REACTIONS OF HYDROCARBONS ON OXIDE CATALYSTS

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Submitted for the degree of Doctor of Philosophy.

Faculty of Science, University of Edinburgh
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To Susan
Prelude

"... Tho' I to foreign lands must hie,
Pursuing fortune's sliddry ba',
With melting heart and brimful eye,
I'll mind you still, tho' far awa'."

The Farewell
Robert Burns
1759-1796
This thesis is a written account of work carried out at Edinburgh University between October 1983 and September 1986. It is all my own work, except where made clear in the text; and some sections have been published in research journals.

Robert Bird
Acknowledgment

First and foremost I thank my wife, Susan, for her patience and encouragement during my time at University and particularly while compiling this thesis. I thank my parents as well for always showing interest in my work.

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Ian Grant carried out some of the experiments with ZrO$_2$(I) and the sample was prepared by Ronald Brown. Figure 2.2 was drawn by Ronald Brown and I thank him for giving permission to use it.
Courses attended

The following courses were attended during the time spent on my Ph.D. course:

Catalysis Group conferences at Firbush Point Field Centre 1984, 1985 and 1986
Aspects of Structural Chemistry
Homogeneous Catalysis
Electron Spectroscopy and Surfaces
Molecular Electronics
Microcomputers with Instrumentation
Chemical Technology and Industrial Chemistry
Organic Industrial Chemistry
Modern Organometallic Chemistry
Scientific German
Abstract

The addition, exchange and isomerization reactions of hydrocarbon molecules on the oxide catalysts lanthana, zirconia and titania (anatase) have been studied using a variety of analytical techniques including gas chromatography, mass spectrometry and deuterium-n.m.r. spectroscopy.

Reactions of ethene, propene, butenes, 2-methylpropene, cyclopentene and some C₆-alkenes with hydrogen, and sometimes deuterium, were investigated on lanthana. The alkene/lanthana system showed evidence of self-poisoning which was more marked with straight-chain than branched hydrocarbons and the rate of addition was shown to depend on the preferred type of adsorbed surface intermediate. The reaction of alkanes, in the C₁-C₅ range, with deuterium was investigated at temperatures above 750K. The main process was stepwise exchange which was accompanied by some multiple exchange and dehydrogenation to form alkene molecules with a high deuterium content.

The hydrogenation of various alkenes, the equilibration of hydrogen and deuterium and the isomerization of some C₆-alkenes was studied on both zirconia and anatase. The rate of hydrogenation only varied to a small extent for the different alkenes on zirconia and the supply of hydrogen to the surface appeared to be rate-determining. As a catalyst, anatase was less active than zirconia for hydrogenation but it was more active for isomerization of 3,3-dimethylbut-1-ene.

Deuterium-n.m.r. studies were used to examine the products from reactions of 2-methylpropene with deuterium on lanthana, zirconia, anatase and other oxide catalysts. Information was obtained on the rates of exchange and addition, and on the location of deuterium in the alkene and alkane products.

Mechanistic schemes for the various reactions of alkenes on oxide catalysts have been suggested in order to justify results.
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Appendix
CHAPTER 1

Introduction
1.1 INTRODUCTION

In this thesis results obtained from the study of reactions of hydrocarbons on three solid metal oxide catalysts have been described and discussed. Since the reactions occur at the solid-gas interface, the process is termed heterogeneous catalysis.

It is the intention of this introductory Chapter to describe some of the general theory of catalysis that may be applied in later sections of the work. Some of the previous literature which is of general relevance to the reactions studied in the present research is also discussed and some properties of the oxide catalyst used in this work (lanthana, zirconia and titania) are also described. A relatively small amount of the available literature concerns the application of n.m.r. spectroscopy as an analytical technique for use in catalytic studies. This technique was widely used in the present study; therefore a brief introduction to the general principles of n.m.r. spectroscopy is given in this Chapter.

A short introductory section also appears at the beginning of each of Chapters 3 to 7. The idea of this section is to review some of the main results from past literature which was considered to be of particular relevance to the work of that particular Chapter.

1.1.1 Definition of Catalysis

One of the earliest research papers to be concerned with the subject of catalysis was presented by Berzelius in 1835 (1). The author defined a catalyst as a substance that increases the rate at which a chemical reaction reaches equilibrium and catalysis is the word used to describe the action of the catalyst. A more modern definition would add that the
catalyst is not consumed in the process; thus it does not appear in the stoichiometric equation for the reaction.

Catalysts may be homogeneous or heterogeneous but all should comply with the following criteria:

(a) Although the catalyst affects the kinetics and rate of reaction, it cannot change the position of equilibrium in a reversible reaction.

(b) In theory the catalyst can be recovered chemically unchanged at the end of the reaction, although it may be changed physically.

The word catalysis is derived from the Greek words 'cata-', meaning down and 'lysein', meaning to split or break. The Chinese words 'tsoo mei' are used for catalyst and they also mean marriage broker. As G.C. Bond (2) pointed out, the latter description is probably a good reflection of the layman's idea of a catalyst.

1.1.2 Historical Outline of Catalysis

Since the early days of Berzelius the phenomenon of catalysis has been a source of extensive study and today about nine-tenths of the chemical manufacturing processes throughout the world are made possible by using catalysts. The study of modern day catalysis requires a knowledge of many techniques of physical chemistry which are used to characterize both the catalysts themselves and the reactions they are affecting. In many cases organic reactants are studied and it is useful to have an appreciation of the reactivity and structure of such molecules. Bearing in mind that most catalysts are made from inorganic materials, it is important that the catalytic chemist has some familiarity with all three classical branches of chemistry.
Many text-books have been written on the subject of catalysis and obviously they go into various degrees of detail. Books by Bond (2) and Thomas and Thomas (3) offer an extensive description of the applications and general principles. Some of the techniques used to study catalytic systems were discussed in a series of monographs (4) and a more recent collection of papers relating to methods used in catalyst characterization is available (5). In recent times the development of analytical techniques such as Fourier transform infrared spectroscopy and deuterium n.m.r. spectroscopy has enabled research workers to obtain detailed information about the nature and composition of adsorbed surface species and the elucidation of reaction mechanisms. In fact, catalysis may be loosely branched into surface studies and reaction mechanisms and, although it is important to have a good idea of both these topics, more attention is paid to the latter in the present work.

1.2 INTRODUCTION TO ADSORPTION AND CATALYSIS

1.2.1 Adsorption

From the definition of heterogeneous catalysis it follows that the reactants become attached in some way to the catalyst. The process of attachment is known as adsorption and this phenomenon forms the basis of heterogeneous catalysis since adsorption acts as a precursor to catalysis. A detailed discussion on the interaction between adsorption and catalysis is extremely complex and beyond the scope of the present work. Information on this subject is available in a monograph by Clark (6) and some of the main ideas of adsorption are now described.

Atoms appearing at the surface of a solid have a smaller co-ordination number than those in the bulk. Whenever a gas comes into contact with the
solid, the forces acting at the surface provide a seat of free energy and adsorption is favourable. Since both the entropy ($\Delta S$) and the free energy ($\Delta G$) of the system decrease, equation (1.1) suggests that the enthalpy of adsorption ($\Delta H_{ads}$) must be negative:

$$\Delta G = \Delta H_{ads} - T\Delta S$$

(1.1)

where $T$ is the temperature. The process of adsorption leads to a larger concentration of the gas molecules on the surface compared with that in the gas phase. The substance adsorbed is known as the adsorbate and that upon whose surface the process occurs is the adsorbent.

Adsorption is divided into two main types depending on how strongly the molecules become attached. For physical adsorption (physisorption) the forces of attraction between the adsorbate and adsorbent are weak and similar in nature to van der Waals forces. The second type is chemical adsorption (chemisorption) where chemical bonds are formed between the adsorbate and adsorbent. There is no sharp divide between the two types of adsorption, but one difference is that more heat is released for chemisorption than for physisorption. Physisorption acts as a precursor to chemisorption and both processes are involved in catalysis.

The essential property of a catalyst is that it provides an energetically favourable reaction pathway for the conversion of reactants to products. The potential energy profile in Figure 1.1 (a) demonstrates the lowering of the activation energy by a catalyst compared with that of a non-catalysed reaction. In the Figure, $E_a$ represents the activation energy and $\Delta H$ is the enthalpy. The figure is based on Figure 1.2 of reference 2. Note that the position of equilibrium is not affected by the catalyst. The reactant will form an adsorbed intermediate on the surface of the catalyst during the reaction and this aspect is illustrated in Figure 1.1 (b),
Figure 1.1

Schematic diagrams for a typical conversion of reactants (R) to products (P): (a) shows the effect of having a catalyst present; (b) shows the effect of having reaction intermediates where (A) is too weakly adsorbed, (B) is too strongly adsorbed and (C) is of intermediate strength.
which is based on Figure 1 of reference 7. The strength of adsorption of the intermediate species is a crucial factor; if adsorption is too weak (curve A) then the activated complex will be too high in energy for formation of the intermediate. If adsorption is too strong (curve B) then the intermediate will be very stable and difficult to convert into products. The ideal situation is shown as curve C where a medium strength of adsorption allows formation of the intermediate from the reactants and comparatively little energy is required to convert it into gas phase products. In many catalytic reactions strongly adsorbed species become irreversibly attached to the surface and in such cases the term poisoning (or fouling) is used.

1.2.2 Adsorption Isotherms

The rate at which a molecule adsorbs is not of any great concern for catalytic processes because it is usually much faster than the reaction rate. However, it is useful to have some knowledge of the relationship between the quantity of gas adsorbed and the gas phase pressure observed when equilibrium is reached. For a constant temperature, such a relationship is called an adsorption isotherm. Brunauer (8) has classified adsorption isotherms into five characteristic types and these have also been discussed by Shaw (9).

If \( x \) is the amount of adsorbate adsorbed at a pressure, \( p \) and \( x_m \) is the maximum amount that the surface can take up, then

\[
\frac{x}{x_m} = \theta \tag{1.2}
\]

where \( \theta \) is the fractional surface coverage. It can be shown (2) that

\[
\theta = \frac{b p}{1 + bp} \tag{1.3}
\]

where \( b \) is a constant known as the adsorption coefficient of the
adsorbent and is equal to the ratio of the rate coefficients for adsorption and desorption \( \frac{k_a}{k_d} \). The relationship between fractional surface coverage and pressure shown in equation (1.3) is known as the Langmuir equation. The Langmuir equation is usually obeyed when adsorption is restricted to one monolayer.

A second relationship known as the BET (after Brunauer, Emmett and Teller) equation is useful for the determination of catalyst surface areas. This method is described in Chapter 2.

1.2.3 Reaction Kinetics

Reaction kinetics is a complex subject and, not surprisingly, a great deal of work is published on the theory (e.g. 10). In the present context the term kinetics is used to describe how the rate of reaction is expressed as a function of concentration (or pressure) and specific rate constants. The relationship is known as a rate law.

In heterogeneous catalysis the reaction essentially occurs on the catalyst surface. However it is more practical to measure the rate of change of pressure of the reactant or products. The rate law in terms of surface concentration can be called the true rate law and that of a gas phase pressures is known as the apparent rate law.

It is often useful to examine the effect that the nature of adsorption has on the apparent kinetics of catalytic reactions. In order to carry out such an examination it is usually assumed that the Langmuir isotherm applies. As an example we may investigate the case of a unimolecular conversion of a species A, which is adsorbed without dissociation, to a product B which is not adsorbed at all. The rate \( (-dp/dt) \) of removal of A will depend only on the concentration of A that is adsorbed, i.e.
on surface coverage, $\theta$. By substituting equation (1.3) we have:

$$-\frac{dp}{dt} = k\theta = \frac{kbp}{1+bp} \quad (1.4)$$

where $k$ is a rate constant. Two features arise from the above relationship:

(a) When the pressure is large, $\theta$ tends towards one (i.e. monolayer coverage) and reaction rate is independent of the pressure.

(b) When the pressure is small, $\theta<1$ and the rate is dependent on pressure.

If (a) applies then the reaction is zero order in $A$; if (b) is relevant then it is a first order reaction. Between the two approximations the reaction can have fractional order and it may be assumed that

$$-\frac{dp}{dt} = -k_r(p)^n \quad (1.5)$$

where $k_r$ is the initial rate of reactant loss, $n$ is the order and $p$ the pressure at time $t$.

Equations (1.4) and (1.5) are used for calculation of some alkene hydrogenation rates in later Chapters. In these experiments the pressure of hydrogen was ignored as it was much greater than that of the alkene. The rate equations are further discussed in the relevant sections of the text. Kinetic information was also obtained from catalytic exchange reactions and the methods used to obtain results are also discussed later.

1.2.4 Activation Energies

Earlier it was mentioned that the lowering of activation energy is a fundamental property required from a catalyst. Just as the surface and apparent kinetics are related through the adsorption isotherm, the surface (true) and apparent activation energies are related through the heat of adsorption. The apparent activation energy, $E_a'$ may be derived from
the Arrhenius equation:

\[ k_r = A \exp \left( -\frac{E_a}{RT} \right) \]  

(1.6)

where \( A \) is the pre-exponential factor, \( k_r \) is the rate at temperature \( T \) and \( R \) is the gas constant. \( E_a \) is interpreted as the difference in energy between that of the most energetic activated complex and the reactants (see Figure 1.1). The apparent activation energy may include a contribution from the temperature dependence for the coverage of adsorbed gas and this can be corrected to give an approximate value for the true activation energy, \( E \), using:

\[ E = E_a - \Delta H_{\text{ads}} \]  

(1.7)

where the symbols have been defined previously. As adsorption is an exothermic process, \( \Delta H_{\text{ads}} \) is negative.

In the case of a homogeneous gas phase reaction the value of \( A \) depends on steric factors such as the molecular diameter of the reactants and collision theory can be applied to the system. However, this theory is not applicable for reactions between molecules that are adsorbed on a catalyst surface and transition state theory can be used to calculate a theoretical approximation for the value of \( A \). More details on this topic are available elsewhere (e.g. 11).

1.3 GENERAL INTRODUCTION TO THE OXIDES

1.3.1 Lanthanum Sesquioxide

Lanthanum is the first member of the lanthanide series of elements. The word derives from the Greek verb 'lanthanein' meaning to hide. This relates to the fact that the element was concealed in cerium oxide when first discovered (ironically the investigator in charge of the research group was J J Berzelius). Lanthanum forms a series of compounds where the metal is in the +3 state.
Lanthanum sesquioxide (La$_2$O$_3$), or lanthana, is a white crystalline ionic solid which is the most basic of the rare earth oxides. The chemistry and physical properties of the rare earth element oxides are described in considerable detail in several textbooks (e.g. 12, 13). Lanthana exists as a hexagonal (A type) structure (14) with seven co-ordination of oxygen around each metal ion. The MO$_7$ groups each form a distorted cube in conjunction with an eighth oxide ion which is located considerably further from the metal ion.

**Preparation and uses**

Lanthanum is separated (using chromatography or ion exchange) from the naturally occurring mineral monozite. Burning the element in air produces a high purity sesquioxide which has a low surface area (< 1 m$^2$ g$^{-1}$). For use as a catalyst the resulting oxide is converted to one of several salts (e.g. nitrate, oxalate) which may then be precipitated to form lanthanum trihydroxide. Heating the hydroxide leads to an oxide with a larger surface area.

Lanthana is used as a glass polish and a high temperature refractory material. There is growing interest with respect to the industrial application of lanthana as a support material for catalysts used in the petroleum industry.

1.3.2 **Zirconium Dioxide**

Zirconium appears in the second row of group IVa in the periodic table. The word derives from the Persian 'zargun' which means gold-coloured and was originally used to describe the yellowish mineral zircon (a zirconia
silicate). Most zirconium compounds contain the metal in the +4 state, although bonds tend to be covalent in character.

Zirconium dioxide (ZrO₂), or zirconia, is the most stable oxide although a rare form of ZrO is also known. At ambient temperatures the crystal form of pure zirconia consists of seven oxide atoms surrounding the central zirconium atom in a monoclinic lattice (15). At higher temperatures (> 1273K) it undergoes a phase change to a cubic fluorite structure. The degree of crystallinity depends on the method of preparation and zirconium dioxide is often amorphous.

Preparation and Uses

Zirconium dioxide exists naturally as the mineral baddeleyite, although it is obtained commercially from the mineral zircon. Dissolving the oxide in water leads to solutions of the general formula ZrO₂ nH₂O. A detailed summary of the preparation and properties of hydrous zirconia is available elsewhere (16). Dehydration of the hydrous zirconia (which usually contains some Zr(OH)₄) by heating produces ZrO₂ but a higher surface area oxide may be obtained by using a salt (e.g. ZrOCl 8H₂O) as a source material.

Zirconia is used to coat pigments such as titania, where it improves durability of paints. It is also used as an opacifier in glazes and enamels; and, due to it having a high thermal stability, the oxide is often found as a refractory in high temperature furnaces.
1.3.3 Titanium Dioxide

Titanium is the first member of the group IVa elements in the periodic table. The metal most commonly shows a valence of 4+, although it can also appear with di- and tri-valency. The element was named after the Greek God Titan.

Titanium dioxide (TiO_2), or titania, is the most commonly used oxide of titanium and it occurs naturally in three different crystalline forms, anatase (tetragonal prismatic), rutile (tetragonal) and brukite (rhombic). An in-depth description of the reactions, thermodynamic properties, preparations and industrial applications of titania is available (17).

Most of the research relating to titania is concerned with rutile and, to a lesser extent, anatase because these forms are commonly used in industry.

The presence of transition metal impurities (Fe, Cr, V etc) means that titania occurs naturally as a black solid although the purified powder is white. Although anatase and rutile are both tetragonal, they are not isomorphous. Anatase forms near-regular octahedral crystals, whereas those of rutile are a slender prismatic type which are often twinned. The formal crystallographic descriptions of the unit cells are D_4h^19 4TiO_2 and D_4h^12 2TiO_2 for anatase and rutile respectively (17). There are several ways in which the structures can be illustrated and a simplified diagram of both are shown in Figure 1.2. More information on the crystal structure of titania and other oxides is available in the publication by Wells (15). Each titanium atom has six oxygen atoms surrounding it in a slightly distorted arrangement. However, anatase is slightly more distorted than rutile.
ANATASE

RUTILE

Figure 1.2
Octahedral arrangement of Ti and O atoms in anatase and rutile.
The stoichiometry of the titanium-oxygen system is greatly influenced by reduction at different temperatures. Reduction of TiO₂ with hydrogen yields products of variable compositions. For example, heating at 1573K produces a black Ti₃O₅ species, whereas formation of the yellow solid TiO takes place on heating at 2273K. Reduction at temperatures between 285 and 1773K gives a mixture of titanium sesquioxide (Ti₂O₃), which is violet, and some TiO.

Rutile is the only oxide of titanium which is thermally stable at all temperatures below 2500K. The transformation from anatase to rutile is accompanied by the evolution of about 32 kJmol⁻¹ but the rate of change is greatly affected by the temperature and the presence of catalysts. The lowest temperature at which partial conversion takes place is 973K.

The hydroxides of titanium are unstable and readily oxidise back to oxide. However infrared spectrometry (18) has been used to show that hydroxyl groups are present on the surface of anatase and rutile. These groups are thought to act as sites for catalytic activity. TiO₂ is more acidic than ZrO₂ because the Ti⁴⁺ ion is smaller than Zr⁴⁺. This is explained by the fact that a more concentrated positive charge on the former atom increases the Lewis acidity of the compound.

Preparation and Uses

Chemically pure TiO₂ is best prepared by oxidation of titanium tetrachloride using a method known in industry as the chloride process. Alternatively, the raw mineral such as ilmenite may be dissolved in sulphuric acid (sulphate process). More recently organic titanates have been used as source materials for titania (17).
Due to the compound's high refractive index and non-toxicity, large quantities of titanium dioxide are used as pigments in the paints, paper and plastics industries. Titania is also used as enamel coatings and catalyst supports.

1.4 REACTIONS OF HYDROCARBONS ON OXIDE CATALYSTS

A textbook by Germain (19) serves as a good introduction to the catalytic conversion of hydrocarbons. More specialized books on the subjects of catalytic hydrogenation (20) and the oxidation of hydrocarbons (21) have been published. Some of the general principles of catalysis by metals were discussed in a monograph by Bond (22) although parts of this work are now outdated. The main conclusions from the study of the reactions of saturated hydrocarbons with deuterium on metal catalysts have been reviewed (23, 24).

The work of the present study is concerned with the reactions (addition, exchange and isomerization) of alkenes and alkanes on oxide catalysts. Thus it was felt that there should be a useful exercise to briefly survey some of the literature published on the subject. More specific reference to previous work directly relevant to particular Chapters is made at appropriate parts of the text.

In the past twenty-five years there has been considerable interest in the reactions of hydrocarbons on oxide catalysts. In early work by Harrison, Nicholls and Steiner (25) the activities of a group of the oxides of first series transition elements were compared for the hydrogenation of ethene. It was suggested from the results that the rate of hydrogenation depended on the d-electron configuration of the metal. Kemball, Nisbet, Robertson and Scurrell (26) investigated the reaction of ethene with
deuterium on a broader range of oxide catalysts than had been previously studied. In addition to the transition metal oxides, the catalysts included magnesium oxide and γ-alumina. The situation was entirely different to that found for transition metal catalysts. For metals, ethene almost always underwent addition to produce ethane and sometimes this was accompanied by exchange of the alkene. With oxides, exchange may be as much as $10^4$ times faster (e.g. MgO) or $10^3$ times slower (e.g. Cr$_2$O$_3$) than addition.

More recently Khodakov and Minachev (27) compared the relative activities of metal oxides as catalysts for the hydrogenation and isomerization of alkenes and the dehydrogenation of alkanes. The results led to the proposal that activity was related to the basicity of active sites on the catalyst. However, other factors must be considered when oxides are compared because anomalies appear. For example, magnesium oxide is basic although it was a poor catalyst when used for hydrogenation of ethene (26).

There is considerable evidence in the literature for different types of hydrocarbon intermediates which adsorb on the surface of oxides during catalytic conversion. The use of exchange studies has been successful in determining the nature of these intermediates. In an earlier review Kemball (28) summarised some of the results relating to the exchange reactions of alkenes (ethene and propene) on metal oxide catalysts. Mechanistic details of hydrogenation and isomerization reactions of alkenes on metal oxide catalysts were discussed by Kokes (29). In particular, the author highlighted the fact that the application of infrared spectroscopy is a useful technique for the study of pre-adsorbed hydrocarbon molecules on the catalyst surface. Some mechanistic studies of hydrocarbons on metal.
oxide catalysts (particularly those having basic properties) were recently reviewed by Kemball (30).

The introduction of advanced analytical techniques in the past ten years has increased the amount of mechanistic information that can be obtained from catalytic studies. This was especially true for investigations involving deuterium exchange work. For example, Hughes, Kemball and Tyler (31) used microwave spectroscopy in order to study the reaction between deuterium and/or deuterium oxide with propene on oxide catalysts. Depending on the catalyst used, there was evidence for five different adsorbed intermediates of propene (i.e. carbenium ion, propen-1-yl, propen-2-yl, σ-allyl and π-allyl). Similarly, evidence for numerous intermediates resulting from the exchange and addition of deuterium with cyclopentene has been detected by deuterium n.m.r. spectroscopy on oxides such as ZnO (32) and CaO (33).

A considerable amount of research concerning the reactions of 3,3-dimethylbut-1-ene (I) has been published. The isomerization reaction of this molecule to give 2,3-dimethylbut-1-ene (II) and 2,3-dimethylbut-2-ene (III) was carried out on alumina catalysts by Pines and Haag (34). It was shown that the rate of isomerization increased with the acidity of the catalyst. The result was explained in terms of a general mechanism similar to the one shown in Scheme 1.1. According to the Scheme, the reaction requires donation of a proton (or deuteron) from the acid surface to the alkene. This leads to the formation of a secondary carbonium intermediate and is followed by rearrangement to give a more stable tertiary carbonium intermediate. Kemball and various co-workers (e.g. 35-38) examined the isomerization of (I), in the presence of
Scheme 1.1

Reaction Scheme for dimethylbutene isomerization (35) in the presence of an acid.
deuterium and deuterium oxide, on catalysts including zeolites and silica/alumina and thereby demonstrated the acidic nature of these oxides. In contrast, magnesium oxide (36, 37) was ineffective for the isomerization reaction - as was expected for a basic catalyst. Some exchange results were also reported, although no reference was made to hydrogenation or deuteration of the dimethylbutenes.

The isomerization of n-butenes is a useful test reaction to obtain information about the type of adsorbed surface intermediates and the probable mode of reaction involved on oxide catalysts. Many investigations have been conducted on this subject and results are published elsewhere (e.g. 39-42). The reactions can be used to distinguish between metal oxide catalysts that are acidic or basic in nature. Isomerization of but-1-ene produces cis- and trans- but-2-ene in different amounts depending on the catalyst used. A high ratio of the products cis/trans is characteristic of a basic catalyst, whereas a ratio which approximates to one is more common to acid catalysts (42).

Some of the results obtained from the exchange reactions of alkanes on metal catalysts were reviewed in the past (7, 23, 24). More relevant work with respect to reactions on oxide catalysts are surveyed in Chapter 5.

1.5 INTRODUCTION TO n.m.r. SPECTROSCOPY

As has been mentioned, a major part of the work in the present investigation involves the use of deuterium n.m.r. spectroscopy for the identification and estimation of the amounts of deuterium atoms in the various different hydrocarbons. Therefore it was felt useful to briefly summarise some of the principles of nuclear magnetic resonance.
More information on the experimental technique used in the present study is given in Chapter 2. For more details on n.m.r. spectroscopy the reader may be referred to text books by Banwell (43) and by Brevard and Kintzinger (44).

1.5.1 Principles of Nuclear Magnetic Resonance

In the presence of a strong external magnetic field certain nuclei possess magnetic moments resulting from their having both electrostatic charge and spin angular momentum. The magnetic moment of a nucleus precesses round the field direction and, provided the field is both uniform and steady, degeneracy of the nuclear energy levels is removed so that a series of quantized energy states relating to discrete orientations of the spinning nucleus is formed.

A nucleus of spin I can take \( 2I + 1 \) orientations when in an external magnetic field and the symbol \( M_1 \) takes values \( I, I-1, I-2 \ldots -I \). \( I \) depends on the number of protons and neutrons in the nucleus and can only have a value of \( 0, \frac{1}{2}Z \) or \( Z \) where \( Z \) is an integer. Selection rules only permit transitions between adjacent energy levels with \( M_1 = \pm 1 \).

The amount of energy required for a transition between levels is related to the external field in the following manner:

\[
\Delta E = \hbar \gamma B_0 / 2\pi
\]

where \( \Delta E \) is the energy difference between the quantized nuclear levels, \( \gamma \) is the gyromagnetic ratio (different for each nucleus), \( B_0 \) is the magnetic field strength, in gauss, and \( \hbar \) is Planck's constant.

According to the Bohr frequency condition, \( \Delta E = \hbar \nu \), hence:

\[
\nu = \gamma B_0 / 2\pi
\]

where \( \nu \) is the frequency of the corresponding electromagnetic resonance in Hz.
1.5.2 n.m.r. Spectroscopy

Spectroscopy may be defined as the interaction between matter and electromagnetic radiation such that energy is absorbed or emitted according to the Bohr frequency condition. In the n.m.r. spectrometer a strong field creates nuclear energy levels and the sample is then submitted to an additional weak oscillating magnetic field produced by passing electromagnetic radiation, in the radiofrequency range, through a surrounding coil. The frequency of this second field is scanned over the appropriate scale. At certain precise frequencies the nuclear magnets resonate with the field; this is associated with undergoing transitions between the magnetic energy levels. This resonance is detected by a search coil and is amplified and recorded as a n.m.r. spectrum depicting intensity against magnetic field.

Chemical shift

The exact frequency at which a nucleus absorbs depends on where in the molecule it is located. An important factor which determines the peak position is the electronic environment around the nucleus.

The chemical shift (δ) is defined as an atoms position relative to a standard reference:

\[
\delta = \left( \frac{v_x - v_{\text{ref}}}{v_{\text{ref}}} \right) \times 10^6
\]

where δ is the chemical shift for nucleus X in p.p.m. \(v_x\) and \(v_{\text{ref}}\) are the observed frequencies for X and the standard which contains some X nuclei. Provided δ is measured this way it is independent of the spectrometer frequency.
Shielding

Electrons surrounding the observed nucleus circulate in a plane that is perpendicular to $B_o$ and so induce a field which either opposes (i.e. shields the nucleus) or augments (i.e. deshields the nucleus) the external field. In turn the external field is modified to an effective field strength $B_{eff}$ where:

$$B_{eff} = B_o (1 - \sigma)$$

\(\sigma\) is known as the shielding constant and it depends on the electronic density around the nucleus.

Since each set of equivalent nuclei has a slightly different environment from all other sets, a change of applied field strength is required to produce the effective field strength at which the absorption occurs. It is the applied field strength which appears on the spectrum.

Shielded nuclei have a high \(\sigma\) and appear at a low frequency; deshielded protons appear at a high frequency on the spectrum.

Spin-spin coupling

If adjacent atoms are chemically non-equivalent, magnetic interaction causes a splitting of peaks giving a fine structure on the n.m.r. spectrum. The separation between these peaks is the coupling constant, $J$ (inHz). The magnitude of $J$ depends on the number of bonds between the related atoms.

1.5.3 Deuterium n.m.r. Spectroscopy

Naturally occurring hydrogen is predominantly $^1H$ which is a favourable nucleus for n.m.r. because it has spin $I = \frac{1}{2}$ and a high receptivity. The low natural abundance and low resonant frequency of $^2D$ ($I = 1$) originally meant that the use of the deuteron in n.m.r. was limited.
The recent availability of $^2$D-enriched species and the introduction of Fourier transform n.m.r. spectroscopy have enabled detailed study to be conducted on molecules that contain deuterium atoms.

The $^2$D coupling constants are usually small ($J_{DD} \approx 0.2$ Hz) so each anisochronous deuteron appears as a single peak. Although $J_{DD}$ cannot usually be measured from the spectrum, information can be gained about the isotopic shifts of various different deuteriums in molecules such as labelled hydrocarbons. The isotopic shifts for deuterium species parallel those for corresponding protons.

Broad-band decoupling by irradiation of the entire proton $\delta$ range may be deployed to produce a simple first order spectrum.

Fourier Transform n.m.r. Spectrometer.

$^2$D n.m.r. may be studied using a Fourier transform n.m.r. spectrometer provided it is capable of supplying the appropriate resonance frequencies. Here all resonances are probed simultaneously by effectively applying each of the frequencies in the $\delta$ range at once using a short pulse. The sample is magnetised and a signal resulting from all the individual transverse magnetic vectors (My) decaying to zero is recorded.

Each My decay is superimposed to form a total signal called a free induction decay (FID) which is then digitised and stored in a computer before being converted to a conventional spectrum using Fourier transformation.

1.6 THE PRESENT INVESTIGATION

Results are reported for the reactions of alkenes and alkanes on the three oxide catalysts. As far as possible comparisons have been made between the behaviour of the different molecules on each of the catalysts
and between identical molecules on the different catalysts. Attempts were made to compare the results with those reported in previous literature concerning other metal oxide catalysts.

In some cases the main hydrocarbon intermediates have been identified and reaction schemes were suggested. Reaction kinetics were also studied wherever possible.
1.7 REFERENCES


9. Shaw, D.J. Introduction to Colloid and Surface Chemistry, Ch. 6 (Butterworths, London, 1966).


CHAPTER 2

Experimental
2.1 INTRODUCTION

In the present study the reactions of a number of alkene and alkane molecules were investigated on oxide catalysts. Products from the isomerization, hydrogenation and deuteration experiments were analysed using gas chromatography. Exchange of alkenes and alkanes with deuterium and the equilibration of hydrogen and deuterium involved analysis by mass spectrometry. In some of the reactions where deuterium appeared in the product hydrocarbons deuterium n.m.r. spectrosocopy was used for analysis. The analytical techniques are described in the following Chapter.

The catalysts were prepared and subsequently pretreated in order to maximize their respective activities and methods used are described along with characterization techniques. Experimental details specific to a particular investigation are given in a short experimental section in the relevant Chapter.

2.2 GAS HANDLING APPARATUS AND EXPERIMENTAL PROCEDURE

2.2.1 Vacuum Lines

Three different vacuum lines were used to carry out the experiments. Two of these contained static reaction systems and the third was a recirculation line. The apparatus used for experiments depended on the nature of the reaction being investigated and the type of analysis required.

Mass spectral analysis could be carried out using static line (I) and a schematic diagram of the vacuum apparatus is shown in Figure 2.1. A silica vessel was connected to the line by a Young's B24 greaseless joint and the total reaction volume was 210 cm$^3$. The cone of the vessel was surrounded by a water-cooled jacket. The vacuum line contained Springham's greaseless metal valves.
Figure 2.1
Schematic diagram of static line (I).
The recirculating apparatus was connected to a gas chromatograph; a schematic diagram of the recirculation section is shown in Figure 2.2. This consisted of a silica vessel with a 1 cm diameter sinter attached via a ball and socket joint, a liquid nitrogen trap and a connection through a three-way trap and a Carle valve to the gas chromatograph. The volume of the apparatus was 335 cm$^3$ and a Metal Bellows (240V) recirculation pump with a flow meter was used. An accurately measured (4.18 cm$^3$) doser section was positioned above the reaction vessel. Poisoning experiments could be carried out by the introduction of measured doses of the poison molecule into the main gas streams. The vacuum line contained Springham's ground glass stopcocks lubricated with Apiezon L and N high vacuum grease. The remaining sections of the recirculation apparatus were identical to those of static line (I). Both systems contained a palladium-silver alloy thimble for purification of hydrogen or deuterium.

Static line (II) was used for reactions requiring gas chromatographic analysis and this system was broadly similar to static line (I) except that greased taps were used and the closed reaction volume was 180 cm$^3$. The bulk of reactions followed by gas chromatography were conducted on the recirculation line. In experiments where a large amount of catalyst was required the gas flow was restricted in this apparatus and static line (II) was used instead.

All reactions were carried out by using low pressures of gases (<10 kPa); hence a high background vacuum was required. This was achieved by using a liquid nitrogen trapped three-stage rotary pump (Edwards). This set-up produced pressures of less than 1.3 x 10$^{-6}$ kPa. The vacuum lines each contained two sets of pumps - one for evacuation of the gas handling side of the line and the other to pump the reaction vessel.
Figure 2.2

Schematic diagram of the recirculating reactor (●, calibrated volume).
The gas handling sections consisted of a series of permanently attached storage bulbs for keeping the gaseous hydrocarbons and a mixing section where the reactants were prepared. Liquids were fed into the system by detachable ampoules and the gases which were not contained in the storage bulbs were supplied from cylinders.

Hydrocarbon pressures were measured using either a mercury monometer or a diaphragm pressure gauge. A MacLeod gauge was used to measure the pressure in the reaction vessel during catalyst evacuation. This was calibrated so as to indicate a pressure of $1.3 \times 10^{-6}$ kPa or less.

2.2.2 Sampling Systems

Samples to be analysed by gas chromatography were taken at suitably chosen time intervals. They were removed from the reaction vessel by way of a three-way tap which was connected to the Carle valve via a short piece of capillary glass tubing. This section could be evacuated whenever necessary. When the Carle valve was opened the hydrocarbon passed into a stainless steel capillary loop and the carrier gas was fed directly into the column (thus avoiding the sample loop). On closing the valve the carrier gas was redirected into the loop in order to flush the hydrocarbons into the column for separation.

Analysis by mass spectrometry involved continuous sampling of the hydrocarbons. A capillary leak connected the reaction vessel to the mass spectrometer. The leak was approximately one metre long which meant a relatively large time interval had elapsed between the samples leaving the vessel and arriving in the spectrometer. As a result, a short induction period was observed for the exchange reactions.
Material was lost at a rate of 2% hr\(^{-1}\) for the continuous sampling and a loss of 1% sample\(^{-1}\) was found for gas chromatographic analysis.

2.2.3 Control of Temperature

All catalyst pretreatments and most reactions were carried out at elevated temperatures which were achieved by heating the reaction vessel using a close-fitting electrical furnace. The temperature of the furnace was controlled by a Eurotherm proportional controller with a chromel-alumel thermocouple fitted to the outside of the vessel. A second thermocouple linked to a Comark digital thermometer was inserted into the pocket of the reaction vessel and this gave an accurate measurement of the temperature just above the catalyst bed.

Some of the reactions were carried out at temperatures below 273K and in these cases the catalyst was cooled by immersing the reaction vessel into a slush bath. These were prepared by semi-freezing the appropriate organic solvent with liquid nitrogen. The temperatures attained by the different slush baths are shown in Table 2.1.

2.2.4 Experimental Procedure

In each experiment a weighed amount of catalyst was placed in the reaction vessel and then evacuated at the chosen temperature for a specific time interval. In some experiments oxygen was passed over the catalyst after thermal treatment and this is indicated later in the relevant Chapters. Following pretreatment the furnace was removed and the reaction vessel allowed to cool to room temperature. A second furnace was used to raise the temperature to the value required for the reaction; alternatively a slush bath was used to cool the vessel.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>256</td>
</tr>
<tr>
<td>o-xylene</td>
<td>247</td>
</tr>
<tr>
<td>Arklone</td>
<td>237</td>
</tr>
<tr>
<td>Chloroform</td>
<td>208</td>
</tr>
</tbody>
</table>
Reactant hydrocarbons were purified by vacuum distillation involving several freeze/pump/thaw cycles. In order to completely remove air from the sample, the initial 10% of the gas phase was evacuated when the hydrocarbon was melted and similarly the final fraction was discarded when freezing the compound. Pressures of the gases were either allowed to mix for about 30 minutes (static gas-line) or recirculated for a few minutes. In the static system the reactants were expanded into the reaction vessel via an entrance tap which was closed after 15 seconds. The mixture came into contact with the catalyst by redirecting the flow after mixing on the recirculation apparatus. A clock was started as soon as the gases entered the reaction vessels.

Before removing samples for analysis by gas chromatography the capillary section between the Carle valve and the sampling tap was evacuated. The three-way tap was then rotated to allow the gases to pass from the vessel into the capillary section, as far as the valve. The time was noted and after 15 seconds the sampling tap was closed, the Carle valve opened and the gas chromatograph switched on. After a further 15 seconds, to allow the sample to be flushed into the column, the Carle valve was closed.

Mass spectra were recorded by operating a scan control switch on the front panel of the spectrometer and simultaneously starting the recorder.
2.3 ANALYTICAL TECHNIQUES AND TREATMENT OF EXPERIMENTAL DATA

2.3.1 Gas Chromatography

The Gas Chromatograph

Gas chromatographic analysis was carried out using a Perkin-Elmer (type F11) gas chromatograph fitted with a flame-ionisation detector. After a sample from the reaction vessel had entered the sample loop it was transferred into the adjoining column by nitrogen carrier gas. The resolved components were ionised in the hydrogen/air flame of the detector on reaching the end of the column. This produced a current signal which was amplified and recorded as peaks on a potentiometric recorder (Servoscribe). The area under the peaks and the retention times are printed out by a Venture Mk II digital integrator.

Details of the columns and operation conditions used for the separation of the various hydrocarbon molecules are shown in Table 2.2. Two types of column are mentioned and they were prepared in different ways. In the packed column the active material was dispersed on to a support compound, whereas it was spread along the walls of a capillary column. Figure 2.3 is a typical trace showing the dimethylbutenes and dimethylbutanes peaks separated by the squalane capillary column.

Treatment of Results

The amounts of each hydrocarbon in the sample was proportional to the area under the peak. The alkenes and alkanes had different sensitivities in the detector; therefore it was necessary to calculate a correction factor to account for this. This was achieved by sampling from a 1:1 mixture of the two compounds and recording the average integral obtained for a series of different pressures. The integral was plotted
Table 2.2
Conditions used for Gas Chromatography

<table>
<thead>
<tr>
<th>Compound</th>
<th>Column</th>
<th>Length/m</th>
<th>T/K</th>
<th>Total p/kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>A</td>
<td>2</td>
<td>293</td>
<td>177</td>
</tr>
<tr>
<td>Propene (I)</td>
<td>A</td>
<td>2</td>
<td>348</td>
<td>308</td>
</tr>
<tr>
<td>Propene (II)</td>
<td>A</td>
<td>2</td>
<td>368</td>
<td>342</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>A</td>
<td>2</td>
<td>313</td>
<td>225</td>
</tr>
<tr>
<td>3,3-Dimethylbut-1-ene</td>
<td>B</td>
<td>50</td>
<td>273</td>
<td>163</td>
</tr>
<tr>
<td>2,3-Dimethylbutene</td>
<td>C</td>
<td>4</td>
<td>318</td>
<td>239</td>
</tr>
<tr>
<td>cis-But-2-ene</td>
<td>C</td>
<td>4</td>
<td>313</td>
<td>225</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>C</td>
<td>4</td>
<td>313</td>
<td>225</td>
</tr>
<tr>
<td>Cyclopentene (I) &amp; (II)</td>
<td>D</td>
<td>2</td>
<td>313</td>
<td>225</td>
</tr>
</tbody>
</table>

a A = 3% squalane on activated alumina, B = squalane capillary, C = 13.5% bis-2-methoxyethyl adipate + 6.5% di-2-ethylhexylsebacate on Chromosorb P, D = 15% squalane on Chromosorb P.

b Nitrogen carrier gas.

c 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene.
Figure 2.3

Gas chromatographic spectrum for the C₆-alkenes using a squalane capillary column:
(a) 3,3-dimethylbut-1-ene, (b) 2,2-dimethylbutane,
(c) 2,3-dimethylbut-1-ene, (d) 2,3-dimethylbutane
and (e) 2,3-dimethylbut-2-ene.
against partial pressure and the sensitivity factors were obtained from the slopes, with the reactant alkene given a value of 1.00. A typical plot is shown for propene and propane in Figure 2.4 and this gave sensitivity factors of 1.00 and 0.94 for the respective molecules.

Isomerization, hydrogenation and deuteration reactions of alkenes were studied using gas chromatography. The gas samples from the reaction vessel were analysed at different time intervals and the experimental data was plotted as percentage composition against time.

2.3.2 Mass Spectrometry

The Mass Spectrometer

Results from experiments involving exchange of hydrocarbons with deuterium and the hydrogen-deuterium equilibration were analysed by mass spectrometry using a micromass MM601 (Vacuum Generators) spectrometer. An advantage of using this apparatus is that continuous sampling of the reaction mixture is possible.

The analyser section of the instrument was pumped by a water-cooled oil-vapour diffusion pump (Edwards), backed by a two stage rotary pump. Pressure measurement was by a Pirani-ion gauge and a minimum pressure of about $1.3 \times 10^{-10}$ kPa was achieved.

The gas molecules from the reaction vessel were ionized, by electron impact, on entering the ion source in the spectrometer. This results in a parent ion, $C_m X_n^+$ ($X = H$ or $D$). The ionizing energy and focus of the electron beam can be varied by means of a source control and the conditions used depend on the molecule being investigated.

Some of the ions were then accelerated out of the ionization chamber by application of a potential, $V$ (Ca 2kV). After acceleration, the ions
Figure 2.4

Plot used to determine the relative sensitivities of propene, $\bigcirc$, and propane, $\square$, towards the flame in the G.C. apparatus.
traverse a magnetic field, $H$, where they are deflected through $90^\circ$. A series of slits ensures that only those ions which travelled a path of radius, $r$, arrive at the detector. The magnetic field was varied using a constant accelerating voltage and the mass of the ions are given by:

$$m = H^2r^2e/2V$$

(2.1)

where $e$ is the charge on the electron.

The ions were detected by means of a Faraday cup collector. The current was amplified and spectra were then recorded using a fast response potentiometric recorder (Chessel Ltd).

The instrument was capable of operating in the mass range 1-400 a.m.u. and the time taken to scan any mass range could be varied. In experiments the scan time for recording one spectrum was usually between one and three minutes.

The ionizing voltages were suitably chosen in order to achieve a compromise between high sensitivity and minimal fragmentation. The parent ions of 2-methylpropane, 2-methylpropene and 2,2-dimethylpropane did not give adequate sensitivity for detailed examination. Results of experiments with these molecules were obtained in terms of the pseudoparent ions which formed by loss of a methyl fragment.

Calibration experiments with equimolar samples of alkane and alkene were used to calculate relative sensitivities of the two compounds. The resulting sensitivity factors are shown in Table 2.3 for the relevant hydrocarbons.

The ionizing voltage used for the equilibration of hydrogen and deuterium was 22eV. Sensitivity of the apparatus for these experiments was calibrated by using 1:1 mixtures of the two gases.
### Table 2.3

**Ionizing voltages, fragmentation factors and hydrocarbon sensitivities used for analysis by mass spectrometry**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>eV</th>
<th>Ion + used</th>
<th>Number of H atoms lost</th>
<th>Alkene sensitivity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Relative peak size</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>M⁺</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CH₄</td>
<td>16</td>
<td>CH₄⁺</td>
<td>0.659</td>
<td>0.250</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>12</td>
<td>C₃H₈⁺</td>
<td>0.775</td>
<td>0.139</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>12</td>
<td>C₃H₆⁺</td>
<td>0.968</td>
<td>0.247</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>20</td>
<td>C₄H₁₀⁺</td>
<td>0.182</td>
<td>0.052</td>
</tr>
<tr>
<td>C₄H₈ c</td>
<td>20</td>
<td>C₄H₈⁺</td>
<td>0.411</td>
<td>0.066</td>
</tr>
<tr>
<td>(CH₃)₃CH</td>
<td>15</td>
<td>C₃H₇⁺</td>
<td>0.347</td>
<td>0.236</td>
</tr>
<tr>
<td>(CH₃)₂CCH₂</td>
<td>15</td>
<td>C₃H₅⁺</td>
<td>0.088</td>
<td>0.255</td>
</tr>
<tr>
<td>Cyclo C₅H₁₀</td>
<td>25</td>
<td>C₅H₁₀⁺</td>
<td>0.038</td>
<td>0.019</td>
</tr>
<tr>
<td>Cyclo C₅H₈</td>
<td>25</td>
<td>C₅H₈⁺</td>
<td>2.162</td>
<td>0.157</td>
</tr>
<tr>
<td>(CH₃)₄C</td>
<td>35</td>
<td>C₄H₉⁺</td>
<td>0.046</td>
<td>0.028</td>
</tr>
</tbody>
</table>

- **a** Relative to an assigned value of 1.000 for ion which had not lost H.
- **b** Peak size relative to 1.00 for alkane.
- **c** Using trans-but-2-ene.
Treatment of Results

Mass spectra consisted of several sets of peaks which had varying intensities, each set corresponding to a different time. The heights of the peaks were measured manually to the nearest 0.5 mm and converted to a common sensitivity. The intention of the experiments was to accurately assess how the nature of the peaks were changing with time. But before this could be achieved it was necessary to correct the raw spectral data. In order to do this the results from the hydrocarbon reactions were treated in a different way to those from hydrogen-deuterium equilibration and the methods used are described below.

(a) Reactions of Hydrocarbons.

In these experiments the data was corrected to account for two complicating factors. One set of corrections took account of the presence of naturally occurring isotopes and the other compensated for the occurrence of molecular fragmentation.

Both sets of corrections were carried out using a modification of a computer programme written by Dowie (1). The main principles used for the programme are described below.

In the exchange reaction of hydrocarbons the mass of the parent (P) will increase by one a.m.u. each time a hydrogen atom is replaced by a deuterium atom in the molecule. Hence peaks will appear with mass (P+1) and (P+2) and so on. The heavy isotopes, carbon-13 and deuterium, will be present in the hydrocarbon molecules with natural abundances of 1.069% and 0.016% respectively (2). Therefore the mass spectra of the hydrocarbons contain peaks with masses of one and two a.m.u. larger than that of the
parent peak and this fact must be taken into account. In the correction use was made of the binomial expression for the hydrocarbon molecule $C_mH_n$:

$$(0.98931 + 0.01069X)^m (0.99984 + 0.00016X)^n$$

(2.2)

The expected intensity ratio of peaks containing natural isotopes relative to that of the parent may be calculated in this way. Expansion of the binomial expression leads to a number of terms in $X$ raised to different powers. The term in $X^0$ (i.e. 1) corresponds to the fraction of natural isotope in the parent peak, and those in $X^1$ and $X^2$ correspond to the fractions in $(P+1)$ and $(P+2)$ etc. During the course of a reaction the deuterium content of the hydrocarbons increases and this reduces the amount of naturally occurring deuterium. Hence, for any isotopically labelled species, $C_mH_{n-r}D_r$, the value of $(n-r)$ substitutes $n$ in equation (2.2) so that the relative quantities of the heavier molecules can be calculated.

Thus the first stage in determining the true extent of exchange involved the subtraction of the isotope contributions due to hydrocarbons appearing at lower masses from the intensities observed for the products. The procedure was carried out in the computer programme using a systematic manner starting with the lowest masses, correcting them and then working upwards to the peaks having larger masses.

Bombardment of the hydrocarbon by the ionizing electrons produces a parent ion which has lost one electron. In practice the parent has a chance of losing one or more hydrogen atoms and this produces peaks with $(P-1)$ and $(P-2)$ etc. These peaks are known as fragment ions and their presence must be taken into account in the determination of the composition of the hydrocarbons on the spectrum.
The fragmentation factors \( f_i \) of the light hydrocarbon were measured from the spectrum of the unreacted sample and these were defined by:

\[
f_i = \frac{C_m H_{n-i}}{C_m H_n}
\]

(2.3)
i.e. the ratio of the peak heights of fragment and parent ion after correction for naturally occurring isotope. The loss of deuterium and/or hydrogen is also considered for the labelled molecules and the fragmentation pattern of the heavy hydrocarbons were obtained by multiplying \( f_i \) by 0.65. This figure was obtained from the work of Dowie, Whan and Kemball (3) where the authors assumed that hydrogen is more readily lost than deuterium from isotopically labelled molecules. A detailed description of the different probabilities for the loss of H or D from the various molecules was reported in reference 3. Statistical factors were incorporated into the computer programme with \( A = 1.1 \) and \( B = 0.9 \) where \( A \) and \( B \) were defined in the previous work (3).

Once both types of correction were carried out the peak heights were expressed as a percentage.

The experimental conditions used for the analysis by mass spectrometry are summarised in Table 2.3. Exchange of the molecules n-butane, 2-methylpropane, propane and cyclopentane was accompanied by dehydrogenation with formation of heavily exchanged alkene. The values given in the Table are reported for equal pressures of unreacted alkane or alkene at 625K.

(b) Equilibration of Hydrogen and Deuterium.

The sensitivity of the peak having \( m/e = 3 \) for HD was found by allowing an equimolar mixture of hydrogen and deuterium to reach equilibrium over
zirconia for 48 hours at 293K and choosing a calibration factor so that the equilibrium constant for the reaction

\[ H_2 + D_2 \rightleftharpoons 2HD \]

agreed with the value given by Urey and Rittenberg (4). This procedure was based on earlier work of Brookes (5) and gave relative sensitivities for \( H_2 : HD : D_2 \) of 1.0 : 2.2 : 3.7. These values were independent of the temperature used for the reaction. It took four minutes to run the mass spectrum and so in the kinetic experiments it was necessary to interpolate the observed peak heights in order to obtain sets of values for \( m/e = 2, 3 \) or 4 at the appropriate times.

No increase in the initial 0.5% HD present as impurity in the deuterium was observed after overnight mixing of the \( H_2 \) and \( D_2 \), in contact with the pyrex glass at room temperature. But blank experiments without catalyst showed that slow equilibration reactions occurred in the silica reaction vessel after the usual pretreatment procedures for zirconia and anatase had been carried out.

2.3.3 Deuterium n.m.r. Spectroscopy

Deuterium n.m.r. spectra were obtained in a Bruker WH 360 spectrometer operated at 55.28 MHz using an Aspect 2000 data system. Spectra were acquired at 298K in the unlocked mode and both broad band proton decoupling and Fourier transformation of the signal were carried out. The presence of 5% D-chloroform solvent provided sufficient signal for optimisation of the homogeneity of the sample on the FID from a single 90° pulse and provided an internal reference taken as \( \delta = 7.25 \) p.p.m. Other details of the operating conditions are available elsewhere (6).
In all cases line-narrowed spectra were obtained by carefully selecting the function parameters (LB and GB in the Bruker n.m.r. programme FTQ 82060) to give optimum resolution. Spectra were run by Dr I H Sadler using the SERC high field facility at Edinburgh University.

Samples for analysis were obtained by following the reactions to an appropriate conversion, determined by gas chromatography, and the contents of the reaction vessel were expanded into a large volume through a trap immersed in liquid nitrogen. The deuterium gas was then evacuated and the hydrocarbons were condensed and subsequently distilled under vacuum. After outgassing by three or four freeze/pump/thaw cycles, the hydrocarbons were transferred into a sample tube containing the 5% D-chloroform solvent at 77K and this was sealed by melting under vacuum.

2.4 CHARACTERIZATION TECHNIQUES

2.4.1 Surface Area Measurements

Surface areas of the catalysts were determined using nitrogen adsorption at 77K and the BET method (7). The vacuum apparatus consisted of a manometer, a sample holder and a series of five dosing bulbs of different volume. The volume of each section of the gas-line was calibrated using successive expansion of air from a bulb of known volume and by applying Boyle's Law. Fresh samples of catalyst (0.5 g) were accurately weighed into the vessel and it was melted on to the apparatus. The neck of the sample holder was made from capillary tubing which was cut in order to remove the catalyst from the gas line after experiments. A nitrogen-trapped three-stage mercury diffusion pump backed by an oil rotary pump was used to obtain a pressure of less than $1.3 \times 10^{-6}$ kPa in the system.
The catalyst sample was pretreated in an identical way to that used for reactions and the reaction vessel was immersed in a Dewar vessel containing liquid nitrogen before the surface area was measured. An initial dose of nitrogen gas was expanded into a closed volume and on to the catalyst with the dosing bulbs empty. The equilibrium adsorbate gas pressure \( p \) was then measured at room temperature using the manometer and the volume of gas adsorbed on the catalyst \( V \) was calculated (and converted to standard temperature and pressure). The volume of the apparatus was then reduced by a known amount by filling the first dosing bulb with mercury. The new equilibrium pressure was measured and the amount of gas adsorbed was again calculated. This procedure was repeated until all the dosing bulbs were filled with mercury.

The experimental data was treated in terms of the following form of the BET equation:

\[
p/V(p_o-p) = (1/(V_mC)) + (((C-1)p/V_mCp_o)
\]

(2.4)

where \( p_o \) is the saturation vapour pressure of the adsorbate (101.32 kPa for nitrogen at 77K), \( V_m \) is the volume required to give a complete monolayer by adsorption, \( p \) and \( V \) are as described above and \( C \) is given by the relationship:

\[
C \cong \exp \left( \frac{\Delta H_{ads} - \Delta H_{liq}}{RT} \right)
\]

(2.5)

where the symbols \( \Delta H_{ads} \) and \( \Delta H_{liq} \) represent the heats of adsorption and the latent heat of liquefaction of the adsorbate respectively. A plot of \( p/V(p_o-p) \) against relative pressure \( (p/p_o) \) gave a straight line of slope,

\[
S = (C-1)/V_mC
\]

(2.6)

and intercept,

\[
I = 1/V_mC
\]

(2.7)
such that \( V_m = 1/(S+I) \). A typical plot obtained for the catalyst \( \text{La}_2\text{O}_3(II) \) is shown in Figure 2.5.

The required surface area \((A/m^2)\) was given by:

\[
A = \left( \frac{V_m \cdot N_A \cdot \sigma}{V_s} \right)
\]

where \( \sigma \) is the cross-sectional area of nitrogen which was taken to be \( 16.2 \times 10^{-20} \text{ m}^2 \), after McClellan and Harnsberger (8), \( N_A \) is the Avagadro number and \( V_s \) is the standard molar gas volume. The surface area was quoted in \( \text{m}^2 \text{g}^{-1} \).

The areas observed for the catalysts used in the present investigation are given later in the experimental section of the relevant Chapters.

2.4.2 Thermogravimetric Analysis

Further characterization of the lanthana catalyst was obtained by thermogravimetry using a Stanton Redcroft TG 770 analyser with a heating rate of 10 deg min.\(^{-1}\). This apparatus consisted of a weight balance and thermal programmer connected to a potentiometric recorder. Samples (5 mg) were held in a furnace in the presence of flowing air. Full-scale deflection was set at 50% of the starting weight.

Thermograms showing the percentage weight change with heating temperature were plotted in the range 290-1273K.

2.5 MATERIALS

2.5.1 Reactants

The suppliers of the various alkenes and alkanes (all at least 99% pure) are listed in Table 2.4. With the exception of methane, the hydrocarbons were further purified by vacuum distillation. The second
Figure 2.5

BET plot for adsorption of nitrogen on 0.6 g La$_2$O$_3$ (II) at 77K.
### Table 2.4

**Suppliers of the Hydrocarbon Reactants**

#### Alkenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>Matheson</td>
</tr>
<tr>
<td>Propene (I)</td>
<td>Air Products</td>
</tr>
<tr>
<td>Propene (II)</td>
<td>Matheson</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>Matheson</td>
</tr>
<tr>
<td>3,3-Dimethylbut-1-ene</td>
<td>Fluka AG</td>
</tr>
<tr>
<td>2,3-Dimethylbutene</td>
<td>Fluka AG</td>
</tr>
<tr>
<td>cis-But-2-ene</td>
<td>Fluka AG</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>Matheson</td>
</tr>
<tr>
<td>Cyclopentene (I) &amp; (II)</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

#### Alkanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Cambrian</td>
</tr>
<tr>
<td>Propane</td>
<td>Cambrian</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>Cambrian</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>Fluka AG</td>
</tr>
<tr>
<td>2,2-Dimethylpropane</td>
<td>Cambrian</td>
</tr>
</tbody>
</table>
sample of cyclopentene (II) was further purified by passage through a column packed with basic γ-alumina to remove peroxide impurities.

Deuterium (99.5%) from Matheson Chemicals and hydrogen from BOC were dried in a bed of 4A molecular sieve at 77K and then diffused through a heated palladium-silver alloy thimble.

Carbon dioxide, used in some poisoning experiments on zirconia, was obtained as grade X from BOC and distilled under vacuum before use.

2.5.2 Catalysts

Lanthana (La$_2$O$_3$)

The oxide catalyst was prepared using the method described by Imizu, Sato and Hattori (9). This involved precipitation of the hydroxide (La(OH)$_3$) from the nitrate by addition of ammonia. Lanthanum nitrate, La(NO$_3$)$_3$ 6H$_2$O (99.999%), was obtained from the Aldrich Chemical Company. The precipitate was washed with deionized water, dried at 373K and ground to 24-42 mesh; weighed amounts (usually in the range 15-100 mg) of this material were taken for catalytic experiments and evacuated for three hours to form the oxide. The evacuation temperature and sample weights are given later in the relevant Chapters. Two preparations were made: La(OH)$_3$(I) was stored in the atmosphere and La(OH)$_3$(II) was kept under vacuum in a dessicator.

Zirconia (ZrO$_2$)

Zirconyl chloride, ZrOCl$_2$8H$_2$O, from Aldrich Chemical Company was used to prepare the hydroxide following the procedure described by Wang, Hattori and Tanabe (10). This involved precipitation using aqueous ammonia and the resulting zirconium hydroxide was calcined at 873K and then allowed to
rehydrate by cooling in the atmosphere. Weighed samples (usually in the range 100 to 250 mg) were evacuated for three hours for the catalytic experiments. Most experiments involved evacuation at 873K but in some cases the temperature was less and this is indicated in the relevant text. Two different samples of zirconyl chloride of 98+% and 99.99% purity were used as starting materials and the resulting oxides are described as \( \text{ZrO}_2(\text{I}) \) and \( \text{ZrO}_2(\text{II}) \) respectively.

**Anatase (\( \text{TiO}_2 \))**

Titania (CLDD 1643) was a gift from Tioxide U.K. plc and as the material had a rutile content of less than 0.4% the catalyst is referred to as anatase. Preparation consisted of hydrolysis of isopropyl titanate, \( \text{Ti}[\text{OCH(CH}_3\text{)}_2]_4 \), and the resulting hydroxylated compound was calcined at 773K for 17 hours to produce \( \text{TiO}_2 \). The sample was a white powder and had 0.047% Cl and 0.029% S as impurities.

Pretreatment consisted of overnight evacuation (17 hours) at 723K followed by admission of 13.2 kPa of pure oxygen gas into the catalyst vessel at this temperature. The initial dose of oxygen was then evacuated and a second 13.2 kPa of oxygen was passed on to the catalyst; then the contents of the vessel were allowed to cool to room temperature and left for 15 minutes. Finally the second dose of oxygen was pumped away and the catalyst was heated to reaction temperature under vacuum.

**Calcium oxide (CaO) and \( \gamma \)-Alumina (\( \text{Al}_2\text{O}_3 \))**

Some experiments involving these catalysts are described in Chapter 4. The CaO was identical to the sample of Brown, Kemball, McGillivray and Sadler (11) and the standard alumina, SA 2165, was described by John,
Kemball, Pearce and Pearman (12). Pretreatment of both catalysts followed the methods of the previous authors.

2.6 CALCULATION OF REACTION RATES

2.6.1 Isomerization and Addition Rates

The experimental data was plotted as a percentage of reactants (x) against time (t) and usually the initial slope (-dx/dt) was used to measure the rate, \( k \) in \( \text{min}^{-1} \). In some cases the procedure was different and this is described in the relevant part of the text.

2.6.2 Exchange Rates

The treatment of the data from exchange reactions was detailed by Kemball (13), and only the most important equations and definitions are described here.

The deuterium content of a hydrocarbon is defined by \( \phi \) where:

\[
\phi = \sum \text{iD}_i = n \times 100d \tag{2.9}
\]

and \( \text{D}_i \) is the percentage of alkene with \( i \) deuterium atoms; \( d \) is the average chance of any atom being deuterium at a particular time and \( n \) is number of exchangeable hydrogen atoms.

The course of an exchange reaction may be followed in two ways - either by the rate of incorporation of deuterium into the molecule or by the rate of disappearance of the reactant hydrocarbon.

The initial rate of entry of deuterium into the hydrocarbon is given by the first order reversible equation:

\[ -\log (\phi_{\infty} - \phi) = k_{\phi} t / 2.303 \phi_{\infty} - \log (\phi_{\infty} - \phi_0) \] \( \tag{2.10} \)

where \( \phi \) and \( \phi_{\infty} \) represent the deuterium content of the alkane at
time \( t \) (min) and equilibrium, \( \Phi_0 \) is the initial value of \( \Phi \) and \( k_0 \) is the initial rate of exchange (D atoms acquired by 100 molecules in unit time).

A second rate \( k_o \) refers to the rate of disappearance of light hydrocarbon in % min\(^{-1}\). This is defined by:

\[
\log \left( \frac{x-x_\infty}{100-x_\infty} \right) = k_o \frac{t}{2.303} - \log (100-x_\infty)
\]

(2.11)

where \( x \) is the percentage of reactant at time \( t \) (min) and 100 and \( x_\infty \) refer to the initial and equilibrium percentages respectively. A plot of \( \log \left( \frac{x-x_\infty}{100-x_\infty} \right) \) against time gives a straight line with gradient \(-k_o/2.303 (100 - x_\infty)\).

The ratio of the two rate constants, \( M = \frac{k_0}{k} \), represents the mean number of hydrogen atoms being replaced by deuterium atoms in each hydrocarbon molecule undergoing exchange.

### 2.6.3 Rate of Equilibration of Hydrogen and Deuterium

The course of the equilibration reactions with time followed the usual first order reversible equation (14):

\[
\log \left[ [\text{HD}] - [\text{HD}]_\infty \right] = -kt/2.303[\text{HD}]_\infty + \log [\text{HD}]_\infty
\]

(2.12)

where \([\text{HD}]\) and \([\text{HD}]_\infty\) represent the percentages of hydrogen deuteride present at time \( t \) (min) and at equilibrium, and \( k \) is the initial rate of reaction in % min\(^{-1}\). A plot of \( \log ([\text{HD}]_\infty - [\text{HD}]) \) against time gives a straight line with gradient \(-k/2.303[\text{HD}]_\infty\).

### 2.6.4 Units of Rates

All rates of reaction were expressed in molecules s\(^{-1}\) m\(^{-2}\). The number of molecules, \( n \), in the static system was calculated from the gas equation:

\[
n = \frac{pV}{AT} \times 273/760 \times 22400 \times T
\]

(2.13)

where \( p \) (mm Hg) is the pressure of gas in volume \( V \) (cm\(^3\)), \( T \) (K) is the
reaction temperature and \( N_A \) is the Avogadro number. For reactions carried out on the recirculation line, \( n \) was calculated by substituting \( T \) with room temperature.

A charge in the order of \( 10^{20} \) molecules was used and more accurate numbers are given in the respective Chapters.

The rates of reactions involving hydrocarbons \( (r/\text{molecules s}^{-1} \text{ m}^{-2}) \) were then calculated using the relationship:

\[
r = nk/100 \times 60 \times AW
\]

where \( k \) is the slope in \( \% \text{ min}^{-1} \), \( A \) is the surface area in \( \text{m}^2 \text{g}^{-1} \), and \( W \) is the sample weight in grams. However, the absolute rate is sometimes quoted as \( k \) (rather than \( r \)) in molecules \( s^{-1} \text{ m}^{-2} \).

The absolute initial rate of the equilibration of hydrogen and deuterium was calculated using:

\[
r = 2k n_H/60 \times 100 \times AW
\]

where \( n_H \) is the charge of hydrogen molecules and the other symbols were defined previously. The factor 2 was introduced to allow for the fact that with a 50:50 mixture of \( \text{H}_2: \text{D}_2 \) only half of the exchanges will lead to observable product, neglecting isotope effects (15).

### 2.6.5 Calculation of Activation Energies

Activation energies \( (E_a) \) were calculated from the Arrhenius equation (1.6). Taking logarithms of both sides of the equation leads to:

\[
\log k = \log A - E_a/2.303 RT
\]

where the symbols are as defined in Chapter 1. Provided that \( k \) and \( A \) are expressed in molecules \( s^{-1} \text{ m}^{-2} \), the gas constant is in \( \text{JK}^{-1} \text{ mol}^{-1} \) and temperature is in \( K \), the activation energy has units \( J \text{ mol}^{-1} \).
2.7 REFERENCES

1. Dowie, R.S. Computer Programmes for Catalytic Studies (Chemistry Department, University of Edinburgh, 1973).


CHAPTER 3

Reactions of Alkenes on Lanthana.
3.1 INTRODUCTION

Rosynek (1) has given a general review of the catalytic properties of lanthana and his report showed that the oxide was an effective catalyst for the hydrogenation and isomerization of selected alkenes. Minachev, Khodakov and Nakhshunov (2) reported some results for the hydrogenation of ethene at low temperatures as part of a study of the catalytic activities of rare earth oxides. High activity for hydrogenation was found at 195K and rates were dependent on the temperature at which the catalyst was pretreated. A maximum rate of about $1.7 \times 10^{17}$ molecules s$^{-1}$m$^{-2}$ after pretreatment at 1073K was reported but activities were estimated only by taking rates at 50% conversion. Khodakov, Makarov, Delzer and Minachev (3) used thermal programmed desorption to provide evidence for at least two adsorbed forms of ethene on the surface after exposure to the gas at 195K and the amounts of these species were dependent on pretreatment temperatures. They also showed that carbon monoxide, carbon dioxide and water reduced the rate of hydrogenation of ethene. Topchieva and Ibragimova (4) reported that the hydrogenation of propene took place on lanthana between 415 and 483K but gave no detailed results. The most extensive work involving alkene hydrogenation was carried out by Jensen (5) who used ethene, propene and but-1-ene and showed that at 273K the rate of reaction of ethene was about $10^4$ times faster than the rates for the other molecules.

The isomerization of but-1-ene and related reactions has been studied by a number of groups (5-10). There is a high initial preference for the formation of cis-but-2-ene and this demonstrates a kinetic control of selectivity which has been attributed to a mechanism involving π-allylic
intermediates. Similar results have been found on other basic oxide catalysts such as calcium oxide (11) and magnesia (12). Experiments with mixtures of undeuterated and deuterated butenes on lanthana showed that double-bond movement occurred by intramolecular transfer of H or D with little contribution from intermolecular reaction.

In Chapter 4 mechanistic studies of the reactions of 2-methylpropene and deuterium are reported. Exchange of the alkene occurred about 10 times faster than addition at 414K and the distribution of deuterium atoms in 2-methylpropene was consistent with a π-allyl species as intermediate. The n.m.r. results showed that the chances of acquiring D or H at the primary and tertiary positions of 2-methylpropene in the addition process were not the same. It was suggested that the species adding to these positions originated from different pools of H or D on the surface with different partial charges.

The original intention of this research was to obtain information on the hydrogenation of a wide range of alkenes on lanthana and also to examine the isomerization of 3,3-dimethylbut-1-ene on the catalyst. Preliminary results showed that two complicating features were important. The first of these was a tendency for self-poisoning to occur with alkene/hydrogen mixtures on lanthana and the extent of this depended not only on temperature but also on the alkene. The second complication was the sensitivity of the catalysts to ageing as a result of uptake of water or carbon dioxide. With some of the alkenes, experiments were carried out using deuterium instead of hydrogen and, where appropriate, products were examined by $^2$D-n.m.r. spectroscopy.
3.2 EXPERIMENTAL

Catalyst pretreatment consisted of heating weighed amounts of hydroxide (usually in the range from 15 to 60 mg) for three hours for catalytic experiments. Fresh samples were used for each experiment except where indicated in the text. The BET-N\_2 surface area of La\_2O\_3 (I) was measured after pretreatment at different outgassing temperatures and results are reported later.

Reactions were followed on the recirculation system and analysis was by gas chromatography. Some samples were also analysed using \^2D-n.m.r. spectroscopy by condensing the hydrocarbon after a specific amount of alkene was converted. The technique used has been described in Chapter 2.

The reaction mixture consisted of a 5:1 ratio of hydrogen (or deuterium):hydrocarbon with a pressure of 2.4 kPa of alkene corresponding to a charge of about 2.0 \times 10^{20} molecules of hydrocarbon.

Reaction rates were usually measured by plotting percentage of reactant against time, although fractional plots were used for some analyses and these are described later in the text.

3.3 RESULTS

3.3.1 Catalyst Characterization

Thermograms for various catalyst samples showing the percentage weight changes with temperature are given in Figure 3.1. Since the samples contained different but significant amounts of carbonate, it was preferable to convert observed weight changes to percentages of the final weight attained around 1173K as this was assumed to correspond to La\_2O\_3\textsuperscript{3}. Trace A shows the sequence of events when a sample of La(OH)\textsubscript{3}(II) which had been stored in vacuum was heated. A loss of 3 to 4\% occurred at 353 to 393K.
Figure 3.1

Thermograms for samples of lanthanum hydroxide; (A) La(OH)$_3$(II), (B) La(OH)$_3$(II) exposed to 500 Torr CO$_2$ for 48 hours, (C) La$_2$O$_3$(II) fresh from vacuum line after degassing at 873K for 3 hours, (D) La$_2$O$_3$(II) treated as for (C) but after 24 hours in the atmosphere.
Since a monolayer of water would amount to only 1.1% of the oxide weight, it is likely that some water is lost from the bulk in this temperature region. The substantial loss between 573 and 683K can be attributed to completion of the decomposition of the hydroxide. By 700K the loss of weight of 15% was approaching the expected value of 16.6% for conversion of hydroxide to oxide. The significant further loss between 823 and 1073K was ascribed to decomposition of carbonate. Since a monolayer of carbon dioxide would only account for a decrease of 1.6%, the fall of 10.5% observed provides strong evidence for some bulk carbonate.

Traces B, C and D show the effect of treating the samples in various ways. Exposure of La(OH)$_3$(II) to 500 torr of carbon dioxide for 48 hours gave trace B which was similar to A except for a larger weight loss in the high temperature region. Trace C corresponds to a sample evacuated at 873K for three hours and then rapidly transferred to the TG apparatus. There was a significant increase in weight observed up to 400K which shows the rapid uptake of atmospheric water by this sample. In contrast, there was a smaller weight loss in the high temperature region indicating that the sample contained less carbonate after evacuation at 873K. A sample treated as for C but allowed to stand in the atmosphere for 24 hours gave trace D which showed characteristics more similar to those for the hydroxide.

There was a good correlation between the age of catalyst samples and the percentage loss of weight in the high temperature region due to carbonate decomposition and the results are given in Table 3.1. Infrared studies carried out by Professor Rochester and Mr Anderson at Dundee University on a sample of La$_2$O$_3$(I) confirmed that temperatures of 1000K were necessary to free the surface of carbonate species. After evacuation of
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight loss in range 823-1023K (as % of La$_2$O$_3$ weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) La$_2$O$_3$(II) after degassing at 873K for 3 hours</td>
<td>4.4</td>
</tr>
<tr>
<td>(2) As for (1) after 24 hours in atmosphere</td>
<td>7.4</td>
</tr>
<tr>
<td>(3) La(OH)$_3$(II) one week after preparation and storage under vacuum</td>
<td>10.5</td>
</tr>
<tr>
<td>(4) As for (3) exposed to 500 torr CO$_2$ for 48 hours</td>
<td>13.9</td>
</tr>
<tr>
<td>(5) La(OH)$_3$(I) six weeks after preparation and storage in atmosphere</td>
<td>21.6</td>
</tr>
<tr>
<td>(6) As for (5) but exposed to 500 torr CO$_2$ for 48 hours</td>
<td>22.9</td>
</tr>
</tbody>
</table>
the sample at 873K bands were detected in the range 1300 to 1600 cm\(^{-1}\) but these disappeared when the catalyst was degassed at 1023K.

The BET plots for nitrogen adsorption were linear in the range of relative pressure (\(p/p_0\)) from 0.05 to 0.20 and the derived surface areas are given in Table 3.2 for a number of pretreatment temperatures.

### 3.3.2 Alkene Reactions

A general feature observed with most of the catalytic reactions was a fall in rate during the course of the reaction. Such a decrease may arise from an approach to equilibrium which is easily recognised, from a kinetic dependence on the pressure of alkene which will only become appreciable after more than 15% conversion, or from some poisoning of the catalyst. When a reduction in rate was observed at low conversions the most probable course was self-poisoning of the system.

**n-Butenes**

As there are many results in the literature, only a few experiments were carried out to show that the present catalysts were comparable to those of other workers for the isomerization of the butenes. Reactions of but-1-ene and cis-but-2-ene at 273K are shown in Figures 3.2 and 3.3 respectively. There was a fast isomerization of but-1-ene which decreased by a factor of about 10\(^3\) after a few minutes even although the amount of reactant was still well in excess of the equilibrium percentage (1.4%). On the other hand, with cis-but-2-ene there was a decrease in rate in the first 10 or 15 minutes which was largely associated with the establishment of the equilibrium between cis-but-2-ene and but-1-ene, and the subsequent conversion to
Table 3.2
Surface Areas of Lanthana (I)

<table>
<thead>
<tr>
<th>Outgassing temp. / K</th>
<th>673</th>
<th>823</th>
<th>873&lt;sup&gt;a&lt;/sup&gt;</th>
<th>923</th>
<th>973</th>
<th>1073</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area m²g⁻¹ (of La₂O₃)</td>
<td>40 ± 1</td>
<td>35 ± 1</td>
<td>29 ± 1</td>
<td>16 ± 1</td>
<td>8.4 ± 0.6</td>
<td>1.4 ± 0.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> A sample of La₂O₃(II), outgassed at 873K had an area of 42±2 m²g⁻¹.
Figure 3.2
Isomerization of but-1-ene over 13 mg La_2O_3(l) at 273K:
O, but-1-ene, □, cis-but-2-ene, △, trans-but-2-ene.
Figure 3.3

Reaction of cis-but-2-ene over 13 mg La₂O₃(II) at 273K:
○, but-1-ene, □, cis-but-2-ene, △, trans-but-2-ene.
trans-but-2-ene continued at a steady rate which was about one-tenth of the rate of the initial reaction. Rates are given in Table 3.3.

**Ethene**

Figure 3.4 shows successive hydrogenations of ethene at 247K. Between each experiment the reaction mixture was pumped away at 293K and the catalyst evacuated for 30 minutes. The catalytic activity was high but fell by more than 50% between runs and during each run there was a decrease in rate, even in the case of the third reaction when the conversion was only some 25%.

In order to study the influence of temperature, it was decided to measure initial rates for a series of second reactions between 208 and 273K. Prior to each of these, the catalyst sample was "conditioned" by running a first reaction at 247K. Rates obtained in this way are shown as an Arrhenius plot in Figure 3.5 which also includes some rates on fresh catalysts and on a twice-conditioned catalyst. Arrhenius parameters for ethene and other alkenes are brought together in Table 3.4. Experiments were carried out on the hydrogenation of ethene on catalyst samples which had been used for the hydrogenation of 2-methylpropene and propene at 414K. Subsequent rates of reaction of ethene were 12 and 15 times slower respectively at 273K than for the reaction at this temperature after the catalyst had been used for hydrogenation of ethene at 247K.

The effect of catalyst ageing was examined by using a sample of La$_2$O$_3$(I) which had been stored in the atmosphere for 18 months. The rate of hydrogenation of ethene at 273K was more than $10^2$ times slower than for reaction on fresh lantha and there was more significant poisoning during the course of the reaction.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate $10^{18}$ molecules s$^{-1}$ m$^{-2}$</th>
<th>$\text{La}_2\text{O}_3$(I)</th>
<th>$\text{La}_2\text{O}_3$(II)</th>
<th>ref. 10$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>but-1-ene $\rightarrow$ but-2-enes</td>
<td></td>
<td>1.6</td>
<td>5.3</td>
<td>6.7</td>
</tr>
<tr>
<td>cis/trans ratio</td>
<td></td>
<td>7-8</td>
<td>4-5</td>
<td>7-8</td>
</tr>
<tr>
<td>cis-but-2-ene $\rightarrow$ but-1-ene</td>
<td></td>
<td>-</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>cis-but-2-ene $\rightarrow$ trans-but-2-ene</td>
<td></td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The rates taken from reference 10 refer to catalysts outgassed at 873K - the temperature used in the present work.
Figure 3.4

Hydrogenation of ethene over 22 mg $\text{La}_2\text{O}_3$(I) at 247K:

- $\bigcirc$, first reaction,
- $\boxplus$, second reaction,
- $\Delta$, third reaction.

Figure 3.4

Hydrogenation of ethene over 22 mg $\text{La}_2\text{O}_3$(I) at 247K:

- $\bigcirc$, first reaction,
- $\boxplus$, second reaction,
- $\Delta$, third reaction.
Figure 3.5

Arrhenius plots for the hydrogenation of ethene: ○, ● and □, results on La$_2$O$_3$(I) used as fresh catalyst or after one or two 'conditioning' reactions at 247K respectively; ■, La$_2$O$_3$(II) after one 'conditioning' reaction at 247K.
Table 3.4

Arrhenius Parameters for Hydrogenation

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Temp. range T/K</th>
<th>Activation energy E/kJ mol⁻¹</th>
<th>Frequency factor log(A/molecules s⁻¹ m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>208-273</td>
<td>36 ± 2</td>
<td>24.6 ± 0.4</td>
</tr>
<tr>
<td>3,3-Dimethylbut-1-ene</td>
<td>245-273</td>
<td>23 ± 2</td>
<td>21.1 ± 0.3</td>
</tr>
<tr>
<td>Propene</td>
<td>311-414</td>
<td>43 ± 3</td>
<td>22.6 ± 0.4</td>
</tr>
<tr>
<td>2-Methylpropene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>335-414</td>
<td>42 ± 2</td>
<td>22.3 ± 0.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Results for a reaction on catalysts 'conditioned' by hydrogenation of ethene at 247K.

<sup>b</sup> Results from Chapter 4.
3,3-Dimethylbut-1-ene

The vapour pressure of this compound was too low to permit experiments with the usual pressures to be carried out below 245K but hydrogenation was followed between this temperature and 273K. Only a small decrease in rate was observed after high conversion had occurred as shown by the plot in Figure 3.6. This was attributed to a kinetic dependence on the pressure of alkene and the course of the reaction conformed to an equation based on a power rate law. Following the procedure used by Brown, Kemball and Taylor (13), the effect of changes in the pressure of hydrogen are ignored so that the rate is given by

\[
\frac{dx}{dt} = -k_{r} \left(\frac{x}{100}\right)^{n}
\]

(3.1)

where \(x\) is the percentage of alkene present at time \(t\), \(k_{r}\) is the initial rate of reaction expressed as % per unit time and \(n\) is the order of reaction with respect to alkene. Integration of equation (3.1) gave

\[
x^{(1-n)} - x_{0}^{(1-n)} = -(1-n)k_{r} t/(100)^{n}
\]

(3.2)

where \(x_{0}\) is the percentage of alkene at \(t = 0\). A satisfactory linear plot was obtained for the reaction of 3,3-dimethylbut-1-ene at 273K by using \(n = 0.4\), as shown in Figure 3.6. The rates for the reaction at different temperatures are given as an Arrhenius plot in Figure 3.7.

Since the hydrogenation of this compound seemed to be a well-behaved catalytic reaction which was not subject to self-poisoning, it was used as a test reaction to study the influence of pretreatment temperature on the activity of lanthana. The results shown in Figure 3.8 indicated that maximum activity was obtained after pretreatment at 950K.

An attempt was made to follow the isomerization of 3,3-dimethylbut-1-ene to 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene, a reaction which is
Figure 3.6
Hydrogenation of 3,3-dimethylbut-1-ene over 52 mg LaO$_3$(l) at 273K:
O, percentage alkene, □, plot to test equation (3.2) using $n = 0.4$. 
Figure 3.7

Arrhenius plots for the hydrogenation of the alkenes: □, 2-methylpropene, ○, propene (I), ●, propene (II) and △, 3,3-dimethylbut-1-ene on La$_2$O$_3$(I); ■, 2-methylpropene and ⬤, propene (II) on La$_2$O$_3$(II).
Figure 3.8

Effect of pretreatment temperature on the rate of hydrogenation of 3,3-dimethylbut-1-ene on 52 mg $\text{La}_2\text{O}_3(\ell)$ at 273K.
thought to require acidic catalytic sites (14). But on 85 mg of La$_2$O$_3$(I)
less than 1% reaction was observed in two hours at 510K.

2-Methylpropene

As reported in Chapter 4, the hydrogenation of 2-methylpropene was
studied in the temperature range 335 to 414K. The reaction was
well behaved and second runs on the same catalyst sample gave rates only
slightly lower than those for first runs. An Arrhenius plot is included in
Figure 3.7 for comparison with the other alkenes. A sample of La$_2$O$_3$(I)
stored for 18 months gave a rate 10$^2$ times less than the rate for a fresh
catalyst at 414K.

Propene

The hydrogenation of propene occurred in the same temperature range and
at similar rates to those found for 2-methylpropene. But the behaviour of
the two alkenes differed in other respects. Some decrease in rate with
time was noted with all propene reactions and second runs were usually at
least ten times slower than first runs. These points are illustrated in
Figure 3.9 and an Arrhenius plot for first runs is included in Figure 3.7.

Cyclopentene

Less than 1% hydrogenation was found after one hour at 312K for
cyclopentene(I), i.e. the sample which was not treated to remove peroxides.
With cyclopentene(II) a rapid reaction was observed at 312K with some decrease
in rate at higher conversions. The results conformed to equation (3.2) with
n = 0.6 and the initial rate of reaction of 5.9 x 10$^{16}$ molecules s$^{-1}$ m$^{-2}$ was
Figure 3.9

Hydrogenation of propene (I) over 22 mg La$_2$O$_3$(I) at 338K:
○, first reaction, □, second mixture.
an order of magnitude larger than the extrapolated rate for 2-methylpropene at the same temperature. A different behaviour was found for cyclopentene(II) at 382K as shown in Figure 3.10. The initial reaction was faster than at 312K but poisoning became obvious after a few minutes so that conversion at times greater than 40 minutes were actually less than at the lower temperature.

2,3-Dimethylbut-1-ene

Results for reaction of this compound with hydrogen at 373K are shown in Figure 3.11. A very rapid \( (>10^{18} \text{ molecules s}^{-1} \text{m}^{-2}) \) isomerization to 2,3-dimethylbut-2-ene took place in the first few minutes and then hydrogenation of the two alkenes to 2,3-dimethylbutane followed at a steady rate of \( 5.5 \times 10^{15} \text{ molecules s}^{-1} \text{m}^{-2} \).

3.3.3 Experiments with Deuterium - Results and Interpretation

Experiments using deuterium instead of hydrogen were carried out with ethene, propene and 3,3-dimethylbut-1-ene. The procedure in each case involved following reactions at a selected temperature by gas chromatography until about 20% of the alkene had been converted to alkane then the hydrocarbons were condensed and subsequently analysed by n.m.r. spectroscopy. In this way, it was possible to determine the amount and position of the deuterium atoms in the alkenes and, when exchange occurred, in the alkenes as well. In some cases it was possible to identify grouping of deuterium atoms in the products because the resonances were displaced by isotopic shifts caused by other deuterium atoms in neighbouring positions \((15, 16)\).
Figure 3.10
Hydrogenation of cyclopentene (II) over 22 mg La₂O₃(l):
○, 312K, □, 382K.
Figure 3.11

Isomerization and hydrogenation of 2,3-dimethylbut-1-ene over 52 mg La2O3(l) at 373K:

○, 2,3-dimethylbut-1-ene, Δ, 2,3-dimethylbut-2-ene,
□, 2,3-dimethylbutane.
Ethene and 3,3-Dimethylbut-1-ene

In both cases deuterium was observed only in the alkanes formed and not in the alkenes. Reaction of ethene at 222K to 30% conversion gave the simple n.m.r. spectrum with a single resonance shown in Figure 3.12. The position of this resonance at $\delta = 0.834$ p.p.m. corresponds closely with the expected value (15), $\delta = 0.836$ p.p.m., for the compound CH$_2$DCH$_2$D in which the two deuterium atoms are equivalent but subject to a $\beta$-shift due to the neighbouring deuteron. Clearly, the reaction involved simply the addition of deuterium to the alkene without any detectable alkene exchange.

Two experiments were carried out at 243K using 3,3-dimethylbut-1-ene with conversions of 14% and 27% to 2,2-dimethylbutane respectively. In both cases the spectra had two resonances of similar size with $\delta = 0.811$ p.p.m. and $\delta = 1.196$ p.p.m. as shown in Figure 3.12. These positions suggested that the product of the deuteration contained one primary and one secondary deuterium atom so that again the reaction involved simply addition of deuterium across the double bond to give (CH$_3$)$_3$CCHDCH$_2$D and no exchange of the alkene.

Propene

The n.m.r. spectrum of the products from the conversion of 20.2% propene to propane at 380K was complex but readily interpreted. Significant amounts of deuterium were present in the alkene and the positions of the resonances were identical with those previously found for the exchange of propene with deuterium over calcium oxide (16) together with some evidence of a small amount of exchange of the H atom on the central carbon atom. The resonances due to deuterium present in the propane were less well resolved but showed evidence for D atoms in both
Figure 3.12
Deuterium n.m.r. spectra of alkanes formed over La$_2$O$_3$(II):
(a) ethane after 30.3% conversion of ethene at 222K,
(b) 2,2-dimethylbutane after 14% conversion of 3,3-dimethylbut-1-ene at 243K.
The line narrowing parameters used were (a) LB = 0.50 and GB = 0.350, and (b) LB = 0.30 and GB = 0.30.
secondary and primary positions in various groupings which were established from the isotopic shifts (15). The full analysis of the spectrum from this experiment is given in Table 3.5.

The distribution of deuterium atoms in the propene is considered first. Although some exchange had taken place of the H atom on the central carbon, the percentage of D in this position was much less than the 16.7% expected for a random distribution of D over all six positions. Thus, the main exchange had occurred in the five terminal positions and the agreement between experimental distribution 2 and the calculated distribution confirmed that exchange over these five positions was random. The relative amounts of the two groupings of primary D atoms in the propane -CH₂CH₂D and -CHDCH₂D showed that only 90% of the propane had a D atom on the central carbon and 10% had not. On this evidence a value of 0.90 was assigned for the number of secondary D atoms in the propane molecules. Comparison of the sizes of the various resonances then indicated that each propane had 0.92 primary D atoms and that the propene molecules had an average of 0.30 D atoms. Thus in the period of the experiment during which 20% of the propene was deuterated some 30% of the alkene acquired a D atom. It follows that the exchange reaction was some 1.5 times faster than the addition process.

The chances of acquiring D at the secondary and primary positions of propene in the formation of propane can also be estimated. Since the exchange on the central carbon of the alkene was small, the final value of 0.90 secondary D in each propane indicated a 90% chance of acquiring D at the secondary position of the alkene. Some of the 0.92 primary D observed in the propane would have originated from exchange of the alkene. It can be assumed that the average deuterium content of the propene during the experiment was half the final value, i.e. 0.15 D/molecule. This suggested
Table 3.5
Analysis of the n.m.r. Spectrum for the Reaction of Propene with Deuterium after 20.2% Conversion to Propane

(A) Deuterium in propene

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Chem. shift δ/p.p.m.</th>
<th>%D</th>
<th>Expt.1</th>
<th>Expt.2</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X -C-X</td>
<td>5.8551</td>
<td>2.1</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CX₃-C-D</td>
<td>5.0570</td>
<td>17.3</td>
<td></td>
<td>17.6</td>
<td>18.1</td>
</tr>
<tr>
<td>D -C-H</td>
<td>5.0428</td>
<td>2.1</td>
<td>2.1</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>CX₃-C-X</td>
<td>4.9638</td>
<td>19.0</td>
<td></td>
<td>19.4</td>
<td>18.1</td>
</tr>
<tr>
<td>D -C-D</td>
<td>4.9481</td>
<td>2.6</td>
<td>2.7</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>CX₃-C-X</td>
<td>1.7135</td>
<td>49.1</td>
<td></td>
<td>50.2</td>
<td>49.3</td>
</tr>
<tr>
<td>-CH₂D</td>
<td>1.6945</td>
<td>7.8</td>
<td>8.0</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>-CD₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

a X refers to H or D.

b Distribution in terminal positions scaled to 100%.

c Calculated for a random distribution over the five terminal positions with a chance of a D in each position of 0.095.
Table 3.5 (contd.)

(B) Deuterium in propane

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Chem. shift $\delta$/p.p.m.</th>
<th>%D</th>
<th>D/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^\circ$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CHD}$</td>
<td>1.3058</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)(\text{CH}_2\text{D})\text{CHD}$</td>
<td>1.2990</td>
<td>40.2</td>
<td>0.90$^b$</td>
</tr>
<tr>
<td>$1^\circ$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{CH}_2\text{CH}_2\text{D}$</td>
<td>0.8919</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>$-\text{CHDCH}_2\text{D}$</td>
<td>0.8831</td>
<td>40.7</td>
<td>0.92</td>
</tr>
<tr>
<td>$-\text{CHXCHD}_2$</td>
<td>0.8642</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

*a X refers to H or D.

*b Assigned on the relative amounts of the primary deuterium groupings $-\text{CH}_2\text{CH}_2\text{D}$ and $-\text{CHDCH}_2\text{D}$. 
that the 0.92 value was a sum of 0.15 from exchanged alkene and 0.77 from the addition process so that only 77% of the atoms adding to the methylene group of the alkene were D. The appreciable chance (23%) of acquiring an H atom at the methylene group on addition explains why 19% of the secondary deuterium in propane had no primary deuterium neighbour.

3.4 DISCUSSION

In order to obtain maximum catalytic activity for lanthana a compromise has to be made between removal of surface impurities and loss of surface area consequential on a high pretreatment temperature. Treatment at 873K clearly removed water but some carbonate remained as confirmed both by the thermogravimetric and infrared results obtained. Treatment at 1073K removed all impurities but gave oxide with a surface area of <2 m^2 g^-1. The experiments on the hydrogenation of 3,3-dimethylbut-1-ene indicated an optimum pretreatment temperature of 950K. In terms of characterization the catalyst used here was similar to the sample prepared by Rosynek and Magnuson (17) using the 'dehydration/rehydration' method. The catalytic activity and the selectivity observed in this work for the isomerization of but-1-ene were comparable to those reported by Rosynek et al. (10), see Table 3.3. Furthermore, the extrapolated rate for the hydrogenation of ethene in a first reaction of over 10^{18} molecules s^{-1}m^{-2} on La_2O_3(l) is in line with the rate of 4 x 10^{18} at 273K from Jensen's results (5).

Much of the emphasis in previous investigations involving reactions of alkenes on lanthana has been on effects of outgassing temperature, on selectivity and on the influence of poisons on activity. Several groups (4, 7, 9) have reported that lanthana was greatly sensitive to traces of impurities. Rosynek and Fox (7) ascribed curvature at low
conversions in the kinetic plots to self-poisoning by but-1-ene and
Goldwasser and Hall (9) observed stable and reproducible activities only
for samples of butene which had been repeatedly purified. The present
results confirm the very substantial loss of activity which occurs when
lanthana is stored under atmospheric conditions.

3.4.1 Self-poisoning in Alkene Reactions

A main conclusion from the results is that stable catalytic activity
for reactions of alkenes on lanthana is the exception rather than the
norm. One advantage of a recirculation system is that the course of
reactions can be followed with time and changes of rate readily
determined. Even allowing for kinetic dependence on the pressure of
alkene where appropriate, falling rates do appear to be a general feature
of the alkene/lanthana systems. The degree to which rates diminish depends
on the nature and purity of the alkene, the reaction temperature and the
storage of the catalyst sample.

The overall behaviour of reactants with branched structures, such as
3,3-dimethylbut-1-ene and 2-methylpropene, was better than that found with
the straight-chain molecules. One possible cause of falling rates may
be some oligomerization of the alkene on the catalyst surface.
Straight-chain molecules would be more likely to exhibit such a reaction
than branched molecules. Certainly the most stable catalytic activity was
observed with 3,3-dimethylbut-1-ene at 273K (Figure 3.6) and much steadier
and more reproducible activity was found at 414K with 2-methylpropene than
with propene. The worst behaviour was found with cyclopentene(I) where the
presence of peroxide impurities probably enhanced oligomerization.
A further potential course of self-poisoning with alkene oxide systems is breakdown of the hydrocarbon by reaction with the surface of the oxide to form surface carboxyl entities and adsorbed water. Catalytic activity depends on the formation of adsorbed intermediates which can then be converted to other hydrocarbons. At higher temperatures or on oxides such as lanthana with high affinity for carbon dioxide the intermediates may break down irreversibly and the surface become poisoned.

3.4.2 Activity for Hydrogenation and Mechanistic Considerations

Results in Table 3.6 show the temperatures required to give a rate of hydrogenation of the various alkenes of $10^{16}$ molecules s$^{-1}$ m$^{-2}$. The two most easily hydrogenated alkenes are ethene and 3,3-dimethylbut-1-ene and the common property linking these compounds probably relates to the fact that neither can form an allyl species. The fact that no exchange was detected with either alkene in the experiments using deuterium is another feature in common. The absence of exchange with these alkenes shows that no reversible dissociation occurs to adsorbed vinyl species at low temperatures and also that the formation of the alkyl species is probably rate-determining in the addition process. Any alkyl species formed is converted to alkane without significant back reaction to adsorbed alkene. This behaviour is comparable to results reported for ethene (18) and cyclopentene (19) on zinc oxide for which there was evidence against any contribution from alkyl reversal processes.

The inverse correlation between ability to form allylic species and rate of hydrogenation is further confirmed by the fact that cyclopentene was the next most readily hydrogenated molecule after ethene and 3,3-dimethylbut-1-ene. The formation of a \( \pi \)-allyl species is possible.
Table 3.6

Temperatures Required for Hydrogenation of Different Alkenes on Lanthana

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Temperature for hydrogenation at $10^{16}$ molecules s$^{-1}$m$^{-2}$</th>
<th>T/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene (second reaction)</td>
<td></td>
<td>222</td>
</tr>
<tr>
<td>3,3-Dimethylbut-1-ene</td>
<td></td>
<td>240</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td></td>
<td>&lt;312</td>
</tr>
<tr>
<td>Propene</td>
<td></td>
<td>342</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td></td>
<td>345</td>
</tr>
<tr>
<td>2,3-Dimethylbutenes</td>
<td></td>
<td>&gt;373</td>
</tr>
</tbody>
</table>
from cyclopentene but does not occur to any appreciable extent on zinc oxide (19, 20) or on γ-alumina (21). The remaining alkenes studied in this work may dissociate to allyl species without difficulty and the lower rates of hydrogenation observed may be associated with a significant fraction of surface sites being occupied by such species which cannot, of course, contribute to the formation of alkane. The difference between the fast hydrogenation of ethene and the much lower rates for propene and 2-methylpropene on lanthana is in accord with the relative rates reported by Jensen (5) for ethene, propene and but-1-ene. A similar difference was observed between the rates of hydrogenation of ethene and of other alkenes on zinc oxide (13) and attributed to the consequences of allyl formation with the C₃- and C₄-alkenes.

The rapid isomerization of 2,3-dimethylbut-1-ene at 373K probably occurred through the reversible formation of allylic species although the alternative mechanism involving tertiary carbocations cannot be entirely excluded. Further evidence for the role of allylic intermediates came from the exchange of 2-methylpropene with deuterium which takes place at 5 to 10 times the rate of the addition reaction (see Chapter 4); and from the present results with propene for which a process leading to the random exchange of the five terminal positions in the molecule exceeds addition at 380K. The small amount of exchange of the central position found with propene may be due to some alkyl reversal occurring at this temperature which is over 100° above the temperatures used for the n.m.r. studies on ethene and 3,3-dimethylbut-1-ene. The different chances of acquiring a D atom at the secondary and primary positions of propane in the addition reaction
may indicate that two pools of H/D species are present on the surface although the evidence for this was clearer in the other work with 2-methylpropene (see Chapter 4). The suggestion is that the species (possibly with a partial positive charge) acquired at the primary position is more likely to be diluted with hydrogen through the alkene exchange process than the species (partial negative charge) taken up on the secondary carbon atom.

3.4.3 Isomerization

The high initial ratio of cis/trans products from the fast isomerization of but-1-ene exemplifies the basic nature of lanthana. But the striking difference between the reaction of but-1-ene and those of cis-but-2-ene and of 2,3-dimethylbut-1-ene is the much greater degree of self-poisoning observed. These facts substantiate the suggestion that less self-poisoning is associated with alkenes having more alkyl groups linked to carbon atoms at the ends of the double bond.

The absence of detectable isomerization of 3,3-dimethylbut-1-ene even at 510K was perhaps not surprising since it is a reaction which occurs readily only on catalysts with acidic sites and is not found to occur on basic oxides (14). The present results support the conclusions in the literature that the mechanism of alkene isomerization on lanthana is the reversible formation of carbanionic allylic species - a process which cannot occur with 3,3-dimethylbut-1-ene.
3.5 REFERENCES


CHAPTER 4

Reactions of 2-Methylpropene on Lanthana and Zirconia.
4.1 INTRODUCTION

The objective of this research is to use the technique of $^2$D-n.m.r. spectroscopy combined with either mass spectrometry or gas chromatography to obtain detailed information on the distribution of deuterium atoms on the products from catalytic reactions on oxides. The n.m.r. technique in favourable cases can provide quantitative results not only on the location of deuterium in various positions in molecules but also on the groupings of such atoms. This kind of information is of importance in establishing the nature and reactivity of the adsorbed intermediates involved in the reactions and providing a good indication of probable mechanisms. Brown, Kemball, McGillivray and Sadler (1) gave results for the reactions of propene and cyclopentene on calcium oxide and on some other oxides. The present investigation is concerned with reactions of 2-methylpropene on lanthana or zirconia, both of which show activity for exchange and addition processes with this alkene.

Only a limited amount of work has been published on the exchange of 2-methylpropene or its conversion to 2-methylpropane on oxide catalysts despite the fact that it is an interesting reactant because of the range of intermediates which it can form on surfaces. Results reported by Robertson, Scurrell and Kemball (2) show that on basic oxides, such as magnesia, 2-methylpropene exchanges with deuterium readily even at temperatures as low as 200K. The reaction occurs by the stepwise replacement of hydrogen atoms with deuterium but all eight hydrogen atoms are exchangeable at the same rate. The mechanism is thought to involve the reversible dissociation of the alkene to an adsorbed allyl species - a process which allows interconversion of methyl and methylene hydrogen on deuterium atoms as well as providing a route to the exchange of all eight...
atoms in the molecule. The exchange results do not provide any direct evidence about possible charge on the allyl species which might in principle be cationic, neutral or anionic. However, the most likely reaction on the strongly basic oxide is an acidic dissociation of the alkene:

\[ \text{CH}_2=\text{C(\text{CH}_3)}_2 \rightarrow [\text{CH}_2=\text{C(\text{CH}_3)}=\text{CH}_2^-]_a + (\text{H}^+)_a \]

leading to an adsorbed carbanionic allyl species associated with a surface cation and an adsorbed hydrogen ion combined with a surface oxide ion. Experiments with labelled propene (which undergoes a similar kind of exchange process on magnesia) have shown that there is an appreciable, but not unexpected, isotope effect such that C-H bonds break more rapidly than C-D bonds with \( k_H/k_D = 11 \) at 195K (3). Exchange of 2-methylpropene has also been reported over zinc oxide by Brown, Kemball and Taylor (4), and this catalyst shows a similar behaviour to magnesia except that the temperature range required is 270 to 326K instead of 195 to 273K and a slow addition reaction also takes place at about \( 10^{-2} \) times the rate of exchange.

Owing to the presence of the tertiary carbon atom in 2-methylpropene another mechanism of exchange likely to be favoured on acidic oxides or other types of acid catalyst is the reversible formation of the alkyl tertiary carbocation \( \text{C}^+(\text{CH}_3)_3 \). This process also provides a means of interconverting methylene and methyl hydrogen atoms as well as exchanging all atoms and has consequences which are similar to those of the allyl mechanism. Since both the associative alkyl mechanism and the dissociative allyl mechanism produce the same results, a distinction between them depends on additional information, either on the probable nature of the catalyst or the relative rates of reaction with different alkenes.
The relative rates of exchange with D$_2$O or D$_2$ are often useful in determining the nature of the catalyst. In an investigation by Kemball and McCosh (5), rapid exchange with 2-methylpropene and D$_2$ was observed on X-type zeolites containing cobalt or cerium ions and the reaction was much faster than the corresponding exchange with propene and D$_2$O. These results are consistent with a mechanism on the zeolites involving alkyl carbocations as intermediates.

There has been some confusion about mechanisms of exchange of 2-methylpropene on titania (rutile). Similar rates of exchange were observed by Lake and Kemball (6) for propene and 2-methylpropene with deuterium at temperatures in the range 523 to 723K and interpreted in terms of an allyl mechanism. Subsequently, Halliday, Kemball, Leach and Scurrell (7) found that the use of D$_2$O in place of D$_2$ as the source of the labelling atoms in reactions with mixtures of the two alkenes on rutile at 530K gave exchange of 2-methylpropene at 30 times the rate for propene, and this demonstrated that the mechanism with the C$_4$-alkene involved the tertiary carbocation as intermediate. The equality of the rates of exchange of the two alkenes in the earlier work is now thought to be a consequence of the rate of supply of deuterium atoms from the D$_2$ gas which is the rate-determining reaction, according to Ferrier, John, Leach, Kennedy and Tyler (8). One interesting feature of rutile was that, like zinc oxide, it had some activity for the conversion of alkene to alkane although the rate was some 10$^{-2}$ times slower than exchange at 600K.

There is comparatively little evidence of selective exchange of 2-methylpropene either by reversible formation of vinyl intermediates leading to replacement of methylene hydrogen atoms or by reversible formation of \( \sigma \)-allyl species giving replacement of the methyl hydrogen
atoms. Some evidence of preferential exchange of methylene hydrogen atoms was reported by Hightower and Hall for reaction on γ-alumina at 296K but a more recent investigation by John, Kemball, Paterson and Rajadhyaksha (9) using microwave spectroscopy showed a random distribution of deuterium atoms in the products for exchange on a different alumina at 296 to 313K. These latter results were attributed to a tertiary carbocation mechanism on evidence from experiments in the presence of hydrogen sulphide which is a selective poison for allylic mechanisms on alumina. Gallium oxide is known (Carleton, Gilmore and Rooney (10)) to be an effective catalyst for alkene exchange by σ-allyl mechanisms but no evidence of any break in the product distribution corresponding to the exchange of three or six deuterium atoms was detected with 2-methylpropene at 553K. The failure to detect selective exchange with 2-methylpropene may be a consequence of fast double bond movement, through either an allyl or alkyl mechanism, obscuring the selectivity.

In this Chapter results are reported for hydrogenation of 2-methylpropene on lanthana and zirconia. Since addition reactions with this alkene are comparatively unusual on oxides, it was decided to investigate the system in more detail using deuterium to obtain information on both exchange and addition. The system deuterium/2-methylpropene is difficult to study by the mass spectrometric technique (Brown et al. (4)) because of overlapping peaks from the alkenes and alkanes. So in this work gas chromatography was used to follow addition and $^2$D-n.m.r. spectroscopy to determine the rate of the exchange as well as the character of the exchange and addition reactions.
4.2 EXPERIMENTAL

Pretreatment of lanthana consisted of heating 25 mg La(OH)$_3$ at 873K under vacuum for three hours. The subsequent oxide had a measured BET-N$_2$ surface area of $29 \pm 1$ m$^2$g$^{-1}$. Zirconium hydroxide, Zr(OH)$_4$ was subjected to calcination in air at 873K for three hours and then samples in the range 40-100 mg (measured as hydroxide) were outgassed for a further three hours at 873K for catalytic experiments. The surface areas were 69$\pm$7 and 74$\pm$7 m$^2$g$^{-1}$ for ZrO$_2$ (I) and ZrO$_2$ (II) respectively. A few experiments were investigated on calcium oxide (19 mg) and γ-alumina (196 mg) and the source and pretreatment of these catalysts were given in Chapter 2.

Experiments using lanthana and zirconia were run in the recirculation system with analysis by gas chromatography. Samples from experiments involving deuterium were also analysed using deuterium n.m.r. spectroscopy. Static line (I) was used for the experiments carried out on CaO and γ-Al$_2$O$_3$ and the course of reaction was examined by mass spectrometry with further inspection using $^2$D-n.m.r.

The experiments with La$_2$O$_3$ and ZrO$_2$ used 5:1 mixtures of hydrogen (or deuterium):alkene with a pressure of 2-methylpropene of 2.4 kPa corresponding to about $2 \times 10^{20}$ molecules of hydrocarbon in the apparatus. For CaO and γ-Al$_2$O$_3$ an identical pressure ratio was used with an alkene pressure of 3.6 kPa and a charge of $2.1 \times 10^{20}$ molecules.

Rates of hydrogenation and deuteration were calculated from the slopes of percentage against time plots, and exchange rates on lanthana and zirconia were obtained from results on the n.m.r. spectra. Details of the method for evaluation of the spectra are given later. The rate of exchange ($k_\text{ex}$) of
2-methylpropene on CaO and $\gamma$-Al$_2$O$_3$ was calculated from the slope of the first order graph showing the loss of reactant versus time (Kemball (11)).

### 4.3 RESULTS

#### 4.3.1 Lanthana

Hydrogenation of 2-methylpropene occurred at conveniently measurable rates on samples of catalyst in the temperature range from 335K to 414K. Typical results on the course of the reactions with time are shown in Figure 4.1. With fresh samples of catalyst there was a decrease in the rate amounting to some 20 to 25% of the initial value over a period of 10 to 20 minutes. However, second reactions on a sample of catalyst which had been used for a first reaction (usually at 414K) and evacuated at room temperature gave steady rates which were about 75% of that for the fresh samples (see Figure 4.1). For faster reactions in which a large percentage of the alkene reacted the rate of reaction showed a dependence on the 0.5 power of the alkene pressure (see Chapter 3). The rates from first and second reactions are shown as Arrhenius plots in Figure 4.2 and the derived parameters are given in Table 4.1.

#### Procedure for the evaluation of the $^2$D n.m.r. spectra

A detailed procedure was developed for the analysis of the results obtained from the deuterium n.m.r. spectra of the partially deuterated samples of 2-methylpropene. The methods used are described in relation to experiment 3B - a second experiment carried out at 380K on a catalyst "conditioned" by a first reaction at 414K. The experiment was stopped after 19% of the alkene had been converted to alkane and the n.m.r. spectrum is shown in Figures 4.3 and 4.4 and the assignments of the various
First, ○, and second, □, hydrogenation reactions of 2-methylpropene on 21.5 mg La₂O₃ at 414K.
Figure 4.2

Arrhenius plots for hydrogenation (open symbols) and deuteration (filled symbols) of 2-methylpropene on La$_2$O$_3$:
- O and ●, first reactions;
- □ and ■, second reactions.
Table 4.1

Arrhenius Parameters for Reactions of 2-Methylpropene on La$_2$O$_3$ and ZrO$_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temp. Range</th>
<th>E/kJ mol$^{-1}$</th>
<th>Log A/molecules s$^{-1}$m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st hydrogenation</td>
<td>335 to 414</td>
<td>42 $\pm$ 2</td>
<td>22.3 $\pm$ 0.3</td>
</tr>
<tr>
<td>2nd hydrogenation</td>
<td>341 to 401</td>
<td>47 $\pm$ 1</td>
<td>22.9 $\pm$ 0.1</td>
</tr>
<tr>
<td>2nd deuteration</td>
<td>367 to 414</td>
<td>30 $\pm$ 6</td>
<td>20.3 $\pm$ 0.4</td>
</tr>
<tr>
<td>Exchange associated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with 2nd deuteration</td>
<td>367 to 414</td>
<td>40 $\pm$ 8</td>
<td>22.6 $\pm$ 0.9</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrogenation</td>
<td>273 to 432</td>
<td>16 $\pm$ 1</td>
<td>17.0 $\pm$ 0.1</td>
</tr>
<tr>
<td>deuteration</td>
<td>246 to 433</td>
<td>21 $\pm$ 1</td>
<td>17.8 $\pm$ 0.1</td>
</tr>
</tbody>
</table>
Part of the deuterium n.m.r. spectrum of the products from reaction 3B on $\text{La}_2\text{O}_3$ in which 19% of 2-methylpropene was converted to alkane. The spectrum was line-narrowed using $\text{LB} = -0.20$ and $\text{GB} = 0.40$ as the values of the function parameters of the Bruker n.m.r. programme FTQ 820601. The assignments of the peaks are given in Table 4.2.

(a) resonances for deuterium in the methylene group of the alkene.

(b) resonances for deuterium in the methyl groups of the alkene and on the tertiary carbon of the alkane.
Figure 4.4

The n.m.r. spectra for the primary deuterium atoms in the 2-methylpropane formed in experiments on La₂O₃.

(a) From experiment 3B using the line-narrowing parameters given for Figure 4.4; the assignments of the peaks are given in Table 4.2.
(b) From experiment 4B using LB = -0.30 and GB = 0.35; this spectrum is similar to that for experiment 3B but also shows the small broad peak at $\delta = 0.833$ corresponding to the groupings CD₃CH and CD₃CD.
resonances are given in Table 4.2. There was some variation in the absolute positions of the resonances from sample to sample but the deuterium isotope shifts were constant. Analysis of the various grouping of deuterium ions in 2-methylpropene was made without difficulty except for the overlap between the resonance for deuterium in CD₃ and one of the resonances for the tertiary deuterium in the alkane. The α-shifts associated with deuterium in the methylene and methyl groups of the alkene were -15.2 ± 0.1 and -19.3 ± 0.1 p.p.b. respectively. The α- and β-shifts for primary deuterium atoms in the alkane were -20.7 ± 0.3 and -8.2 ± 0.3 p.p.b. respectively in good agreement with values already reported by Brown, Kemball, Oliver and Sadler (12) of -20.9 and -8.5 p.p.b. An accurate value for the β-shift for the tertiary deuterium in the alkane was not obtainable because of the overlap with the alkene resonance but the results were consistent with the value of -7.6 p.p.b. reported by Brown et al.(12).

The relative amounts of the various resonances for the deuterium groupings in the alkene showed a random distribution of the H and D atoms over the eight positions in the molecule. If d is the chance of D and h (= 1-d) is the chance of H in any position, the expected proportions of the deuterium in the groups =CHD and =CD₂ will be 2hd and 2d² respectively. Similarly the relative proportions of deuterium in -CH₄D, -CHD₂ and -CD₃ will be 6h²d, 12hd² and 6d³ respectively bearing in mind that there are two methyl groups in the alkene but only one methylene group. The observed peak integrals for the various resonances are given in Table 4.3 and they provided two independent values of d. The relative amount of deuterium in =CHD and =CD₂ gave d = 0.200 and the corresponding ratio for deuterium in -CH₂D and -CHD₂ gave d = 0.206. The agreement between these values was satisfactory and using the mean value d = 0.203 it
Table 4.2

Positions of Various Resonances in the n.m.r. Spectrum (Figures 4.3 and 4.4) for the Alkene/Alkane Products from Experiment 3B

<table>
<thead>
<tr>
<th>Type of D</th>
<th>Grouping</th>
<th>Chemical shift $\delta$/p.p.m.</th>
<th>Type of D</th>
<th>Grouping</th>
<th>Chemical shift $\delta$/p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene</td>
<td>=CHD</td>
<td>4.6887</td>
<td>tertiarly</td>
<td>$(CH_3)_2CD$</td>
<td>1.6901</td>
</tr>
<tr>
<td></td>
<td>$=CD_2$</td>
<td>4.6736</td>
<td></td>
<td>$(CH_3)(CH_2D)CD$</td>
<td>(1.684)$^a$</td>
</tr>
<tr>
<td>methyl</td>
<td>$-CH_2D$</td>
<td>1.7237</td>
<td>primary</td>
<td>$CH(CH_2D)$</td>
<td>0.8837</td>
</tr>
<tr>
<td></td>
<td>$-CHD_2$</td>
<td>1.7044</td>
<td></td>
<td>$CD(CH_2D)$</td>
<td>0.8754</td>
</tr>
<tr>
<td></td>
<td>$-CD_3$</td>
<td>(1.684)$^a$</td>
<td></td>
<td>$CH(CHD_2)$</td>
<td>0.8627</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$CD(CHD_2)$</td>
<td>0.8546</td>
</tr>
</tbody>
</table>

$^a$ These resonances coincided.
Table 4.3

The Percentages of Deuterium in the Various Groupings for the Alkene from Experiment 3B

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Peak integral</th>
<th>Experimental % of D</th>
<th>Calculated (using d = 0.203) % of D</th>
</tr>
</thead>
<tbody>
<tr>
<td>=CHD</td>
<td>4.902</td>
<td>20.4</td>
<td>20.8</td>
</tr>
<tr>
<td>=CD$_2$</td>
<td>0.929</td>
<td>4.1</td>
<td>4.2</td>
</tr>
<tr>
<td>-CH$_2$D</td>
<td>12.485</td>
<td>52.0</td>
<td>51.8</td>
</tr>
<tr>
<td>-CHD$_2$</td>
<td>5.153</td>
<td>21.4</td>
<td>21.1</td>
</tr>
<tr>
<td>-CD$_3$</td>
<td>(0.515)$^a$</td>
<td>(2.1)$^a$</td>
<td>2.1</td>
</tr>
</tbody>
</table>

$^a$ Fraction of peak assigned to give the expected percentage.
was possible to calculate the distribution of deuterium over all the groupings. The only adjustment required in making comparison between experimental and calculated results was to assign the appropriate fraction of the unresolved peak to match the calculated percentage of deuterium in the grouping -CD₃; once that had been done, there was good agreement between the two sets of values (Table 4.3).

The initial rate of exchange was obtained from the usual first order reversible equation (2.10). The value of $\Phi$ for the mixture analysed by n.m.r. spectroscopy was given by:

$$\Phi = \text{ID}_i = 8 \times 100 \text{ d}$$

(4.1)

where $D_i$ was defined in Chapter 2. An estimate of $\Phi_\infty$ based on the assumption that in the equilibrium distribution the hydrogen and deuterium are randomly dispersed in the hydrocarbon and hydrogen mixture is given by:

$$\Phi_\infty = x_D \times n \times 100$$

(4.2)

where $x_D$ is the fraction of deuterium atoms in the total number of hydrogen and deuterium atoms in the system and $n$ is the total number of exchangeable hydrogens in the molecule. In the present case the value of $\Phi$ was estimated by assuming that at equilibrium the ratio of (D/H) in the 'alkene' was greater than (D/H) in the 'hydrogen' by a factor of 2.2 (Meyer and Kemball (13)); this assumption gave $\Phi = 530$ for the reaction mixture used.

Analysis of the relative amounts of the various groupings of deuterium in the alkane was used to establish the chances of acquiring an H or D atom at the tertiary carbon atom and on the methylene group of the alkene in the addition reaction. The results in Figure 4.4 for experiments 3B and 4B show that it was possible to identify a number of different groupings of primary deuterium atoms. A less detailed analysis of the tertiary deuterium atoms
was obtained and they were estimated in two groups only - those without a primary deuterium neighbour and those with one or more such neighbours. The observed and calculated distribution of deuterium atoms in the 2-methylpropanes formed in two experiments are given in Table 4.4.

A simple method depended on comparing the total tertiary deuterium in the 19% alkane with the estimated total deuterium ($\Omega/100 = 1.62$ atoms per molecule) in the 81% alkene. This gave 0.86 tertiary deuterium atoms per alkane molecule in experiment 3B. A similar calculation gave 1.14 primary deuterium atoms per alkane molecule but this value had to be corrected for the average deuterium content of the alkene throughout the experiment since all alkene deuterium is converted to primary deuterium in the alkane when addition takes place. The estimated average deuterium content of the alkene was 0.75 deuterium atoms per molecule so that only $1.14 - 0.75 = 0.39$ deuterium was acquired by the methylene group on conversion to alkane.

It was possible to confirm this rather surprising result by a detailed calculation of the amounts of the various groupings of deuterium atoms in the alkane. The steps in the calculation were as follows:

(a) The evidence that deuterium was randomly spread in the alkene at the end of the experiment and the known deuterium content at that stage was used to estimate the average amounts of various deuto-alkenes throughout the course of the experiment.

(b) It was assumed that in the addition process the average chance of acquisition of D or H at the tertiary position was $d_3$ or $1-d_3$ respectively. Similarly, the average chance of acquiring D or H at the methylene position was assumed to be $d_1$ or $1-d_1$ respectively.
Table 4.4

Groupings of Deuterium Atoms in the 2-Methylpropanes from Experiments 3B and 4B

<table>
<thead>
<tr>
<th>Grouping</th>
<th>% of D</th>
<th>expt. 3B</th>
<th>calc.</th>
<th>expt. 4B</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3\text{O}}\text{D}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CDC}_3\text{H}_9$</td>
<td></td>
<td>9.4</td>
<td>10.8</td>
<td>5.0</td>
<td>5.4</td>
</tr>
<tr>
<td>$\text{CDC}_3\text{H}_9\text{-nD}_n$</td>
<td></td>
<td>33.0</td>
<td>32.3</td>
<td>30.4</td>
<td>28.1</td>
</tr>
<tr>
<td>$^{1\text{O}}\text{D}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2\text{DCH}$</td>
<td></td>
<td>6.3</td>
<td>7.0</td>
<td>6.7</td>
<td>6.5</td>
</tr>
<tr>
<td>$\text{CH}_2\text{DCD}$</td>
<td></td>
<td>37.7</td>
<td>37.0</td>
<td>35.7</td>
<td>36.7</td>
</tr>
<tr>
<td>$\text{CHD}_2\text{CX}^c$</td>
<td></td>
<td>13.6</td>
<td>12.9</td>
<td>20.3</td>
<td>21.1</td>
</tr>
<tr>
<td>$\text{CD}_3\text{CX}^c$</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1.9</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

- Assuming chances of acquiring D at the tertiary and primary positions of $d_3 = 0.84$ and $d_1 = 0.45$.
- Assuming chances of acquiring D at the tertiary and primary positions of $d_3 = 0.85$ and $d_1 = 0.45$.
- X represents H or D.
(c) Calculation of the expected groupings of deuterium in the alkane was then made on the basis that the conversion to alkane involved merely addition of one atom at the tertiary position and one atom at the primary position and no further exchange.

(d) Values of \(d_3\) and \(d_1\) were chosen to give agreement between the calculated and observed distribution.

The results in Table 4.4 indicate that it was possible to reproduce the experimental results assuming values of \(d_3 = 0.84\) and \(d_1 = 0.45\) in experiment 3B and these values are close to those obtained above by the simple method of 0.86 and 0.39 respectively. Also included in Table 4.4 are results for experiment 4B in which rather greater exchange of alkene had taken place and more of the groupings with two or three deuterium atoms in the methyl groups had formed.

Rates of Reaction and Allied Results for 2-Methylpropene

The data from the five experiments with 2-methylpropene and deuterium on lanthana are shown in Table 4.5; the Arrhenius plots are given in Figure 4.2; and the derived parameters in Table 4.1. First experiments are designated with the letter A and second experiments on catalysts conditioned by use, normally at 414K, are labelled B. Exchange was faster than addition in all cases and the difference between the two rates increased with temperature. In all experiments the deuterium in the alkene was randomly distributed. The addition process was characterized by a comparatively high value of \(d_3\) (the chance of acquiring a deuterium at the tertiary carbon) and a significantly lower value of \(d_1\) (the chance of adding a deuterium to the methylene groups of the alkene). Values of \(d_1\) estimated by the simple method were less reliable when the amount of
Table 4.5
Exchange and Addition Reactions of 2-Methylpropene on Lanthana

<table>
<thead>
<tr>
<th>Expt.</th>
<th>T/K</th>
<th>% Addition</th>
<th>Rate of addition $k_A/10^{16}$ molecules s$^{-1}$m$^{-2}$</th>
<th>Ratio $k_D/k_A$</th>
<th>Chance of acquiring D in addition$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1A</td>
<td>347</td>
<td>14.9</td>
<td>0.78</td>
<td>5.0</td>
<td>0.83</td>
</tr>
<tr>
<td>2B</td>
<td>367</td>
<td>18.6</td>
<td>0.96</td>
<td>6.5</td>
<td>0.97</td>
</tr>
<tr>
<td>3B</td>
<td>380</td>
<td>19.0</td>
<td>1.50</td>
<td>7.4</td>
<td>0.86(0.84)</td>
</tr>
<tr>
<td>4A</td>
<td>414</td>
<td>31.2</td>
<td>4.1</td>
<td>9.4</td>
<td>0.79</td>
</tr>
<tr>
<td>4B</td>
<td>414</td>
<td>30.4</td>
<td>3.0</td>
<td>9.7</td>
<td>0.84(0.85)</td>
</tr>
</tbody>
</table>

$^a$ A refers to first experiments and B to second experiments.

$^b$ Values in parenthesis determined by the detailed method, the others by the approximate method.

$^c$ Values which are less reliable being the difference between two larger numbers.
exchange was substantial as in the two experiments at 414K which were allowed to run to more than 30% addition. For example in experiment 4A, the value of d₁ was derived by subtraction of two larger numbers both subject to some error; for this reaction d₁ = (1.43-1.31) = 0.12.

4.3.2 Zirconia

In order to compare results for the two catalysts, mixtures of reactants identical to those described for lanthana were used in most of the experiments on zirconia. A typical deuteration is shown in Figure 4.5. Some decline in rate was found in the first few minutes but thereafter there was a linear decrease in the percentage of alkene with time and rates were determined from this part of the graph. The rates of the various hydrogenation or deuteration reactions carried out within the temperature range 246K to 433K are shown as Arrhenius plots in Figure 4.6, and the derived parameters are given in Table 4.1. Similar rates were obtained on both samples of zirconia as illustrated in Figure 4.6.

Two successful experiments were carried out using deuterium n.m.r. spectroscopy to analyse the mixtures of alkene and alkane after about 20% addition had taken place. The method of analysis will be described for run Z9 at 415K. In contrast to the results found on lanthana there was relatively little exchange of the alkene although the ratio of (deuterium in the methyl groups):(deuterium in the methylene groups) was close to 3:1. The alkane contained similar amounts of primary and tertiary deuterium and the results indicated that the deuteration reaction approximated to the straightforward addition of D₂ to the alkene. The detailed analysis of the n.m.r. spectrum is given in Table 4.6. The groupings were readily identified from the chemical shifts of the various resonances. The
Figure 4.3

The course of reaction of 2-methylpropene with deuterium on 77 mg \( \text{ZrO}_2 \) (II) at 392K.

Figure 4.5

The course of reaction of 2-methylpropene with deuterium on 77 mg \( \text{ZrO}_2 \) (II) at 392K.
Figure 4.6

Arrhenius plots for hydrogenation (squares) and deuteration (circles) of 2-methylpropene on zirconia; open symbols refer to ZrO$_2$ (I) and filled symbols to ZrO$_2$ (II).
Table 4.6

Amounts and Groupings of Deuterium in the Products from Reaction Z9 of 2-Methylpropene on Zirconia

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grouping</th>
<th>% of D</th>
<th>D/molecule&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkene</td>
<td>=CHD</td>
<td>4.1</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;D</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>alkane (3°D)</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;D)CD</td>
<td>40.3</td>
<td>0.95</td>
</tr>
<tr>
<td>alkane (1°D)</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;DCH</td>
<td>1.9</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;DCD</td>
<td>40.2</td>
<td></td>
</tr>
</tbody>
</table>

Total: 100.0

<sup>a</sup> Analysis made on a mixture containing 83.8% alkene and 16.2% alkane.

<sup>b</sup> Relative to the assigned value of 0.95 for the tertiary deuterium in the alkane.
relative amounts of the two groupings of primary atoms in the alkane showed that 95% of the 2-methylpropane molecules had a D in the tertiary position and only 5% had H. Using these percentages it was possible to make the assignments in the last column of Table 4.6. In experiment Z9 since 8% of the alkene was exchanged at the end of the period which gave 16% deuteration the rate of exchange was half the rate of addition, i.e. $k_E = 0.5 k_A$. The average deuterium content of the alkene during the experiment was 0.04 D/molecule and on conversion to alkane this would have become primary deuterium - a fact which explains the difference between the 0.99 primary deuterium compared with the 0.95 tertiary deuterium in the alkane.

In the other experiment at 433K examined by deuterium n.m.r. spectroscopy after 23% conversion to alkane, the value of $k_E/k_A$ was found to be 0.6 and again the addition process gave about 1 D/molecule in both the primary and tertiary position of the alkane.

### 4.3.3 Other Oxides

For comparison with the results on lanthana and zirconia, reactions of 2-methylpropene with deuterium were also examined on calcium oxide and on γ-alumina. Since little or no formation of alkane was expected, the reactions were run in static system (I) linked to the mass spectrometer and when a convenient amount of exchange had taken place the alkene was collected for n.m.r. analysis (12).

Results for reaction on CaO at 237K and γ-Al₂O₃ at 341K are shown in Table 4.7. The rate of exchange of 2-methylpropene on calcium oxide at 237K was $7.9 \times 10^{16}$ molecules s⁻¹ m⁻² which compares with $1.7 \times 10^{17}$ for propene at 236K (1). The rate of exchange of 2-methylpropene on γ-alumina at
### Table 4.7

**Exchange Reactions of 2-Methylpropene and Deuterium on Calcium Oxide and γ-Alumina**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Oxide weight</th>
<th>T/K</th>
<th>t/min</th>
<th>D₀</th>
<th>D₁</th>
<th>D₂</th>
<th>D₃</th>
<th>D₄</th>
<th>D₅</th>
<th>Mᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20</td>
<td>237</td>
<td>29</td>
<td>75.65</td>
<td>16.00</td>
<td>6.05</td>
<td>1.65</td>
<td>0.60</td>
<td>0.05</td>
<td>1.28</td>
</tr>
<tr>
<td>calculated Aᵃ</td>
<td></td>
<td></td>
<td></td>
<td>69.42</td>
<td>25.93</td>
<td>4.23</td>
<td>0.40</td>
<td>0.02</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>200</td>
<td>341</td>
<td>57</td>
<td>78.25</td>
<td>18.20</td>
<td>3.25</td>
<td>0.25</td>
<td>0.05</td>
<td>0.00</td>
<td>1.11</td>
</tr>
<tr>
<td>calculated Bᵃ</td>
<td></td>
<td></td>
<td></td>
<td>77.03</td>
<td>20.44</td>
<td>2.37</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

- **a** A represents the distribution calculated for stepwise exchange with the same average deuterium content as the results from calcium oxide; B was a similar calculated distribution for comparison with the results for γ-alumina.
- **b** The mean number of deuterium atoms entering each molecule in the initial stages of reaction.
341K was $6.0 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$, and the corresponding rate for propene was $2.1 \times 10^{14}$ at the lower temperature of 293K. The exchange reaction was largely stepwise on alumina but a little multiple exchange occurred with calcium oxide and the value of $M = 1.28$ was identical with that found for propene at 249K.

A slow hydrogenation of 2-methylpropene of $3.2 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$ was observed on calcium oxide at 313K which compares with $5.2 \times 10^{14}$ in the same units for the reaction of propene.

The results of the n.m.r. analyses for the exchange reactions of 2-methylpropene are given in Table 4.8. As with results on lanthana (Table 4.3), the full range of groupings of deuterium atoms were detected and on both oxides the agreement between calculated and observed distributions confirmed that in each of the deutero-alkenes the deuterium atoms were largely randomly distributed throughout the molecule. There was just a slight indication near the limit of experimental error for preferential exchange in the methylene group of the alkene in the reaction over alumina. The ratio of deuterium in methylene to deuterium in methyl was 0.314 on calcium oxide, and values of 0.325, 0.328 and 0.326 were found from various runs with lanthana, but on alumina the ratio was 0.361.

4.4 DISCUSSION

4.4.1 Rates of Reaction

A convenient method of comparing the rates of exchange with deuterium or the addition reaction of 2-methylpropene is to estimate the temperature needed to achieve a specified rate on different oxides. Results of this kind are given in Table 4.9; for exchange, two rates are selected - $10^{17}$ molecules s$^{-1}$ m$^{-2}$ for the more active catalysts and $10^{15}$ in the same units for those less active. The order of activity of exchange is
Table 4.8
Comparison of Experimental and Calculated Distributions of Deuterium Atoms in 2-Methylpropene exchanged on Calcium Oxide (237K) and γ-Alumina (341K)

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Percentages of D</th>
<th>calcium oxide</th>
<th>γ-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs.</td>
<td>calculated (d = 0.121)</td>
<td>obs.</td>
</tr>
<tr>
<td>=CHD</td>
<td>20.7</td>
<td>22.0</td>
<td>24.5</td>
</tr>
<tr>
<td>=CD₂</td>
<td>3.2</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>-CH₂D</td>
<td>58.5</td>
<td>57.9</td>
<td>63.7</td>
</tr>
<tr>
<td>-CHD₂</td>
<td>16.1</td>
<td>16.0</td>
<td>9.8</td>
</tr>
<tr>
<td>-CD₃</td>
<td>1.5</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

100.0 100.0 100.0 100.0
Table 4.9

Comparison of the Catalytic Activity\textsuperscript{a} of Different Oxides for the Exchange or Deuteration of 2-Methylpropene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Exchange $10^{17}$ molecules s\textsuperscript{-1} m\textsuperscript{-2}</th>
<th>Exchange $10^{15}$ molecules s\textsuperscript{-1} m\textsuperscript{-2}</th>
<th>Deuteration $10^{15}$ molecules s\textsuperscript{-1} m\textsuperscript{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>237</td>
<td>ZnO 303</td>
<td>La\textsubscript{2}O\textsubscript{3} 296</td>
</tr>
<tr>
<td>MgO</td>
<td>313</td>
<td>Al\textsubscript{2}O\textsubscript{3} (350)</td>
<td>CaO (330)</td>
</tr>
<tr>
<td>La\textsubscript{2}O\textsubscript{3}</td>
<td>373</td>
<td>ZrO\textsubscript{2} 425</td>
<td>ZrO\textsubscript{2} 383</td>
</tr>
<tr>
<td>ZnO</td>
<td>(390)</td>
<td>TiO\textsubscript{2} (Rutile) (743)</td>
<td>ZnO 398</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Temperature required to give rate specified in molecules s\textsuperscript{-1} m\textsuperscript{-2}. (Numbers in parentheses are less accurate.)
CaO>MgO>La$_2$O$_3$>ZnO>Al$_2$O$_3$>ZrO$_2$>TiO$_2$ (rutile); and for deuteration the order is La$_2$O$_3$>CaO>ZrO$_2$>ZnO>TiO$_2$ (rutile).

These results show that basic oxides tend to be efficient catalysts for the exchange of the alkene but there is no such simple explanation for the order for the addition reaction. Zirconia is unusual in showing slightly greater activity for addition than for exchange; on lanthana exchange is about an order of magnitude faster than addition and the ratio is even larger on the others.

4.4.2 Mechanisms

The dominant characteristic of the exchange reaction of 2-methylpropene with deuterium is that the products show a random distribution of deuterium atoms in each deutero-alkene over the eight positions in the molecule, the two positions in the methylene group and the six positions in the two methyl groups. Hughes, Kemball and Tyler (14) reported that on γ-alumina, which gives preferential exchange of vinylic hydrogen atoms with propene, there is little evidence for a similar reaction with 2-methylpropene and the results are in better agreement with those of John et al. (9) than with the earlier report from Hightower and Hall (15).

The essential feature of the mechanism of exchange is a means of moving the position of the double bond in 2-methylpropene so that eight atoms become randomly distributed between the methylene groups and the two methyl groups. An important aspect of the addition process is the clear evidence that the chances of acquiring deuterium at the primary and tertiary positions differ in the formation of 2-methylpropane over lanthana. Both these points can be covered in terms of the general scheme for the reactions of 2-methylpropene on oxides which will be considered in some
detail (see Scheme 4.1). The following points can be made relating to the application of the Scheme to different catalysts and different conditions:

1. In exchange reactions, the forward and backward steps in each of the reversible processes involved will occur at the same rate. This will apply to reactions (1) and (2), and also to (3) and (4) or (5) and (6).

2. The size of the partial charges on the adsorbed π-allyl and alkyl species need not be the same although for simplicity they are shown as equivalent in the Scheme. The fractional charges are likely to depend on the nature of the catalyst.

3. The Scheme implies that there are two distinct pools of H or D species in the surface. The symbol Y represents those which are involved in the interconversions between alkene and allyl, or between alkene and alkyl. When either of these interconversions takes place rapidly the composition of the Y pool is likely to approximate to the isotopic composition of the alkenes. The composition of the Z pool will depend on the source of these species which may be the compound used to provide the deuterium isotope or, in some circumstances, could be through the dissociation of alkane molecules. The partial charges on the Y and Z species may differ in size as well as sign.

4. Exchange of alkene may occur through reactions (1) and (2) combined with either of the pairs (3) and (4) or (5) and (6). Either route will permit movement of the double bond around the molecule and the exchange of any or all of the hydrogen atoms in the alkene.

5. Since the consequences of exchange by (3) and (4) or by (5) and (6) are similar, it is not easy to determine which route is favoured on a given catalyst. There may be cases when both routes are operative at the same time although not necessarily at the same rate. Comparison
Scheme 4.1

General Scheme for reactions of 2-methylpropene on oxide catalysts.

Both $Y$ and $Z$ represent $H$ or $D$. The fractional charges on the adsorbed species will vary with the nature of the oxide and the magnitude of the charges on the allyl and alkyl species need not be the same.
between the rates of reaction of 2-methylpropene and other alkenes, such as propene, may help to distinguish between the routes.

6. Strongly basic oxides are likely to favour the acidic dissociation of the alkene involved in reactions (3) and (4). Here it is suggested that this pair of reactions comprises the principal mode of exchange on calcium oxide for which similar rates of reaction are found with propene and 2-methylpropene. The same conclusion for the same reason would seem to apply to magnesia (2) and zinc oxide (4).

7. Exchange by the pair of reactions (5) and (6) is likely to be predominant on acidic oxide catalysts or in cases where a potentially good supply of D⁺ is available, e.g. when the source of the isotopic label is provided in the form of D₂O. A more rapid rate of exchange of 2-methylpropene than of propene is an indication of reaction via (5) and (6) because the formation of the alkyl carbocation is easier with the C₄⁻molecule. An example where the use of D₂O instead of D₂ was required to enhance the rate of exchange of 2-methylpropene relative to the rate for propene was mentioned earlier for rutile catalysts (7).

8. Transfer of H atoms around the molecule by either pair of reactions (3) and (4) or (5) and (6) can provide a means of partially randomizing the distribution of D between the methylene and methyl groups (complete equilibration with molecules containing -CD₃ or =CD₂ requires the transfer of D as well as H). At low temperatures such transfer of H atoms is likely to be faster than exchange between alkene molecules because of the kinetic isotope effect on the relative rates of dissociation of C-H and C-D bonds.
9. The absence of appreciable multiple exchange on a catalyst suggests that reactions (1) and (2) take place more rapidly than (3) and (4) or (5) and (6). The converse applies when multiple exchange is substantial.

10. The Scheme provides an explanation of the results found for the nature of the deuteration reaction on lanthana. What occurs is an example of the consequences of the suggestions in paragraph 3 above. When substantial amounts of alkene exchange are occurring, the composition of the Y pool will be less rich in D than the Z pool and less D is added to the primary carbon than to the tertiary carbon.

11. The Scheme can also explain why exchange of 2-methylpropane with heavy water on acidic oxides (Hindin, Mills and Oblad (16); Hansford, Waldo, Drake and Honig (17); Kemball and McCosh (5)) gives multiple exchange with up to 9 but not 10 deuterium atoms in the products. The slow step is the dissociation of the alkane by reaction (8); there follows a rapid series of interconversions by reactions (5) and (6) leading to the replacement of all 9 primary hydrogen atoms if a sufficient supply of D⁺ is available. The final step of the exchange is reaction (7) which adds an atom to the tertiary position to reform the alkane; this atom is much more likely to arise as an H⁻ from the dissociation of another hydrocarbon than as a D⁻ from D₂O.

12. The examples quoted refer to conditions where (5) and (6) are rapid in relation to (7) and (8). With alkenes, other than 2-methylpropene, the evidence suggests that the rate-determining step for alkane formation is reaction (5) - the formation of the adsorbed alkyl species. The alkyl species is then rapidly converted to alkane (reaction 7) and does not revert to alkene (reaction 6). Evidence for this type of behaviour was found for ethene by Kokes and Dent (18) and also for
cyclopentene by Brown, Kemball and Taylor (19) on zinc oxide. It seems probable that the relative rates of reactions (5), (6) and (7) with 2-methylpropene may vary significantly from catalyst to catalyst, and with the conditions used.

13. The Scheme does not include dissociation of alkene to adsorbed vinyl species. By analogy with the behaviour of propene and cyclopentene, such a reaction might be expected on alumina but little evidence for it was found in the present work.

The scrambling of H and D atoms in 2-methylpropene appears to be an efficient process on alumina as on the other oxides but there is some doubt about the mechanism involved. The scrambling may occur through reactions (3) and (4) but the evidence from studies with propene is against the formation of π-allyl species at low temperatures. Alternatively, the scrambling may involve reactions (5) and (6) since the results discussed by John et al. (9) indicate the likelihood of such processes with molecules capable of forming tertiary carbocations. But, if this associative mechanism is involved, it is surprising that the exchange of 2-methylpropene is not faster than the exchange of propene on alumina.

14. On zirconia, the comparatively simple nature of the deuteration reaction which adds D at both the primary and tertiary positions of the alkene shows that for this catalyst the Y and Z pools are similar. This may be a consequence of the comparatively low rate of exchange, i.e. reaction (6) is slower than (7) and the interconversion to allyl is unimportant. It is also possible that the partial charge on the alkyl species is smaller on zirconia so that the addition reaction
approximates more closely than on lanthana to the successive uptake of two more or less neutral atoms of deuterium.

4.4.3 n.m.r. Results

The spectra show that 2-methylpropene is readily analysed by deuterium n.m.r. spectroscopy. The spectra are simple because of the absence of D on the central carbon atoms. Consequently, deuterons, whether in the methylene group or the methyl groups, are subject only to $\alpha$-shifts which are of sufficient size (15 to 20 p.p.b.) to be easily detected and measured or $\gamma$-shifts which are small enough to be neglected. Under these circumstances, it is possible to identify and estimate all the relevant groupings of deuterium in the molecules.

The situation is more complex with 2-methylpropane and the achievement of adequate resolution of the various peaks is easier for the primary deuterons which are subject to not more than one $\beta$-shift. The peaks for the tertiary deuterons, influenced by up to six $\beta$-shifts, cannot be completely resolved because $\beta$-shifts (ca. 8 p.p.b.) are similar to the natural line-width of the resonances.

The combination of n.m.r. analysis with either gas chromatography or mass spectrometry provides a reasonably complete picture of the location and grouping of deuterium atoms in the products from reactions of 2-methylpropene with $D_2$. 
4.5 REFERENCES


CHAPTER 5

High Temperature Reactions of Alkanes with Deuterium on Lanthana.
5.1 INTRODUCTION

A considerable amount of work relating to the exchange reactions of alkanes with deuterium on oxide catalysts is published in past literature. Robertson, Scurrrell and Kemball (1) studied the exchange behaviour of a series of alkanes on γ-alumina and established that catalyst activity for the reaction increased with the acidity of the hydrocarbon. For n-butane and 2-methylpropane reactants the different types of hydrogen atom within the same molecule reacted at different rates. This evidence led to the belief that the reaction mechanism involved formation of carbanionic intermediates, resulting from heterolytic dissociation of the C-H bond. Further research involved the exchange of cyclopentane with deuterium on γ-alumina (John, Kemball, Pearce and Pearman (2)) and results indicated that the temperature used to activate the catalyst had a significant effect on activity. Hydrocarbon exchange reactions on magnesium oxide were investigated by Robertson, Scurrrell and Kemball (3) and the activity pattern shown by a number of alkane molecules resembled that found for γ-alumina. Therefore carbanionic alkyl intermediates were also envisaged on this catalyst. Interesting results were reported (Halliday, Kemball, Leach and Scurrrell (4)) for rutile at temperatures above 700K. Alkane exchange was the main reaction in the presence of deuterium and it was accompanied by dehydrogenation to give alkene products.

The results for the reaction of alkanes with deuterium studied on lanthana, using mass spectrometry and deuterium n.m.r. spectroscopy, are given in this Chapter.
Utiyama, Hattori and Tanabe (5) studied the exchange of alkanes with deuterium on a group of metal oxide catalysts. The hydrogen atoms in methane were replaced on lanthana at 573K and activity was dependent on the temperature at which the catalyst was pretreated. The sample was most active following evacuation at 923K and a rate of $2.4 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$ was obtained from the results. The multiplicity factor, $M (= k/ k_0)$, was 1.2 compared with a value of 1.0 expected for a stepwise exchange process. Exchange of 2-methylpropane took place at 573K on lanthana and during the course of reaction the products were analysed by proton n.m.r. Results obtained showed that the hydrogen atoms on the methyl position of the alkane were exchanged at a faster rate than those in the methyne group.

In recent work by Brown, Kemball, Oliver and Sadler (6), the products from the reaction of alkanes (ethane, propane, 2-methylpropane and 2,2-dimethylpropane) with deuterium on some supported metal catalysts were analysed by deuterium n.m.r. spectroscopy. Results obtained by this method were useful for elucidation of reaction mechanisms.

Apart from the work of Utiyama and co-workers, the catalytic activity of lanthana for the exchange of alkanes has not been studied. Therefore the original purpose of this research was to compare the behaviour of n-butane, 2-methylpropane, propane, cyclopentane, 2,2-dimethylpropane and methane on the oxide. Preliminary experiments showed that reactions could be conveniently studied at temperatures above 570K and under such conditions exchange was accompanied by dehydrogenation for all alkanes except 2,2-dimethylpropane and methane. Using mass spectrometry and deuterium n.m.r. spectroscopy both types of reaction were followed simultaneously.

Some of the work is discussed in relation to the results in the other Chapters (7, 8).
5.2 EXPERIMENTAL

Catalyst pretreatment consisted of heating about 95 mg of La(OH)$_3$(I) to 923K under vacuum followed by outgassing for three hours at this temperature. The resulting oxide had a measured BET-N$_2$ surface area of $16 \pm 1$ m$^2$g$^{-1}$.

The course of most experiments was analysed by mass spectrometry and in some cases the sample was condensed, after about 15% conversion, and the deuterium n.m.r. spectrum was obtained using the technique described in Chapter 2. Experiments were conducted using static line (I).

A pressure ratio of 5:1 for deuterium:alkane was used with hydrocarbon pressures of 2.4 kPa and 3.6 kPa for kinetic and n.m.r. type reactions respectively. This corresponds to the use of $1.9 \times 10^{19}$ molecules for the investigation of reaction kinetics and $8.9 \times 10^{19}$ molecules where n.m.r. spectra were obtained.

The molecules n-butane, 2-methylpropane, propane and cyclopentane underwent dehydrogenation and the amount of alkene expected for thermodynamic equilibrium was calculated using equation (5.1):

$$K = \frac{P_A P_D}{P_B}$$

(5.1)

where $K$ is the equilibrium constant for dehydrogenation of the alkane, as obtained from equilibrium constants of formation of the corresponding hydrocarbons quoted in the literature (9). $P_A$, $P_B$ and $P_D$ represent the pressures (in atm.) of alkene, alkane and deuterium respectively.

In many experiments substantial stepwise exchange was accompanied by a small amount of multiple exchange and some dehydrogenation of the alkane. The value of $\bar{Q}$ was calculated for alkane molecules produced from the exchange reactions and this gave the rate $k_\bar{Q}$ (see Chapter 2).
M, the multiplicity of the exchange reaction expressed in D atoms per molecule, was calculated from the ratio $k_φ/k_0$. Both $k_φ$ and $k_0$ were further broken down into a stepwise and a multiple exchange component and the method employed is described later.

5.3 RESULTS

Some general points emerged from the experiments with n-butane. Therefore the initial part of the results section relate to this molecule. The main features observed for the other alkanes are described later.

5.3.1 n-Butane

The reaction of n-butane with deuterium was conveniently studied between 571K and 721K. Results obtained from the mass spectrum after a time interval of 40 minutes are given in Table 5.1 for a typical experiment carried out at 625K.

In the first stage of analysis the peaks on the spectrum were corrected by subtracting the background contributions from naturally occurring carbon-13 and deuterium isotopes in the hydrocarbons. The corrected peak heights were expressed as percentages. Substantial peaks appeared with m/e = 59 and 60 and these corresponded to alkane. Some peaks also appeared in the higher mass range (m/e = 67 and 68). A maximum percentage also appeared at m/e = 64 and this was attributed to alkene.

The results indicate that the main reaction is alkane exchange although simultaneous dehydrogenation takes place. Lanthana is an effective catalyst for exchange of alkenes at temperatures lower than 420K (7, 8). Therefore any butene present would be highly exchanged and the peaks at m/e 63 and 64 were attributed to the butenes C₄HD₇ and C₄D₈. To take the
Table 5.1
Hydrocarbon distributions for the reaction of n-butane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T/K</th>
<th>Time(min)</th>
<th>m/e</th>
<th>58</th>
<th>59</th>
<th>60</th>
<th>61</th>
<th>62</th>
<th>63</th>
<th>64</th>
<th>65</th>
<th>66</th>
<th>67</th>
<th>68</th>
</tr>
</thead>
<tbody>
<tr>
<td>But/1</td>
<td>625</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>experimental^a</td>
<td>83.40</td>
<td>11.75</td>
<td>1.42</td>
<td>0.21</td>
<td>0.34</td>
<td>0.30</td>
<td>0.98</td>
<td>0.09</td>
<td>0.09</td>
<td>0.38</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>But/2</td>
<td>721</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>experimental^b</td>
<td>84.21</td>
<td>11.90</td>
<td>1.43</td>
<td>0.14 (0.06)</td>
<td>0.11</td>
<td>0.36</td>
<td>0.09</td>
<td>0.09</td>
<td>0.38</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>calculated^c</td>
<td>83.35</td>
<td>13.38</td>
<td>0.97</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

% Species

<table>
<thead>
<tr>
<th>% Alkane</th>
<th>% Alkene</th>
<th>% Alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_0</td>
<td>D_1</td>
<td>D_2</td>
</tr>
<tr>
<td>84.21</td>
<td>11.90</td>
<td>1.43</td>
</tr>
</tbody>
</table>

^a Peak heights were corrected for isotope.
^b Results worked out on the assumption that peaks with m/e = 63 and 64 are due to the alkenes C_4HD_7 and C_4D_8 respectively and that all other peaks correspond to alkane. The values in parenthesis are estimated by assuming no alkene with m/e = 62 was present.
^c For a binomial distribution totalling 97.74% with $\phi = 15.4$.
^d The distribution given for the reaction at 721K was interpolated from a graph in order to estimate the composition of the n.m.r. sample.
analysis a stage further it was assumed that the other peaks corresponded entirely to alkane molecules and the mass spectrum was corrected using the relevant fragmentation factors for n-butane and trans-but-2-ene. Final percentages of the isotopic species are shown in Table 5.1.

The experimental results for products containing four or less deuterium atoms per butane molecule gave an average D content \( d \) of 0.0158. The calculated distribution given in the Table shows the amounts of each compound expected for a completely stepwise reaction. The agreement between the two sets of data indicates that stepwise exchange is the main reaction but the results show that some multiple exchange must also occur.

Exchange rates for the alkane were calculated from logarithmic plots. A typical example of the graph for the reaction carried out at 625K is shown in Figure 5.1. The values of \( \%D_0 \) and \( \bar{D} \) were calculated by considering alkane species only; the presence of alkene was ignored. After an initial inhibition period lasting less than ten minutes the system settles and the graph is linear for about an hour. Rates were obtained from the slope and \( k_0 \) and \( M \) are given in Table 5.2. After approximately one hour, the plot curves and the fall in rate associated with this is ascribed to poisoning.

The results in Figure 5.2 show how \( k_0 \) varies with reaction temperature. The reaction had an activation energy of \( 66^{+3} \) kJmol\(^{-1}\) and \( \log A \) was \( 21.3^{+0.3} \) molecules s\(^{-1}\)m\(^{-2}\).

Further breakdown of the reaction rates into stepwise and multiple components was carried out for the reaction at 625K. This involved measurement of the initial slopes of plots showing percentage product against time for each of the isotopically labelled compounds. \( k_1 \) was then calculated by combining the individual rates of formation of the species.
Figure 5.1

The exchange of n-butane on 73 mg La$_2$O$_3$(I) at 625K plotted according to the first order kinetic equations.
### Table 5.2

**Activities for the reactions of different alkanes with deuterium at 625K**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Exchange Rate/10^{15} molecules s^{-1} m^{-2}</th>
<th>Dehydrogenation Rate/10^{14} molecules s^{-1} m^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_o M k_1(M_1) k_2(M_2)</td>
<td>k_D</td>
</tr>
<tr>
<td>n-Butane</td>
<td>6.1 1.8 5.3(1.1) 0.6(9.6)</td>
<td>1.6</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>2.7 1.7 2.2(1.1) 0.3(6.9)</td>
<td>0.9</td>
</tr>
<tr>
<td>Propane</td>
<td>3.1 1.6 2.6(1.0) 0.3(7.5)</td>
<td>0.4</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>1.8 1.1 1.6(1.1) 0.02(9.5)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- k_1 and k_2 relate to product alkane containing less than four or more than five D atoms per molecule respectively.

- M_1 and M_2 associated with 2-methylpropane used the C_3X_7^+ alkion.
Figure 5.2
Arrhenius plot for alkane exchange on La$_2$O$_3$(l).
O, n-butane; Δ, 2-methylpropane; •, propane;
□, 2,2-dimethylpropane; ▲, cyclopentane; and ■, methane.
associated with stepwise exchange and the multiplicity factor $M_1$ was calculated using:

$$M_1 = \sum \frac{r_i}{k_1}$$  \hspace{1cm} (5.2)

where $r_i$ is the rate of formation of alkane containing $i$ deuterium atoms per molecule. A similar procedure for multiple exchange gave values for $k_2$ and $M_2$.

The rate data obtained is shown in Table 5.2 and the results provide further evidence for two separate exchange mechanisms. Rates are consistent with the relationships:

$$k_0 = k_1 + k_2$$  \hspace{1cm} (5.3)

and

$$k_\circ = k_1 M_1 + k_2 M_2$$  \hspace{1cm} (5.4)

The course of reaction with time is presented in Figure 5.3 for the experiment at 625K. The graph shows the general characteristics of the butane/deuterium system catalyzed by lanthana. The rate of dehydrogenation ($k_D$) was calculated from the initial slope of the alkene formation curve and this is reported in Table 5.2. The amount of alkene increases until reaching 0.45% of the hydrocarbon phase, although this value is less than that expected for an equilibrium composition (0.68%) at 625K. Once a maximum is achieved the amount of butene detected in the gas phase gradually falls with time. This is accompanied by a drop in formation of exchanged alkane, particularly for molecules with a large deuterium content.

**n.m.r. studies of the reaction of butane**

Products from an experiment carried out at 721K were investigated by $^2$D-n.m.r. spectroscopy and results from the spectrum are shown in
Figure 5.3
Formation of products from the reaction of n-butane with deuterium on 73 mg La$_2$O$_3$(l) at 625K. 
•, (stepwise) and △, (multiple) are alkane from exchange and □, is alkene from dehydrogenation.
Table 5.3. The mass spectrometric data for the sample, extrapolated to the time it was isolated from the catalyst, is shown in Table 5.1.

The n.m.r. evidence confirms the presence of butenes in the hydrocarbon phase. Some 27% of the deuterium in the butenes is contained in but-1-ene and the equilibrium amount of this alkene at 721K corresponds to 21% of the total butene.

The chemical shifts (δ) obtained from the n.m.r. spectrum of n-butane are given in Table 5.3. A number of exchanged alkane resonances appeared, the secondary deuterium had δ values in the range 1.26-1.20 p.p.m., and primary atoms occurred with δ = 0.88-0.82 p.p.m. Groupings of deuterium in the butanes were assigned with the help of α-, β- and γ-shifts reported from experiments with labelled propanes by Brown et al. (6). In fact, on comparing the data obtained from the propane experiments with that of n-butane, it appeared that the isotopic shifts of the alkanes were similar.

In agreement with the mass spectrometric data most of the deuterium in the butane was present in molecules containing one or two D atoms. Terminal exchange of butane is favoured since the alkane has eight times more primary D than secondary species, and for molecules with only a single deuterium atom the ratio is 11. Results from the mass spectrum indicate an average of 0.71 D/molecule in the 98.3% alkane. Knowing the relative amounts of deuterium in the alkene and alkane from the n.m.r. analysis, it was possible to calculate an average of 6.1 D/molecule in the 1.7% alkene. This value suggests that a majority of the butenes are heavily exchanged, although the details of the n.m.r. spectrum show that some of the compound contains only small amounts of deuterium atoms.
Table 5.3
Analysis of n.m.r. spectrum of n-butane exchanged at 721K

<table>
<thead>
<tr>
<th>But-1-ene</th>
<th>Chemical Shifts (δ/p.p.m.)</th>
<th>%D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3.5</td>
</tr>
<tr>
<td>But-2-enes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grouping</td>
<td>Chemical shifts (δ/p.p.m.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>But-1-ene</td>
<td></td>
</tr>
<tr>
<td>But-2-enes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grouping</td>
<td>Chem. shift Isotope shift Components</td>
<td></td>
</tr>
<tr>
<td>expt.</td>
<td>calc.</td>
<td>-Δδ/p.p.b.</td>
</tr>
<tr>
<td>Components</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Chem. shift δ/p.p.m.</th>
<th>Isotope shift expt. calc.</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>2°D</td>
<td>CH₃CHDCH₂⁻</td>
<td>1.2699</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CH₂DCHCH₂⁻</td>
<td>1.2625</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>CH₃CHDCHD⁻</td>
<td>1.2083</td>
<td>61.6</td>
</tr>
<tr>
<td>1°D</td>
<td>CH₂DCH₂⁻</td>
<td>0.8809</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CH₂DCH⁻</td>
<td>0.8716</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>CHD₂CH₂⁻</td>
<td>0.8608</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>CHD₂CHD⁻</td>
<td>0.8516</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>CHD₂CD₂⁻</td>
<td>0.8408</td>
<td>39.0</td>
</tr>
<tr>
<td></td>
<td>CD₃CH₂⁻</td>
<td>0.8208</td>
<td>40.1</td>
</tr>
<tr>
<td></td>
<td>CD₃CD₂CD₂⁻</td>
<td>0.8193</td>
<td>61.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X represents H or D</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
</tbody>
</table>
5.3.2 2-Methylpropane

Products from the reaction of 2-methylpropane at 680K were analysed by mass spectrometry and deuterium n.m.r. spectroscopy, and the composition of the sample taken after 160 minutes is shown in Table 5.4. The results show that alkane exchange is accompanied by dehydrogenation.

General analysis of the mass spectrum was conducted using the $C_3X_7^+$ ($X = H$ or $D$) pseudoparent ions but a complicating factor arose because the peak with m/e = 46 would have contributions from both alkane ($C_3H_4D_3^+$) and alkene ($C_3D_5^+$). Therefore the amounts of the latter two species were obtained from the parent ion spectrum by measuring the peaks with m/e = 61 ($C_4H_7D_3$) and m/e = 64 ($C_4D_8$).

The n.m.r. results confirm the presence of 2-methylpropene and chemical shifts were in agreement with those reported before (8). Analysis of the results is complicated by the fact that resonances corresponding to deuterium atoms in the methyl group of 2-methylpropene and those of the methine group in 2-methylpropane both appear with $\delta = 1.68$ p.p.m. However, the percentages of these species were estimated by assuming that deuterium is randomly distributed in the alkene molecule (8). In order to estimate the amount of deuterium contained in the methyl group of the alkene, the integral for the $=CD_2$ resonance was multiplied by three. Subtraction of this number from the total integral for resonances with $\delta = 1.68$ p.p.m. gave an indication of the amount of deuterium on the methine position of 2-methylpropane.

The mass spectral data for the $C_3X_7^+$ fragment ion gave a $\phi$ value of 22.0 which indicates an average of 0.31 D atoms per alkane molecule. The 0.42% alkene had an average of 6.6 D/molecule which is slightly less than the amount of deuterium expected for the eight positions.
Table 5.4

Results for the reaction of 2-methylpropane with deuterium at 680K after 160 minutes

(A) Analysis by mass spectrometry

<table>
<thead>
<tr>
<th>( %C_3X_7^+ ) Ions ( a )</th>
<th>( D_0 )</th>
<th>( D_1 )</th>
<th>( D_2 )</th>
<th>( D_3 )</th>
<th>( D_4 )</th>
<th>( D_5 )</th>
<th>( D_6 )</th>
<th>( D_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>experimental</td>
<td>83.27</td>
<td>14.57</td>
<td>1.20</td>
<td>(0.36)</td>
<td>-</td>
<td>0.07</td>
<td>0.08</td>
<td>0.45</td>
</tr>
</tbody>
</table>

(Also \( C_3D_5^+ \)
  0.42)

(B) Analysis by \(^2\text{D-n.m.r. spectroscopy} \( b \)

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Grouping</th>
<th>Chem. shift ( \delta/p.p.m. )</th>
<th>( %D )</th>
<th>Alkane</th>
<th>Grouping</th>
<th>Chem. shift ( \delta/p.p.m. )</th>
<th>( %D )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>=CD(_2)</td>
<td>4.6763</td>
<td>2.1</td>
<td></td>
<td>-CH(_2)D</td>
<td>0.8862</td>
<td>71.1</td>
</tr>
<tr>
<td></td>
<td>-CD(_3)</td>
<td>1.68</td>
<td>6.4</td>
<td></td>
<td>-CHD(_2)</td>
<td>0.8650</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>&gt;CD</td>
<td></td>
<td></td>
<td></td>
<td>-CD(_3)</td>
<td>0.8280</td>
<td>12.6</td>
</tr>
</tbody>
</table>

\( a \) The amount of \( C_3H_4D_3^+ \) and \( C_3D_5^+ \) species are estimated from the parent spectrum; for all other species analysis is in terms of the \( C_3X_7^+ \) pseudoparent.

\( b \) The amounts of species that overlap with \( \delta = 1.68 \) p.p.m. are estimated by assuming a random distribution of \( D \) in the alkene.
There is some evidence for preferential exchange in the primary position of 2-methylpropane since the ratio for the amounts of \(-\text{CH}_2\text{D}:\text{-CD}\) from the n.m.r. spectrum was 34 and in total there was about 42 times more primary than tertiary deuterium in the alkane.

A kinetic experiment with 2-methylpropane was carried out at 625K in order to compare the behaviour with that of n-butane. Rates were measured in the usual way and are given in Table 5.2. The value of \(k_0\) fell gradually although less than 15% reactant was converted, but the rate obtained from the initial slope is represented in Figure 5.2.

Alkene amounted to a maximum of some 0.56% of the gas phase composition for the dehydrogenation reaction. A value of 0.58% 2-methylpropene was expected for equilibrium between alkene, alkane and deuterium at this temperature.

### 5.3.3 Other molecules

The reactions of propane and cyclopentane with deuterium were studied at 625K and the general behaviour of these molecules was similar to that of the C\(_4\)-alkanes. The rates of exchange and dehydrogenation are compared in Table 5.2 and values of \(k_0\) gave the results plotted in Figure 5.2.

Once small amounts of cyclopentene were formed, no further dehydrogenation or multiple exchange took place, although the reaction system had not reached equilibrium.

The percentage of exchanged alkene that resulted from experiments conducted at various temperatures was compared with the calculated equilibrium amounts for all four hydrocarbons studied and results are presented in Table 5.5.
Table 5.5

Experimental amounts of alkene compared with amounts calculated for an equilibrated mixture of alkane and alkene

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Temp/K</th>
<th>% Alkene</th>
<th>Experiment&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Calc&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>625</td>
<td></td>
<td>0.45</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>721&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>1.68</td>
<td>4.48</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>625</td>
<td></td>
<td>0.52</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>680&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>0.42</td>
<td>2.15</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>625</td>
<td></td>
<td>0.27</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>721</td>
<td></td>
<td>0.29</td>
<td>22.00</td>
</tr>
<tr>
<td>Propane</td>
<td>625</td>
<td></td>
<td>0.11</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<sup>a</sup> Maximum amount observed.

<sup>b</sup> Theoretical values taken from reference 9.

<sup>c</sup> Using the experimental conditions of n.m.r. type study.
As an extension of the research, the reaction of 2,2-dimethylpropane with deuterium was studied at temperatures ranging from 625K to 724K. Analysis was carried out in terms of the C₄ X₉⁺ fragment ion.

The initial product distribution plot for a kinetic experiment carried out at the lowest temperature is shown in Figure 5.4. It appears from the large amount of D₁⁻ ion that exchange is stepwise but some of the alkane did contain two D atoms per molecule. As was observed for the other molecules studied, three characteristic regions were identified on the first order plots for exchange of 2,2-dimethylpropane. A short induction period was followed by a steady reaction, which lasted one hour, then activity gradually fell. k₀ and kₚ were calculated from the linear part of the graph and the former rate at 625K is compared with the results for the other molecules in Figure 5.2. The initial value (k₀ = 2.49 X 10¹⁵ molecules s⁻¹ m⁻²) was halved after a time interval of two hours, yet less than 15% alkane was exchanged. The value of M for this experiment was 1.02 and an alternative way used to obtain the multiplicity gave M_D = 1.02. In the latter method M_D was calculated by examination of the initial product distribution and using the relationship:

\[ M_D = \Sigma n \, d_n \]  

where \( d_n \) is the fractional contribution of \( n \) deuterium atoms to the distribution.

The evidence from the reaction at 625K suggests that exchange of 2,2-dimethylpropane is almost entirely stepwise. However there was some indication that a small amount of multiple exchange took place. In order to
Figure 5.4

Initial products obtained from the mass spectrum after exchange of 2,2-dimethylpropane on 73 mg La_2O_3(I) at 625K. ○, and □, represent C_4H_8D^+ and C_4H_7D_2^+ respectively.
take the investigation a stage further, products from an experiment carried out at 626K were analysed by deuterium n.m.r. spectroscopy.

The distribution obtained from the mass spectral analysis after 215 minutes is shown in Table 5.6. The value of $\phi$ was 20.39 for the $C_4X_9^+$ ion and this figure was used to calculate the percentages of species expected for a random distribution of deuterium over nine positions, as shown in the Table. The main resonance that appeared on the n.m.r. spectrum had $\delta = 0.9235$ p.p.m. and this amounted to some 92.8% of the deuterium in the alkane. This peak was assigned to 2,2-dimethylpropane with one D atom and the chemical shift was in agreement with the value of $\delta = 0.9279$ p.p.m. reported for $\text{-CH}_2\text{D}$ by Brown et al. (6). One other resonance was observed with $\delta = 0.9026$ p.p.m. and this was ascribed to alkane containing two D atoms in the same methyl group. The results gave a value for the $x$-shift in 2,2-dimethylpropane of -20.9 p.p.b. compared with -20.7 p.p.b. reported in the previous work (6).

According to the mass spectral data 0.203 D atoms/ion were present and this gives a chance of 0.023 D atoms in each position for an even spread of deuterium in the ion. Using this value, the ratio of D in $\text{-CHD}_2$ compared with that in $\text{-CH}_2\text{D}$ would be 0.047 for a random distribution of deuterium atoms. Inspection of the n.m.r. spectrum gave a ratio of 0.077; in other words, slightly more $\text{-CHD}_2$ formed than was expected for straightforward stepwise exchange.

The hydrocarbon distribution obtained after 43 minutes from the mass spectrum of a reaction carried out at 724K is shown in Table 5.6. The experimental results gave $\phi = 71.4$ for the alkion fragment and this corresponds to an average of 0.95 D atoms per molecule. The percentages of each isomers expected for a random distribution over nine exchangeable
Table 5.6

Alkane distributions for the reaction of 2,2-dimethylpropane with deuterium

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T/K</th>
<th>time/min.</th>
<th>D$_0$</th>
<th>D$_1$</th>
<th>D$_2$</th>
<th>D$_3$</th>
<th>D$_4$</th>
<th>D$_5$</th>
<th>D$_6$</th>
<th>D$_7$-D$_9$</th>
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</thead>
<tbody>
<tr>
<td>DMP/1</td>
<td>626</td>
<td>215</td>
<td></td>
<td></td>
<td>82.04</td>
<td>15.73</td>
<td>2.03</td>
<td>0.20</td>
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<td>81.33</td>
<td>17.00</td>
<td>1.58</td>
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<tr>
<td>DMP/2$^c$</td>
<td>724</td>
<td>43</td>
<td></td>
<td></td>
<td>55.23</td>
<td>26.40</td>
<td>12.19</td>
<td>4.52</td>
<td>1.30</td>
<td>0.29</td>
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<td></td>
<td></td>
<td>47.68</td>
<td>36.81</td>
<td>12.63</td>
<td>2.53</td>
<td>0.32</td>
<td>0.03</td>
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</table>

a Analysis in terms of the C$_4$X$_9^+$ ions.

b Calculated values are based on random distributions over nine positions with chances of $\hat{d} = 0.023$ ($\hat{\phi} = 20.4$) and $\hat{d} = 0.079$ ($\hat{\phi} = 71.0$) for temperatures of 626K and 724K respectively.

c The experimental results at 724K are based on extrapolation for an n.m.r. sample.
positions with $d = 0.079$ are shown for comparison in Table 5.6.

Inspection of the two sets of data shows that a relatively large number of molecules contains more than one D atom. It is also clear that the experimental distribution of the ions deviates quite significantly from the amounts expected for stepwise exchange. At this temperature $k_o = 1.64 \times 10^{16}$ molecules $s^{-1} m^{-2}$ and $M$ was 1.24.

There was no evidence for alkene product at any of the temperatures studied. This would only occur after rearrangement of the 2,2-dimethylpropane to n-pentane or 2-methylbutane.

The reaction of methane was studied at 625K and stepwise exchange ($M = 1.00$) was observed. The initial rate ($k_o = 1.27 \times 10^{15}$ molecules $s^{-1} m^{-2}$) is shown in Figure 5.2, although this fell to 0.4 times the original value after less than 10% reactant was converted.

5.4 DISCUSSION

Comparison of the results obtained at 625K showed that the rates of exchange of the different alkanes only varied by a factor of ca. five. With methane the exchange rate can be compared with results reported for lanthana by Utiyama and co-workers (5). A rate of $2.8 \times 10^{14}$ molecules $s^{-1} m^{-2}$ at 573K was obtained from the results of the Japanese workers and this is a factor of 4.5 times less than the rate at 625K reported in the present work. It was surprising that Utiyama et al. did not report any evidence for dehydrogenation or multiple exchange of 2-methylpropane but the reaction was studied at lower temperature and this may explain the differences between the two sets of results.
In the following sections the general mechanism of the reactions are discussed for lanthana and the intermediates involved are compared with those reported on other oxide catalysts. Some reference is also made in connection with catalyst poisoning when alkanes react with deuterium on lanthana.

5.4.1 Reaction Mechanism

For the alkanes capable of forming alkenes directly, dehydrogenation accompanied the main exchange reaction. The results for these molecules can be understood in terms of Scheme 5.1. The reaction Scheme is based on a similar suggestion used to explain results obtained for the reaction of alkanes on rutile (4).

At the beginning of the reaction, alkyl is formed by dissociative adsorption which if reversed gives stepwise exchange. Alkene formation takes place on the catalyst surface by dissociation of the alkyl. Rapid reversible dissociation of alkene via reactions (7) and (8) produces molecules that contain several deuterium atoms. Some alkene desorbs via step (5) but the evidence also indicates that a small amount of the molecules go by the reverse of step (4) to give alkane which is highly exchanged.

The main exchange route for the reactants 2,2-dimethylpropane and methane does not involve alkene-related species and probably involves interconversion of steps (1) and (2) in the reaction Scheme.

5.4.2 Reaction Intermediates and Activities

The deuterium atoms gave preferential exchange of primary hydrogen in both n-butane and 2-methylpropane and this is consistent with a mechanism
Scheme 5.1

General scheme for the high temperature reactions of n-butane, 2-methylpropane, propane and cyclopentane with deuterium on La$_2$O$_3$. 
involving carbanionic intermediates. If, after heterolytic dissociation, an alkyl group possesses a negative charge on a carbon atom then intermediates which result after cleavage of a primary C-H bond will be more stable than those species formed by secondary or tertiary bond rupture. An alternative way of explaining the results is by considering steric factors since the hydrogen atoms on the methyl groups of both C_4-alkanes are less hindered and will be more labile.

The formation of stable carbanionic intermediates on lanthana does seem reasonable considering that previous work (e.g. 10) has shown that an important feature of this catalyst is the basic properties of the surface. A similar conclusion was reached by Utiyama et al. (5) where the authors proposed that the basic sites of the oxide were responsible for abstraction of a proton from the alkane in the rate determining step of the exchange reactions. They also suggested that the nature of the active sites on lanthana were identical to those of the alkaline earth metals (MgO, CaO, SrO and BaO).

Carbanionic species were also envisaged on γ-alumina (1) and magnesium oxide (3) where large variations observed for exchange rates of a number of molecules gave a relationship that associated activity with acidity of the hydrocarbons. Results on lanthana did not point towards a correlation of this nature because the reaction rates for the different molecules were too similar. The absence of such a trend was not surprising considering the results for lanthana are probably connected with a poisoned catalyst surface and bearing in mind that hydrocarbon acidities calculated by Robertson et al. (1, 3) relate to room temperature. In contrast, the relative activities for the exchange of
alkanes on rutile (4) were consistent with homolytic dissociation of the hydrocarbon on the acidic surface.

2,2-dimethylpropane can form a number of different types of intermediates in exchange reactions and these were originally discussed in a study on metal catalysts by Kemball (11). The main reaction on lanthana involved a simple exchange process where one hydrogen was replaced by one deuterium atom at a time with the likely intermediate being an \( \text{a-alkyl} \). In agreement with the results given by Kemball (11), the contribution from multiple exchange was small at lower temperatures but increased as the temperature was raised. The products from the latter reaction probably involve \( \text{a,a-} \) and/or \( \text{a,a,a-} \) monoadsorbed intermediates. If the molecule adsorbed by a two-point \( \text{a,\gamma-} \) species then this would not be detected by deuterium n.m.r. spectroscopy (6) but it is possible that this intermediate also contributes towards the multiple exchange reaction. A more detailed examination of the exchange of 2,2-dimethylpropane requires further experiments to be carried out.

Lanthana is an effective catalyst for the exchange of alkenes with deuterium at temperatures below 420K, provided the reaction can proceed via \( \pi \)-allyl intermediates (7, 8). Bearing this in mind, it is suggested that adsorbed \( \pi \)-allyl species are responsible for multiple exchange of the alkenes formed during the reactions of n-butane, 2-methylpropane, propane and cyclopentane with deuterium.

5.4.3 Molecule Stabilities

Each of the molecules studied demonstrated self-poisoning on the catalyst surface but this was not unexpected for reactions conducted at such high temperatures. In the case of 2,2-dimethylpropane the fall in catalyst activity can be ascribed to some irreversible adsorption of the
hydrocarbon but such a suggestion does not explain the poisoning of the reaction involving methane. Lanthana is easily deactivated by contact with molecules such as CO₂ or H₂O (7), and contamination of the surface by impurities of this sort cannot be ruled out when methane was investigated. Vacuum distillation cannot be used for purification of the reactant in such cases.

The alkene/lanthana system showed varying degrees of self-poisoning in previous research (7); hence some deactivation of the oxide is expected when dehydrogenation of alkanes occur. An interesting feature observed from Figure 5.3 was an apparent fall in the amount of butene present during the latter stages of the experiment. This discovery is due to a loss of alkene as it adsorbs, and sticks to, the catalyst surface. The process that leads to formation of both butene and heavily exchanged butanes occurs on identical sites on lanthana, thus the drop in the amount of the latter molecules that desorb into the gas phase was expected.

The severity of catalyst deactivation attributed to alkene adsorption will increase as reaction temperature is raised and accordingly the amounts of exchanged alkene arising from alkane dehydrogenation at the higher temperatures are further from the equilibrium concentrations shown in Table 5.5. Another thing that was clear from the results in the Table is the indication that cyclopentene has a particularly adverse effect on the catalyst activity. The poor ability of lanthana in catalyzing dehydrogenation of cyclopentane is probably related to the fact that cyclopentene is very unstable on the surface, as was also observed in hydrogenation of this molecule reported in the other work (7). Despite these observations, the degree of poisoning of the stepwise exchange of cyclopentane was no worse than that found for the other alkanes studied.
5.5 REFERENCES


7. See Chapter 3.

8. See Chapter 4.


CHAPTER 6

Reactions of Alkenes and the Equilibration Hydrogen and Deuterium on Zirconia.
6.1 INTRODUCTION

A considerable amount of literature has been published in relation to the adsorption and reaction of various carbon-containing molecules on zirconia catalysts but only a small proportion of this work concerns the reaction of alkenes with either deuterium or hydrogen. The purpose of the present Chapter was to study a range of alkenes (ethene, propene, 3,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene) with deuterium and hydrogen in order to obtain kinetic and mechanistic information.

In early work by Tret’yakov, Pozdnyakov, Oranskaya and Filimonov (1) and also by Agron, Fuller and Holmes (2), infrared spectroscopy was used to study the surface of zirconia. At room temperature two adsorption bands that appeared in the region 3800-3600 cm\(^{-1}\) were ascribed to surface hydroxyl groups and these species were still present after evacuating the catalyst at temperatures up to 773K. Yamaguchi, Nakano, Iizuka and Tanabe (3) investigated the reaction between adsorbed D\(_8\)-isopropyl alcohol and the surface hydroxyl groups and results showed that dehydration to form propene was accompanied by exchange of the deuterium atoms in the alcohol. Since the catalyst was able to extract both OH\(^-\) and H\(^+\) from the terminal methyl group, the authors concluded that zirconia possessed sites that were of moderate acid and basic strength. Exchange of the -OH groups by some labelled alcohols and other oxygen-containing compounds was reported by Yamaguchi, Nakano and Tanabe (4) and results for the exchange of propene with a deuterated catalyst sample provided evidence that the two types of hydroxyl groups reacted at different rates. The different types of -OH group were attributed to bridged and terminal species similar to those on rutile proposed by Jackson and Parfitt (5).
Wang, Hattori and Tanabe (6) and Nakano, Iizuka, Hattori and Tanabe (7) obtained information about the acid-base and catalytic properties of zirconia by examining the adsorption and reaction of selected molecules. Inspection of the infrared spectra of adsorbed pyridine and adsorption of carbon dioxide gave measures of the number of basic and acidic sites, and values observed differed when the temperature of catalyst pretreatment was varied. A maximum concentration of acid sites ($3.9 \times 10^{-8}$ mole m$^{-2}$) was reported after outgassing at 673K but a maximum for the number of basic sites ($1.7 \times 10^{-7}$ mole m$^{-2}$) was associated with the higher temperature of 973K. Nakano et al. (7) also studied the isomerization of but-1-ene and activity correlated best with the basic properties of the catalyst. The predominant product was cis-but-2-ene; hence it was suggested that the reaction proceeds via a basic carbanion mechanism. Results obtained from coisomerization of $D_0$- and $D_8$-but-1-ene were consistent with an intramolecular hydrogen transfer mechanism.

Onishi, Abe, Maruya and Domen (8) published evidence for infrared bands due to Zr-H and Zr-D species resulting from the dissociative adsorption of hydrogen over the catalyst at 298K. The hydrogenation of conjugated dienes using two different hydrogen sources was studied by Yamaguchi and Hightower (9) and later by Nakano, Yamaguchi and Tanabe (10). Zirconia was an active catalyst for hydrogenation with both $H_2$ and cyclohexadiene (catalytic transfer hydrogenation) although alkene product selectivity varied for the two source molecules. According to Yamaguchi and Hightower, neither equilibration of hydrogen and deuterium nor alkene exchange occurred when the molecules propene, 2-methylpropene, n-butene or 1,3-butadiene were passed over the catalyst in the presence of a mixture of $H_2$ and $D_2$ or just $D_2$. Addition to the alkenes between temperatures of 273-348K produced
alkane molecules containing two deuterium atoms. In the subsequent publication (10) catalyst activities for addition to the dienes were measured on samples which had been pretreated at different outgassing temperatures and maximum rates were observed at 873K and 1073K for hydrogenation using H₂ and cyclohexadiene respectively; H₂-D₂ equilibration was reported in the temperature range 323-348K and was fastest after evacuating the oxide at 873K. The observed change in product n-butenes found for ZrO₂, when cyclohexadiene was used instead of hydrogen, was not found for other oxide catalysts such as CaO, LaO and MgO (Shima and Yamaguchi (11)). In the latter cases, addition gave similar products irrespective of the hydrogen donor.

Results published in relation to the reactions of but-1-ene and 1,3-butadiene were in broad agreement with those reported by Halcom (12). His results were part of a general study of hydrogenation, oxidation and isomerization reactions involving hydrocarbons and carbon monoxide on zirconia.

The reactions of CO and CO₂ with hydrogen on zirconia has been a major source of study for numerous authors, particularly after 1986 when advanced analytical techniques such as FTIR, TPD and TPDE have become available (for example see He and Ekerdt (13-15) and Onishi and various co-workers (16-19)). Many surface species have been detected for the reaction, including methanol, dimethylether and 2-methylpropane, although product selectivity depends on catalyst preparation (18).

The reaction of alkenes with deuterium were studied in some detail in two reports. Products from the exchange of propene with either D₂ or D₂O on a series of oxide catalysts were examined using microwave spectroscopy by Hughes, Kemball and Tyler (20). Some experiments were conducted on an
industrial catalyst consisting of zirconia with 9.1 wt.% γ-alumina and <0.3 wt.% sulphur and the evidence suggested that the main intermediates on this sample were carbocations - in other words the catalyst acted as an acid by donating a proton to the alkene. Results for the reaction of 2-methylpropene with deuterium (and hydrogen), studied by gas chromatography and 2D-n.m.r. spectroscopy, are reported in Chapter 4. Alkene containing deuterium atoms was detected by n.m.r., although exchange was half as fast as addition at 415K and this contrasts with results found for basic oxides such as La₂O₃ and CaO, where exchange was the faster reaction.

Initial work relating to the present Chapter showed hydrogen (and deuterium) adding at similar rates for all alkenes studied. Therefore it was also decided to investigate H₂-D₂ equilibration on the sample in order to compare the rate of this reaction with those of the alkenes. The previous literature has indicated that both basic and acidic properties of zirconia are important in the catalytic reactions and with this in mind some of the experiments carried out in the present study involved isomerization of 3,3-dimethylbut-1-ene (33DMB1) since this reaction is known to occur on acid sites but not on basic sites (21). Some work on the reaction of 33DMB1 on zirconia has been reported (Tolvaj, Halasz and Gati (22)) but only at the rather high reaction temperature of 773K. As the influence of pretreatment temperature had been extensively studied in the earlier work, most of the present results were obtained after outgassing at 873K - the value which gave maximum rates for H₂-D₂ exchange and for hydrogenation of butadiene (10).
6.2 EXPERIMENTAL

Weighed samples of hydroxide (usually in the range 100 to 250 mg) were evacuated for three hours at 873K for catalytic experiments. The BET-N$_2$ surface areas were $69 \pm 7$ and $74 \pm 7$ m$^2$g$^{-1}$ for ZrO$_2$(I) and ZrO$_2$(II) respectively. Unless otherwise stated, runs were carried out using ZrO$_2$(I).

A pressure ratio of 5:1 hydrogen (or deuterium):alkene was used with 2.4 kPa of hydrocarbon corresponding to a change of ca. $2 \times 10^{20}$ molecules. The isomerization of 33DMB1 was followed using a pressure of 2.5 kPa ($8 \times 10^{19}$ molecules). Equal pressures of 3.5 kPa ($1.7 \times 10^{20}$ molecules) of hydrogen and deuterium were admitted to adjacent sections of the vacuum line and allowed to mix overnight at room temperature prior to equilibration experiments.

Reactions involving 33DMB1 were carried out on static line (II); all other experiments involving alkenes were followed on the recirculation system and static line (I) was used to study the equilibration of hydrogen and deuterium.

In some experiments hydrocarbon samples were analysed by $^2$D-n.m.r. and the technique described in Chapters 2 and 3 was employed. The procedure used to obtain results from the equilibration of hydrogen and deuterium is reported in Chapter 2.

6.3 RESULTS

6.3.1 Hydrogenation of Alkenes

Typical experiments for the hydrogenation of ethene are shown in Figure 6.1. At 273K there was a small decrease in rate during a period of about 20 minutes, followed by a steady reaction. This behaviour was common
Figure 6.1

The hydrogenation of ethene over 77 mg ZrO$_2$(l): □, 273 K; ○, 325 K.
to all alkene addition reactions in which less than 15% of the reactant was converted. Rates were calculated from the steady region. At 325K no initial fall in rate was detectable but some decline occurred at conversions above 50%. This was attributed to a small kinetic dependence of the rate on the alkene pressure and confirmed by plotting the results according to equation (2) of reference 23. A good straight line was obtained assuming $n = 0.2$ for the order of the hydrogen reaction with respect to alkene pressure.

The rates of reaction at various temperatures of ethene, propene and 33DMB1 are given as Arrhenius plots in Figure 6.2 which also includes results from the work in Chapter 4 with 2-methylpropene. There was good agreement between the results on ZrO$_2$(I) and ZrO$_2$(II) and the derived Arrhenius parameters are reported in Table 6.1. No isomerization of 33DMB1 was detected at 378K or below. The hydrogenation of 2,3-dimethylbut-2-ene (23DMB2) is reported in a later section.

### 6.3.2 Equilibration of Hydrogen and Deuterium

At 294K the silica vessel contributed 10% of the total observed rate and the net rate of equilibration on the zirconia was $2.8 \times 10^{15}$ molecules s$^{-1}$m$^{-2}$. At 348K the blank reaction contributed 15% and the net rate was $6.6 \times 10^{15}$ molecules s$^{-1}$m$^{-2}$. These rates were only slightly greater than the rates of hydrogenation of ethene as may be seen in Figure 6.2, and approximate values of the Arrhenius parameters for the equilibration derived simply from the two rates are included in Table 6.1.
Figure 6.2
Arrhenius plots for hydrogenation of alkenes and hydrogen/deuterium equilibration: open symbols ZrO$_2$(I), filled symbols ZrO$_2$(II); ◊, ethene; □, propene; Δ, 33DME1; ▲, H$_2$/D$_2$ equilibration. The dashed line is for 2-methylpropene from Chapter 4.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reactant</th>
<th>Temp. range T/K</th>
<th>Activation energy E/kJ mol$^{-1}$</th>
<th>Frequency factor log(A/molecules s$^{-1}$m$^{-2}$)</th>
<th>Rate at 300K r/molecules s$^{-1}$m$^{-2}$</th>
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<td>hydrogenation</td>
<td>ethene</td>
<td>246-425</td>
<td>18 ± 1</td>
<td>18.3 ± 0.2</td>
<td>1.5 x 10$^{15}$</td>
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<td>propene</td>
<td>291-414</td>
<td>16 ± 1</td>
<td>17.8 ± 0.1</td>
<td>1.0 x 10$^{15}$</td>
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<tr>
<td></td>
<td>33DMB1</td>
<td>294-378</td>
<td>20 ± 1</td>
<td>18.1 ± 0.2</td>
<td>5.6 x 10$^{14}$</td>
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<td>23DMB2$^a$</td>
<td>329-426</td>
<td>16 ± 1</td>
<td>16.3 ± 0.3</td>
<td>3.3 x 10$^{13}$</td>
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<td>2-methylpropene$^b$</td>
<td>273-432</td>
<td>16 ± 1</td>
<td>17.0 ± 0.1</td>
<td>1.6 x 10$^{14}$</td>
</tr>
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<td>294 and 348</td>
<td>14</td>
<td>17.9</td>
<td>2.9 x 10$^{15}$</td>
</tr>
<tr>
<td>isomerisation</td>
<td>33DMB1</td>
<td>410-528</td>
<td>23 ± 5</td>
<td>16.1 ± 0.5</td>
<td></td>
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</tbody>
</table>

$^a$ The alkene was rapidly converted to an equilibrium mixture of 23DMB2 and 23DMB1.

$^b$ Results from Chapter 4.
6.3.3 Poisoning with Carbon Dioxide

The technique described by Brown et al. (23) was used to study the effect of doses of carbon dioxide on the rate of hydrogenation of ethene at 273K. The steady rate of hydrogenation was measured for about one hour, a known amount of carbon dioxide was released into the reaction line from a 4.2 cm$^3$ doser positioned upstream from the catalyst and then after an interval of about 15 minutes the new lower rate of reaction was obtained. Results are shown in Figure 6.3 as percentage of the original rate against the amount of carbon dioxide admitted, expressed as a surface concentration. A small amount of carbon dioxide caused a sharp reduction in rate consistent with the existence of some active but easily poisoned sites and then activity declined linearly with the volume of carbon dioxide admitted. Extrapolation of the linear section of the curve indicated that $1.0 \pm 0.2 \times 10^{18}$ molecules m$^{-2}$ of carbon dioxide eliminated the catalytic activity. If the cross-sectional area of the molecule is assumed (24) to be 0.22 nm$^2$ this amount of carbon dioxide would have covered 22 $\pm$ 5% of the zirconia surface.

The surface of the catalyst was black after poisoning with carbon dioxide. The colouration remained after degassing the catalyst for three hours at 873K and little activity for hydrogenation of ethene ($<10^{13}$ molecules s$^{-1}$ m$^{-2}$) was found at 273K. But removal of the hydrogen-ethene mixture and treatment for three hours with 13 kPa of oxygen at 873K removed the black colour and restored the normal activity ($8.3 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$) for the hydrogenation of ethene at 273K.
Figure 6.3

Poisoning of ethene hydrogenation on 39mg ZrO$_2$(I) at 273K by addition of carbon dio
6.3.4 Further Results with Dimethylbutenes

Isomerization of 33DMB1 to 23DMB2 and 23DMB1 was slow in the temperature range 410 to 528K. Steady rates of reaction were found at the lower temperatures but at 528K a fall in activity was observed over two hours, even although the conversion had reached only 4% - well below the equilibrium value. This fall was attributed to self-poisoning and the catalyst was black at the end of the experiment. Rates used for the Arrhenius plot in Figure 6.4 were taken from the initial part of the reactions and the derived parameters are given in Table 6.1. The product ratio \( R = \frac{23DMB2}{23DMB1} \) was 4.7 at 448K but only 1.5 at 528K.

Some experiments were carried out with 33DMB1 on catalysts pretreated at 723K instead of the usual 873K. Such catalysts had a surface area of \( 143 \pm 10 \text{ m}^2\text{g}^{-1} \). They gave a rate of isomerization at 448K of \( 2.3 \times 10^{13} \text{ molecules s}^{-1}\text{m}^{-2} \) which was 20% faster than the rate on catalysts pretreated at 873K. In contrast, the rate of hydrogenation of 33DMB1 at 325K was only \( 1.5 \times 10^{12} \text{ molecules s}^{-1}\text{m}^{-2} \) which was 70 times slower than the rate for the normal catalysts.

Some reactions were carried out with 23DMB2 and either hydrogen or deuterium and a run at 430K is shown in Figure 6.5. A fast isomerization (\( >10^{16} \text{ molecules s}^{-1}\text{m}^{-2} \)) to 23DMB1 was observed but the rate declined rapidly as the equilibrium between the two alkenes was approached. Meanwhile, a slow but increasing rate of conversion to the alkane (23DMB) occurred and the shapes of the curves suggested that the route to alkane was through the 23DMB1 isomer. Arrhenius plots for the addition reaction are shown in Figure 6.4 and the derived parameters are given in Table 6.1. At the lower temperature of 328K, the initial rate of isomerization of 23DMB2 was \( 5 \times 10^{14} \text{ molecules s}^{-1}\text{m}^{-2} \) (see Figure 6.4).
Figure 6.4
Arrhenius plots for reactions of the dimethylbutenes on ZrO$_2$(I). The dashed line refers to hydrogenation of 33DMB1 (see Figure 6.2); Δ, deuteration of 33DMB1; □, hydrogenation and □, deuteration of 23DMB2 (and the isomer 23DMB1); ○, isomerization of 33DMB1; ■, isomerization of 23DMB2.
Figure 6.5

Reaction of 23DMB2 with deuterium at 430K over 116 mg ZrO₂(l): 
O, 23DMB2; □, 23DMB1; Δ, 23DMB.
6.3.5 Deuterium n.m.r. Spectroscopy

Deuterium n.m.r. spectroscopy was used to analyse the products from the reaction of four alkenes (ethene, propene, 33DMB1 and 23DMB2) with deuterium. In each case the reaction was followed by gas chromatography until about 15% to 25% of the alkene had been converted to alkane and the hydrocarbons were frozen and subsequently analysed.

The results with ethene and 33DMB1 indicated that addition occurred without detectable exchange of the alkene. The rate of deuteration of ethene at 312K was $9.8 \times 10^{14}$ molecules s$^{-1}$m$^{-2}$ (2.4 times slower than the rate of hydrogenation) and a sample containing 17% ethane gave a single resonance at $\delta = 0.835$ p.p.m. This value corresponds to that expected for the deuterium atoms in CH$_2$DCH$_2$D and showed that the reaction involved simple addition across the double bond of ethene. Rates of deuteration of 33DMB1 at 313 and 368K are shown in Figure 6.4. The n.m.r. spectrum of a sample from the higher temperature after 20% conversion to alkane had two resonances of similar intensity with $\delta = 1.193$ p.p.m. and $\delta = 0.804$ p.p.m. These values can be assigned to the secondary and primary deuterium atoms in (CH$_3$)$_3$CCHDCH$_2$D and again provide evidence for straight addition across the double bond. No evidence for exchanged alkene was found and 0.04 D/molecule would have been readily detected.

The deuteration of propene occurred at about half the rate of hydrogenation in the temperature range from 298 to 433K; the activation energy was $13 \pm 3$ kJmol$^{-1}$ and the frequency factor $\log A = 17.0 \pm 4$ molecules s$^{-1}$m$^{-2}$. N.m.r. spectra were obtained on samples at three temperatures. The chemical shifts associated with the various groupings of deuterium atoms in propane and the distribution of deuterium between these groupings are given in Table 6.2. The assigned values for the number of D atoms per molecule
Table 6.2
Groupings of Deuterium in Propane from the n.m.r. Spectra for the Reactions of Propene with Deuterium

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Chem. shift $\delta$/p.p.m.</th>
<th>Temp. (% conversion to alkane)</th>
<th>305K (12%)</th>
<th>394K (23%)</th>
<th>433K (28%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>305K (12%)</td>
<td>394K (23%)</td>
<td>433K (28%)</td>
<td></td>
</tr>
<tr>
<td>CHD(CX$_3$)$_2$</td>
<td>1.2997</td>
<td>49.9</td>
<td>47.0</td>
<td>47.0</td>
<td>0.90</td>
</tr>
<tr>
<td>CH$_2$DCH$_2$</td>
<td>0.8935</td>
<td>-</td>
<td>3.2</td>
<td>5.3</td>
<td>1.01</td>
</tr>
<tr>
<td>CH$_2$DCHD</td>
<td>0.8839</td>
<td>50.1</td>
<td>49.8</td>
<td>47.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

a X represents H or D.
b Values for secondary D are based on the relative amounts of the two types of primary D.
were based on the ratio of the peaks for primary D in CH₂DCH₂⁻ and
CH₂DCHD⁻. For example, for the sample obtained from reaction at 394K the
relative percentages for these two types of primary D were 6% and 94%.
Therefore, it was assumed that each molecule contained 0.94 secondary D
atoms.

No evidence for the exchange of propene was obtained from the n.m.r.
spectrum of the products from the reaction at 305K but small amounts of
deuterium in the propenes were observed in the samples from the two higher
temperatures. Results for the highest temperature, 433K, are given in
Table 6.3. The chemical shifts were similar to those observed previously
for propene exchanged over calcium oxide (26). Deuterium was present in
all possible positions of the molecule including that on the central carbon
atom. A comparison of the peak sizes for the propene and propane
resonances indicated that the total deuterium content of the propene was
0.08 D/molecule assuming 1.91 D/molecule (see Table 6.2) for the propane.
Since this amount of exchange had occurred during the time required to
convert 28% of the alkene to alkane, the addition reaction was about 3.5
times faster than exchange. A corresponding analysis of the sample from
the experiment at 394K showed 0.03 D/propene and a rate of addition 7 times
faster than exchange.

Even at 433K the exchange of propene contributed very little to the
amount of deuterium detected in the propane. It was assumed that the
average D/propene was half the final value of 0.08 and distributed as 0.01
on the central carbon and 0.03 on the terminal carbon atoms. Subtracting
those values from the figures in the last column of Table 6.2 gave 0.89 and
0.98 as the amounts of secondary and primary D acquired by the propane in
the addition process.
Table 6.3

Distribution of Deuterium in Propene from the n.m.r. Spectrum for the Reaction at 433K (28% Conversion to Propane)

<table>
<thead>
<tr>
<th>Position</th>
<th>Chem. shift δ/p.p.m.</th>
<th>%D</th>
<th>Relative amounts a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CD=CH₂</td>
<td>5.8545</td>
<td>19.2</td>
<td>1.12</td>
</tr>
<tr>
<td>D-C-H II</td>
<td>5.0563</td>
<td>15.3</td>
<td>0.89</td>
</tr>
<tr>
<td>CH₃-C-H</td>
<td>5.0563</td>
<td>15.3</td>
<td>0.89</td>
</tr>
<tr>
<td>H-C-D II</td>
<td>4.9631</td>
<td>14.2</td>
<td>0.83</td>
</tr>
<tr>
<td>CH₃-C-H</td>
<td>4.9631</td>
<td>14.2</td>
<td>0.83</td>
</tr>
<tr>
<td>-CH₂D</td>
<td>1.7131</td>
<td>51.3</td>
<td>3.00</td>
</tr>
</tbody>
</table>

a Relative to -CH₂D = 3.00.
Analysis of a sample from the reaction of 23DMB2 with deuterium, shown in Figure 6.5, provided information on alkene exchange and the nature of the addition reaction. Deuterium was readily detected in the methyl groups of 23DMB2, all of which are equivalent; it was also found in the two types of methyl group of 23DMB1 in the expected 2:1 ratio but was not detected in the tertiary position or in the methylene group. Both alkenes had similar values for total D/molecule and this showed that the isomerization was mainly intramolecular. If there had been participation of deuterium in the formation of 23DMB1, it would have had a higher deuterium content than the reactant 23DMB2.

It was assumed that each alkane molecule (23DMB) had one tertiary deuterium atom in order to calculate the relative numbers of D/molecule given in the last column of Table 6.4. Simple addition of deuterium across the double bond of 23DMB2 would lead to alkane with only tertiary deuterium but simple addition to 23DMB1 would give alkane with equal amounts of primary and tertiary deuterium. Clearly, the experimental results agreed more closely with the latter alternative and confirmed that the route to alkane was through the isomer 23DMB1. The build-up of about 0.065 D/molecule in the alkenes during a period which gave 5% addition showed that for this system exchange was some 30% faster than addition.

6.4 DISCUSSION

The catalysts used in this work can be compared with those used by Nakano et al. (7). ZrO₂(II) and ZrO₂(III) had a greater surface area by factors of about two with values of 69 and 74 m² g⁻¹ for samples pretreated at 873K compared with their value of 32.1 m² g⁻¹. On the other hand, the amount of carbon dioxide, 1.0 x 10¹⁸ molecules m⁻², needed to
<table>
<thead>
<tr>
<th>Compound</th>
<th>(%)</th>
<th>Position</th>
<th>Chem. shift $\delta$/p.p.m.</th>
<th>%D</th>
<th>D/molecule $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23DMB2</td>
<td>75.8</td>
<td>CDX$_2^-$</td>
<td>1.640</td>
<td>27.2</td>
<td>0.062</td>
</tr>
<tr>
<td>23DMB1$^b$</td>
<td>19.2</td>
<td>CDX$_2$C=</td>
<td>1.70</td>
<td>2.6</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CDX$_2$)CX(CX$_3$)$^-$</td>
<td>1.02</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>23DMB</td>
<td>5.0</td>
<td>CD(CX$_3$)$_2^-$</td>
<td>1.376</td>
<td>29.2</td>
<td>1.00$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CDX$_2$)CX(CX$_3$)$^-$</td>
<td>0.824</td>
<td>35.5</td>
<td>1.20</td>
</tr>
</tbody>
</table>

$a$ X represents H or D.

$b$ No signals were detected apart from D atoms in the methyl groups.

$c$ Relative to an assumed value of 1.00 for the tertiary D in the alkane.
poison the hydrogenation of ethene at 273K on ZrO$_2$(l) was lower than the amount, $2.3 \times 10^{18}$ molecules m$^{-2}$, which they reported for irreversible adsorption of carbon dioxide at 373K. Likewise, the rate, $2.6 \times 10^{16}$ molecules s$^{-1}$ m$^{-2}$ of H$_2$-D$_2$ exchange found by the Japanese group (10) for zirconia outgassed at 873K was about four times greater than the present rate at 348K of $6.6 \times 10^{15}$ in the same units but the details about conditions used in their work are not available to enable the two sets of experiments to be compared accurately.

The poisoning experiments which were carried out using carbon dioxide can only provide an upper limit to the number of catalytic sites because adsorption is likely to occur simultaneously on other sites. These considerations may explain why the amount of carbon dioxide needed to eliminate activity for the hydrogenation of ethene is an order of magnitude greater than the number of basic sites on zirconia ($10^{17}$ m$^{-2}$) determined by the formation of diphenylnitroxide radicals from adsorbed diphenylamine (7). The present results for poisoning of zirconia are not unlike those reported for zinc oxide (23) for which $2.3 \times 10^{18}$ molecules m$^{-2}$ of carbon dioxide were required to prevent the hydrogenation of ethene at 273K. Assuming a cross-sectional area of 0.22 nm$^2$ for the molecule of carbon dioxide, some 50% of the zinc oxide was covered compared with 22% for zirconia.

6.4.1 Hydrogenation and Isomerization of Alkenes

In this section the rates of reaction of the various alkenes on zirconia will be discussed and the catalytic behaviour of zirconia will be compared with some other oxides. More detailed consideration of probable adsorbed intermediates and possible mechanisms will be discussed in the following section.
The results in Figure 6.2 show that the rate of the $\text{H}_2\text{-D}_2$ equilibration reaction is only slightly faster than the rate of the fastest hydrogenation (that of ethene) on zirconia. So it is possible that the ability of the catalyst to activate hydrogen, as measured by the $\text{H}_2\text{-D}_2$ reaction, may be a controlling factor in relation to the activity of the catalyst for the hydrogenation of alkenes. If the supply of hydrogen, either as molecules or in the dissociated form, is the limiting step in the addition process, the similarity of the activation energies for the equilibration reaction and for the hydrogenation of the different alkenes (Table 6.1) may be explained. The fact that the rates for all the alkenes studied (with the exception of the special case of 23DMB2 to be discussed later) show a spread of less than a factor of 10 is further support for a common rate-determining process which is not greatly influenced by the nature or the shape of the alkene molecule. It is also relevant to note that the rates of the direct hydrogenation of butadiene were found by Nakano and co-workers (10) to be about 25% of the rate of the $\text{H}_2\text{-D}_2$ reaction (assuming that the two sets of data shown in their Figure 1 were obtained under comparable conditions). So with the diene as with the alkenes, the supply of hydrogen may be the controlling process for hydrogenation on zirconia.

The possible rate-determining role of hydrogen activation on zirconia is not unlike the situation found on titanium dioxide (rutile) for the reactions of alkenes, except that much higher temperatures are needed to achieve appreciable rates with rutile catalysts. The $\text{H}_2\text{-D}_2$ equilibration occurs at $10^{15}$ molecules s$^{-1}$m$^{-2}$ at 260K on zirconia but a temperature (27) of over 500K was required for this rate on rutile. Again, even at 673K the rates of hydrogenation (Lake and Kemball (28)) of ethene or propene on...
rutile were only $10^{14}$ and $10^{13}$ molecules s$^{-1}$m$^{-2}$ respectively, whereas rates of this magnitude were obtained on zirconia below 300K (see Table 6.1).

Comparisons can also be made between the rates of hydrogenation of ethene or propene on zirconia and corresponding data determined under similar conditions for the same reactions on zinc oxide (23) and on lanthana (see Chapter 3). For zinc oxide, the rates at 300K for the hydrogenation of ethene or propene are $2.7 \times 10^{15}$ or $4.0 \times 10^{13}$ molecules s$^{-1}$m$^{-2}$, and for lanthana, $2.2 \times 10^{18}$ or $1.3 \times 10^{15}$ in the same units. So at 300K zirconia and zinc oxide exhibit similar efficiency as catalysts for the hydrogenation of ethene while zirconia and lanthana show comparable activity for the hydrogenation of propene. The factor which varies markedly with the three oxides is the ratio of the ethene/propene rates at 300K; these ratios are 1.5, 70 and >1000 for ZrO$_2$, ZnO and La$_2$O$_3$ respectively. The high ratios on zinc oxide and lanthana have been attributed to the blocking of the sites needed for hydrogenation by the formation of adsorbed allyl species from propene. The absence of a high ratio on zirconia may be a consequence of the rate-limiting supply of hydrogen or of a lesser tendency for propene to dissociate to form allyl species.

Zirconia is not an efficient catalyst for the isomerization of 33DMB1 as a temperature of around 570K was needed to attain a rate of $10^{14}$ molecules s$^{-1}$m$^{-2}$, and the ratio of hydrogenation/isomerization was about 300 at 400K (see Figure 6.4). Previous work (21, 29) has demonstrated that a catalyst must have acidic properties, which can involve Bronsted acidity or possibly Lewis acidity, in order to isomerize 33DMB1 and so it is not surprising that zirconia pretreated at 873K is a poor catalyst for this reaction. In contrast to the results for hydrogenation of alkenes, rutile (27) is one of the more active oxides.
for the isomerization of 33DMB1 as a rate of $10^{14}$ molecules $s^{-1} m^{-2}$ is attained at 350K and the same rate can be achieved around 400K on alumina (29). On the other hand, zinc oxide and lanthana, like zirconia, are not effective catalysts for the reaction. A temperature of 520K was needed to give a rate of $10^{14}$ molecules $s^{-1} m^{-2}$ on zinc oxide (30) and no appreciable reaction was detected on lanthana (Chapter 3) at 510K. The use of temperatures in excess of 500K with the alkene/oxide systems can lead to self-poisoning as observed in the present work with 33DMB1 on zirconia at 528K. The fact that the isomerization was marginally faster on zirconia outgassed at 723K rather than 873K is consistent with the earlier work (7) which indicated that acidic properties were associated with lower outgassing temperature, preferably around 673K.

The relative rates of isomerization and addition with 2,3DMB2 are shown in Figure 6.4 and they contrast markedly with those for 33DMB1. The isomerization was a rapid reaction on zirconia at 328K but addition took place ten times more slowly. The evidence from the deuterium n.m.r. experiment with 23DMB2 showed that the route to the alkane was through the isomer 23DMB1 and indicated the probability of considerable steric hindrance for the direct hydrogenation of 23DMB2.

6.4.2 Exchange Results and Possible Mechanisms

For the discussion of the results on the exchange of the alkenes with deuterium and the evidence from n.m.r. spectroscopy about the distribution and groupings of deuterium atoms in the products, it is helpful to relate the behaviour of individual alkenes to the possible reactions set out in Scheme 6.1. This shows the main routes by which alkene exchange may take place, the possible steps in the formation of alkane, and includes the
Scheme 6.1

General scheme for the reactions of alkenes with deuterium on zirconia.
intermediates which are likely to be involved in the isomerization reactions as well. The scheme is simplified by the omission of reference to any charges or partial charges on the adsorbed intermediates but such charges may have an important bearing on what is likely to happen with some reactants, particularly on the more highly ionic oxides. In general, exchange may occur through reversible dissociation either to vinyl or allyl species or by reversible association to alkyl species. The position of deuterium atoms in the product molecules formed at low conversions can be a useful guide to likely mechanisms but equally the absence of exchange of a particular type is just as valuable as an indication of the reactions which do not contribute.

The absence of any detectable exchange with ethene and 33DMB1 shows that these molecules do not readily undergo reversible dissociation to adsorbed vinyl species. Furthermore, if we accept that alkane formation occurs by the stepwise route through reactions (5) and (7), the alkyl reversal reaction (6) must be slow compared with (7). Behaviour of this kind was found for the reaction of ethene (31) and cyclopentene (32) on zinc oxide and, for these systems, the rate-determining step in the addition process was reaction (5), the formation of adsorbed alkyl. But for zirconia we should not exclude the possibility that the addition reaction takes place by a one-step process, not shown in the Scheme, involving the addition of a molecule of hydrogen or deuterium. This suggestion would be in keeping with the facts, i.e. that no alkene exchange occurs and that each alkane formed has two deuterium atoms in the expected places, and has been put forward as a possible mechanism for ethane formation on zinc oxide (33). An alternative to the concept of direct molecular addition is stepwise reactions involving the two hydrogen or deuterium atoms which are
to be added being held on pair sites in the surface (31, 32). Activation of hydrogen or deuterium by adsorption on a pair site would enable the addition reaction to occur without accompanying either exchange of the alkene or the $H_2$-$D_2$ equilibration reaction.

The results with propene are important as a guide to possible mechanisms. Exchange was not detected at 305K but at 433K it occurred at about 25% of the rate of the addition reaction. The interesting feature was that the hydrogen atom on the central carbon was exchanged just as readily as the remaining five hydrogen atoms (see Table 6.3). This behaviour is in marked contrast to results for propene exchange on calcium oxide or alumina (26), both of which gave negligible exchange on the central carbon and on lanthana (see Chapter 3), which gave little such exchange.

The replacement of the hydrogen atom on the central carbon of propene cannot be achieved by reversible formation of either allyl or prop-2-yl adsorbed species, but must involve either vinyl or prop-1-yl species. When a vinyl mechanism occurs, e.g. on alumina (26), exchange of the terminal methylene group is more rapid than the replacement of the hydrogen on the central carbon. Steric factors may be responsible for this difference in rate since the linking of a propen-2-yl species to the surface may be more difficult than the corresponding process with a propen-1-yl intermediate. Since preferential exchange of the methylene hydrogen atoms was not found with zirconia, a vinyl mechanism is less likely than a process involving prop-1-yl intermediates. It follows that there must be a limited amount of alkyl reversal at temperatures of 400K or above. The slightly greater degree of exchange of the hydrogen on the central carbon suggests that reversible formation of prop-1-yl occurs somewhat more readily than the same process with prop-2-yl. This suggests that the alkyl species is unlikely to
be cationic in character because a positive charge would facilitate the formation of the 2-yl species rather than 1-yl. The type of propene exchange observed in the present work with pure zirconia contrasts with earlier results for the reaction carried out on sulphur-treated zirconia or zirconia-alumina catalysts (20). Those results showed exchange limited to the five terminal hydrogen atoms and were consistent with acidic type catalysis via secondary carbocationic alkyl species.

While alkyl reversal would be a sufficient mechanism to account for the exchange of all hydrogen atoms of propene, it is not possible to exclude a contribution from a \( \pi \)-allyl mechanism to the exchange of the five terminal hydrogen atoms but it is clearly not the dominant mechanism on zirconia. The importance of \( \pi \)-allyl mechanisms on zirconia may increase with the size of the alkene. Results from Chapter 4 for 2-methylpropene, which showed exchange at 433K at about half the rate of the addition reaction, were consistent with a \( \pi \)-allyl mechanism since the deuterium was randomly distributed in the alkene. The isomerization, which took place with 23DMB2 relatively rapidly, compared with either exchange or formation of alkane was essentially an intramolecular process because the product isomer, 23DMB1, contained no more deuterium than the reactant. The most likely mechanism for this reaction on zirconia is hydrogen transfer through the reversible formation of \( \pi \)-allyl intermediates, although for more acidic surfaces an associative route through tertiary carbocationic alkyl species could be important.

The principal conclusions about mechanisms of alkene reactions with deuterium on zirconia are:
120.

(1) Alkane formation occurs in such a manner that the products contain two deuterium atoms in the expected positions. Adsorption of deuterium on pair sites may be involved.

(2) The extent of alkene exchange only becomes significant at temperatures of 400K or above. The reaction must involve some degree of alkyl reversal with propene.

(3) The reversible formation of π-allyl intermediates contributes to exchange and isomerization to an extent which varies with the nature of the alkene. Even in the presence of deuterium, isomerization tends to involve intramolecular reaction as shown by the present results with 23DMB2 and previous work with but-1-ene (7, 12).
6.5 REFERENCES


30. Housley, J.D., unpublished work.
CHAPTER 7

Reactions of Alkenes on Titania (Anatase).
7.1 INTRODUCTION

The surface and catalytic properties of titania have been the subject of many previous investigations. However, in some of the published work the authors did not indicate which crystal form of the oxide was used. Most of the literature concerned rutile samples, although a considerable amount relates to anatase. In this Chapter some catalytic reactions (hydrogenation and isomerization) of different hydrocarbon molecules on anatase have been investigated.

Infrared studies of the surface hydroxyl groups of TiO₂ have been carried out by many schools of workers. The main results were summarised by Parkyns (1) and it was shown that numerous infrared bands appeared after heating the oxide under vacuum. For example, on a pure anatase sample Parkyns reported evidence for four different hydroxyl groups (3630-3730 cm⁻¹) and adsorbed water after evacuation at 298K. Following evacuation at 673K all the hydroxyls were still present and the situation remained the same on treating the catalyst in the presence of oxygen. Primet, Pichat and Mathieu (2) related the differences between the types of hydroxyl groups to their position in the crystal lattices and then proposed that isolated and bridged groups appeared on the spectra with different frequencies. The hydroxyl species were completely exchanged by deuterium in D₂O and D₂ at temperatures below 473K, although the catalysts themselves were reduced (with formation of Ti³⁺ and D₂O) by exposure to D₂ at 523K. The reaction between the surface hydroxyl groups of rutile and deuterium was studied in greater detail with the use of mass spectrometry (Brookes (3), Lake and Kemball (4)). The latter authors calculated a population of 3.4 OH/A² for a surface outgassed at 723K. Boehm and Herrmann (5) used deuterium exchange and thermogravimetric analysis
to calculate a value of $4.9 \, \text{OH}/\text{Å}^2$ for an anatase sample which was evacuated at 423K; however these hydroxyls were thermally decomposed at 623K.

The acidic and basic properties of titania were studied by Primet, Pichat and Mathieu (6) using adsorption of various gas molecules. Anatase showed amphoteric character since adsorption of both acidic (CO$_2$) and basic ((CH$_3$)$_3$N) molecules occurred at room temperature. The main technique used for the investigation was infrared spectroscopy and this was also used to study adsorption of many other molecules on titania including pyridine (7), carbon dioxide (8) and some aliphatic alcohols (9) on anatase, and acetic acid (10), acetone (11) and primary alcohols (12) on rutile. A summary of results of the adsorption studies was provided by Knozinger (13) and Benesi and Winquist (14). Temperature programmed desorption (TPD) of water from the surface of anatase was discussed in a communication by Munuera, Moreno and Prieto (15).

Harris and Rossington (16) carried out a kinetic study of the ortho-para hydrogen conversion (analysed by microthermal conductivity) and the equilibration reaction of hydrogen and deuterium (mass spectrometry) on anatase. Both reactions were first order at temperatures of 773K or less. Hydrogen-deuterium equilibration was studied in the temperature range 93-773K with maximum activities appearing at 123K and 173K. Activation energies for the equilibration varied depending on the temperature range being studied, although approximate values of 4-29 kJmol$^{-1}$ were reported between room temperature and 423K.

Isomerization of butenes on anatase was examined at 393K by Lemberton, Perot and Guisnet (17). The use of deuterium-labelled reactants led to the suggestion that isomerization can proceed through three different
mechanisms involving adsorption on to Bronsted and Lewis acid sites and basic sites, depending on pretreatment temperature.

A three part study of the interaction of some preadsorbed alcohols (e.g. methanol, ethanol and butanol) with TiO$_2$ was reported by Carrizosa and Munuera (18, 19) and Carrizosa, Munuera and Castanar (20). Most of the work was concerned with decomposition of the alcohols on an anatase sample and products were examined using infrared and temperature programmed decomposition studies. The authors proposed that the alcohols from C$_2$ to C$_5$ underwent dehydration, leading to the corresponding alkene, by way of a concerted monomolecular $\beta$-E2 elimination. It was suggested that such a mechanism involved a synchronous weakening of the C-O bond by an acidic site and the abstraction of a $\beta$-hydrogen by a basic site. Bimolecular dehydration of methanol to ether was observed on anatase (20) in the temperature interval 623-673K, although coking of the catalyst prevented a kinetic study from being conducted. There was also some evidence for the presence of alkyl-titanium (Ti-CH$_3$) species which produced propene via a Ziegler-Natta polymerization mechanism from the reaction of either ethene or ethanol with preadsorbed methanol. Al-Mushta, Davanso and Sheppard (21) reported infrared spectroscopic evidence for an alkylidene-titanium (Ti=CR$_2$) polymer end group during polymerization of ethene on a sulphate-anatase catalyst.

The oxidation of alcohols including propan-2-ol (22) and butan-2-ol (23) has been studied on anatase and the catalyst showed low activity for dehydrogenation of cyclohexane at temperatures above 673K (24).

Rutile was a useful catalyst for mechanistic studies of hydrocarbons and much of the work has been described in various theses (e.g. 3, 25-28). Isomerization of n-butenes was studied by Shannon, Lake and Kemball (29) at temperatures above 373K and the mechanisms were thought to involve ionic
intermediates with formation of carbanions and carbocations from base- and acid-catalyzed reactions respectively. In fact these results are similar to those reported on anatase (17). The acidic nature of rutile was also highlighted by Brookes (3) since the catalyst was active for isomerization of 3,3-dimethylbut-1-ene.

Exchange and addition reactions of ethene, propene and 2-methylpropene with deuterium over rutile were examined by Lake and Kemball (4). Although deuteration was observed in the temperature range 523-723K the most interesting results related to the exchange reaction where the formation of radical intermediates on the surface was proposed. In fact, literature relating to the mechanism of exchange of 2-methylpropene on rutile was discussed in more detail in Chapter 4. Lake and Kemball (4) also examined the exchange of benzene, toluene and m-xylene and within each molecule hydrogen atoms were replaced at different rates depending on their location. More detailed mechanistic studies of propene were carried out using microwave spectroscopy; exchange using D₂ and D₂O (Hughes, Kemball and Tyler (30)) led to the belief that a rapid double bond shift took place via an allyl intermediate. The reaction of D₂-propene in the absence of deuterium gas was studied by John, Kemball, Dickinson and Tyler (31) and they reported that the deuterium was scrambled throughout the alkene by way of an intramolecular double bond shift. High temperature exchange reactions of alkanes were studied by Halliday, Kemball, Leach and Scurrrell (32) and the main exchange process was thought to involve an adsorbed radical species. Dehydrogenation of the alkane and multiple exchange of the resulting alkene were also reported.

Since anatase and rutile are both tetragonal crystal systems, they are anisotropic materials. In effect the physical properties such as
refractive index and thermal conductivity of the two forms of titania are often quite different. Therefore in the present work it was decided to study some of the catalytic reactions of anatase in order to compare results with those reported for rutile.

7.2 EXPERIMENTAL

The catalyst (0.5-1.0g) was pretreated at 723K using the method described in Chapter 2. Following this procedure the oxide had a measured BET-$N_2$ surface area of $50 \pm 5 \text{ m}^2\text{g}^{-1}$.

The course of each hydrocarbon experiment was followed using gas chromatography and the equilibration of hydrogen and deuterium was analysed using mass spectrometry. The $^2D$-n.m.r. spectrum of products from the reaction of 2-methylpropene with deuterium was obtained using the method described in Chapter 2. For the latter experiments the recirculation system was used and the $H_2$-$D_2$ equilibration was studied on static line (I). All other experiments were carried out on static line (II).

A pressure ratio of 10:1 for hydrogen (or deuterium):alkene was used with 1.2 kPa hydrocarbon corresponding to a charge of ca. $3.8 \times 10^{19}$ molecules. For reactions involving 3,3-dimethylbut-1-ene (33DMB1) a hydrocarbon pressure of 2.5 kPa ($8.0 \times 10^{19}$ molecules) was used and the experiments with hydrogen and deuterium had 3.5 kPa ($1.7 \times 10^{20}$ molecules) of each gas.

Reaction rates were usually measured using plots of percentage reactants versus time and a more detailed analysis of the hydrogenation of ethene is described later. The data obtained from mass spectral analysis of the equilibration experiments was treated in the way described in Chapters 6 (for zirconia) and 2.
7.3 RESULTS

After pretreatment in oxygen at 723K the fresh catalyst appeared a yellow colour and it was only after the second dose of the gas at room temperature that the samples were white.

7.3.1 Hydrogenation of Alkenes

Hydrogenation of ethene was studied in the temperature range 383-499K. The course of reaction at 395K and 499K is shown in Figure 7.1. At the lower temperature a short induction period lasting ten minutes was followed by a steady reaction. The rate was obtained from the linear part of the graph. At the higher temperature a fast reaction took place with a constant rate until ca.50% alkene was converted. The rate then decreased as the reactant was used up but the initial slope gave a value of $1.29 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$.

Tests were carried out to see how well the course of the reaction at 499K could be interpreted in terms of the Langmuir isotherm. The method used is identical to that described by Brown, Kemball and Taylor (33) for the reactions of alkenes on zinc oxide. If adsorption of the alkene obeys the Langmuir isotherm and the rate of hydrogenation (dp/dt) is proportional to the amount of surface covered by alkene ($\theta$) then equation (1.3), the Langmuir equation, is applicable. In the present context we have:

$$-\frac{dp}{dt} = k_L \theta = k_L \frac{bp}{1+bp} \quad (7.1)$$

Where $p$ is the pressure of alkene, $k_L$ is a rate constant and $b$ is the adsorption coefficient. The above expression only applies to unimolecular reactions and ignores the effect that changes in hydrogen pressure may have on adsorption of the reactants during the course of the
Figure 7.1

The course of reaction for hydrogenation of ethene on 1 g anatase at 395\textdegree\text{K}, \(\Box\), and 499\textdegree\text{K}, \(\bigcirc\).
reaction. Integration of equation (7.1) gives:

$$\frac{1}{b} \ln p + p = -k_L t + c$$  \hspace{1cm} (7.2)

where $c$ is a constant. By drawing tangents to the plots of conversion against time in the later stages of the reaction it was possible to obtain values of $dp/dt$ at a series of different values of $p$, once the percentage of alkene at time $t$ was converted into a pressure. A plot of $dt/dp$ against $1/p$ was used to derive $b$ and the value obtained was used to plot the results for $p$ and $t$ according to equation (7.2). The final graph is shown in Figure 7.2 and the straight line serves as evidence that the Langmuir isotherm is valid. From this experiment $b$ was calculated as 410 atm$^{-1}$ and $k_L = 1.51 \times 10^{14}$ molecules s$^{-1}$ m$^{-2}$. The initial pressure (0.011 atm) was used to calculate a value of 0.82 for $\Theta_0$, the initial coverage. The constant $b$ is related to $\Delta G^0$, the standard free energy of adsorption of 1 atm of material from the gas phase on to a half covered surface as follows:

$$\Delta G^0 = RT \ln \frac{p_2}{p_1}$$

and since $\Theta = 0.5$, $p_2 = 1/b$

$$\Delta G^0 = -RT \ln b$$  \hspace{1cm} (7.3)

Using equation (7.3) a value of $\Delta G^0 = -25.0$ kJmol$^{-1}$ was calculated.

The initial rates for ethene hydrogenation are shown as an Arrhenius plot in Figure 7.3 and activation parameters are given in Table 7.1.

Hydrogenation of propene was studied in the temperature interval 403-514K. The catalyst behaved in a way similar to that observed for hydrogenation of ethene, and rates obtained from the percentage against time plots are compared for different temperatures in the Arrhenius plot in Figure 7.3. Activation parameters are given in Table 7.1.

Hydrogenation of cyclopentene (I) was studied at 420K and 524K. At the lower temperature the initial rate was $1.9 \times 10^{12}$ molecules s$^{-1}$ m$^{-2}$ but the graph was non-linear and the reaction appeared to poison the catalyst.
Figure 7.2

Plot to test the applicability of the Langmuir isotherm to ethene hydrogenation at 499K on 1 g anatase.
Figure 7.3
Arrhenius plot for hydrogenation reactions on anatase. 
\(\triangle\), ethene; \(\square\), propene; and \(\bullet\), cyclopentene. 
\(\nabla\), and \(\nabla\), refer to formation of 2,3-dimethylbutane from the reaction of 2,3DMB1 with \(H_2\) and after isomerization of 3,3DMB1 in the presence of \(H_2\) respectively; \(\bigcirc\), equilibration of \(H_2\) and \(D_2\).
Table 7.1
Activation parameters for reactions of alkenes and $\text{H}_2$-$\text{D}_2$ equilibration on anatase

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temp. Range</th>
<th>Activation Energy ($E / \text{kJmol}^{-1}$)</th>
<th>Frequency Factor (Log(A/molecules s$^{-1}$ m$^{-2}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenation of Ethene</td>
<td>383-499</td>
<td>45 ± 4</td>
<td>18.9 ± 0.5</td>
</tr>
<tr>
<td>Hydrogenation of Propene</td>
<td>403-514</td>
<td>47 ± 3</td>
<td>18.7 ± 0.3</td>
</tr>
<tr>
<td>Isomerization of 33DMBl</td>
<td>332-381</td>
<td>61 ± 2</td>
<td>21.5 ± 0.9</td>
</tr>
<tr>
<td>Isomerization of 33DMBl (In the presence of hydrogen)</td>
<td>317-385</td>
<td>57 ± 3</td>
<td>23.1 ± 0.3</td>
</tr>
<tr>
<td>Hydrogen-deuterium equilibration</td>
<td>374-480</td>
<td>25 ± 12</td>
<td>18 ± 2</td>
</tr>
</tbody>
</table>
After two hours, less than 2% cyclopentane was produced and the reaction rate had fallen to $1.1 \times 10^{12}$ molecules $s^{-1} m^{-2}$. At 524K the graph showing the course of reaction with time also indicated catalyst poisoning. The initial rate ($6.8 \times 10^{12}$ molecules $s^{-1} m^{-2}$) at the higher temperature is compared with the results for ethene and propene in Figure 7.3. The catalyst was black after the reactions involving cyclopentene and, in order to investigate the amount of gas phase hydrocarbon being lost by adsorption on to the surface, plots of integrator counts against sample number were constructed. Figure 7.4 shows a comparison between results observed under different conditions. The slopes for the reactions on the catalyst at 420K and 524K indicated losses of 2.6 and 4.8% sample$^{-1}$ respectively, compared with an expected loss of 1.0% sample$^{-1}$ for the empty vessel at room temperature.

The reaction of 2-methylpropene was studied at temperatures of 414K and 500K on the static vacuum line and, although less than 1% of 2-methylpropane was produced in the first five minutes of the run, there was no further reaction. In the presence of 0.5g catalyst the height of the peaks from the spectrum fell to less than 25% of their original value in 30 minutes at both temperatures. Inspection of the catalyst after the experiments showed that a black residue had formed on the surface.

An attempt was made to study the reaction of 2-methylpropene with deuterium at 575K and, in order to try and improve the experimental conditions, the recirculation apparatus was used. With a 0.9 g catalyst sample a slow, but well behaved, reaction was observed. The rate of addition was $7.01 \times 10^{12}$ molecules $s^{-1} m^{-2}$, i.e. 33 times slower than that ($2.34 \times 10^{14}$ molecules $s^{-1} m^{-2}$) obtained for hydrogenation of propene by extrapolation of the data from Figure 7.3.
Figure 7.4

Loss of cyclopentene(I) due to sampling: $\bigcirc$, at 524K and $\bullet$, at 420K in the presence of 1 g anatase; $\Box$, without catalyst at 298K.
A hydrocarbon sample consisting of 96.84% 2-methylpropene and 3.16% 2-methylpropane was collected for $^2$D-n.m.r. analysis after 162 minutes. Treatment of the results from the spectrum of the alkene was identical to that given in Chapter 4, and the distribution of deuterium in the different positions is given in Table 7.2. The chance of having a deuterium atom in each position ($d$) was calculated as 0.222 which indicates that 1.78 D atoms were present in each molecule. For comparison, the results expected for a random distribution of deuterium atoms are also given in the Table.

Inspection of the data shows good agreement between the two sets of results. Assuming a $\phi_\infty$ value of 530 (see Chapter 4), it appeared that on average the alkene contained 0.98 D/molecule during the experiment and the rate of exchange was calculated as $6.24 \times 10^{14}$ molecules $^{-1}$m$^{-2}$ s$^{-1}$ i.e. 89 times faster than addition.

Since the amount of 2-methylpropane present in the sample was small, it was not possible to identify deuterium in the tertiary position of the alkane. However, on close inspection of the spectrum a small peak appeared with $\delta = 0.88$ p.p.m. and this resonance was assigned to deuterium on the methyl group of 2-methylpropane. It was not possible to accurately measure the intensity of the peak, although a rough estimation indicated that it corresponded to some 3-5% of the total amount of deuterium atoms in the methyl groups of the alkene.

7.3.2 Equilibration of Hydrogen and Deuterium

Equilibration of hydrogen and deuterium was studied in the temperature range 374-480K and a typical first order plot obtained from the reaction conducted at the lowest temperature is shown in Figure 7.5. Rates are reported in the form of an Arrhenius plot in Figure 7.3 and the approximate
Table 7.2

Groupings of deuterium atoms in 2-methylpropene from the n.m.r. spectrum\textsuperscript{a}

<table>
<thead>
<tr>
<th>Grouping</th>
<th>% Expt.</th>
<th>%Calc.\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>=CHD</td>
<td>18.6</td>
<td>19.4</td>
</tr>
<tr>
<td>-CD\textsubscript{2}</td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td>-CH\textsubscript{2}D</td>
<td>45.5</td>
<td>45.4</td>
</tr>
<tr>
<td>-CHD\textsubscript{2}</td>
<td>25.1</td>
<td>25.9</td>
</tr>
<tr>
<td>-CD\textsubscript{3}</td>
<td>5.3</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} After 162 minutes at 575K.

\textsuperscript{b} Calculated for a random distribution with a chance of d = 0.222.
Figure 7.5

First order reversible plot for equilibration of H₂ and D₂ over 1 g anatase at 374K.
activation energy is given in Table 7.1. Some reaction occurred on the walls of the empty reaction vessel and the rate was 10% of the values observed with the catalyst present. The results given in the Arrhenius plot took account of the latter observation. The blank reaction took place at a rate ten times slower when the vessel had been treated in oxygen at 723K than when it was simply outgassed at 873K (see Chapter 6).

7.3.3 Reactions of Dimethylbutenes

3,3-dimethylbut-1-ene

Isomerization of 33DMB1 to produce 2,3-dimethylbut-1-ene (23DMB1) and 2,3-dimethylbut-2-ene (23DMB2) was studied between 332K and 381K and plots of log (% composition) against time were linear for the initial period of the reaction. This suggested that the reaction followed first order kinetics as described by the equation:

$$\log (x) = -\frac{kt}{230.3} + \log 100$$

(7.4)

where x is the percentage of 33DMB1 at time, t and k is the rate constant for isomerization in % min\(^{-1}\). The reaction was well behaved at the lower temperatures in the range inspected but a gradual fall in rate with conversion was observed at temperatures of 354K and above. The catalyst was black after these experiments. Results are shown in the Arrhenius plot in Figure 7.6, and activation parameters are given in Table 7.1. The results reported for rutile (Brookes (3)) are shown for comparison in Figure 7.6 and these results gave an activation energy of approximately 70 kJmol\(^{-1}\) with log A = 24.3 molecules s\(^{-1}\)m\(^{-2}\). The ratio of the products 23DMB2/23DMB1 from the reaction on anatase was close to the value calculated for equilibrium; for example at 332K the experiment
Figure 7.6

Arrhenius plot for isomerization of 3,3DMB1 on titania. The dashed line is for rutile from reference 4. ○, and □, anatase in the absence and presence of hydrogen respectively.
gave a ratio of 4.8 compared with a theoretical value of 4.1
(Kilpatrick, Prosen, Pitzer and Rossini (34)).

The reaction of 33DMB1 in the presence of hydrogen was studied between 317K and 385K and results for the isomerization are shown in Figure 7.6 and Table 7.1. There was no evidence for hydrogenation of the alkene in this temperature range. After the isomerization reaction had been followed to 25% conversion at 383K, the temperature was increased to 526K in order to investigate whether addition occurred. Direct hydrogenation of 33DMB1 would lead to 2,2-dimethylbutane (22DMB) but there was no evidence for this product. However, formation of 2,3-dimethylbutane (23DMB) took place at a rate of 1.7 x 10^{14} molecules s^{-1} m^{-2} (see Figure 7.3), although the reaction poisoned and the rate fell to 3.7 x 10^{13} molecules s^{-1} m^{-2} after one hour.

2,3-dimethylbutenes

Results for the reaction of 23DMB1 on the present sample of anatase were reported previously by Capitelli (35). Rapid isomerization to give 23DMB2 (r>10^{17} molecules s^{-1} m^{-2}) took place on 50 mg catalyst at 273K. The reaction reached equilibrium after 30 minutes with a gas phase composition of 86% 23DMB2 and 14% 23DMB1. Less than 0.5% of the 33DMB1 isomer was detected.

The reaction of 23DMB1 with hydrogen was studied at 383K and, after rapid isomerization to give 23DMB2, 23DMB was produced at a rate of 7.8 x 10^{12} molecules s^{-1} m^{-2}. The latter result is shown in Figure 7.3.
7.4 DISCUSSION

In order to compare the catalysts as far as possible, the pretreatment of anatase followed that used for rutile by Kemball, Nisbet, Robertson and Scurrell (36). The initial intention of this procedure was to "burn off" any hydrocarbon or related impurities from the surface using oxygen at the high temperature, in an attempt to obtain a clean surface. The yellow colour of the anatase sample at 723K was due to the presence of some TiO species and the purpose of the second dose of oxygen (at room temperature) was to convert it back to TiO$_2$ by oxidation.

It must be borne in mind that a direct comparison between the two crystal forms of titania would require the catalysts to be prepared by an identical method and this is not possible. The extent to which results may be compared is restricted by the fact that any sample of anatase will always contain some rutile as impurity and vice versa.

7.4.1 Equilibration of Hydrogen and Deuterium

The rate of equilibration of hydrogen and deuterium on anatase obtained from Figure 7.3 was approximately $1 \times 10^{15}$ molecules s$^{-1}$m$^{-2}$ at 473K and this compares well with a value of $2.5 \times 10^{15}$ molecules s$^{-1}$m$^{-2}$ obtained from the data of Harris and Rossington (16). Anatase was more effective than rutile for this reaction since a rate of $10^{15}$ molecules s$^{-1}$m$^{-2}$ on the latter catalyst would require a temperature greater than 500K according to the results of Lake and Kemball (4).

7.4.2 Hydrogenation of Alkenes

The straight line obtained in Figure 7.2 confirmed the validity of the Langmuir isotherm for adsorption of ethene when the reaction was taken to a
high conversion. The ratio of initial:Langmuir rates was less than one (0.85) and this observation was expected since $k_L$ is defined for a fully covered surface and the results gave an initial coverage of only 0.82. In other words, the evidence shows that the rate of hydrogenation of ethene is dependent on the coverage of the adsorbed alkene. Similar conclusions were reached by Brown et al. (33) when the hydrogenation of a series of alkenes was studied on zinc oxide.

Hydrogenation of both ethene and propene was a convenient reaction for study in terms of catalyst activity and behaviour. Both molecules reacted at similar rates; for example ethene was hydrogenated at a rate of $3.8 \times 10^{13}$ molecules s$^{-1}$ m$^{-2}$ at 450K compared with a value of $1.6 \times 10^{13}$ in the same units for propene. These rates are approximately 2.5 and 340 times faster than those obtained for deuteration of ethene and propene respectively on rutile from Lake and Kemball's (4) results.

The rate of hydrogenation of ethene was 10-50 times slower than the equilibration of hydrogen in the temperature range studied and the activation energies for the reactions involving ethene and propene were very similar. These results are in line with the suggestion that the rate-determining step for hydrogenation of the alkenes is associated with the activation of the hydrogen molecule on the anatase surface. A similar conclusion was reached for the reactions on zirconia discussed in Chapter 6, although the rates of hydrogenation were closer to those for equilibration and activation energies were about three times lower on the latter catalyst. Although it was a more active catalyst than rutile for hydrogenation of ethene and propene, anatase was about two orders of magnitude less active than zirconia. At 450K the rates of hydrogenation of ethene and propene
were predicted as $1.6 \times 10^{16}$ and $8.8 \times 10^{15}$ molecules s$^{-1}$m$^{-2}$ respectively on ZrO$_2$. There was also some evidence to show that alkenes shared a common rate-determining process for reactions with deuterium on rutile, which was associated with activation of the D$_2$ molecule (4).

Ethene was marginally faster than propene for hydrogenation on anatase and this may relate to a steric difference where the double bond of the former molecule is more accessible. However, the last explanation does not account for the similar rates found for formation of 23DMB and ethane and it may be that differences in the type of adsorbed intermediates of the two molecules also affect the rate of reaction.

Since the activity of anatase was low for the alkene hydrogenation reactions, it was necessary to obtain a compromise of experimental conditions whereby the reaction could be suitably examined. In particular, high temperatures were required before any significant reactivity could be achieved and alkene molecules can be unstable under such conditions. The poisoning observed during the reactions of 2-methylpropene and cyclopentene with hydrogen is the result of irreversible adsorption of hydrocarbon on to the catalyst surface. The results relating to the latter molecule show that adsorption increases as temperature is raised; this fact is not surprising considering that the cyclopentene molecule was also unstable at temperatures above 320K on lanthana (see Chapter 3). The poisoning of the cyclopentene/La$_2$O$_3$ system was thought to be associated with some oligomerization on the catalyst surface and it appears that a similar process operates on anatase.

Deuterium was spread throughout the methyl and methylene positions of 2-methylpropene in a random manner on anatase and, as was pointed out in Chapter 4, this feature can result from a mechanism which involves a
variety of intermediates. Lake and Kemball (4) originally suggested that exchange of 2-methylpropene involved an allyl intermediate, although later results (Halliday et al. (32)) indicated that a tertiary carbocation species was responsible. The evidence from the $^2$D-n.m.r. spectrum of the alkene from the reaction on anatase was not sufficient to enable differentiation between the two types of mechanism but the high degree of catalytic poisoning observed may point towards the involvement of a tertiary carbocation species. Halliday et al. (32) further argued that irreversible adsorption of the latter intermediate was responsible for poisoning of rutile which accompanied the exchange of 2-methylpropane at high temperatures. Therefore it is tentatively suggested that exchange of 2-methylpropene on anatase includes an alkyl reversal step involving a tertiary carbocation.

The rate of exchange of 2-methylpropene was 130 times faster than that of hydrogenation on rutile (4), compared with a factor of 89 for anatase, and both exchange and addition were ten times more rapid on the latter catalyst.

The present results imply that anatase is a more efficient catalyst for the addition reaction of propene compared with that of 2-methylpropene. This is expected since propene would not form a particularly stable carbocation and is therefore less likely to poison the surface.

7.4.3 Isomerization of Dimethylbutenes

Primet et al. (2) attempted to explain their infrared results by constructing a model of the anatase and rutile surfaces. It was argued that the oxygen atoms on the surface of titania would polarize nearby hydroxyl groups so that the hydrogen atom tends towards a proton-like
state. According to the model, the oxygen atoms of anatase were closer to the hydroxyl groups than those of rutile and in effect the former catalyst is more acidic. This conclusion may explain the result that anatase was the more active catalyst form of titania for the isomerization of 33DMB1 because the mechanism is known to involve the donation of a proton from the catalyst surface to the hydrocarbon in order to produce a tertiary carbonium ion (Kemball, Leach, Skundric and Taylor (37)).

The presence of hydrogen had no significant effect on the isomerization reaction of 33DMB1. Judging from the results of the equilibration reaction the catalyst would not be very effective for dissociation of the H₂ molecule at the lower temperatures (ca.320K) of the range investigated for isomerization, and this may explain the apparent lack of alkane formation from the C₆-alkene. 2,3-dimethylbutane is the only alkane that can result from hydrogenation of 23DMB1 and 23DMB2 and temperatures in the order of 526K were required to instigate the reaction after isomerization of 33DMB1. The absence of 3,3-dimethylbutane during the reaction may result from a steric factor since the double bond of 23DMB1 is less hindered than that of 33DMB1.

It was mentioned above that isomerization of 33DMB1 is often enhanced by catalysts that supply a proton to the alkene. However, admitting hydrogen into the reactant mixture failed to increase the reaction rate and this result may also be due to the fact that the hydrogen was not readily activated by anatase. Isomerization of 23DMB1 occurred more rapidly than that of 33DMB1 and it appears that the two reactions proceed by different mechanisms. For example, the 2,3-dimethylbutenes are capable of formation of π-allylic intermediates whereas this is not possible for 33DMB1. The difference in mechanisms and their relationship to the structure of the C₆-alkenes has been discussed in previous literature (37).
7.5 REFERENCES


Appendix

Published Paper
Mechanistic studies on oxide catalysts. II. Reactions of 2-methylpropene on lanthana and zirconnia

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Deuterium nmr spectroscopy and gas chromatography have been used to examine the products from the reactions of 2-methylpropene with hydrogen or deuterium on lanthana, zirconnia and other oxides. Information was obtained on the number, location and grouping of deuterium atoms in both the exchanged alkenes and the 2-methylpropanes formed by addition. The alkenes were particularly suitable for examination by the nmr technique.

Exchange of 2-methylpropene was about 5–10 times faster than deuteration on lanthana between 350 and 420 K, but only half the rate of the addition reaction on zirconnia, which was a less active catalyst.

On all oxides studied, the exchange of 2-methylpropene produced deutero-alkenes in which the deuterium atoms were randomly distributed. Two main mechanisms of reaction were responsible for these results: (a) the reversible interconversion of adsorbed alkene and adsorbed π-allyl species; and (b) the reversible interconversion of adsorbed alkene and adsorbed alk-2-yl species. It is suggested that the relative importance of these mechanisms depends on the nature of the oxide catalyst and the source of the labelling isotope. Selective exchange with 2-methylpropene tends to be masked by efficient scrambling of H and D atoms through intramolecular reactions.

The formation of alkane on zirconnia approximated to the simple addition of D atoms to both the primary and tertiary carbon atoms of the alkene. In contrast, on lanthana there were different chances of acquiring H or D at these positions when 2-methylpropene was saturated, and evidence for two pools of adsorbed hydrogen of differing isotopic composition.

The present results, together with previous investigations, provide a comprehensive mechanistic scheme for the reactions of 2-methylpropene and 2-methylpropane on oxide catalysts.

INTRODUCTION

The objective of this research is to use the technique of ²H nmr spectroscopy combined with either mass spectrometry or gas chromatography to obtain detailed information on the distribution of deuterium atoms in the products from catalytic reactions on oxides. The nmr technique, in favourable cases, can provide quantitative results not only on the location of deuterium in various positions in molecules but also on the groupings of such atoms. This kind of information is of
importance in establishing the nature and reactivity of the adsorbed intermediates involved in the reactions and providing a good indication of probable mechanisms. In Part I (Brown et al. 1986), results were presented for the reactions of propene and cyclopentene on calcium oxide and on some other oxides. The present investigation is concerned with reactions of 2-methylpropene on lanthana or zirconia, both of which show activity for exchange and addition processes with this alkene.

Only a limited amount of work has been published on the exchange of 2-methylpropene or its conversion to 2-methylpropane on oxide catalysts, despite the fact that it is an interesting reactant because of the range of intermediates which it can form on surfaces. On basic oxides such as magnesia, 2-methylpropene exchanges with deuterium readily even at temperatures as low as 200 K (Robertson et al. 1977). The reaction occurs by the stepwise replacement of hydrogen atoms with deuterium, but all eight hydrogen atoms are exchangeable at the same rate. The mechanism is thought to involve the reversible dissociation of the alkene to an adsorbed allyl species, a process that allows interconversion of methyl and methylene hydrogen on deuterium atoms as well as providing a route to the exchange of all eight atoms in the molecule. The exchange results do not provide any direct evidence about possible charge on the allyl species that might in principle be cationic, neutral or anionic. However, the most likely reaction on the strongly basic oxide is an acidic dissociation of the alkene

$$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3 + (\text{H}^+)_a,$$

leading to an adsorbed carbanionic allyl species associated with a surface cation, and an adsorbed hydrogen ion combined with a surface oxide ion. Experiments with labelled propene, which undergoes a similar kind of exchange process on magnesia, have shown that there is an appreciable, but not unexpected, isotope effect such that C—H bonds break more rapidly than C—D bonds with $k_H/k_D \approx 11$ at 195 K (John et al. 1976). Exchange of 2-methylpropene has also been reported over zinc oxide, which shows a similar behaviour to magnesia except that the temperature range required is 270–326 K instead of 195–273 K, and a slow addition reaction also takes place at about $10^{-2}$ times the rate of exchange (Brown et al. 1983).

Owing to the presence of the tertiary carbon atom in 2-methylpropene, another mechanism of exchange likely to be favoured on acidic oxides or other types of acid catalyst is the reversible formation of the alkyl tertiary carbocation $\text{C}^+(\text{CH}_3)_3$. This process also provides a means of interconverting methylene and methyl hydrogen atoms as well as exchanging all atoms, and has consequences that are similar to those of the allyl mechanism. Since both the associative alkyl mechanism and the dissociative allyl mechanism produce the same results, a distinction between them depends on additional information either on the probable nature of the catalyst, the relative rates of exchange with $\text{D}_2\text{O}$ or $\text{D}_2$, or the relative rates of reaction with different alkenes. Rapid exchange with 2-methylpropene and $\text{D}_2\text{O}$ was observed on X-type zeolites containing cobalt or cerium ions, and the reaction was much faster than the corresponding exchange with propene and $\text{D}_2\text{O}$ (Kemball et al. 1983).
Reactions of 2-methylpropene on oxides

& McCosh 1971). These results are consistent with a mechanism on the zeolites involving alkyl carocations as intermediates.

There has been some confusion about mechanisms of exchange of 2-methylpropene on titania (rutile). Similar rates of exchange were observed for propene and 2-methylpropene with deuterium at temperatures in the range 523–723 K, and interpreted in terms of an allyl mechanism (Lake & Kemball 1967). Subsequently, it was found that the use of D$_2$O in place of D$_2$ as the source of the labelling atoms in reactions with mixtures of the two alkenes on rutile at 530 K gave exchange of 2-methylpropene at 30 times the rate for propene (Halliday et al. 1977), and this demonstrated that the mechanism with the C$_4$-alkene involved the tertiary carbocation as intermediate. The equality of the rates of exchange of the two alkenes in the earlier work is now thought to be a consequence of the rate of supply of deuterium atoms from the D$_2$ gas, which is the rate-determining reaction (Ferrier et al. 1978). One interesting feature of rutile was that, like zinc oxide, it had some activity for the conversion of alkene to alkane although the rate was some 10$^{-2}$ times slower than exchange at 600 K.

There is comparatively little evidence of selective exchange of 2-methylpropene either by reversible formation of vinyl intermediates leading to replacement of methylene hydrogen atoms or by reversible formation of σ-allyl species giving replacement of the methyl hydrogen atoms. Some evidence of preferential exchange of methylene hydrogen atoms was reported by Hightower & Hall (1969) for reaction on γ-alumina at 296 K, but a more recent investigation using microwave spectroscopy showed a random distribution of deuterium atoms in the products for exchange on a different alumina at 296–313 K (John et al. 1977). These latter results were attributed to a tertiary carbocation mechanism on evidence from experiments in the presence of hydrogen sulphide, which is a selective poison for allylic mechanisms on alumina. Gallium oxide is known (Carleton et al. 1977) to be an effective catalyst for alkene exchange by σ-allyl mechanisms, but no evidence of any break in the product distribution corresponding to the exchange of three or six deuterium atoms was detected with 2-methylpropene at 553 K. The failure to detect selective exchange with 2-methylpropene may be a consequence of fast double-bond movement, through either an allyl or alkyl mechanism, obscuring the selectivity.

In the course of a study of alkene reactions on lanthana and on zirconia, we discovered that both were catalysts for the hydrogenation of 2-methylpropene. Since addition reactions with this alkene are comparatively unusual on oxides, we decided to investigate the system in more detail using deuterium to obtain information on both exchange and addition. The system deuterium–2-methylpropene is difficult to study by the mass spectrometric technique (Brown et al. 1983) because of overlapping peaks from the alkenes and alkanes. So in this work we decided to use gas chromatography to follow addition, and $^1$H NMR spectroscopy to determine the rate of the exchange as well as the character of the exchange and addition reactions.
Experimental

Materials

Deuterium (99.5%) from Matheson Chemicals and hydrogen from BOC were purified by diffusion through palladium–silver thimbles. 2-Methylpropene (99%), also from Matheson, was further purified by vacuum distillation. Lanthanum nitrate, La(NO$_3$)$_3$6H$_2$O (99.999%), was obtained from the Aldrich Chemical Co. and converted to the hydroxide by the method used by Imizu et al. (1982). This involved precipitation of the hydroxide from an aqueous solution of the nitrate by addition of ammonia. The precipitate was washed with deionized water, dried at 373 K and ground to 24–42 mesh; weighed amounts of this material were taken for the catalytic experiments and evacuated at 873 K for 3 h to form the oxide.

Zirconyl chloride, ZrOCl$_2$8H$_2$O, also from Aldrich, was used to prepare the hydroxide following the procedure described by Wang et al. (1983). This method was similar to that outlined for lanthanum, except that the zirconium hydroxide was subjected finally to calcination in air at 873 K for 3 h, and then allowed to rehydrate by cooling in the atmosphere. Weighed samples of the hydroxide were evacuated for 3 h at 873 K for the catalytic experiments. Two different samples of zirconyl chloride of 98+% and 99.99% purity were used as starting materials and the resulting oxides are described as ZrO$_2$(I) and ZrO$_2$(II) respectively.

Surface areas of the catalysts were determined by nitrogen adsorption; the values expressed in terms of weights of oxide were 29±1 m$^2$ g$^{-1}$ for La$_2$O$_3$ and 69±7 and 74±7 m$^2$ g$^{-1}$ for ZrO$_2$(I) and ZrO$_2$(II) respectively.

Apparatus

Reactions were followed in a greased-tap recirculation line containing a silica vessel with a 1 cm diameter sinter attached via a ball-and-socket joint, a liquid nitrogen trap, and a connection through a three-way tap and a Carle valve to the gas chromatograph. The volume of the apparatus was 355 cm$^3$, and a Metal Bellows (240 V) recirculation pump with a flow meter was used. Gas chromatographic analyses were carried out using a 2 m column containing 3% squalane on activated alumina operated at 368 K under a pressure of 240 kPa of nitrogen carrier gas, and attached to a Perkin Elmer F11 flame ionization detector. Samples for analysis by NMR spectroscopy were obtained by condensing the hydrocarbons in the liquid nitrogen trap and subsequently distilling them into an NMR sample tube containing 5% D-chloroform. Subsequent procedure was identical to that described in Part I.

Results

Lanthana

Hydrogenation of 2-methylpropene occurred at conveniently measurable rates on samples of catalyst (25 mg of La(OH)$_3$) in the temperature range 335–414 K, by using 5:1 mixtures of hydrogen:alkene and a pressure of alkene of 2.4 kPa, corresponding to about $2 \times 10^{29}$ molecules of hydrocarbon in the apparatus. Typical results on the course of the reactions with time are shown in figure 1. With
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Figure 1. (a) The course of reaction of 2-methylpropene with deuterium on 77 mg ZrO$_2$(II) at 392 K. (b) First (○) and second (□) reactions on 21.5 mg La$_2$O$_3$ at 414 K.

Fresh samples of catalyst there was a decrease in the rate amounting to some 20–25% of the initial rate over a period of 10–20 minutes. However, second reactions on a sample of catalyst that had been used for a first reaction (usually at 414 K) and evacuated at room temperature gave steady rates that were about 75% of that for the fresh samples (see figure 1). For faster reactions in which a large percentage of the alkene reacted, the rate of reaction showed a dependence on the 0.5 power of the alkene pressure (Brown et al. 1983). The rates from first and second reactions are shown as Arrhenius plots in figure 2, and the derived parameters are given in table 1.

Figure 2. Arrhenius plots for hydrogenation (open symbols) and deuteration (filled symbols) of 2-methylpropene on La$_2$O$_3$; ○ and ●, first reactions; □ and ■, second reactions.
Procedure for the evaluation of the $^2\text{H}$ NMR spectra

A detailed procedure was developed for the analysis of the results obtained from the deuterium NMR spectra of the partially deuterated samples of 2-methylpropene. The methods used are described in relation to experiment 3B, a second experiment carried out at 380 K on a catalyst ‘conditioned’ by a first reaction at 414 K. The experiment was stopped after 19% of the alkene had been converted to alkane; the NMR spectrum is shown in figures 3 and 4, and the assignments of the various resonances are given in table 2. There was some variation in the absolute positions

![Graph](image-url)

**Figure 3.** Part of the deuterium NMR spectrum of the products from reaction 3B on La$_2$O$_3$ in which 19% of 2-methylpropene was converted to alkane. The spectrum was line-narrowed by using $LB = -0.20$ and $GB = 0.40$ as the values of the function parameters of the Bruker NMR program FTQ 820601. The assignments of the peaks are given in table 2. (a) Resonances for deuterium in the methylene group of the alkene. (b) Resonances for deuterium in the methyl groups of the alkene and on the tertiary carbon of the alkane.

| Table 1. Arrhenius parameters for reactions of 2-methylpropene on La$_2$O$_3$ and ZrO$_2$ |
|---------------------------------|-----------------|-----------------|-----------------|
| reaction                        | temp. range     | $E/(kJ \cdot mol^{-1})$ | $\log_{10} A$ |
| La$_2$O$_3$                     |                 |                 |                |
| 1st hydrogenation               | 335–414         | 42 ± 2           | 22.3 ± 0.3     |
| 2nd hydrogenation               | 341–401         | 47 ± 1           | 22.9 ± 0.1     |
| 2nd deuteration                 | 367–414         | 30 ± 6           | 20.3 ± 0.4     |
| exchange associated with 2nd deuteration | 367–414 | 40 ± 8           | 22.6 ± 0.9     |
| ZrO$_2$                         |                 |                 |                |
| hydrogenation                   | 273–432         | 16 ± 1           | 17.0 ± 0.1     |
| deuteration                     | 246–433         | 21 ± 1           | 17.8 ± 0.1     |
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FIGURE 4. The NMR spectra for the primary deuterium atoms in the 2-methylpropane formed in experiments on La₂O₃. (a) From experiment 3B by using the line-narrowing parameters given for figure 3; the assignments of the peaks are given in table 2. (b) From experiment 4B by using \( \Lambda_B = -0.30 \) and \( \Omega_B = 0.35 \); this spectrum is similar to that for experiment 3B but also shows the small broad peak at \( \delta = 0.833 \) corresponding to the groupings CD₃CH and CD₃CD.

TABLE 2. POSITIONS OF VARIOUS RESONANCES IN THE NMR SPECTRUM (FIGURES 3 AND 4) FOR THE ALKENE/ALKANE PRODUCTS FROM EXPERIMENT 3B

<table>
<thead>
<tr>
<th>2-methylpropene</th>
<th>2-methylpropane</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of D</td>
<td>chemical shift</td>
</tr>
<tr>
<td>grouping</td>
<td>( \delta ) (p.p.m.)</td>
</tr>
<tr>
<td>methylene</td>
<td></td>
</tr>
<tr>
<td>( =\text{CHD} )</td>
<td>4.6887</td>
</tr>
<tr>
<td>( =\text{CD}_2 )</td>
<td>4.6736</td>
</tr>
<tr>
<td>methyl</td>
<td></td>
</tr>
<tr>
<td>( =\text{CHD}_2 )</td>
<td>1.7044</td>
</tr>
<tr>
<td>( =\text{CD}_3 )</td>
<td>( (1.684)⁴ )</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

⁴ These resonances coincided.

of the resonances from sample to sample but the deuterium isotope shifts were constant. Analysis of the various grouping of deuterium ions in 2-methylpropene was made without difficulty except for the overlap between the resonance for deuterium in CD₃ and one of the resonances for the tertiary deuterium in the alkane. The \( \alpha \)-shifts associated with deuterium in the methylene and methyl groups of the alkene were \( -15.2 \pm 0.1 \) and \( -19 \pm 0.1 \) p.p.b.† respectively. The

† p.p.b. = parts per billion; in this paper a billion represents \( 10^9 \).
and \( \beta \)-shifts for primary deuterium atoms in the alkane were \(-20.7 \pm 0.3\) and \(-8.2 \pm 0.3\) p.p.b. respectively, in good agreement with values already reported (Brown et al. 1985) of \(-20.9\) and \(-8.5\) p.p.b. An accurate value for the \( \beta \)-shift for the tertiary deuterium in the alkane was not obtainable because of the overlap with the alkane resonance, but the results were consistent with the reported values of \(-7.6\) p.p.b. (Brown et al. 1985).

The relative amounts of the various resonances for the deuterium groupings in the alkene showed a random distribution of the H and D atoms over the eight positions in the molecule. If \( d \) is the chance of D and \( h = (1 - d) \) is the chance of H in any position, the expected proportions of deuterium in the groups \( =CHD \) and \( =CD_3 \) will be \( 2hd \) and \( 2d^2 \) respectively. Similarly, the relative proportions of deuterium in \( -CH_2D \), \( -CHD_2 \) and \( -CD_3 \) will be \( 6h^2d \), \( 12h^2d^2 \) and \( 6d^3 \) respectively, bearing in mind that there are two methyl groups in the alkene but only one methylene group. The observed peak integrals for the various resonances are given in table 3, and they provide two independent values of \( d \). The relative amount of deuterium in \( =CHD \) and \( =CD_3 \) gave \( d = 0.200 \), and the corresponding ratio for deuterium in \( -CH_2D \) and \( -CHD_2 \) gave \( d = 0.206 \). The agreement between these values was satisfactory, and by using the mean value \( d = 0.203 \) it was possible to calculate the distribution of deuterium over all the groupings. The only adjustment required in making comparison between experimental and calculated results was to assign the appropriate fraction of the unresolved peak to match the calculated percentage of deuterium in the grouping \( -CD_3 \); once that had been done, there was good agreement between the two sets of values (table 3).

The initial rate of exchange was obtained from the usual first order reversible equation (Kemball 1959)

\[
\ln (\phi_t - \phi) = -k_\varphi t/\phi_\infty + \ln \phi_\infty, \tag{1}
\]

where \( \phi \) and \( \phi_\infty \) represent the deuterium content of the alkene at time \( t \) and at equilibrium, and \( k_\varphi \) is the initial rate of exchange (D atoms acquired by 100 molecules in unit time). The value of \( \phi \) for the mixture analysed by NMR spectroscopy was given by

\[
\phi = \sum_i iD_i = 8 \times 100 \, d, \tag{2}
\]
where $D_i$ was the percentage of alkene with $i$ deuterium atoms, and $d$ the average chance of any atom being deuterium at time $t$. The value of $\phi_\infty$ was estimated by assuming that at equilibrium the ratio of (D/H) in the ‘alkene’ was greater than (D/H) in the hydrogen by a factor of 2.2 (Meyer & Kemball 1965); this assumption gave $\phi_\infty = 530$ for the reaction mixture used.

Analysis of the relative amounts of the various groupings of deuterium in the alkene was used to establish the chances of acquiring an H or D atom at the tertiary carbon atom and on the methylene group of the alkene in the addition reaction. The results in figure 4 for experiments 3B and 4B show that it was possible to identify a number of different groupings of primary deuterium atoms. A less detailed analysis of the tertiary deuterium atoms was obtained, and they were estimated in two groups only: those without a primary deuterium neighbour and those with one or more such neighbours. The observed and calculated distribution of deuterium atoms in the 2-methylpropanes formed in two experiments are given in table 4.

**Table 4. Groupings of deuterium atoms in the 2-methylpropanes from experiments 3B and 4B**

<table>
<thead>
<tr>
<th>grouping</th>
<th>expt 3B</th>
<th>calc.</th>
<th>expt 4B</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>tertiary D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDC$_n$H$_9$</td>
<td>9.4</td>
<td>10.8</td>
<td>5.0</td>
<td>5.4</td>
</tr>
<tr>
<td>CDC$<em>n$H$</em>{9-n}$D$_n$</td>
<td>33.0</td>
<td>32.3</td>
<td>30.4</td>
<td>28.1</td>
</tr>
<tr>
<td>primary D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$DCH</td>
<td>6.3</td>
<td>7.0</td>
<td>6.7</td>
<td>6.5</td>
</tr>
<tr>
<td>CH$_2$DCD</td>
<td>37.7</td>
<td>37.0</td>
<td>35.7</td>
<td>36.7</td>
</tr>
<tr>
<td>CHD$_4$CX$^{(3)}$</td>
<td>13.6</td>
<td>12.9</td>
<td>20.3</td>
<td>21.1</td>
</tr>
<tr>
<td>CD$_4$CX$^{(3)}$</td>
<td>—</td>
<td>—</td>
<td>1.9</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

$^{(1)}$ Assuming chances of acquiring D at the tertiary and primary positions of $d_3 = 0.84$ and $d_1 = 0.45$.

$^{(2)}$ Assuming chances of acquiring D at the tertiary and primary positions of $d_3 = 0.85$ and $d_1 = 0.45$.

$^{(3)}$ X represents H or D.

A simple method depended on comparing the total tertiary deuterium in the 19% alkane with the estimated total deuterium ($\phi/100 = 1.62$ atoms per molecule) in the 81% alkene. This gave 0.86 tertiary deuterium atoms per alkane molecule in experiment 3B. A similar calculation gave 1.14 primary deuterium atoms per alkane molecule, but this value had to be corrected for the average deuterium content of the alkene throughout the experiment because all alkene deuterium is converted to primary deuterium in the alkane when addition takes place. The estimated average deuterium content of the alkene was 0.75 deuterium atoms per molecule, so that only $1.14 - 0.75 = 0.39$ deuterium was acquired by the methylene group on conversion to alkane.

It was possible to confirm this rather surprising result by a detailed calculation of the amounts of the various groupings of deuterium atoms in the alkane. The steps in the calculation were as follows.

(a) The evidence that deuterium was randomly spread in the alkene at the end
of the experiment, and the known deuterium content at that stage were used to estimate the average amounts of various deuterio-alkenes throughout the course of the experiment.

(b) It was assumed that in the addition process the average chance of acquisition of D or H at the tertiary position was $d_3$ or $1 - d_3$ respectively. Similarly, the average chance of acquiring D or H at the methylene position was assumed to be $d_1$ or $1 - d_1$ respectively.

(c) Calculation of the expected groupings of deuterium in the alkane were then made on the basis that the conversion to alkane involved merely addition of one atom at the tertiary position and one atom at the primary position and no further exchange.

(d) Values of $d_3$ and $d_1$ were chosen to give agreement between the calculated and observed distribution.

The results in table 4 indicate that it was possible to reproduce the experimental results assuming values of $d_3 = 0.84$ and $d_1 = 0.45$ in experiment 3B, and these values are close to those obtained above by the simple method of 0.86 and 0.39 respectively. Also included in table 4 are results for experiment 4B in which rather greater exchange of alkene had taken place and more of the groupings with two or three deuterium atoms in the methyl groups had formed.

Rates of reaction and allied results for 2-methylpropene

The data from the five experiments with 2-methylpropene and deuterium on lantha are shown in table 5, the Arrhenius plots are given in figure 1 and the

| Table 5. Exchange and addition reactions of 2-methylpropene on lantha |
|---|---|---|---|---|
| Expt | Temp/K | Percentage addition | Rate of addition, $k_A$ | Ratio $k_A/k_A$ | Chance of acquiring D in addition | $d_3$ | $d_1$ |
| 1A | 347 | 14.9 | 0.78 | 5.0 | 0.83 | 0.48 |
| 2B | 367 | 18.6 | 0.96 | 6.5 | 0.97 | 0.45 |
| 3B | 380 | 19.0 | 1.50 | 7.4 | 0.86(0.84) | 0.39(0.45) |
| 4A | 414 | 31.2 | 4.1 | 9.4 | 0.79 | 0.12(3) |
| 4B | 414 | 30.4 | 3.0 | 9.7 | 0.84(0.85) | 0.19(3)(0.45) |

(1) A refers to first experiments and B to second experiments.
(2) Values in parenthesis determined by the detailed method, the others by the approximate method.
(3) Values that are less reliable being the difference between two larger numbers.
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deuterium at the tertiary carbon but a significantly lower value of $d_1$, the chance of adding a deuterium to the methylene groups of the alkene. Values of $d_1$ estimated by the simple method were less reliable when the amount of exchange was substantial as in the two experiments at 414 K that were allowed to run to more than 30 \% addition. For example in experiment 4A, the value of $d_1$ was derived by subtraction of two larger numbers both subject to some error; for this reaction $d_1 = 1.43 - 1.31 = 0.12$.

**Zirconia**

Mixtures of reactants identical to those described for lanthana were used in most of the experiments on zirconia, and weights of the catalyst samples were in the range 40–100 mg (measured as hydroxide). A typical deuteration is shown in figure 1. Some decline in rate was found in the first few minutes but thereafter there was a linear decrease in the percentage of alkene with time, and rates were determined from this part of the graph. The rates of the various hydrogenation or deuteration reactions carried out within the temperature range 246–433 K are shown as Arrhenius plots in figure 5 and the derived parameters are given in table 1. Similar rates were obtained on both samples of zirconia, as illustrated in figure 4.

\[ \text{FIGURE 5. Arrhenius plots for hydrogenation (squares) and deuteration (circles) of 2-methylpropene on zirconia; open symbols refer to ZrO}_4(\text{I}) \text{ and filled symbols to ZrO}_4(\text{II}). \]

Two successful experiments were carried out by using deuterium NMR spectroscopy to analyse the mixtures of alkene and alkane after about 20 \% addition had taken place. The method of analysis will be described for run Z9 at 415 K. In contrast to the results found on lanthana, there was relatively little exchange of the alkene although the ratio of (deuterium in the methyl groups):(deuterium in the methylene groups) was close to 3:1. The alkane contained similar amounts of primary and tertiary deuterium and the results indicated that the deuteration
reaction approximated to the addition of D₂ to the alkene. The detailed analysis of the NMR spectrum is given in table 6. The groupings were readily identified from the chemical shifts of the various resonances. The relative amounts of the two groupings of primary atoms in the alkane showed that 95% of the 2-methylpropane molecules had a D in the tertiary position and only 5% had H. These percentages enabled us to make the assignments in the last column of table 6. In experiment Z9, because 8% of the alkene was exchanged at the end of the period that gave 16% deuterium, the rate of exchange was half the rate of addition, i.e. \( k_E = 0.5 \frac{k_A}{2} \). The average deuterium content of the alkene during the experiment was 0.04 D per molecule, and on conversion to alkane this would have become primary deuterium, a fact that explains the difference between the 0.99 primary deuterium compared with the 0.95 tertiary deuterium in the alkane.

**Table 6. Amounts and groupings of deuterium in the products from reaction Z9 of 2-methylpropene on zirconia**

<table>
<thead>
<tr>
<th>compound</th>
<th>grouping</th>
<th>% D</th>
<th>D/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkene</td>
<td>−CHD</td>
<td>4.1</td>
<td>0.08</td>
</tr>
<tr>
<td>alkene</td>
<td>−CH₃D</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>alkane (3)</td>
<td>(CH₃)₂(CH₂D)CD</td>
<td>40.3</td>
<td>0.95</td>
</tr>
<tr>
<td>alkane (4)</td>
<td>CH₃DCH</td>
<td>1.9</td>
<td>0.99</td>
</tr>
<tr>
<td>alkane (4)</td>
<td>CH₃DCD</td>
<td>40.2</td>
<td></td>
</tr>
</tbody>
</table>

Analysis made on a mixture containing 83.8% alkene and 16.2% alkane.

Relative to the assigned value of 0.95 for the tertiary deuterium in the alkane.

Tertiary D.

Primary D.

In the other experiment at 433 K examined by deuterium NMR spectroscopy after 23% conversion to alkane, the value of \( k_E/k_A \) was found to be 0.6, and again the addition process gave about 1D per molecule in both the primary and tertiary position of the alkane.

**Other oxides**

For comparison with the results on lanthana and zirconia, reactions of 2-methylpropene with deuterium were also examined on calcium oxide and on γ-alumina. Because little or no formation of alkane was expected, the reactions were run in a static system linked to a mass spectrometer, and when a convenient amount of exchange had taken place the alkene was collected for NMR analysis (Brown et al. 1985). The source and pretreatment of the calcium oxide and the γ-alumina have been given in Part I.

Results for reaction on calcium oxide at 237 K and γ-alumina at 341 K are shown in table 7. The rate of exchange of 2-methylpropene on calcium oxide at 237 K was \( 7.9 \times 10^{16} \) molecules s⁻¹ m⁻², which compares with \( 1.7 \times 10^{17} \) for propene at 236 K. The rate of exchange of 2-methylpropene on γ-alumina at 341 K was \( 6.0 \times 10^{14} \) molecules s⁻¹ m⁻², and the corresponding rate for propene was \( 2.1 \times 10^{14} \) at the lower temperature of 293 K. The exchange reaction was largely stepwise
Reactions of 2-methylpropene on oxides

TABLE 7. EXCHANGE REACTIONS OF 2-METHYLPROPENE AND DEUTERIUM ON CALCIUM OXIDE AND γ-ALUMINA

<table>
<thead>
<tr>
<th>catalyst</th>
<th>oxide mass</th>
<th>T/K</th>
<th>t/min</th>
<th>D₀</th>
<th>D₁</th>
<th>D₂</th>
<th>D₃</th>
<th>D₄</th>
<th>D₅</th>
<th>M⁽²⁾</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20</td>
<td>237</td>
<td>29</td>
<td>75.65</td>
<td>16.00</td>
<td>6.05</td>
<td>1.65</td>
<td>0.60</td>
<td>0.05</td>
<td>1.28</td>
</tr>
<tr>
<td>calculated A⁽¹⁾</td>
<td></td>
<td></td>
<td></td>
<td>69.42</td>
<td>25.93</td>
<td>4.23</td>
<td>0.40</td>
<td>0.02</td>
<td>0.00</td>
<td></td>
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<tr>
<td>Al₂O₃</td>
<td>200</td>
<td>341</td>
<td>57</td>
<td>78.25</td>
<td>18.20</td>
<td>3.25</td>
<td>0.25</td>
<td>0.05</td>
<td>0.00</td>
<td>1.11</td>
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<tr>
<td>calculated B⁽¹⁾</td>
<td></td>
<td></td>
<td></td>
<td>77.03</td>
<td>20.44</td>
<td>2.37</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
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</tbody>
</table>

⁽¹⁾ A represents the distribution calculated for stepwise exchange with the same average deuterium content as the results from calcium oxide; B was a similar calculated distribution for comparison with the results for γ-alumina.

⁽²⁾ The mean number of deuterium atoms entering each molecule in the initial stages of reaction.

on alumina, but a little multiple exchange occurred with calcium oxide and the value of \( M = 1.28 \) was identical with that found for propene at 249 K.

A slow hydrogenation of 2-methylpropene of \( 3.2 \times 10^{14} \) molecules \( \text{s}^{-1} \text{m}^{-2} \) was observed on calcium oxide at 313 K, which compares with \( 5.2 \times 10^{14} \) in the same units for the reaction of propene.

The results of the NMR analyses for the exchange reactions of 2-methylpropene are given in table 8. As with results of lanthana (table 3), the full range of groupings of deuterium atoms were detected and on both oxides the agreement between calculated and observed distributions confirmed that in each of the deuterio-alkenes the deuterium atoms were largely randomly distributed throughout the molecule. There was just a slight indication near the limit of experimental error for preferential exchange in the methylene group of the alkene in the reaction over alumina. The ratio of deuterium in methylene to deuterium in methyl was 0.314 on calcium oxide, and values of 0.325, 0.328 and 0.326 were found from various runs with lanthana, but on alumina the ratio was 0.361.

TABLE 8. COMPARISON OF EXPERIMENTAL AND CALCULATED DISTRIBUTION OF DEUTERIUM ATOMS IN 2-METHYLPROPENE EXCHANGED ON CALCIUM OXIDE (237 K) AND ALUMINA (341 K)

<table>
<thead>
<tr>
<th>grouping</th>
<th>calcium oxide</th>
<th>γ-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc. ((d = 0.121))</td>
<td>calc. ((d = 0.072))</td>
</tr>
<tr>
<td>=CHD</td>
<td>20.7</td>
<td>24.5</td>
</tr>
<tr>
<td>=CD₂</td>
<td>3.2</td>
<td>2.0</td>
</tr>
<tr>
<td>=CH₂D</td>
<td>58.5</td>
<td>63.7</td>
</tr>
<tr>
<td>=CHD₂</td>
<td>16.1</td>
<td>9.8</td>
</tr>
<tr>
<td>=CD₃</td>
<td>1.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\[100.0 \quad 100.0 \quad 100.0 \quad 100.0\]
A convenient method of comparing the rates of exchange with deuterium or the addition reaction of 2-methylpropene is to estimate the temperature needed to achieve a specified rate on different oxides. Results of this kind are given in Table 9; for exchange, two rates are selected, $10^{17}$ molecules s$^{-1}$ m$^{-2}$ for the more active catalysts and $10^{15}$ in the same units for the less active. The order of activity of exchange is

$$\text{CaO > MgO > La}_2\text{O}_3 > \text{ZnO > Al}_2\text{O}_3 > \text{ZrO}_2 \gg \text{TiO}_2 \text{ (rutile)},$$

and for deuteration the order is

$$\text{La}_2\text{O}_3 > \text{CaO} > \text{ZrO}_2 > \text{ZnO} \gg \text{TiO}_2 \text{ (rutile)}.$$

These results show that basic oxides tend to be efficient catalysts for the exchange of the alkene but there is no such simple explanation for the order for the addition reaction. Zirconia is unusual in showing slightly greater activity for addition than for exchange; on lanthana exchange is about an order of magnitude faster than addition and the ratio is even larger on the others.

**Mechanisms**

The dominant characteristic of the exchange reaction of 2-methylpropene with deuterium is that the products show a random distribution of deuterium atoms in each deuto-alkene over the eight positions in the molecule, the two positions in the methylene group and the six positions in the two methyl groups. On γ-alumina, which gives preferential exchange of vinylic hydrogen atoms with propene (Hughes *et al.* 1975; Part I), there is little evidence for a similar reaction with 2-methylpropene and our results are in better agreement with those of John *et al.* (1977) than with the earlier report from Hightower & Hall (1969).

The essential feature of the mechanism of exchange is a means of moving the position of the double bond in 2-methylpropene so that eight atoms became randomly distributed between the methylene groups and the two methyl groups. An important aspect of the addition process is the clear evidence that the chances
Reactions of 2-methylpropene on oxides

of acquiring deuterium at the primary and tertiary positions differ in the formation of 2-methylpropane over lanthana. Both these points can be covered in terms of the general scheme (scheme 1) for the reactions of 2-methylpropene on oxides that

\[
\begin{align*}
\text{gas} &
\begin{array}{c}
\text{alkene} \\
\text{alkane}
\end{array} \\
\begin{array}{c}
(1) \\
(2) + Z^+ \\
(5) - Z^-
\end{array}
\begin{array}{c}
\text{surface} \\
(\pi\text{-allyl})_2^+ \\
(\text{alkene}) \\
(\text{alk}-2\text{-yl})_2^+
\end{array}
\end{align*}
\]

Scheme 1. General scheme for reactions of 2-methylpropene on oxides. Both Y and Z represent H and D. The fractional charges on the adsorbed species will vary with the nature of the oxide and the magnitude of the charges on the allyl and alkyl species need not be the same.

will be considered in some detail. There are a number of points that have to be made relating to the application of the scheme to different catalysts and different conditions.

1. In exchange reactions, the forward and backward steps in each of the reversible processes involved will occur at the same rate. This will apply to reactions (1) and (2), and also to (3) and (4) or (5) and (6).

2. The size of the partial charges on the adsorbed π-allyl and alkyl species need not be the same, although for simplicity they are shown as equivalent in the scheme. The fractional charges are likely to depend on the nature of the catalyst.

3. The scheme implies that there are two distinct pools of H or D species in the surface. The symbol Y represents those that are involved in the interconversions between alkene and allyl, or between alkene and alkyl. When either of these interconversions takes place rapidly, the composition of the Y pool is likely to approximate to the isotopic composition of the alkenes. The composition of the Z pool will depend on the source of these species, which may be the compound used to provide the deuterium isotope or, in some circumstances, could be through the dissociation of alkane molecules. The partial charges on the Y and Z species may differ in size as well as sign.

4. Exchange of alkene may occur through reactions (1) and (2) combined with either of the pairs (3) and (4), or (5) and (6). Either route will permit movement of the double bond around the molecule and the exchange of any or all of the hydrogen atoms in the alkene.

5. Because the consequences of exchange by (3) and (4) or by (5) and (6) are similar, it is not easy to determine which route is favoured on a given catalyst. There may be cases when both routes are operative at the same time although not necessarily at the same rate. Comparison between the rates of reaction of 2-methylpropene and other alkenes, such as propene, may help to distinguish between the routes.

6. Strongly basic oxides are likely to favour the acidic dissociation of the alkene involved in reactions (3) and (4). We believe that this pair of reactions comprises the principal mode of exchange on calcium oxide for which similar rates of reaction
are found with propene and 2-methylpropene. The same conclusion for the same reason would seem to apply to magnesia (Robertson et al. 1977) and zinc oxide (Brown et al. 1983).

7. Exchange by the pair of reactions (5) and (6) is likely to be predominant on acidic oxide catalysts or in cases where a potentially good supply of D⁺ is available, e.g. when the source of the isotopic label is provided in the form of D₂O. A more rapid rate of exchange of 2-methylpropene than of propene is an indication of reaction via (5) and (6), because the formation of the alkyl carbocation is easier with the C₄-molecule. An example where the use of D₂O instead of D₃ was required to enhance the rate of exchange of 2-methylpropene relative to the rate for propene was mentioned earlier for rutile catalysts (Halliday et al. 1977).

8. Transfer of H atoms around the molecule by either pair of reactions (3) and (4) or (5) and (6) can provide a means of partly randomizing the distribution of D between the methylene and methyl groups (complete equilibration with molecules containing —CD₃ or —CD₂ requires the transfer of D as well). At low temperatures, such transfer of H atoms is likely to be faster than exchange between alkene molecules because of the kinetic isotope effect on the relative rates of dissociation of C—H and C—D bonds.

9. The absence of appreciable multiple exchange on a catalyst suggests that reactions (1) and (2) take place more rapidly than (3) and (4) or (5) and (6). The converse applies when multiple exchange is substantial.

10. The scheme provides an explanation of the results found for the nature of the deuteration reaction on lanthana. What occurs is an example of the consequences of the suggestions in paragraph 3 above. When substantial amounts of alkene exchange are occurring, the composition of the Y pool will be less rich in D than the Z pool, and less D is added to the primary carbon than to the tertiary carbon.

11. The scheme can also explain why exchange of 2-methylpropane with heavy water on acidic oxides (Hindin et al. 1951; Hansford et al. 1952; Kemball & McCosh 1971) gives multiple exchange with up to nine but not ten deuterium atoms in the products. The slow step is the dissociation of the alkane by reaction (8); there follows a rapid series of interconversions by reactions (5) and (6) leading to the replacement of all nine primary hydrogen atoms if a sufficient supply of D⁺ is available. The final step of the exchange is reaction (7), which adds an atom to the tertiary position to reform the alkane; this atom is much more likely to arise as an H⁵⁻ from the dissociation of another hydrocarbon than as a D⁵⁻ from D₂O.

12. The examples just quoted refer to conditions where (5) and (6) are rapid in relation to (7) and (8). With alkenes, other than 2-methylpropene, the evidence suggests that the rate-determining step for alkane formation is reaction (5), the formation of the adsorbed alkyl species that is then rapidly converted to alkane (reaction 7) and does not revert to alkene (reaction 6). Evidence for this type of behaviour was found for ethene (Kokes & Dent 1972) and also for cyclopentene (Brown et al. 1982) on zinc oxide. It seems probable that the relative rates of reactions (5), (6) and (7) with 2-methylpropene may vary significantly from catalyst to catalyst, and with the conditions used.

13. The scheme does not include dissociation of alkene to adsorbed vinyl species.
By analogy with the behaviour of propene and cyclopentene, such a reaction might be expected on alumina but little evidence for it was found in the present work.

The scrambling of H and D atoms in 2-methylpropene appears to be an efficient process on alumina as on the other oxides, but there is some doubt about the mechanism involved. The scrambling may occur through reactions (3) and (4), but the evidence from studies with propene is against the formation of π-allyl species at low temperatures on alumina. Alternatively, the scrambling may involve reactions (5) and (6) because the results discussed by John et al. (1977) indicate the likelihood of such processes with molecules capable of forming tertiary carbocations. But if this associative mechanism is involved, it is surprising that the exchange of 2-methylpropene is not faster than the exchange of propene on alumina.

14. On zirconia, the comparatively simple nature of the deuteration reaction, which adds D at both the primary and tertiary positions of the alkene, shows that for this catalyst the Y and Z pools are similar. This may be a consequence of the comparatively low rate of exchange, i.e. reaction (6) is slower than (7) and the interconversion to allyl is unimportant. It is also possible that the partial charge on the allyl species is smaller on zirconia so that the addition reaction approximates more closely than on lanthana to the successive uptake of two more or less neutral atoms of deuterium.

NMR results

The spectra show that 2-methylpropene is readily analysed by deuterium NMR spectroscopy. The spectra are simple because of the absence of D on the central carbon atoms. Consequently, deuterons, whether in the methylene group or the methyl groups, are subject only to α-shifts that are of sufficient size (15–20 p.p.b.) to be easily detected and measured, or γ-shifts that are small enough to be neglected. Under these circumstances, it is possible to identify and estimate all the relevant groupings of deuterium in the molecules.

The situation is more complex with 2-methylpropane, and the achievement of adequate resolution of the various peaks is easier for the primary deuterons that are subject to not more than one β-shift. The peaks for the tertiary deuterons, influenced by up to six β-shifts, cannot be completely resolved because β-shifts (ca. 8 p.p.b.) are similar to the natural line width of the resonances.

The combination of NMR analysis with either gas chromatography or mass spectrometry provides a reasonably complete picture of the location and grouping of deuterium atoms in the products from reactions of 2-methylpropene with D₂.

We are grateful to Dr I. H. Sadler for expert advice on the NMR spectra, which were obtained through the SERC high field facility at Edinburgh. R. Bird held an SERC studentship, and we are indebted to Mr I. H. Grant for carrying out some of the runs on zirconia.
REFERENCES