. Since each hydrogen represents a surface metal atom, the ratio \(H/m\), that of adsorbed hydrogen atoms to total metal atoms present on the catalyst, gives an idea of the dispersion of the metal on the catalyst surface. Only surface metal atoms are useful for catalytic reactions, so the hydrogen adsorption can measure exactly how many of the total metal atoms can be used. Using the value of 633 pm\(^2\) for the cross sectional area of the hydrogen atom then the total metal surface area can be calculated.

The values for monolayer adsorption were calculated in the present study by drawing the best straight line through the adsorption isotherm. This gave a value about 10% lower than that by Sinfelt's method and therefore lies about half way between the 'extrapolation' and 'subtraction' methods. The catalyst was reduced at 693 K before being lowered to room temperature to obtain the adsorption isotherm. Values obtained for monolayer coverage are tabulated in Table 4.1 with a summary of the data obtained from these measurements. The ratio of surface metal atoms...
to total metal atoms, the dispersion $H/m$, is near unity for all catalysts only falling significantly below this on iridium itself. This means that nearly all metal atoms present are surface atoms. Values of $H/m$ greater than unity are probably due to metal atoms at edge sites and corners which may adsorb more than one hydrogen atom\(^{(7)}\). The values for the number of surface metal atoms were used to calculate the rates of reaction in terms of turnover numbers. Metal dispersions are in fair agreement with those found recently by Sinfelt for alumina supported platinum-iridium catalysts.\(^{(7)}\)

Before the adsorption isotherms were measured the catalysts were reduced at 693 K a lower temperature than that used for reduction before reaction, 773 K. The temperature difference should not cause appreciable sintering or loss of accessibility on these metals as long as the temperature does not rise above 873 K\(^{(7,8)}\).

4.2 Temperature Programmed Reduction (T.P.R.)

This sensitive technique involves measuring the hydrogen consumption on reducing an oxidised metal catalyst over a temperature range determined by linear temperature programming. Temperature programmed reduction has been found to be very useful for examining highly dispersed, supported metal catalysts and the method is described in detail elsewhere\(^{(9,10)}\). All the catalysts and the salts used in their preparation (bis(acetylactenato)platinum II) and tris(acetylacetanato)iridium III) were characterised by T.P.R. and the resulting spectra are illustrated in
figures 4.1 to 4.8. The platinum salt gave a single sharp peak at 443 K which can be assigned by previous work on platinum catalysts\(^{(11,12)}\) as divalent platinum. The iridium salt sublimed during reduction. T.P.R. spectra of the catalysts are all very similar with two reduction peaks between 373-433 K and 623-683 K.

These catalysts appear to have two types of reducible metal. One, more easily reduced, is probably due to metal associated with other metal atoms in the bulk. The other is more difficult to reduce, more highly dispersed and has a greater interaction with the support. On platinum\(^{(11)}\) these can be assigned to \(\text{Pt}^{2+}\) and \(\text{Pt}^{4+}\) respectively. Strong bonding to the support is also indicated by the fact that iridium is not lost during reduction as with the iridium salt. Iridium itself seems to have a stronger support interaction as shown by the higher temperature peak broadening. Evidence of greater interaction with the support by iridium has been found by Rasser\(^{(13)}\). The reduction peaks for iridium can be tentatively associated with \(\text{Ir}^{4+}\) and \(\text{Ir}^{7+}\)\(^{(12)}\).

The peak areas were measured and normalised to 0.5\% weight metal loading and plotted on figure 4.9. Up to about 50\% platinum content both peak areas are fairly linear but after this they begin to decrease in size. This could be another indication of increased metal-support interactions on iridium rich catalysts.

The temperature at which the peak maxima occur are plotted in figure 4.10. Both increase from platinum to iridium but have maxima about the 50\% iridium. Hence the
1:1 atom ratio seems to be the most stable point on the platinum-iridium series, and the most likely for chemical interaction to form a bimetallic species. Evidence in the literature\(^1\)\(^4\),\(^1\)\(^5\) confirms the 50:50 ratio to be the most stable composition in the series. Mossbauer spectroscopy\(^7\) has indicated the formation of bimetallic clusters at 50% metal iridium content for platinum/iridium catalyst supported on alumina where nearly all metal atoms are surface atoms.
References

Chapter 4

### TABLE 4.1

**Hydrogen Adsorption - Surface Data**

<table>
<thead>
<tr>
<th>Catalyst No.</th>
<th>% Ir</th>
<th>% Total Metal g⁻¹ Catalyst</th>
<th>No. Metal Atoms x 10¹⁹ g⁻¹ Catalyst</th>
<th>Monolayer Metal mol g⁻¹ Catalyst</th>
<th>No. Surface Atoms x 10¹⁹ g⁻¹ Catalyst</th>
<th>H/m</th>
<th>Metal Area m² g⁻¹ Catalyst</th>
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<td>238</td>
<td>0</td>
<td>0.51</td>
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<td>242</td>
<td>54</td>
<td>0.46</td>
<td>1.43</td>
<td>0.261</td>
<td>1.40</td>
<td>0.98</td>
<td>0.89</td>
</tr>
<tr>
<td>243</td>
<td>73</td>
<td>0.41</td>
<td>1.29</td>
<td>0.209</td>
<td>1.12</td>
<td>0.87</td>
<td>0.71</td>
</tr>
<tr>
<td>244</td>
<td>100</td>
<td>0.39</td>
<td>1.22</td>
<td>0.176</td>
<td>0.95</td>
<td>0.78</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 4.1  T.P.R. Bis(acetyl acetonato) platinum (II)
Figure 4.2  T.P.R. 100% platinum.

Hydrogen uptake/arb. units.

Temp/°C.
Figure 4.3  T.P.R. 19% iridium

Hydrogen uptake/(arbitrary units)

0 100 200 300 400 500 600 700 Temp./°c.
Figure 4.4  T.P.R.  39% iridium.
Figure 4.5 T.P.R. 46% iridium.
Figure 4.6  T.P.R. 54% iridium.
Figure 4.7  T.P.R. 73% iridium.
Figure 4.8  T.P.R. 100% iridium.
Figure 4.9  Temperature programmed reduction - peak areas.

- X - High temperature peak
- O - Low temperature peak.
Figure 4.10  Temperature programmed reduction - peak temperatures.
5.1 **Mechanism of Exchange Reactions**

In order to understand the mechanism of catalytic reactions it is necessary to know the nature and stability of intermediates formed. A handy experimental method that gives information on intermediates and the rates of formation and rupture of carbon-hydrogen bonds, is found in the exchange of saturated alkanes with deuterium. The initial percentages of exchange reactions allow the type and reactivity of catalytically formed intermediates to be determined.

The two molecules used in this study were methane and cyclopentane, the reactions of which have been reviewed by Kemball\(^(1)\) and Burwell\(^{(2)}\) respectively. Early experiments with methane\(^{(3,4)}\) showed striking differences in the distribution of initial products on different metals e.g. reaction on tungsten gives \(\text{CH}_3\text{D}\) while on nickel \(\text{CD}_4\) is the major product. Examination of the initial products from reactions at various temperatures and partial pressures of deuterium showed reaction occurred by two mechanisms:-

1) 'Stepwise' exchange which exchanges only one hydrogen giving \(\text{CH}_3\text{D}\) via a mono-adsorbed methyl radical.

2) 'Multiple' exchange where two or more hydrogens are exchanged on one residence on the catalyst's surface. This involves at least two types of
intermediates and depends on how easily these can interconvert on the surface. These are the adsorbed methylene radical \( \text{CX}_2 \) and the multiply bonded \( \text{CX} \) and \( \text{C} \) radicals.

The methyl radical is stable and does not tend to react further, however the methylene radical is more reactive and undergoes further dissociation so all hydrogen atoms are replaced and the major product is \( \text{CD}_4 \) on desorption.

The mechanism of cyclopentane exchange with deuterium on metal catalysts is well understood\(^{(5-7)}\). The exchange of methane gives an indication of the rate of C-H bond cleavage on a catalyst without any carbon-carbon bond rupture. In addition to the rates of bond breaking it is useful to know if the metal surface is one type of active site or several, and how these are affected by the addition of a second metal. The isotopic distribution patterns of cycloalkanes are rich in detail and provide a means for determining the different mechanisms that take place on a catalyst surface. This gives an indication of the different types of active site.

Cyclopentane exchange with deuterium takes place by several mechanisms, leading to products \( \text{d}_1 \), \( \text{d}_2 \) to \( \text{d}_5 \), \( \text{d}_6 \) to \( \text{d}_{10} \) and probably result from reactions on different sites. There is a combination of single and multiple exchange for one metal and different intermediates play a role in each type of exchange. Reaction intermediates are illustrated in figure 5.1. The isotope \( \text{d}_1 \) is produced by a singly adsorbed intermediate, isotopes \( \text{d}_2 \) to \( \text{d}_5 \) are produced by a second adsorption on the \( \beta \) carbon atom on the same side of the sterically flat
cyclopentane molecule. If the probability of desorption to second point adsorption (α-β diadsorption) is low, then all five hydrogens on that side of the ring will be exchanged and the isotopic distribution will show a maxima at d_5. The diadsorbed molecule can at any time in this process of 'repeated second point adsorption' adsorb on the other side of the ring in a similar manner, as illustrated in figure 5.1. This leads to exchange of the other five hydrogens on the opposite side of the ring and is commonly called the 'turnover' process. All ten hydrogens can now be exchanged on one residence on the catalyst surface.

5.2 Methane Exchange - Water Interference in the Mass Spectrometer

Initial experiments with methane exchange showed apparent initial percentages of isotopes d_1 to d_4 at zero time of reaction despite correction for background and naturally occurring isotopes. An example is shown in figure 5.2. There are three explanations for this;

1) There is a type of site on the catalyst which is very active for exchange but is very quickly poisoned, so all reaction on these sites has ceased by the time of the first reading.

2) Water isotopes (H_2O, DHO, D_2O) are formed on the catalyst surface by reaction of oxygen with the reaction mixture.
3) Water isotopes are displaced by reaction mixture deuterium from species in the mass spectrometer.

If either of alternatives (2) and (3) are the dominant source of interference then the errors in the isotope percentages are not caused by methane isotopes but by water isotopes ($\text{H}_2\text{O}$, $\text{DHO}$ and $\text{D}_2\text{O}$) which have the same masses as the deuterated methanes and cannot be distinguished by mass spectroscopy.

Before each experiment the mass spectrometer was baked out overnight. Background was determined by measuring the mass range m/e 12 to 20 before the reaction mixture was admitted and after this was pumped away when the experiment was completed. The average of both sets of peaks was substracted from the heights of peaks obtained at each experimental reading and hence correction for background was obtained.

The previous experiments had shown a proportional rise in the background interference with the chronological order in which the experiments were carried out, implying a build up of heavy water isotopes in the mass spectrometer which increased with every experiment carried out - a 'memory' effect. If this is so then option (3), that of the exchange of oxygen species with deuterium in the mass spectrometer is the source of the trouble.

To investigate this possibility 8.0 kPa of deuterium (the same pressure as used for reaction) was placed in the reaction vessel, without catalyst and at room temperature, and allowed to bleed into the mass spectrometer. The
background was monitored over a period of time on two separate occasions, an example is given in figure 5.3. Time zero refers to the time at which deuterium was admitted. After admission of deuterium, isotopes 18, 19 and 20 rise rapidly but 19 and 20 rise faster than 18 showing the background to be deuterating with time. This clearly shows interference of type 3 i.e. exchange of water isotopes on the mass spectrometer surfaces with reaction mixture deuterium.

Normal baking had not been enough to remove this 'memory' effect in the mass spectrometer and background measurements before and after admission of the reaction mixture could not detect the reaction on the instrument surfaces. Therefore to overcome this problem the spectrometer had to be stripped of residual adsorbed water and hydrogen more thoroughly than normal baking could achieve. This was accomplished by baking out with 8.0 kPa of light hydrogen, purified by passing through a palladium silver thimble, leaking into the spectrometer from the vessel not used for the catalyst reduction. Leak rate was about two per cent per hour.

After overnight baking with hydrogen 8.0 kPa of deuterium was again admitted and the background followed with time with the result illustrated in figure 5.4. The initial background has been reduced but there is still an increase of masses 18, 19 and 20 with time and so the exchange of reaction mixture deuterium with residual water isotopes has still not been prevented. This exchange in the mass spectrometer cannot be distinguished from that over the catalyst.
In order to overcome this unwanted exchange reaction 8.0 kPa of light hydrogen, purified by a palladium silver thimble, was leaked simultaneously with the reaction deuterium, through the second capillary leak. Both capillaries have similar leak rates and the reaction vessels are independent of each other. Hence by introducing a pool of light hydrogen in the spectrometer, exchange of deuterium with the adsorbed species would be kept to a minimum. Figure 5.5 shows the background with time when 8.0 kPa of light hydrogen was leaked in with 8.0 kPa of deuterium and the spectrometer had been baked overnight in light hydrogen. Now there is no dramatic rise in masses m/e 18, 19 and 20 and peaks 19 and 20 do not rise faster than 18 showing there is no deuterium exchange in the mass spectrometer.

All methane exchange experiments were carried out with these measures in force and normal reaction kinetics were observed for the production of the deuterated species. On the 100% platinum and 81% platinum catalysts methane exchange was carried out with and without the hydrogen treatment and both gave similar reaction rates but in the absence of light hydrogen the initial products were not as accurate, due to the error from water isotopes.

5.3 Methane Exchange Reactions

The reaction of methane with deuterium was carried out at 473 K with a ionising voltage of 20 eV and methane:deuterium ratio of 1:10. Experimental data was analysed as described in Chapter 3 and rates of deuterium entry
$k_\phi$ and rates of disappearance of light methane calculated from the first order rate equation given before. Table 5.1 summarises the $k_o$ rates in turnover frequencies (molecules per second per surface metal atom), multiplicities $m = k_\phi/k_o$, and the initial product distributions. A value of $m$ was calculated from the initial products by the relationship:

$$m = \frac{\sum_{n=1}^{n} n d_n}{100}$$  \hspace{1cm} 5.1$$

where $d_n$ represents the percentage of the isotope containing $n$ deuterium atoms.

Typical reaction course with time plots are given in figures 5.6 to 5.8 and the first order rate plots from which the rates were calculated are shown in figure 5.9. Reaction rates decrease linearly as iridium content is increased, which is clearly shown on the plot of reaction rate against percent iridium on figure 5.10. Platinum has the highest activity, being about twice as fast as iridium.

The initial products obtained on platinum show stepwise exchange to be the dominant mechanism although there is a little multiple exchange. The bimetallic catalysts show similar isotopic distributions to platinum but as iridium content increases, multiple exchange character increases slightly. On all catalysts, however, single exchange is the dominant mechanism. A similar sequence of products i.e. $\text{CH}_3D > \text{CH}_2D_2 > \text{CHD}_3 > \text{CD}_4$ has been found on reaction on platinum films (8).
Table 5.2 lists the literature comparisons with methane exchange reactions. Haining (9) carried out methane exchange on a platinum/alumina/chlorine catalyst on the apparatus at Edinburgh using a methane to deuterium ratio of 1:10. Assuming similar metal dispersions and correcting for metal loading and catalyst sample weight, Haining's platinum catalyst gives a very similar rate to the one used in the present study. Initial products show the same pattern, the dominant exchange mechanism is that of single exchange.

Methane exchange with deuterium on iridium has been carried out on films (10) and on a silica support (11). Both use a higher partial pressure of hydrocarbon and consequently the extent of multiple exchange is greater than that found in the present study.

Methane exchange shows that iridium has a slightly greater tendency to form multiple carbon to metal bonds, but there is very little difference across the catalyst series. Only reaction rate, which is indicative of product desorption, alters to any significant extent and indicates that the desorption step becomes more difficult as iridium content is increased.

5.4 Cyclopentane Exchange with Deuterium

The exchange of cyclopentane with deuterium is a much more facile reaction than that of exchange of methane (5, 6, 10). This is shown by the low reaction temperature required to produce a similar rate to that of methane exchange, as all cyclopentane reactions were carried out at 303 K. Other reaction conditions were as
described earlier. Rates of reaction, $k_0$, are illustrated in figure 5.10 and tabulated with multiplicities in Table 5.3. Figure 5.11 shows typical rate plots obtained and figure 5.12 displays the reaction course with time for the reaction on iridium. At this temperature all rate plots gave a good straight line and did not indicate any self poisoning of the reaction. The initial products are summarised in Table 5.4. Exchange products $d_6$ to $d_{10}$ were summed and are displayed with the ratio of isotopes $d_2:d_5$ in Table 5.3. Two early experiments were carried out with a hydrocarbon:deuterium ratio of 1:25 and these are indicated in the appropriate tables.

The rate of exchange is faster on platinum than on iridium but not markedly so. The bimetallic catalysts are all very similar for rates of reaction and there is not such a progressive decrease in rate with iridium content as was found for methane exchange reactions. Although overall rate is quite similar on all catalysts, the distributions of isotopic products show interesting differences. Platinum displays the usual combination of processes leading to single and multiple exchange; the monodeuterated product formed by a monoadsorbed intermediate, products $d_2$ to $d_5$ formed by $\alpha\beta$ diadsorption and $d_6$ to $d_{10}$ formed by this with the 'roll over' process. There is an increase in percentage from $d_2$ to $d_5$ and again from $d_6$ to $d_{10}$ which shows a greater tendency for repeated second point adsorption before desorption of the deuterated hydrocarbon molecule.
On iridium there is a greater tendency for single exchange and $d_1$ is much more prominent with a corresponding decrease in multiply exchanged products. There are no maxima at $d_5$ and $d_{10}$, although these species are produced, but now a decrease in percentage from $d_2$ to $d_5$ and $d_6$ to $d_{10}$. The same processes operate on iridium as on platinum but there is a lower tendency for adsorption on a second point on the carbon ring before desorption of the molecular product. The bideutero isotope, $d_2$, has increased in importance on iridium and this may indicate the formation of an $\alpha\alpha$ diadsorbed intermediate species in preference to an $\alpha\beta$. A doubly deuterated product could be formed by one $\alpha\beta$ diadsorption which subsequently desorbs; however, methane exchange has shown iridium to be slower for product desorption and better for creating multiple carbon to metal bonds. The existence of multiple surface to hydrocarbon bonding has been reported in the literature $^{(12)}$, for iridium catalysts.

On the monometallic catalysts there are three processes involved for multiple exchange. These have been characterised by Burwell $^{(13)}$.

1) Initial monoadsorbed cyclopentane forms a cis diadsorbed cyclopentene and if the ratio $C_5H_9^* \rightarrow C_5H_8^{**}$ to that of desorption of $C_5H_9D$ is low then the $\% d_2 > \% d_3 > \% d_4 > \% d_5$. A high $\% d_1$ is a sign of a high probability of desorption.
2) A process as in (1) but the ratio is large, then \( \% d_2 < \% d_3 < d_4 < \% d_5 \). A maxima at \( d_5 \) shows a high probability of diadsorption at the \( \beta \) carbon atom.

3) A 'roll over' process leading to similar type of exchange of the five hydrogens on the other side of the ring.

Processes (2) and (3) describe the exchange on platinum while process (1) partly describes the reaction on iridium although there appears to be an \( \alpha \alpha \) diadsorption process in operation on this catalyst.

The isotopic distribution of the bimetallic catalysts are quite similar to that on platinum itself with maximas at \( d_5 \) and \( d_{10} \). There is a greater contribution from the monoadsorbed intermediate, \( d_1 \) increases with iridium content, and from the \( \alpha \alpha \) diadsorbed surface species as \( d_2 \) increases almost linearly across the series. Both modes of diadsorption, \( \alpha \alpha \) and \( \alpha \beta \), now compete with one another and a measure of this competition can be gained from the \( d_2/d_5 \) ratio, Table 5.3. If the \( \alpha \alpha \) mode of adsorption is dominant then the exchange will go no further than \( d_2 \), if \( \alpha \beta \) is the mechanism responsible then exchange will mostly carry on until \( d_5 \). The amount of \( d_2 \) increases with iridium content until at about 50% iridium composition the two processes contribute equally. After this the ratio rises steeply until on iridium itself, \( \alpha \alpha \) diadsorption is the dominant process.

The presence of iridium also inhibits the 'roll over' mechanism as shown by the sums of isotopes \( d_6 \) to
in Table 5.3. This is high on platinum, fairly constant across the bimetallics and then drops sharply on iridium. The relatively high percentages of $d_6$ and $d_7$ on iridium may indicate an $\alpha\alpha$ turnover process after the replacement of one or two hydrogens and this may prevent 'roll over' by an $\alpha\beta$ intermediate.

The isotopic distributions show very marked changes between the monometallic and bimetallic catalysts. The presence of only 17% platinum is enough to increase the $d_5$ percentage three times and the $d_{10}$ species four times, these being indicative of the repeated $\alpha\beta$ diadsorption and $\alpha\beta$ 'roll over' respectively. Between the iridium and 17% platinum catalysts the $d_2/d_5$ ratio shows a change from a situation where the $\alpha\alpha$ process of adsorption is four times as important as that of the $\alpha\beta$ to one where the two processes make about equal contributions. This break in character is also noticeable between platinum and 19% iridium where the $d_2/d_5$ ratio doubles. A similar change in activity is only noticeable between 19% and 73% iridium i.e. across the whole of the bimetallic series. The competing mechanisms of adsorption do not show an additive effect (i.e. the percentage of an isotope on a bimetallic catalyst is not the sum of the activities on platinum and iridium) over the bimetallic series.

Increasing the partial pressure of deuterium does not seem to effect the reaction rate but as expected $^{(6)}$ decreases the extent of multiple exchange. It is clear that the bimetallic catalysts are similar in rate to iridium but similar in reaction character to platinum. Both rate and the nature of exchange are not additive
over the catalyst series and imply bimetallic interaction between the constituent metals.

Recent literature \(^{(13)}\) quotes work carried out on a platinum/alumina catalyst and the results are summarised in Table 5.5. Allowing for the higher temperature the rate obtained is almost 10 times slower than that found in the present study and the initial product distributions are also very similar.

5.5 Comparison of Methane and Cyclopentane Reactions

Cyclopentane exchange with deuterium is one of the easiest reactions to carry out on supported metal catalysts \(^{(5)}\). This is shown by the low reaction temperature required to obtain a similar rate to that for methane exchange. An activation energy for methane exchange on a similar platinum catalyst has been recently determined \(^{(9)}\) (90 kJ mol\(^{-1}\)). If this is used to adjust the rate of methane exchange found at 473 K to one expected at 303 K, the cyclopentane rate is faster by a factor of 10\(^6\).

This difference in rate between the two molecules can be attributed to the bond dissociation energies of the carbon-hydrogen bonds in each molecule. These are \(^{(14)}\):

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Dissociation Energy (C-H)</th>
<th>Exchange rate 303</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>431 kJ mol(^{-1})</td>
<td>3.7 x 10(^{-8})</td>
</tr>
<tr>
<td>C(<em>5)H(</em>{10})</td>
<td>397 kJ mol(^{-1})</td>
<td>6.5 x 10(^{-3})</td>
</tr>
</tbody>
</table>

The difference in dissociation energy is 34 kJ mol\(^{-1}\).
Thus if:

\[
\begin{align*}
\text{rate } \text{CH}_4 &= A e^{-E_1/RT} \quad 5.2 \\
\text{rate } \text{C}_5\text{H}_{10} &= A e^{-E_2/RT} \quad 5.3
\end{align*}
\]

and assuming that the pre-exponential factor, A, is the same in both cases, then

\[
\text{Ratio of the rates} = e^{-\Delta E/RT} \quad 5.4
\]

At 303 K using the difference in bond dissociation energy, 34 kJ mol\(^{-1}\), this gives a value for \(\Delta E\) rate to be \(1.37 \times 10^{-6}\) which is very close to the difference between the exchange rates at this temperature. It appears then, as expected, the exchange rate is determined by the bond dissociation energy of C-H in a molecule.
References

Chapter 5

    To be published.
14) J.G. Calvert and J.N. Pitts, 'Photochemistry'
### TABLE 5.1

**Methane Exchange with Deuterium at 473 K**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>(k_o)</th>
<th>M</th>
<th>(% d_1)</th>
<th>(% d_2)</th>
<th>(% d_3)</th>
<th>(% d_4)</th>
<th>(M^A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>238</td>
<td>0</td>
<td>0.014</td>
<td>1.1</td>
<td>87</td>
<td>9</td>
<td>3</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>239</td>
<td>19</td>
<td>0.012</td>
<td>1.1</td>
<td>82</td>
<td>13</td>
<td>4</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>240</td>
<td>39</td>
<td>0.011</td>
<td>1.2</td>
<td>79</td>
<td>10</td>
<td>8</td>
<td>3</td>
<td>1.4</td>
</tr>
<tr>
<td>241</td>
<td>46</td>
<td>0.013</td>
<td>1.2</td>
<td>83</td>
<td>13</td>
<td>3</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
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<td>54</td>
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<td>85</td>
<td>10</td>
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<td>1.2</td>
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<tr>
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<td>0.011</td>
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<td>84</td>
<td>10</td>
<td>4</td>
<td>2</td>
<td>1.2</td>
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<td>0.0078</td>
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<td>79</td>
<td>14</td>
<td>4</td>
<td>3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\(A\) - calculated from the initial products

\[ M = \Sigma_{n} d_n / 100 \] where \(d_n\) is the percentage of the isotope containing \(n\) deuterium
### TABLE 5.2

Comparison of Methane Exchange Results with Literature

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_0$</th>
<th>d₁</th>
<th>d₂</th>
<th>d₃</th>
<th>d₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238 (a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>0.014</td>
<td>87</td>
<td>9</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Pt/Al₂O₃/Cl (b)</td>
<td>0.016</td>
<td>82</td>
<td>9</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>RC244 (a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir/Al₂O₃</td>
<td>0.0078</td>
<td>79</td>
<td>14</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Ir/SiO₂ (c)</td>
<td>0.00053</td>
<td>64</td>
<td>10</td>
<td>7</td>
<td>19</td>
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<tr>
<td>Ir film (d)</td>
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<td>20.9</td>
<td>22.3</td>
<td>33.0</td>
<td>23.7</td>
</tr>
</tbody>
</table>

(a) Catalysts used in the present study. Exchange carried out at 473 K.


(c) From Wong et al. unpublished. Exchange carried out at 420 K.

## TABLE 5.3

Cyclopentane Exchange with Deuterium at 303 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>$k_o$</th>
<th>$M \left( k_{ph}/k_o \right)$</th>
<th>Sum $d_{6}-d_{10}$</th>
<th>Ratio $d_2/d_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.0065</td>
<td>4.0</td>
<td>17.7</td>
<td>0.29</td>
</tr>
<tr>
<td>RC239</td>
<td>19</td>
<td>0.0040</td>
<td>3.1</td>
<td>12.9</td>
<td>0.59</td>
</tr>
<tr>
<td>RC240</td>
<td>39</td>
<td>0.0039</td>
<td>3.2</td>
<td>11.6</td>
<td>0.46</td>
</tr>
<tr>
<td>RC240</td>
<td></td>
<td>(0.0034&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(3.1&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(17.3&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(0.44&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.0044</td>
<td>2.9</td>
<td>10.0</td>
<td>0.83</td>
</tr>
<tr>
<td>RC242</td>
<td>54</td>
<td>0.0043</td>
<td>2.9</td>
<td>12.0</td>
<td>0.96</td>
</tr>
<tr>
<td>RC243</td>
<td>73</td>
<td>0.0045</td>
<td>2.7</td>
<td>7.8</td>
<td>1.14</td>
</tr>
<tr>
<td>RC244</td>
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<td>0.0047</td>
<td>1.9</td>
<td>4.4</td>
<td>4.58</td>
</tr>
<tr>
<td>RC244</td>
<td></td>
<td>(0.0046&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(1.5&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(2.4&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>(6.6&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

<sup>a</sup> - cyclopentane:deuterium ratio 1:25
### TABLE 5.4

**Cyclopentane Exchange with Deuterium**

**Initial Product Distributions at 303 K**

<table>
<thead>
<tr>
<th>Catalyst Number</th>
<th>Percent Ir</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>
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<sup>A</sup> - cyclopentane:deuterium ratio of 1:25
### Table 5.5

Cyclopentane Exchange - Comparisons with Literature

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**RC238 Pt/Al\(_2\)O\(_3\)**

- Rate \( k_0 \)
  - \( 65 \times 10^{-4} \)

**Pt/Al\(_2\)O\(_3\)\(^A\)**

- Rate \( k_0 \)
  - \( 310 \times 10^{-4} \) (545 K)
  - \( 4.5 \times 10^{-4} \) (303 K)

\(^A\) - from J. Catal., 64, 84, (1980) exchange carried out at 354 K, \( E_a = 75 \text{ kJ mol}^{-1} \).
Figure 5.1 Surface intermediates for exchange reactions.

**Methane Exchange**

- Monoadsorbed
- Diadsorbed

**Cyclopentane Exchange**

- Monoadsorbed leading to a singly exchanged product
- Multiple exchange intermediates
Figure 5.1 (b)

Cyclopentane Exchange

"Roll over"

Mechanism
Figure 5.2 Methane exchange on 100% platinum: background interference due to deuterium/water exchange in the mass spectrometer.
Figure 5.3  Effect of deuterium on water isotopes in the mass spectrometer.
Figure 5.4 Effect of baking with hydrogen on deuterium/water exchange in the mass spectrometer.
Figure 5.5  Deuterium water exchange in the mass spectrometer after baking with hydrogen and with simultaneous light hydrogen leak into the spectrometer.
Figure 5.6  Methane exchange on 100% platinum at 473 K.
Figure 5.7  Methane exchange on 46% iridium at 473 K.
Figure 5.8  Methane exchange on 100% iridium at 473 K.
Figure 5.9  Methane exchange with deuterium - $k_o$ rate plots.
Figure 5.10  Exchange rate vs iridium content.
Figure 5.11  Cyclopentane exchange with deuterium at 303 K.
Figure 5.12  Cyclopentane exchange on iridium at 303 K.
Figure 5.12  Cyclopentane exchange on iridium at 303 K.
6.1 Introduction

Hydrogenolysis reactions are classed as the breaking of chemical bonds in the presence of hydrogen. In this work the bonds broken were carbon to carbon bonds in alkane molecules: ethane, propane, n-butane, n-pentane and cyclopentane. The original hydrogenolysis mechanism put forward by Taylor (1) for ethane hydrogenolysis considered the overall reaction in three stages.

A) Dissociative adsorption of the hydrocarbon to form a dehydrogenated chemisorbed species.

B) Rupture of the carbon-carbon bond on the catalyst surface.

C) Rehydrogenation of the carbon fragments and desorption of methane.

These three steps can be represented diagrammatically for ethane:

\[
\begin{align*}
C_2H_6(g) & \xrightarrow{k_1} C_2H_5(ads) + H(ads) & 6.1 \\
C_2H_5(ads) + H(ads) & \xrightarrow{k_2} C_xH_y(ads) + aH_2 & 6.2 \\
C_xH_y(ads) + H_2 & \xrightarrow{k_3} CH_y(ads) + CH_z(ads) & 6.3 \\
& \downarrow H_2 \\
& CH_4(g)
\end{align*}
\]
The rate determining step is the breaking of the carbon to carbon bond, $k_3$.

Sinfelt$^{(2,3)}$ has reviewed hydrogenolysis over supported group VIII metal catalysts. For ethane hydrogenolysis the rate expression is of the form:

$$\text{rate} = k \cdot p_{C_2H_6}^n \cdot p_{H_2}^m$$  \hspace{1cm} (6.4)

$n$ - order with respect to ethane  
$m$ - order with respect to hydrogen.

Most group VIII metals show an inverse dependence on hydrogen pressure, the values for exponent $m$ vary from metal to metal reaching a maxima on palladium of -2.5. Only iron and rhenium show positive orders with respect to hydrogen. Ethane pressure dependence is generally near first order.

Sinfelt has also compared the activities for group VIII metals for ethane hydrogenolysis$^{(2,3)}$ and this can be closely correlated to electronic effects namely percentage d-character of the metallic bond and/or geometric effects such as lattice spacings. Since percentage d-character of the metal probably determines heat of adsorption of the hydrocarbon to the metal, this could indicate that hydrogenolysis activity increases with increasing strength of adsorption of the intermediate $C_2H_x$ to the surface. Hydrogenolysis activity passes through a maximum as metal crystallite size decreases. For small crystallites edge and corner atoms represent a greater proportion of the total number of metal atoms.
present, and will probably have different bonding properties and catalytic activities from those atoms in the bulk.

Larger hydrocarbons than ethane undergo dissociative adsorption and breaking of one carbon-carbon bond but the resulting fragments containing two or more carbon atoms can now either combine with hydrogen and desorb from the surface or carry out further carbon-carbon bond scission to give smaller carbon units. The more carbon bonds broken per residence of the catalyst surface, the greater the 'depth' of hydrogenolysis.

6.2 Ethane and Propane Hydrogenolysis

The ethane and propane hydrogenolysis were carried out by Mr. Andrew Hopkirk for an honours project in 1980. The rates for ethane hydrogenolysis at 523 K are tabulated in Table 6.1, with rates at 473 K calculated by means of the Arrhenius equation:

\[ \log \left( \frac{r_1}{r_2} \right) = \frac{E_A}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \]

The activation energies determined are given in Table 6.1 and are in fair agreement with those in the literature. Reaction order with respect to ethane was about 0.42 and initial rates were determined by the tangents of the zero order plots in the initial stages of the reaction, typical examples of which are displayed in figure 6.1 and 6.2. The large sample loss of 7% is related to curve shapes by the amount of hydrogen taken from the system. The large negative order in hydrogen expressed in equation 6.4 causes an acceleration in rate
as hydrogen is removed on sampling. After a time however the hydrocarbon content will be so low that adsorbed ethane will be deficient on the surface and the rate determining step becomes adsorption of ethane on the catalyst as shown in equation 6.1 This general reaction scheme describes the reactions on the catalysts as follows:-

1) On platinum the biggest loss of hydrogen is from sampling but the reaction is too slow to show acceleration.

2) On 19% and 39% iridium the reaction rate accelerates due to hydrogen loss by sampling.

3) On 46-73% iridium acceleration of the reaction takes place as in (2) but the reaction rate is so rapid that the ethane concentration is low at the catalyst surface and adsorption becomes the rate determining step.

The rates of hydrogenolysis increase with iridium content but do not vary linearly across the series. Platinum was least active and showed a difference in rate 100 times slower than the 19% iridium catalyst. Across the rest of the series the rate only increased by sixteen times. The addition of iridium to the platinum catalyst does not cause a proportional rise in activity. The peak in activity at the 73% iridium catalyst was strange but reproducible. Rates of hydrogenolysis at 473 K are slower than the rates of methane exchange, Table 5.1, the former rate indicates ease of carbon-carbon bond scission the latter product desorption. This means that for both iridium and platinum
catalysts carbon-carbon bond cleavage is the rate determining step, an observation made by Sinfelt\(^{(2,3)}\).

The activation energies found are in fair agreement with those in the literature\(^{(2)}\) but the relative activities of platinum/iridium are here about \(10^{-3}\) whereas a larger difference, \(10^{-6}\), has been found before.

**Propane Hydrogenolysis**

The hydrogenolysis of propane was carried out on the platinum 19\% iridium, 46\% iridium and iridium catalysts. Rates of reaction and initial products are summarised in Table 6.1. The rate quoted on platinum was obtained at 498 K as the rate at 473 K was almost too small to measure. For iridium the rate quoted is an average of two experiments, the reaction profile for iridium is illustrated in figure 6.3. The deceleration in rate can be attributed to the fact that the rate of hydrogenolysis is about the same as the rate of methane exchange on this catalyst. This means that there is a larger contribution from product desorption and this poisons the hydrogenolysis (i.e. the bond breaking reaction). On the other catalysts the rate determining step is still carbon-carbon bond rupture. Only on iridium does the desorption process challenge this dominance. The large increase in activity between platinum and 19\% iridium is present again but the rate is fairly constant across the rest of the catalyst series.

If only one bond is broken per residence on the catalyst surface, the percentages of methane and ethane
will be about equal; if more than one bond is broken then methane will be more prominent than ethane. All catalysts show single bond cleavage to be the dominant mechanism although iridium shows a slight increase in multiple bond rupture.

6.3 Butane Hydrogenolysis

Butane hydrogenolysis was carried out over the catalyst series at 473 K, rates of reaction and initial products are tabulated in Table 6.2. Typical reaction with time plots are given in figures 6.4 and 6.5 with the first order plots in figure 6.6. Reaction rate is slower on platinum than on the bimetallics and there is a large increase, forty times, between platinum and the 19% iridium bimetallic. After this rate increases only four times over the rest of the catalyst series. The similarities in the pattern of hydrogenolysis activities with catalyst composition for ethane, propane and butane can be clearly seen in figure 6.7. There does not seem to be a great difference between the bimetallic catalysts and iridium. The absence of iridium altogether on the platinum monometallic decreases the rate by about 100 times. Rates for propane hydrogenolysis fall in between those for ethane and butane but lie nearer to the values obtained for butane.

The initial products show that on all catalysts there is very little isomerization in the butane reaction. For hydrogenolysis reactions the pattern of initial products indicates which and how many carbon-carbon bonds are broken per residence on those catalysts surface.
For a butane molecule central bond scission is shown by a large percentage of ethane; terminal scission by equal amounts of methane and propane and multiple rupture by a larger percentage of methane than propane. The percentages of ethane show for all catalysts central bond scission is the dominant process, see Table 6.2. On platinum methane and propane have similar values so only one bond is broken per residence of the hydrocarbon on the surface, the ratio of central:terminal split being about 5:1. The bimetallic catalysts show more central bond scission than platinum, while multiple rupture as shown by the ratio of methane:propane, increases with iridium content. Iridium itself shows the greatest multiple bond breaking but even there, single bond scission and particularly central rupture is the dominant process.

The extent of multiple bond breaking on the 'depth' of hydrogenolysis can be measured by the M factor, first introduced by Ponec and Sachtler (4), where:

\[ M = \sum_{J=2}^{J=3} \frac{(4-J)C_J}{C_1} \]  

where \( C_J \) represents the molar concentration of a hydrocarbon having \( J \) carbon atoms, and \( C_1 \) is methane molar concentration. The value of \( M \) is only of use if one type of bond scission is dominant, this being indicated by the magnitude of \( M \).

- \( M = 1 \) if terminal bond scission is dominant
- \( M < 1 \) if multiple bond scission is dominant
- \( M > 1 \) if median bond fission is dominant.
The M values in table 6.2 show that central bond rupture is the main process with a maximum of activity on 19% iridium. On platinum the value is lower due to the contribution from terminal bond rupture. As iridium is added the percentage of propane stays fairly constant but methane increases showing a greater tendency for multiple bond breaking which lowers the M value. Although the values for M are similar on platinum and iridium, the processes giving this figure are different, the hydrogenolysis is 'deeper' on iridium shown by the higher percentage of methane.

Haining\(^{(5)}\) carried out butane hydrogenolysis on a similar platinum/alumina catalyst. Using his activation energy and correcting for metal loading, catalyst sample weight and assuming a similar number of surface atoms per gram catalyst, the rate at 473 K is much lower than that obtained in the present study. The results are quoted in Table 6.3. Haining's platinum catalyst contained chlorine and the slower rate may be due to an inhibiting effect of the halogen\(^{(6)}\). The initial products in the earlier study show a much greater isomerization activity, again possible due to the presence of chlorine, but the lighter fragments indicate a similar bond rupture process - that of one carbon to carbon bond broken per residence on the catalyst surface and mainly central bond rupture.

The rate obtained by Maurel\(^{(7)}\) for his platinum alumina catalyst is very close to that obtained for the monometallic platinum. Clarke\(^{(8)}\) reported central bond scission to be the dominant process for butane hydrogenolysis on iridium film at 511 K, with little isomerization activity
for this catalyst. Anderson\(^{(9)}\) obtained initial products for iridium, which compare well to those found here and Bernard et al\(^{(10)}\) have reported that platinum and iridium are the best metals for median bond fission. Betizeau et al\(^{(11)}\) found the ratio of activities for platinum/iridium to be \(1.8 \times 10^{-5}\) which is a larger difference than that found between the monometallic catalysts, this being \(6.4 \times 10^{-3}\).

6.4 n-Pentane Hydrogenolysis

Butane hydrogenolysis showed that central bond scission was the dominant hydrogenolysis process on all catalysts, but multiple bond rupture did increase slightly with iridium content. Some n-pentane hydrogenolysis experiments were carried out to see if this selectivity for central bond breaking would be continued here to produce ethane and propane as the principal products and how this would vary with iridium content. The rates of n-pentane hydrogenolysis could also be compared with the cyclopentane hydrogenolysis results.

All hydrogenolysis of pentane was carried out under the same reaction conditions as for butane, typical reaction course with time plates are given in figures 6.8 to 6.9 for the platinum and 46% iridium catalyst. Reaction kinetics were apparent first order and rates were calculated from first order plots as given in figure 6.10. Rate of reaction, initial products and M values, the depth of hydrogenolysis, are tabulated in Table 6.4. Overall rate increases from platinum to iridium across the series and the ratio of activity
of platinum:iridium is about 1:20. Compared to butane hydrogenolysis, platinum doubles in activity while iridium has a rate half of that obtained for butane. These differences cancel each other out on the bimetallics in the middle of the series as these have very similar rates for pentane and butane hydrogenolysis.

The n-pentane initial percentages show ethane and propane to be the major products on all catalysts proving that selectivity for central carbon-carbon bond fission is still high. On platinum, ethane is very nearly equal to propane and the percentages of methane and butane are also very similar. This indicates only one carbon-carbon bond is broken per residence on the catalyst, the ratio of median to terminal split is about 4:1 which is close to the result obtained for butane hydrogenolysis. On iridium the percentage of ethane is larger than propane and that for methane much larger than butane. Although the main reaction is still central bond scission as shown by the magnitudes of ethane and propane percentages, it is clear that the propane and butane being formed by rupture of one median or terminal bond are then broken down further to ethane and methane before desorption from the surface. Hence the hydrogenolysis on iridium is a bit 'deeper', i.e. there is a greater contribution from multiple bond scission.

The bimetallic catalysts do not show a gradual increase in multiple bond scission as iridium content increases as was the case for butane hydrogenolysis. There appears to be a maxima for central bond rupture at the 46% iridium catalyst with a corresponding decrease
in terminal and multiple bond scission. The trend across the series can clearly be seen from the M factor, the 'depth' of hydrogenolysis, which is greater than unity for all catalysts showing central bond breaking to be the dominant process across the series. The magnitude of M goes through a maximum at 46% iridium showing that central bond breaking is greater on this catalyst than the rest of the bimetallics. Temperature programmed reduction, (Chapter 4), has shown that the most stable point on the platinum/iridium catalyst series to be about the 1:1 atomic ratio, and hence this is the most likely composition at which bimetallic interaction will take place. This interaction seems to promote central bond scission for the n-pentane molecule but not for n-butane, so the metal ensembles formed may be selective for the central bond rupture mode of hydrogenolysis in non symmetrical alkane molecules.

As for the reaction of n-butane, isomerization activity was low, isopentane was produced in small amounts on 46% iridium and seemed to increase with iridium content. Although more isomerization may be expected on the platinum rich end of the series, where the metal to hydrocarbon bond strength is probably weaker, but the rates of overall reaction may be too slow to allow isomerization products to be formed in detectable amounts. Isopentane percentage does not increase from 73% iridium to iridium itself but a small amount of isobutane is formed on the latter so total isomerization activity increases.
The variation of the depth of hydrogenolysis gives an indication of metal-metal interactions and such interactions reflect the existence of bimetallic crystallites. Selectivity for hydrocarbon reactions is believed to be due to either or both of the 'geometric' or 'electronic' effects on metallic crystallites, as discussed in Chapter 1. Activity for hydrogenolysis reactions on group VIII metals is best explained by the 'electronic' theory regarding the contribution from the metals d-electrons\(^{(2,3)}\). An interpretation of the electronic effect has been based on the 'softness' of the metal\(^{(12)}\). Transition metals can be considered as soft acids and their softness increases with the polarisability of the metal. An inverse correlation has been found between softness and the extent to which a metal causes alkane hydrogenolysis\(^{(12)}\), and metals can be classified in order of increasing depth of hydrogenolysis and decreasing softness.

\[
\text{Pd, Pt : Ir, Rh : Ru : Os : Re} \\
\text{depth of hydrogenolysis} \\
\text{'softness'}
\]

Increasing depth of hydrogenolysis i.e. multiple bond breaking also shows increasing metal to hydrocarbon bond strength, indicated by the rate of methane exchange. Haining's work\(^{(5)}\) and that of the present study has shown the metal to carbon bond strengths to be in the order Pt<Ir<Re and this fits with the relation to softness of the metals. Rhenium has shown deeper hydrogenolysis for n-butane\(^{(5)}\) and n-pentane\(^{(10)}\) than iridium, which has now been found to have greater tendency for multiple bond scission than platinum.
Although the activities and selectivities of the monometallics for paraffin hydrogenolysis fit well with established 'electronic' theories, the bimetallic reactions are more difficult to explain. Butane hydrogenolysis shows a decrease across the catalyst series for median bond fission while this reaction 'peaks' in activity at 46% iridium for the n-pentane molecule. Selectivity for hydrogenolysis reactions on the bimetallic catalysts seem to be due to some geometric effect.

6.5 Cyclopentane Hydrogenolysis

Cyclopentane hydrogenolysis is a much more difficult reaction to carry out than cyclopentane exchange and requires a temperature of about 453 to 573 K in order to obtain a similar rate to that of exchange. The initial products are quite different for metals of group VIII especially between platinum and iridium. On the former metal only one carbon-carbon bond is broken giving n-pentane as the sole product; iridium breaks more than one bond and gives all the lighter fragment molecules. Cyclopentane hydrogenolysis experiments were carried out under the same conditions as for butane and n-pentane. Reaction was found to follow apparent zero order kinetics, typical reaction plots with time are shown in figures 6.11 to 6.12. Rates of reaction and initial percentages are summarized in Table 6.5.

Overall hydrogenolysis rate increases as before across the series from platinum to iridium. The large increase in rate between platinum and 19% iridium is
still evident, the ratio between these catalysts being about 1:5 while the rate doubles over the rest of the series from 19% to 100% iridium composition. The rate obtained on platinum is very close to that obtained for n-pentane hydrogenolysis but rates on the iridium rich catalysts are about a quarter of that for n-pentane. Comparing the activities for all the alkane molecules the ratio of rates for cyclopentane: n-pentane:n-butane reaction is 1:1:0.7 on platinum and 1:4:5 on the iridium catalyst. Although iridium is faster for hydrogenolysis on any one hydrocarbon than platinum, it seems to be proportionally less active for the cyclic molecule. A higher activity for n-pentane hydrogenolysis than for the cyclopentane reaction has been reported in the literature\(^{(17)}\).

The initial products show that platinum is highly selective towards the ring opening reaction to give n-pentane as the sole product. This means only one carbon-carbon bond is broken per residence on the catalyst surface, what was found for the paraffin molecules and agrees with what is found in the literature\(^{(11,13-16)}\). Addition of iridium causes more than one bond to be broken which results in the formation of the smaller fragments as well as n-pentane formed by the single bond breaking 'ring opening' reaction. The percentages of methane, ethane, propane and butane all increase with iridium content with a corresponding decrease in n-pentane showing the greater tendency for multiple bond scission of the cyclopentane molecule as found previously\(^{(11,16)}\).
Reaction of cyclopentane with hydrogen on this catalyst series can be considered as consisting of two processes, rupture of a single bond-ring opening; or multiple bond scission - hydrogenolysis to smaller fragment molecules. The rates for each process (in terms of carbon units) and the ratio for the rate of multiple hydrogenolysis to that of ring opening are tabulated in Table 6.6. This shows that on all catalysts single bond rupture is the dominant reaction but multiple scission increases with iridium content. In this respect, the cyclic molecule mirrors the pattern of activity found on the alkanes. The ratio of the different hydrogenolysis rates increases six times between platinum and the first bimetallic, then stays fairly constant over the rest of the bimetals and doubles between 73% iridium and iridium itself. Again the activity of this mode of hydrogenolysis is not additive between the two monometals. On iridium hydrogenolysis is faster and more multiple than on platinum so the trend for group VIII metals where decreasing softness increases depth and rate of hydrogenolysis holds for the reaction of cyclopentane on these two metals.

Rates of reaction are fairly close to those found before on similar catalysts by Maurel\(^{(16)}\). Both sets of results are compared in Table 6.7 making the assumption that all catalysts have similar metal dispersions. Platinum is about ten times faster than in the previous study while iridium is almost ten times slower.
The rate of n-pentane hydrogenolysis on iridium is about four times faster than cyclopentane hydrogenolysis yet a substantial amount of n-pentane is observed as an initial product. To investigate the possibility of the cyclopentane molecule blocking the reaction of the paraffin a 50/50 mixture by volume (0.4 kPa cyclopentane and 0.4 kPa n-pentane with 8.0 kPa of hydrogen) was made up and reacted on the iridium catalyst at 473 K. Reaction plots can be seen in figures 6.13 and 6.14. Cyclopentane reacted at a rate of 0.0031 molecules per second per surface metal atom. The percentage of n-pentane increased with time until there was only 5% of the cyclic molecule, and then the alkane underwent hydrogenolysis. Initial rate of formation of the lighter hydrocarbons and n-pentane, when summed, corresponded to the rate of loss of cyclopentane. The initial products for the reaction are:

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<th>% C&lt;sub&gt;3&lt;/sub&gt;</th>
<th>% C&lt;sub&gt;4&lt;/sub&gt;</th>
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</tr>
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The rate and pattern of activity is more like the reaction of cyclopentane then n-pentane, so it appears that the slower cyclic hydrogenolysis blocks the faster reaction on the paraffin. This is probably due to strong adsorption to the surface of cyclopentane, indicated by zero order kinetics, and the slower reaction of the cyclic hydrocarbon.
References

Chapter 6


   Dr. M.A. Day, Petrochemicals Division, I.C.I., personal communication.


## TABLE 6.1

The Reaction of Ethane and Propane with Hydrogen

<table>
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<tr>
<th>Catalyst</th>
<th>% Ir</th>
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<th>$E_A$ (kJ mol(^{-1}))</th>
<th>$E_A$ (kJ mol(^{-1}))</th>
<th>Rates of Ethane hydrogenolysis at 473 K (x10^-4)</th>
<th>Rates of Propane hydrogenolysis at 473 K (x10^-4)</th>
<th>Propane hydrogenolysis initial percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td>238</td>
<td>0</td>
<td>0.084</td>
<td>280</td>
<td>226</td>
<td>0.00011</td>
<td>0.24(^{(B)})</td>
<td>(C)</td>
</tr>
<tr>
<td>239</td>
<td>19</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td>53</td>
</tr>
<tr>
<td>240</td>
<td>39</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>241</td>
<td>46</td>
<td>~25</td>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>53</td>
</tr>
<tr>
<td>242</td>
<td>54</td>
<td>9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>73</td>
<td>210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>244</td>
<td>100</td>
<td>92</td>
<td>192</td>
<td>151</td>
<td>0.85</td>
<td>21</td>
<td>58</td>
</tr>
</tbody>
</table>


\(B\) - at 498 K.

\(C\) - reaction too slow.
### TABLE 6.2

Reaction of n-butane with Hydrogen at 473 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>Rate</th>
<th>% C₁</th>
<th>% C₂</th>
<th>% C₃</th>
<th>% iC₄</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.00018</td>
<td>19.4</td>
<td>67</td>
<td>13.5</td>
<td>0.1</td>
<td>7.6</td>
</tr>
<tr>
<td>RC239</td>
<td>19</td>
<td>0.0071</td>
<td>8.5</td>
<td>85.5</td>
<td>6.0</td>
<td>0.1</td>
<td>20.8</td>
</tr>
<tr>
<td>RC240</td>
<td>39</td>
<td>0.0056</td>
<td>10.9</td>
<td>82.6</td>
<td>6.4</td>
<td>0.1</td>
<td>15.7</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.0093</td>
<td>12.3</td>
<td>80.0</td>
<td>7.0</td>
<td>0.1</td>
<td>13.7</td>
</tr>
<tr>
<td>RC242</td>
<td>54</td>
<td>0.014</td>
<td>13.0</td>
<td>79.8</td>
<td>7.1</td>
<td>0.1</td>
<td>12.8</td>
</tr>
<tr>
<td>RC243</td>
<td>73</td>
<td>0.023</td>
<td>14.5</td>
<td>77.5</td>
<td>7.8</td>
<td>0.2</td>
<td>11.2</td>
</tr>
<tr>
<td>RC244</td>
<td>100</td>
<td>0.028</td>
<td>23.0</td>
<td>70.0</td>
<td>6.8</td>
<td>0.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Rate at 473 K $\times 10^{-4}$</td>
<td>$E_a$ kJ mol$^{-1}$</td>
<td>Initial Product Distributions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------------</td>
<td>-------------------</td>
<td>------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RC238 (c)</td>
<td>1.8</td>
<td>2.0</td>
<td>19.4 67.0 13.5 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td></td>
<td></td>
<td>16.0 24.0 13.5 46.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td></td>
<td>7.3</td>
<td>19.4 67.0 13.5 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td></td>
<td></td>
<td>23.0 70.0 6.8 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RC244 (c)</td>
<td></td>
<td>1.5</td>
<td>15.3 79.4 15.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(a) rates in turnover frequency
(b) rates in mol/hr g\(^{-1}\) metal
(c) from the present study
(d) from J. Chem. Res., 7, 2056, (1977) reaction carried out at 545 K
(e) from J. Catal., 50, 87, (1977) reaction carried out at 573 K
(f) from J. Catal., 59, 325 (1979) reaction carried out at 485 K.
### TABLE 6.4

Reaction of n-Pentane with Hydrogen at 473 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>Rate (A.M)</th>
<th>% C&lt;sub&gt;1&lt;/sub&gt;</th>
<th>% C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>% C&lt;sub&gt;3&lt;/sub&gt;</th>
<th>% iC&lt;sub&gt;4&lt;/sub&gt;</th>
<th>% nC&lt;sub&gt;4&lt;/sub&gt;</th>
<th>% iC&lt;sub&gt;5&lt;/sub&gt;</th>
<th>M&lt;sup&gt;A&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.00059</td>
<td>14.2</td>
<td>39.8</td>
<td>37.8</td>
<td>-</td>
<td>8.5</td>
<td>-</td>
<td>14.3</td>
</tr>
<tr>
<td>RC240</td>
<td>19</td>
<td>0.0069</td>
<td>8.2</td>
<td>47.2</td>
<td>42.2</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>27.9</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.014</td>
<td>4.4</td>
<td>52.8</td>
<td>41.1</td>
<td>-</td>
<td>1.3</td>
<td>0.4</td>
<td>54.9</td>
</tr>
<tr>
<td>RC243</td>
<td>73</td>
<td>0.027</td>
<td>13.9</td>
<td>42.3</td>
<td>39.7</td>
<td>-</td>
<td>3.4</td>
<td>0.8</td>
<td>15.1</td>
</tr>
<tr>
<td>RC244</td>
<td>100</td>
<td>0.037</td>
<td>21.5</td>
<td>46.1</td>
<td>27.6</td>
<td>0.2</td>
<td>3.8</td>
<td>0.8</td>
<td>9.2</td>
</tr>
</tbody>
</table>

\[ A - M = \frac{\sum_{J=2}^{4} (5-J) C_J}{C_1} \] where \( C_J \) is the molar concentration of the hydrocarbon containing \( J \) carbon atoms. \( C_1 \) is methane.
## TABLE 6.5

Reaction of Cyclopentane with Hydrogen at 473 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>Rate</th>
<th>% C₁</th>
<th>% C₂</th>
<th>% C₃</th>
<th>% C₄</th>
<th>% iC₅</th>
<th>% nC₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.00089</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98.0</td>
</tr>
<tr>
<td>RC239</td>
<td>19</td>
<td>0.0040</td>
<td>3.5</td>
<td>4.3</td>
<td>5.6</td>
<td></td>
<td></td>
<td>86.6</td>
</tr>
<tr>
<td>RC240</td>
<td>39</td>
<td>0.0051</td>
<td>6.1</td>
<td>8.5</td>
<td>6.8</td>
<td>0.8</td>
<td></td>
<td>77.7</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.0055</td>
<td>5.7</td>
<td>6.4</td>
<td>7.5</td>
<td>1.8</td>
<td></td>
<td>78.5</td>
</tr>
<tr>
<td>RC242</td>
<td>54</td>
<td>0.0067</td>
<td>8.2</td>
<td>11.1</td>
<td>8.6</td>
<td>2.2</td>
<td></td>
<td>69.9</td>
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<tr>
<td>RC243</td>
<td>73</td>
<td>0.0083</td>
<td>9.2</td>
<td>12.4</td>
<td>8.9</td>
<td>1.4</td>
<td></td>
<td>68.1</td>
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<td>RC244</td>
<td>100</td>
<td>0.0093</td>
<td>25.2</td>
<td>22.0</td>
<td>12.6</td>
<td>2.5</td>
<td>0.1</td>
<td>37.6</td>
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</tbody>
</table>
### Table 6.6

Reaction of cyclopentane with hydrogen at 473 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>Rate of ring opening</th>
<th>Rate of multiple hydrogenolysis</th>
<th>Ratio of rates multiple:opening</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.00088</td>
<td>0.00001</td>
<td>0.011</td>
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<tr>
<td>RC239</td>
<td>19</td>
<td>0.0038</td>
<td>0.00023</td>
<td>0.061</td>
</tr>
<tr>
<td>RC240</td>
<td>39</td>
<td>0.0046</td>
<td>0.00050</td>
<td>0.11</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.0050</td>
<td>0.00050</td>
<td>0.10</td>
</tr>
<tr>
<td>RC242</td>
<td>54</td>
<td>0.0058</td>
<td>0.00087</td>
<td>0.15</td>
</tr>
<tr>
<td>RC243</td>
<td>73</td>
<td>0.0072</td>
<td>0.0011</td>
<td>0.15</td>
</tr>
<tr>
<td>RC244</td>
<td>100</td>
<td>0.0071</td>
<td>0.0022</td>
<td>0.31</td>
</tr>
</tbody>
</table>

All rates in terms of carbon units
### TABLE 6.7

Cyclopentane Hydrogenolysis

Comparison with Literature

| Catalyst    | $E_A$ (kJ mol$^{-1}$) | Rate at 473 K
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>140</td>
<td>0.0014 moles hr$^{-1}$ g$^{-1}$ metal</td>
</tr>
<tr>
<td>Ir/Al$_2$O$_3$</td>
<td>108</td>
<td>1.32 moles hr$^{-1}$ g$^{-1}$ metal</td>
</tr>
</tbody>
</table>

Figure 6.1  Ethane hydrogenolysis at 323 K.
Figure 6.2 Ethane hydrogenolysis.
Figure 6.3  Pentane hydrogenolysis on iridium at 473 K.
Figure 6.4 The reaction of n-butane with hydrogen on platinum at 473 K.
Figure 6.5 Reaction of n-butane with hydrogen on 54% platinum at 473 K.
Figure 6.6  Reaction of n-butane with hydrogen at 473 K.
Figure 6.7 Hydrogenolysis reaction rate vs catalyst composition.
Figure 6.8  The reaction of n-pentane with hydrogen on platinum at 473 K.
Figure 6.9  The reaction of n-pentane with hydrogen on iridium at 473 K.
Figure 6.10 The reaction of n-pentane with hydrogen at 473 K.
Figure 6.11  The reaction of cyclopentane with hydrogen on iridium at 473 K.
Figure 6.12  The reaction of cyclopentane with hydrogen on 46% iridium at 473 K.
Figure 6.13  The reaction of a 50/50 mixture of cyclopentane/n-pentane with hydrogen on iridium at 473 K.
Figure 6.14  The reaction of 50/50 cyclopentane/ n-pentane mixture with hydrogen at 473 K.
CHAPTER 7

COMPARISON OF REACTION RATES

7.1 Comparison of the Rates of Methane Production from Hydrogenolysis to the Rate of Methane Exchange

As discussed in Chapter 1, one of the following reaction steps is rate determining in heterogeneously catalysed reactions:

1) Reactant adsorption
2) Carbon-carbon bond breaking
3) Product desorption.

Methane exchange gives an idea of the ability of methane to desorb from the catalyst surface; the production of methane from alkane hydrogenolysis indicates the rate of carbon-carbon bond breaking. Hence the ratio $R$, that of the initial rate of methane production from hydrogenolysis to the rate of methane exchange will show which of processes (2) or (3) is rate determining\(^{(1)}\).

$$R = \frac{\text{Initial rate of methane production from alkane hydrogenolysis}}{\text{Initial rate of methane exchange}}$$

If $R$ is much smaller than unity then carbon-carbon bond rupture is rate limiting, if $R$ is much greater than unity product desorption is slow and if $R$ is about equal to unity the two processes contribute equally to rate.

The $R$ values for both butane and pentane hydrogenolysis are summarized in Table 7.1 and shown graphically in figure 7.1. Both molecules give similar
results except for the 54% iridium catalyst where the R obtained from pentane experiments is smaller due to the small amount of methane produced on this catalyst. On platinum the value of R, very much less than one, clearly shows that bond rupture is rate limiting on this catalyst. As the catalyst series is traversed the R value increases reaching a maximum on iridium of 0.83. It appears that product desorption has an increasing contribution to rate with increasing iridium content. On iridium itself the two processes contribute about equally to rate; product desorption does not become wholly rate limiting as on rhenium (1).

The conclusions reached for the R values agree with the comparisons of the rates of hydrogenolysis of the lighter hydrocarbons (ethane and propane) to methane exchange, which showed carbon-carbon bond scission to be rate limiting except on iridium where desorption becomes equally as important. Carbon-carbon bond rupture for cyclopentane was much slower than the rate of cyclopentane exchange, indicated by the temperatures required to obtain similar rates of reaction. If the activation energies determined by Maurel (2) are used to adjust the rate of hydrogenolysis to one expected at 303 K, exchange is faster by about $10^7$ on platinum and $10^5$ on iridium.

Haining's result for the R value on his platinum catalyst (1), $R = 0.005$, is in good agreement with that obtained on the platinum catalyst used in this study. For butane (1) and pentane (2) hydrogenolysis, carbon-carbon bond rupture has been proposed as the rate determining
step on a platinum alumina catalyst. Iridium blacks have shown that product desorption is relatively slow for hydrogenolysis reactions.

7.2 Comparison of Bond Breaking Reactions

Deuterium exchange with methane and cyclopentane indicate that as iridium content increases there is a tendency to form multiple carbon to metal bonds. Hydrogenolysis experiments show that multiple carbon-carbon bond scission increases with iridium content although single bond scission is the dominant process on all catalysts. Multiple carbon-metal bond formation is a necessary pre-requisite for the rupture of more than one carbon-carbon bond \(^{(4)}\). The maximum for single bond scission for n-pentane, on the 54% iridium catalyst could be due to a geometric factor on the catalyst surface which the non-symmetrical hydrocarbon exploits.

Rates for all the hydrogenolysis reactions are illustrated in figure 7.2 and show a noticeable pattern. Platinum is much slower than the bimetallics which do not increase much in rate across the series. The rates on the bimetallic catalysts cannot be obtained by an 'additive' effect of the rates on platinum and iridium alone. Rates of breaking a primary to secondary \((C_1-C_{II})\) and those on breaking a secondary to secondary \((C_{II}-C_{II})\) carbon to carbon bond were calculated for the larger molecules and illustrated in figure 7.3. This shows that the two processes have similar trends in activity across the series and that the \(C_{II}-C_{II}\) bond rupture is the preferred process with the higher rate. The largest increase in
rate is between platinum and the 19% iridium catalyst for both processes; the subsequent increase across the rest of the series to iridium is only about half the initial rise to the first bimetallic. It appears that a fairly small amount of iridium, 19%, when added to platinum, increases activity greatly but further addition of iridium does not cause a similar rise in rate.

This pattern of activity indicates bimetallic interaction between the two metals, and can be explained by a geometric effect. On the platinum catalyst the surface is made up of platinum ensembles which have a low hydrogenolysis activity. The addition of 19% iridium creates platinum-iridium bimetallic ensembles which are more active than the platinum ones. Further addition of iridium causes more of these bimetallic ensembles until on the monometallic iridium catalyst the surface is made up of iridium ensembles which do not have a markedly higher activity than the bimetallic ensembles.

The low metal content and high dispersion of these catalysts eliminate any surface enrichment effects as most metal atoms must be considered as surface atoms. Both metals have face-centred cubic (f.c.c.) structures with lattice constraints of 391.6 pm and 383.1 pm for platinum and iridium respectively\(^\text{(5)}\). The interatomic distances are 27.75 pm for platinum and 27.14 pm for iridium\(^\text{(6)}\). Both metals should thus be miscible in any ratio and a series of solid solutions have been reported\(^\text{(7)}\).
Some evidence of bimetallic interaction has been derived from the temperature programmed reduction spectra, (Chapter 4) at the 1:1 atomic ratio, a conclusion reported in the literature\(^8\).

### 7.4 Conclusion

Although temperature programmed reduction suggested the most likely point for bimetallic interaction was the 1:1 atomic ratio, none of the catalytic reactions supported this. Rates for exchange and hydrogenolysis reactions did not vary linearly with iridium content. No evidence could be found for a sample dilution of the more active metal by the less active metal as for Group VIII/Ib bimetallic catalysts. Instead a small amount of iridium (19%) caused an increase in hydrogenolysis rate of 10 times that of the platinum catalyst. As iridium content was increased up to 100% iridium the rate only increased by 1.5 times the rate of 19% iridium. It appears that on the bimetallic platinum/iridium catalysts, ensembles are created that have a much greater activity for hydrogenolysis than platinum alone, but are not much less active than iridium ensembles. Exchange rates did not show such a large trend but no additive effects were noticeable.

Carbon-carbon bond breaking is the rate determining step on all catalysts, product desorption only becomes significant on iridium itself where it is nearly as fast as bond rupture. Single scission on the central bond was the major reaction on all catalysts with a slight
increase of multiple bond rupture on the iridium rich catalysts. This multiple bond rupture and the greater tendency for multiple exchange suggests the formation of multiple carbon to metal bonds on iridium.
References

Chapter 7

TABLE 7.1

R values, the ratio of initial rates of methane production from hydrogenolysis to the rate of methane exchange

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ir</th>
<th>R(Butane)</th>
<th>R(Pentane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC238</td>
<td>0</td>
<td>0.0025</td>
<td>0.0059</td>
</tr>
<tr>
<td>RC239</td>
<td>19</td>
<td>0.051</td>
<td>-</td>
</tr>
<tr>
<td>RC240</td>
<td>39</td>
<td>0.055</td>
<td>0.051</td>
</tr>
<tr>
<td>RC241</td>
<td>46</td>
<td>0.088</td>
<td>0.048</td>
</tr>
<tr>
<td>RC242</td>
<td>54</td>
<td>0.26</td>
<td>-</td>
</tr>
<tr>
<td>RC243</td>
<td>73</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>RC244</td>
<td>100</td>
<td>0.83</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Figure 7.1  R values vs catalyst composition.

X - Butane
O - Pentane
Figure 7.2  Hydrogenolysis turnover frequencies at 473 K.

Iridium \%
Figure 7.3 Rates of $C_1$-$C_{II}$ and $C_{II}$-$C_{II}$ bond breaking vs catalyst composition.
INTEGER N,C
DATA N=100, C=100
DIMENSION E(100), FH(10), PE(10), FER(20), D(20), X(7), YN(20), XN(8)
READ, ISETS
END

S = M + 2
N = N + 1
M = M + 1
WRITE(*, 0.0)
00 CONTINUE
  PPP(I) = PHI
  WRITE(6,440) TIME,TOTAL,PHI
  410 FORMAT(9X,1X,$0.2F9.2X,7X,3F11.2,T13.2)
  WRITE(6,24) PHI
  440 FORMAT(9X,12X,31HOMINOAL DISTRIBUTION WITH PHI=,7F8.2,2X)
  YY = PHI/(100.00)
  XX = 100.00-YY
  L(1) = 100.00*XX
  JEAN = J
  DO 55, JIM=2, JEAN
  55 L(JIM) = D(JIM-1) - (JEAN-JIM+1)*YY)/(XX*(JIM-1))
  WRITE(6,10011) (BLANK,L,LDU=1,N)
  WRITE(6,25) (L(JIM),JIM=1,JEAN)
  CONTINUE
  WRITE(6,10001) C,N,O,MON,NOS
  0000 FORMAT(1X,4X,CONFIDENCE IS C',I7,' N ',I7,' N ',I7,' N ',I7,' N ',I7,' N ',I7)
  9999 FORMAT(15X,6F5.2)
  9999 FORMAT(15X,3F5.2)
  WRITE(6,25) (L(1),1,J=1,8)
  WRITE(6,25) (L(J),J=1,JEAN)
  WRITE(6,9997)
  WRITE(6,9998)
  LG 6688 INOS=1, ISRTS
  WRITE(6,9999) (STORH(INOS,J),J=1,J)
  PPP(I) = INOS
  STOP
END