REACTIONS OF SUBSTITUTED CYCLOPROpanes
ON
MOLECULAR SIEVE ZEOLITES

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SUMMARY

The isomerisation reactions of methylcyclopropane, 1,1 dimethylcyclopropane and 1,2 dimethylcyclopropane were examined over Na13X zeolite and forms prepared by partial exchange of sodium for other ions. Cation replacement was found to result in increased isomerisation activity and correlation between activity and the degree of ion exchange was observed for nickel and copper sieves.

Investigations of the system using water and hydrogen indicated that the reactant ring opening step was irreversible. The induction periods observed for nickel and copper zeolites were attributed to a cation reduction process thought to be associated with the ring scission reaction.

The direction of alkylcyclopropane ring cleavage influenced the observed reaction products and was considered to be a function of the operative mechanism. In general carbonium ion intermediates were thought to be involved; cerium and hydrogen zeolites were regarded as functioning via protonic sites whereas a cation reduction process was thought to be important for the transition metal exchanged zeolites examined. A radical mechanism occurring to a lesser extent than a carbonium ion mechanism was proposed for nickel zeolites.
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Appendix I

Mechanistic Schemes for Alkylcyclopropane Isomerisation

Appendix II

Computer Programs:

(1) methylcyclopropane as reactant

(2) 1,1 dimethylcyclopropane as reactant

(3) 1,2 dimethylcyclopropane as reactant
CHAPTER I

INTRODUCTION TO CATALYSIS

1.1 Historical

Since the earliest civilisations man has utilised processes which are catalytic in nature. Indeed some of the principles underlying the mediaeval fantasies of the philosopher's stone are embodied in our present day understanding of catalysis. However it was not until the end of the eighteenth century that the first scientific observations of the phenomenon of catalysis were reported.

Van Marum (1) discovered in 1796 that alcohol was dehydrogenated by passage over copper and in 1813 Thenaud (2) found that ammonia and hydrogen peroxide (1818) were decomposed by metals. However it was not until 1836 that Berzelius (3) combined these results and those of others in order to formulate concepts which ascribed the mechanism of apparently diverse chemical reactions to a common cause. Subsequently Berzelius invented the term catalysis and awakened further scientific interest in the subject. Ostwald, at the end of the nineteenth century, proposed that the rate of reaction was a measure of catalytic activity and so gave catalysis the quantitative foundation on which our modern ideas are built.

Catalysis has since become the subject of closer scientific investigations and today forms the key to many chemical processes being used in industry.

1.2 Definition/
1.2 Definition

Catalysis describes the action of a substance (the catalyst) which, isothermally and non-radioactively, augments the rate of a chemical reaction without appearing in the stoichiometric equation of the reaction. For reversible reactions a catalyst provides an alternative path but does not alter the chemical equilibrium, both forward and reverse reactions being catalysed to the same extent.

In general catalysed reactions may be classified as heterogeneous or homogeneous, depending on the phase relationship between catalyst and reactants and products.

(i) Heterogeneous catalysis involves reaction at an interfacial layer between distinct phases.

(ii) Homogeneous catalysis involves reaction in which catalyst and reactants are in the same phase.

This thesis is concerned with heterogeneous catalysis and specifically deals with the reactions of gases on solid catalysts.

1.3 Heterogeneous Catalysis

In a study of contact catalysis the general problem of adsorption is of fundamental importance and a large amount of experimental evidence has been accumulated showing that the adsorption of reactant molecules occurs on solid surfaces.

The first hypothesis concerning heterogeneous catalysis proposed that chemical activation was caused by mere mechanical impact of the gas molecules with the solid surface, but this postulate could not explain the high specific action of different surfaces. Faraday (4) proposed that physical attractive forces were operative, between catalyst and reactant, reaction rates being increased/
increased because of the increased concentration of reactants in the
condensed layer. However it was not until Sabatier (5) introduced the
idea that unstable surface intermediates were involved that satisfactory
explanation could be given to the specificity of catalytic action. On the
basis of results obtained from gaseous adsorption on metal surfaces
Langmuir (6) proposed that chemical bonds held molecules to surfaces and
that the nature of adsorption depended on the surface catalytic sites.

Two types of adsorption are thus clearly distinguishable, namely
physical adsorption and chemisorption. (7,8,9)

1.4 Physical Adsorption

In physical adsorption the molecules are held to the surface by forces
similar to those involved in the Van der Waals equation of state for gases.
Heats of adsorption are low (few hundred joules per mole) corresponding to
the latent heat of condensation of adsorbate, and the reactivity of the
adsorbate is not markedly altered. Physical adsorption requires little activation
energy and is thus rapid and reversible at low temperatures. Gases are not
physically adsorbed at temperatures much greater than their critical
temperature; adsorption occurs near the adsorbate boiling point.

Since the forces involved are small and non-specific, physical
adsorption is not of direct importance when considering the surface catalysis
reactions of stable molecules. However, because of the non-selective nature
of physical adsorption and the fact that the adsorbate occupies an area
determined by its size (rather than preferentially occupying certain sites),
the technique of measuring physical adsorption on surfaces at low temperatures
provides a convenient method of determining surface areas. This is exemplified
by the work of Brunauer, Emmett and Teller (10) whose methods are generally
used/
used for surface area determinations.

1.5 Chemisorption

Chemisorption is the result of a chemical reaction, involving some electronic redistribution, between the adsorbate and the adsorbent. The resulting chemical bond may be covalent or ionic in character, the adsorbed species being regarded as an adsorbed ion or an adsorbed dipole.

The forces involved in chemisorption are nearly always similar to those occurring in chemical reactions, the heats evolved in chemisorption being commonly in the order of 40 - 400 kJ/mole. In view of these energy changes chemisorbed species are usually markedly altered in their reactivity as exemplified by the dissociative chemisorption of hydrogen on tungsten.

Chemisorption is confined to a single layer and is specific in nature, hydrogen being chemisorbed on tungsten but not on copper. Chemisorption is a necessary, but not sufficient, condition for catalytic reaction; a too strongly chemisorbed reactant will be difficult to remove and may act as a poison, while a too weakly chemisorbed reactant may not remain on the surface long enough to react.

Like other chemical reactions chemisorption is an activated process, the rate of which increases with temperature. Many chemisorptions are consequently irreversible especially at low temperatures, due to a slow desorption rate.

Another feature of chemisorption reported by Taylor (11) is the variation in adsorptive power shown by catalyst surfaces. These "active" sites, which are responsible, can be identified with certain lattice defects/
defects and can be thought of as chemically unusual sites.

Infra-red spectroscopy (12, 13) and electron spin resonance (14) techniques have been applied to studies of the chemisorbed state. From these and other studies it has been shown that gases chemisorb on surfaces with the formation of a variety of species which may undergo rearrangement. It was also found that the relative concentrations of these adsorbed species could be affected by the presence of other gases.

1.6 The Mechanism of Heterogeneous Catalysis

A heterogeneously catalysed reaction can be considered as occurring in five elementary steps:

(i) Diffusion of reactant from the gas phase to the surface
(ii) Chemisorption of one or more reactant species on the surface
(iii) Chemical reaction on the surface
(iv) Desorption of the products from the surface
(v) Diffusion of the products away from the surface

The slowest of these steps determines the overall reaction rate. Diffusional processes can be important for highly porous catalysts or where the reactants are in the liquid phase. However they rarely influence rates in low pressure laboratory systems, unless the reactions are extremely fast.

A study of the Arrhenius plot over a wide temperature range will indicate if diffusion control is operative in a particular system, since the temperature coefficients are different for activated and diffusion processes. If straight lines are obtained it is unlikely that diffusion effects are important.

Neglecting/
Neglecting steps (i) and (v) (given above) the pathway of the catalytic reaction $X \rightarrow Y$ may be schematically represented as follows; where the steps (ii), (iii), (iv) have been described previously and

(ii) $X + \text{catalyst} \rightarrow X(\text{catalyst})$

(iii) $X(\text{catalyst}) \rightarrow Y(\text{catalyst})$

(iv) $Y(\text{catalyst}) \rightarrow Y + \text{catalyst}$

where $X$ or $Y(\text{catalyst})$ is understood as being species $X$ or $Y$ chemisorbed on the catalyst surface.

Figure 1.1 represents the energy - reaction path diagram for this simple unimolecular reaction with regions (ii), (iii), (iv) appropriately labelled.
It can be seen that by means of a series of three chemical reactions each with its own activation energy and heat of reaction, the catalyst has lowered the overall energy required as compared to the thermal reaction. Due to the exponential nature of the rate equation, the catalytic reaction is faster than the thermal reaction at a given temperature and conversely a lower temperature is required for a catalytic reaction at a given rate.

If the adsorbed species is difficult to form or remove than steps (ii) or (iv) become rate controlling. For reactions involving several molecules the situation becomes more complicated.

For the surface reaction (stepiii) one could envisage chemisorbed species reacting, among themselves, with physically adsorbed species or with molecules colliding with the surface. Two basic mechanisms have been proposed to explain the combination of reactants at the catalyst surface, namely the Langmuir (15,16) and Eley (17,18) mechanisms.

The Langmuir mechanism assumes that the adsorption and desorption processes are in equilibrium and that the rate of reaction is determined by chemical interaction of molecules adsorbed on adjacent catalyst sites. This mechanism applies to reactions which take place at high temperatures where it is reasonable to expect rapid adsorption and desorption. The hydrogen-deuterium exchange reaction would occur by a Langmuir mechanism as follows:

\[
\begin{align*}
\text{H} & \quad \text{D} \\
\text{M} \quad \text{M} & \quad \rightarrow \quad 2\text{M} + \text{HD}
\end{align*}
\]

Eley proposed that only one species is chemisorbed and that another molecule from a physically adsorbed layer or from the gas phase interacts with the chemisorbed species in the surface reaction. The Eley mechanism generally/
generally applies to low temperature reactions. The hydrogen-deuterium exchange reaction would occur by an Eley mechanism as follows:

\[
\begin{array}{c}
\text{H} \\
M \\
\text{D} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{D} \\
M \\
\text{H} \\
\end{array}
\]

Information about surface species is available from spectroscopic studies, for example infra-red and electron spin resonance, but the results can be difficult to interpret. Furthermore it is not easy to derive the properties and concentrations of the various chemical species from the kinetics of the reaction. Surface reaction mechanisms are thus difficult to determine. However indirect experimental methods using deuterium and tracer elements have been found useful in elucidation of surface mechanisms.

1.7 Catalysts and Catalytic Activity

Geometric and Electronic Factors

Around 1930 much significance was attached to the correlation between catalytic activity and the spatial arrangement of the reactant molecule and the crystalline lattice of the catalyst. This view was especially emphasised by Balandin (multiplet theory) and has been reviewed by Trapnell, Griffith, Siegel and by Bond and Wells.

Steric or geometric factors may be applied to consideration of hydrogenation and dehydrogenation reactions on metals involving large reactant molecules. For example the results of cyclohexene dehydrogenation over metals were rationalised on the basis of certain surface geometry requirements, whereby/
whereby a group of surface atoms, suitably spaced and of the necessary activity, chemically adsorbed the reactant in a definitely oriented position. Metals with lattice constants outside certain limits were found to be inactive for the cyclohexane dehydrogenation reaction. The geometric factor may also explain catalyst specificity in the decomposition reactions of alcohols - the lattice spacing determining whether dehydration or dehydrogenation occurs.

However six membered ring compounds also undergo dehydrogenation on oxides and it has become recognised (27) that geometrical criteria are only part of the chemical requirements for catalytic activity. The gross physical catalyst structure (surface area and pore size) has also to be considered. It can be generally assumed that catalyst activity increases with surface area.

In contrast to geometrical considerations the electronic factor places stress on electronic character as the basis for catalytic action. Definite correlation has been found between the extent of d bond character and catalytic activity for an alloy series in certain heterogeneous reactions (27,28). Dowden and Wells (30) have applied Crystal Field Theory concepts to explain the activity patterns observed in a series of transition metal compounds in attempting to arrive at a better correlation between theoretical and experimental catalysis.

Studies on semi-conducting oxides (29) also serve to illustrate the relationship between electrical conductivity and catalytic activity. The observed correlations found for the semi-conducting oxides may be accounted for in terms of the electron theory as proposed by Wolkenstein (31).

Catalyst Classification/
Catalyst Classification

Catalysts are comprised of a very wide range of chemicals represented by elements and compounds, particularly halides, oxides and sulphides. Classification of these types is possible from consideration of their electrical conductivities and in this way catalysts can be grouped into metals, semi-conductors and insulators. The reactions in which these catalysts are normally employed can then be summarised.

Metals are used for dehydrogenation and hydrogenation reactions. The semi-conducting oxides and sulphides are active for oxidation, reduction, dehydrogenation, cyclisation and to a lesser extent hydrogenation.

The insulators, which include salts and stoichiometric oxides, are active for a wide range of reactions including polymerisation, isomerisation, cracking, dehydration, alkylation, halogenation and dehalogenation. These catalysts are thought to function through acid sites with formation of carbonium ions from olefins.

The reactive properties of these catalyst types may be usefully combined to obtain dual function catalysts such as platinum on alumina. These catalysts are active for hydrogenation/dehydrogenation (platinum) and olefin isomerisation (alumina) and find widespread use as reforming catalysts in the petroleum industry.

This thesis is concerned with catalysts, known as zeolites or molecular sieves, which may be regarded as highly ordered crystalline aluminosilicates. They are active for similar reactions as the insulators and may be regarded as functioning through similar acid sites. A large number of synthetically and naturally occurring zeolites are known and further discourse on them is given in the following chapter.
2.1 Occurrence/Definition

Naturally occurring zeolite minerals were discovered and investigated in 1756 by the Swedish metallurgist Baron Cronstedt, who named these materials zeolites because of their intumescent properties (Greek; 'zeo' to boil and 'lithos' a stone). Zeolites are also named molecular sieves, a term applied by McBain (32) because of the selective adsorption properties exhibited by these substances.

Zeolites or molecular sieves may be defined (33) as crystalline aluminosilicates with a well defined pore structure, the cavities within the zeolite contain ions and water, and zeolites undergo ion exchange and reversible dehydration with retention of the crystalline framework.

Both naturally occurring and synthetic zeolites are known. Naturally occurring zeolites may be found associated with the geodes of igneous rocks or in sedimentary deposits of lacustrine and volcanic origins; thirty four such types are currently recognised (34). Many synthetic zeolites, some with structurally analogous natural relations, exist. These synthetic types are generally of greater commercial interest than the natural mineral forms because of their more uniform structure.

Zeolites, and especially the synthetic forms, are found to be useful in fundamental studies of catalysis since they possess a well defined structure in which the catalytic sites are situated in defined positions.

2.2 Synthesis/
2.2 Synthesis

In the late 1930's Barrer (35,36) recognised and investigated the highly selective adsorption properties of dehydrated zeolites. Barrer (37,38) also studied zeolite synthesis and had prepared several zeolites using a high pressure hydrothermal process prior to 1948. At about this time impetus was given to the research on zeolite synthesis by the Linde Division of Union Carbide, who, attracted by the commercial potential of zeolites in gaseous separation, initiated a study of zeolite synthesis and characterisation. It was found that high pressures were not necessary in the hydrothermal process and the Linde workers prepared several hitherto unknown zeolites. By 1952 many different species of zeolite had been prepared (39,40).

Synthetic zeolites are formed when freshly prepared, highly reactive aluminosilicate gels are crystallised at temperatures ranging from 298K to 423K. The best gel mixtures are prepared from the soluble salts of the alkali metals; the gel structures arising from polymerisation of the aluminate and silicate ions. Crystallisation of the gel occurs by depolymerisation caused by the hydroxyl ions present in the reaction mixture. The alkali metal ions and the aluminate and silicate components of the supersaturated gel re-arrange during the crystallisation process to give large numbers of crystalline nuclei. The product is a finely divided white powder consisting of particles a few nanometres in size.

A sodium zeolite would be formed from crystallisation of gels prepared from sodium aluminate, sodium silicate and sodium hydroxide. The type of alkali metal chosen is important. Different zeolite species are formed from crystallisation of potassium aluminosilicate gels.

Different synthetic zeolites also result from controlled variation of the initial gel composition and the temperature of the crystallisation.
The most commonly used synthetic zeolites are coded A, X and Y types, each of which has different Si/Al ratios and structural properties.

2.3 Structure

The determination of zeolite structures has been made possible by the development of X-ray diffraction techniques. Since 1960 about half of the known zeolites have been structurally characterised.

The basic structural building units of the zeolite framework may be regarded as silica and alumina tetrahedra. These silica or alumina tetrahedra share oxygen atoms to form rings, which are observed by X-ray diffraction and which are characteristic of zeolites. According to Loewenstein (41) the alumina tetrahedra only join to one silica tetrahedra so that no Al-O-Al bonding occurs and the Si/Al ratio is never less than unity.

The rings, formed by the basic building units, are regarded as the secondary building units of zeolite frameworks. The nature and occurrence of these rings form the basis of the modern classification of zeolite structures. These rings are analogous in size to the anions (42) thought to be responsible for the growth of zeolite crystals during synthesis and are not to be confused with larger assemblages of tetrahedra such as the β cage in faujasite (which is described below).

There are seven groups of zeolites based on this classification scheme (43, 44) - analcite, natrolite, chabazite, hormatone, heulandite, mordenite and faujasite. Most of these framework groups are based on several types of secondary building unit.

Zeolites may be geometrically visualised as based on chains, layers and polyhedra. The zeolite sodalite (Figure 2.1 (a)) of the chabazite group (44) is based on four and six membered single rings and the framework can be geometrically represented.
Fig. 2.1

(a) Line drawing of sodalite structure
(b) Truncated octahedron or sodalite unit
(c) Structural arrangement of atoms in sodalite unit
(d) Line drawing of Linde A sieve
(e) Line drawing of Linde X sieve
represented in sheets or layers of linked rings of tetrahedra. Zeolites of the mordenite group are based on complex five membered rings and individual alumina tetrahedra. The zeolite mordenite has a two dimensional tubular pore system. (45)

Apart from a recent interest in mordenite (46) most catalytic work has centred on the faujasite class. The synthetic sieves A and ZK-5 belong to this grouping and synthetic zeolites X and Y are isostructurally related. The work described in this thesis has utilised a Linde X sieve and the structure of the faujasite group, and X in particular, will be described in more detail.

The secondary building units of the faujasite group are based on four, six and eight membered single rings and in some cases four and six membered double rings (Linde A and faujasite respectively). The basic building block of the faujasite class is the sodalite unit or β cage which has the shape of a truncated octahedron consisting of silica and alumina tetrahedra. (Figs. 2.1b, 2.1c.) The manner in which these β cages join together determines the type and properties of the zeolite. It should be noted that for the line drawings given in Figure 2.1 the oxygen atoms do not lie on the midpoints of the edges but are displaced to attain tetrahedral configuration around the silicon or aluminum atoms.

In Linde A, the sodalite units share square faces through four bridging oxygen atoms to form a cubic structure. (47) This arrangement of β cages produces an α cage or truncated cubo-octahedron. (Fig. 2.1d.) This cavity has an internal diameter of 1.0nm and is entered through six circular apertures, formed by a nearly regular ring of eight oxygen atoms, with a free diameter of 0.42nm. The β cages have an internal diameter of 0.66nm and are connected/
connected to the α cages by means of distorted rings of six oxygen atoms of
0.22 nm free diameter.

The Linde A structure is also generated by joining the square faces
of the truncated cubo-octahedron or α cage. If the hexagonal faces of the
α cage are joined the structure of ZK-5 is obtained.

Synthetic zeolites X and Y and the natural zeolite faujasite have
similar aluminosilicate structures. In faujasite (48, 49) the β cages form
a diamond type structure, each cage being tetrahedrally surrounded by four
others and joined to each other at the hexagonal faces by six bridging
oxygen atoms. (Fig. 2.1e.) This arrangement of β cages generates large
supercages of about 1.20 nm internal diameter. Each of these large cages opens
into four identical tetrahedrally positioned supercages through a twelve
membered ring 0.80 - 0.90 nm in diameter.

Linde 13X sieves with sodium as the alkali metal present are named NaX
and this zeolite has the unit cell composition

\[ \text{Na}_{86} \cdot (\text{AlO}_2)_{86} \cdot (\text{SiO}_2)_{106} \cdot 264\text{H}_2\text{O} \]

Zeolite Y differs from the X type in having a higher Si/Al ratio
(ranging from 1.5 to 3.0). NaX and modifications of this zeolite prepared
by ion exchange were used as catalysts in this thesis.

2.4 Ion Exchange

Cations are present in a zeolite framework to compensate for the
negative charge which arises due to the presence of an aluminium atom
tetrahedrally co-ordinated to four oxygen atoms. One of the earliest
properties of zeolites to be recognised was their ability to exchange these
cations, usually in aqueous solutions, for a variety of other ions. (49)
Provided that the geometry is correct complex ions (50) can also be introduced
into/
into the zeolite pores.

The ion exchange behaviour of zeolites depends on the nature (size, charge) of the exchanging cation and exchange usually does not proceed to the maximum possible without structural collapse. For the X type sieves a high theoretical maximum exchange value of 4.7 milliequivalents per hydrated gram is expected. However the extent of expected exchange tends to diminish with increasing Debye - Hückel character of the ion. This behaviour can be understood because of the electrostatic nature of the cation - anion bond.

The selectivities of zeolites in ion exchange have been related to structure. The ion exchanging properties of zeolites have found significant commercial use in recovery and purification processes.

Cation exchange in zeolites affects the lattice dimensions to an extent which depends on the degree of exchange and the size and valency of the exchanging cation. Barrer and co-workers observed a change in the lattice constant from 2.49nm to 2.56nm in faujasite on replacement of monovalent sodium ions by divalent cobalt or nickel ions.

In aqueous solutions a zeolite generally exhibits a pH just greater than pH7. Zeolites undergo base exchange and structural collapse of the zeolite framework occurs if the pH of an exchanging solution falls below pH5. This has to be considered in the choice of metal salt for any proposed ion exchange in zeolites and means that exchange for proton in acid media does not occur without structural collapse.

Exchange of the zeolite framework ions for protons is achieved by initial exchange with ammonium ions and subsequent heating at temperatures between 623K and 673K to remove ammonia, leaving the proton in the lattice.
This process is known as decationisation and at the most occurs to about 96% replacement of sodium ions in faujasite type zeolites. However faujasites, with less than 0.1% sodium, which are more stable than conventionally decationated sieves, have recently been prepared by repeating the decationisation and ammonia exchange procedures. (54)

If higher temperatures are used to drive off the ammonia, removal of water or dehydroxylation occurs. The extent of decationisation determines the stability of the zeolite for dehydroxylation, the decationated zeolites being less heat resistant than the sodium forms.

Decationisation is thought by Uytterhoeven (55) and Ward (56) to result in the formation of structural OH groups which act as Brönsted acid centres. Dehydroxylation is thought to result in the formation of tri-co-ordinated aluminium oxide Lewis acid type centres through the removal of lattice oxygen atoms. (57)

The tetrahedral aluminium atom has been removed from Y zeolite frameworks by E.O.T.A. complexing agent with retention of crystallinity and with an increase in thermal stability attributable to the formation of more Si-O-Si bonds. (58)

The cations in a zeolite may also be reduced to the elemental or unusual valence state (59,60) and highly dispersed atoms are obtained in this way. Platinum zeolites prepared by an exchange and reduction process are used industrially as reforming catalysts.

2.5 Cation Locations

The adsorptive and catalytic properties of faujasite type zeolites have been shown to be influenced by the type of cation in the structure. Frilette and others (61) demonstrated that the mechanism of catalytic cracking/
cracking of hydrocarbons on a near faujasite depended on the sieve cation. Carter et al (62) have shown that the infra-red spectral features attributable to adsorbed ethylene in a zeolite were influenced by the choice of zeolite cation.

The nature and environment of these zeolite cations is therefore of great importance to an understanding of the properties of zeolites and this topic is currently of major interest in zeolite research.

The cations appear to be associated with and distributed amongst a number of specific framework positions and may exist either in the hydrated region of the large cages or at points where the framework oxygen atoms provide the highest co-ordination. Seven cation positions are currently recognised and these are depicted in Figure 2.2.

The S₁ or type I sites (either nomenclature will be applicable) are located in the interior of the hexagonal faces joining two sodalite units. Cations in the S₁ sites have six oxygen atoms 0.274nm distant as nearest neighbours and six more oxygen atoms at a further distance. The S₁ sites may be regarded as S₁ sites displaced from the hexagonal face into the sodalite cage.

The S₁₁ sites are slightly displaced from an unshared hexagonal face into the supercage. The S₁₁' and S₁₁* sites are similar except that the latter is considerably displaced into the supercage whereas the S₁₁' site is displaced into the smaller θ or sodalite cage. Cations at S₁₁ have six oxygen atoms in a puckered ring as nearest neighbours; three at 0.249nm and three at 0.254nm. Type II* projects further into the supercage than would be expected for a cation bonded to the oxygen atoms of the puckered six membered oxygen ring.

Type /
Figure 2.2

Schematic Drawing of Cation Positions in Zeolites X and Y
Type V is near the centre of the twelve membered ring which forms the entrance port to the supercage and type U lies at the centre of the sodalite unit and there are 8 of these sites per unit cell.

In earlier work \(^{(59,63)}\) the Linde workers recognised the major sites as being S\(_{11}\), S\(_{11'}\), already described, and a further site, S\(_{111}\) which is given in Figure 2.2 for comparison. This site was thought to be situated at the centre of the square faces of the sodalite cages. The S\(_{111}\) site would have two oxygen atoms, 0.374nm apart, as nearest neighbours and was thought to be populated in the univalent cation form of the zeolite.

The seven sites described may be regarded as modifications of the three major sites recognised earlier. From a catalytic viewpoint two general types of site may be considered; cations in type I, I', II' or U sites are probably less able to influence catalytic reactions involving hydrocarbon molecules than cations in type V, II or II* sites due to the former group being more inaccessible to reactant molecules. However the possibility of ions in the inaccessible sites migrating or having electostatic effect on reactants during catalysis must also be considered.

For the sites described, type I can contain a maximum of 16 cations per unit cell while the other sites could have 32 cations. Type I is the only site permitting a cation to be enclosed by framework oxygens whereas types I', II and II' have a one side co-ordination. So that in assigning cations to various sites, type I would be preferred unless considerations of electrostatic repulsion or cation-molecule attraction became important. Electrostatic repulsion may rule against simultaneous sharing of a polyhedral face as in S\(_1\) and S\(_{11}\) or more acutely S\(_{11'}\) and S\(_{11'1}\). Certain cations can co-ordinate to molecules like water to form hydrated complexes and this is known to influence preferred cation positions in zeolites. The population distribution/
distribution of the cations among the sites also depends on the nature and extent of ion exchange and on the state of hydration of the zeolite.

A variety of physical techniques have been applied to the elucidation of cation distribution and cation site preference in zeolites and a summary of these follows.

X-ray diffraction is perhaps the most reliable method of determination of cation distribution in zeolites. Diffraction experiments are best carried out using single crystals (less satisfactory results are obtained with powders) although the resulting electron density data may be subject to the limitations of personal interpretation. The technique gives information about the positions of cations and water molecules in the zeolite structure and results relating to faujasites in different states of hydration are given in table 2.1.

Table 2.1

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Form</th>
<th>I</th>
<th>I'</th>
<th>II</th>
<th>II'</th>
<th>II*</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX</td>
<td>Hydrated</td>
<td>9Na</td>
<td>8Na</td>
<td>24Na</td>
<td>8H₂O</td>
<td>26H₂O</td>
<td></td>
</tr>
<tr>
<td>Faujasite</td>
<td>Hydrated</td>
<td>16(Na,Ca)</td>
<td>32H₂O</td>
<td>11H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce,Na,Ca-faujasite</td>
<td>Hydrated</td>
<td>18Na</td>
<td>32H₂O</td>
<td>26H₂O</td>
<td>5.8Ca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na,Ce-faujasite</td>
<td>Partly dehydrated</td>
<td>3.4Na</td>
<td>11.5Ca</td>
<td>10.7Na</td>
<td>16H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-faujasite</td>
<td>Strongly dehydrated</td>
<td>10.6</td>
<td>3.2Ni</td>
<td>6.4Ni</td>
<td>1.9Ni</td>
<td>1.9H₂O</td>
<td></td>
</tr>
</tbody>
</table>
In an early study of hydrated NaX zeolites (48) a full $S_1$ occupation was found although a re-evaluation (65) of the data assigned cations to type I, $I'$ and II sites. More recently the cation distributions in a single crystal of hydrated NiX (66) and in strontium, lanthanum and cerium exchanged X zeolites (67, 68) have been determined. Hydrated CeX has cations in type V sites predominantly, due to hydration at this position. On outgassing the zeolite at $623^\circ K$ for 15 hours cerium ions were observed to migrate into the $\beta$ cage where they can octahedrally co-ordinate with three framework oxygens and three water molecules.

Angell and Schaffer (69) have used infra-red techniques to determine the cation occupancy of surface sites. Certain cations in surface sites were observed to give a specific infra-red band on the adsorption of carbon monoxide. For X zeolites the results indicated that divalent copper ions occupied sites inaccessible to carbon monoxide until 35% replacement of sodium by copper whereas cobalt and nickel ions occupied surface sites (accessible to carbon monoxide) after 20% replacement of sodium.

Electron spin resonance studies (70) of divalent manganese, incorporated into zeolites previously exchanged with other divalent cations, have also been used to elucidate the site occupancy in zeolites. The manganese ion in X type exchanged zeolites was found to have no overwhelming site preference. Results for hydrated X type zeolites indicated that $Li^+$, $Mg^{++}$ and $Zn^{++}$ ions occupied surface sites, accessible to water, due to the high heats of hydration of these ions. It was also concluded that these ions had a lower $S_1$ preference than sodium, $Zn^{++}$ being especially unfavourable for $S_1$ occupation since this ion prefers a tetrahedral co-ordination. In dehydrated X zeolites the preference for type I sites was found to depend on the ion field strength and ion size; for the alkali metals the order of type I preference is $K^+ > Na^+ > Li^+$ with $Rb^+$ and $Cs^+$ being excluded on geometric considerations.

Attempts/
Attempts to determine zeolite cation distributions have also been made from studies of catalytic activity (71) and from gaseous adsorption and gas chromatographic measurements (72).

Mössbauer spectroscopy can yield information about valence states of certain atoms and the environment of these atoms (73), and this technique has been applied to the problem of cation valencies and distributions in zeolites. From studies of Mössbauer spectra of Fe$^{3+}$ in Y zeolites, Goldanski et al. (74) proposed that ferric cations are in non-localised positions, the effect of gaseous adsorption being to localise these cations. Delgass and Boudart (75) also observed non-localisation of ferrous ions in ferrous Y zeolite; localisation of the ions occurred on dehydration. Norice and Rees (76) found that ferric ions were reduced to ferrous ions when a ferric Y zeolite was outgassed. The results also indicated that at low levels of exchange, ferric ions (hydrated zeolite) preferred type II sites.

It is clear that although the subject of cation distribution in zeolites is one which has aroused considerable interest, there are still problems in obtaining precise information. Some of the factors influencing the cation distribution in zeolites and some of the methods used to elucidate the nature of the cation population have been presented in the above.

2.6 Dehydration/Stability/Adsorption

The presence of molecular water as a chemically inert entity in zeolites is unlikely. Zeolitic water is known to occupy cation positions and form hydrated complexes with the exchangeable cations (77). The presence of water in zeolites, even in small amounts, has also been shown (78) to influence the cation distribution. Water may also interact with framework oxygens and can also be polarised, by the electrostatic field around the cation, into hydroxyl groups and protons which may then attach to the framework oxygens.
The water present in zeolites is removable by heating and/or evacuation; the process of dehydration causes no major change in lattice structure although the cation distribution may be affected. (68, 76) Zeolites with monovalent cations normally dehydrate more readily than multivalent forms, for which the bonding of the hydrated cation complex is stronger. Dehydrated zeolites exhibit a high degree of thermal stability; temperatures of the order of 973K are required to decompose an X type structure. However structural collapse may occur in the presence of water at lower temperatures. The ability of zeolites to resist thermal decomposition in the presence of water depends on the Si/Al ratio, those zeolites with the higher ratios being the most stable. (79) (i.e. Y better than X type)

The stability of zeolites is also affected by the nature and extent of ion exchange. Rabo (59) has suggested that structural breakdown occurs on dehydration of tervalent ion exchanged zeolites due to hydrolysis in the presence of a sufficiently strong electrostatic field. It has also been found (80) that strontium and cobalt exchanged X zeolites are thermally less stable than monovalent or other divalent forms.

The molecular sized voids which remain on dehydration of a zeolite can selectively adsorb gases or vapours. The adsorption process is controlled by the dimensions of the zeolite windows, so that molecules which are too large to enter the windows are not adsorbed. Thus providing the geometry requirements are fulfilled, a zeolite adsorbs a gas or vapour until the pore volume is completely filled; this behaviour gives a rectangular type of shape to the adsorption isotherm. Examples of limiting adsorption capacities for certain adsorbents in X zeolites, determined from measurements of isotherms of adsorbents at saturation pressures, are given in table 2.2. Molecules which are not normally adsorbed may be encapsulated in the zeolite structure at high temperatures and pressures. Under these conditions adsorption occurs due to an increased window size (resulting from/
from the increased vibrational amplitude) and on cooling the pore windows shrink enclosing the guest molecules in the zeolite pores.

Table 2.2

Limiting Adsorption Capacities for X-type Zeolites (35,52,79)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Kinetic Diameter (nm)</th>
<th>Temperature (K)</th>
<th>Pressure (kN/m²)</th>
<th>No. Adsorbed Mols./Cavity for NaX</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.265</td>
<td>298</td>
<td>3.33</td>
<td>33.0</td>
</tr>
<tr>
<td>Ar</td>
<td>0.340</td>
<td>90</td>
<td>101.31</td>
<td>17.6</td>
</tr>
<tr>
<td>O₂</td>
<td>0.346</td>
<td>90</td>
<td>101.31</td>
<td>18.6</td>
</tr>
<tr>
<td>Kr</td>
<td>0.360</td>
<td>90</td>
<td>91.90</td>
<td>14.5</td>
</tr>
<tr>
<td>N₂</td>
<td>0.364</td>
<td>77</td>
<td>93.33</td>
<td>16.6</td>
</tr>
<tr>
<td>Xe</td>
<td>0.396</td>
<td>195</td>
<td>93.33</td>
<td>9.3</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.430</td>
<td>298</td>
<td>27.32</td>
<td>4.3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.600</td>
<td>298</td>
<td>6.00</td>
<td>3.9</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.600</td>
<td>298</td>
<td>10.13</td>
<td>5.6</td>
</tr>
<tr>
<td>Neopentane</td>
<td>0.620</td>
<td>298</td>
<td>92.33</td>
<td>3.6</td>
</tr>
<tr>
<td>((C₄H₉)_3N)</td>
<td>0.810</td>
<td>298</td>
<td>0.10</td>
<td>2.1</td>
</tr>
<tr>
<td>((C₄F₉)_3N)</td>
<td>1.020</td>
<td>323</td>
<td>0.07</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The factors affecting adsorption in zeolites have been reviewed by Venuto and Landis. (81) Zeolite adsorption behaviour depends generally on the geometry, charge distribution and interaction of the zeolite and/or the sorbate. The different zeolite types have different pore sizes and the effect of temperature on the critical (with respect to adsorption) dimensions has been given above. Zeolites with low Si/Al ratios have relatively high charge distributions and adsorb polar organic molecules less readily than zeolites with higher Si/Al ratios. It has been suggested that the sizes of the rings associated with zeolites also decrease with increase in silica content, due to the Si—O bond being shorter than the Al—O bond. (82)

The number, size, valency and location of zeolite cations also affect the size/
size and shape of the windows which control adsorption in zeolites. Reed and Breck (46) observed an increase in pore diameter from 0.4nm to 0.5nm in zeolite A after 30% - 40% replacement of the monovalent sodium ions by divalent calcium ions. It has also been shown that the pore diameter of sodium X zeolites is reduced on replacement of sodium by calcium or barium. (79) The observed adsorption behaviour of zeolites depends on the cations and consequently factors affecting cation positions and distribution (i.e. dehydration) (83) affect the adsorption properties. Controlled addition of water or ammonia has been shown to affect the sorption behaviour of ethane in chabazite and mordenite. (44, 84, 85)

The geometry and polarity of the sorbate also influence the sorption behaviour. The former feature is of obvious industrial interest and numerous processes utilise the ability of zeolites to exclude molecules from their pores on the basis of size. Polarity of sorbate influences the pore dimensions due to the possible strong interaction of polar or polarisable functional groups (e.g. -OH, -C=O, -NH₂, -C=C) in the sorbate with the zeolite surface. The sorption inhibition reported by Goldstein (86) of zeolites containing eight ring pore entry windows for species such as simple nitriles, carboxylic acids and nitro compounds can be rationalised in such a manner.

2.7 Surface Investigations

The best method of studying hydroxyl groups, adsorbed water and other species which may exist on the surface of zeolites, is infra-red spectroscopy. Investigations utilising this technique have been reviewed by Yates (87) and by Ward. (88) For X type zeolites three infra-red bands are generally observed (89) and these have been associated, in order of decreasing frequency, with SiOH groups, AlOH groups and hydroxyl groups linked with the cations. For the X zeolites studied hydroxyl groups were detected even after outgassing of the zeolite at 873K. Other workers (90) have also confirmed the presence of residual hydroxyl groups.
groups on NaX outgassed at 723K. Angell and Schaffer (91) have reported the existence of residual hydroxyl groups for X and Y zeolites outgassed at high temperatures. The results observed for the Y zeolites were similar to those observed for X zeolites; three hydroxyl bands were generally observed for a series of ion exchanged Y sieves. Ward (92) has published work on spectra of hydroxyl groups on zeolites, particularly alkali metal, alkaline earth and rare-earth exchanged Y zeolites. Structural hydroxyl groups were observed for NaX (the results were in agreement with the data of Habgood (90) above) and for magnesium, calcium, strontium and rare-earth exchanged zeolites. No hydroxyl groups were observed for alkali cation and base exchanged forms.

The infra-red spectra of various inorganic and organic molecules adsorbed on zeolites have also been reported.

(i) Inorganic Molecules

The adsorption of water has been reported by Bertsch and Habgood (93) for sodium, lithium and potassium exchanged X zeolites. They concluded that the adsorbed water was bonded to the zeolite cation via the oxygen atom (of water) and also hydrogen bonded to a zeolite oxygen atom. The hydrogen of the zeolite hydroxyl groups (described above) has been found to be exchangeable with heavy water (94) or deuterium (89) with the resultant formation of deuteroxy groups. The reversible adsorption of water on zeolites is not generally accompanied by reversible infra-red spectra. The spectral differences observed by Ward (92) during dehydration, rehydration and subsequent dehydration cycles of group IA and IIA Y zeolites were explained in terms of changes of cation location or co-ordination or hydrogen bonding. Zhdanov (94) has found that the frequency and ease of removal of adsorbed water depends on the Si/Al ratio and reported that hydroxyl band frequency decreased with increasing cation radius, indicative of the cation polarising influence.

The/
The work of Angell and Schaffer (69) in relation to carbon monoxide adsorption on X, Y zeolites has already been described (2.5); the adsorbed carbon monoxide was considered to be bonded via a carbon - cation bond and polarised by the cation electric field.

Habgood has studied the adsorption of carbon dioxide on X type zeolites (93). Two types of adsorbed species were found; one was attributed to an intact carbon dioxide molecule which was reversibly adsorbed at room temperature and the other to a carbonate species formed by chemisorbed carbon dioxide. The alkaline earth zeolites did not exhibit the carbonate type band and it was proposed that carbonate species were found at less shielded surface cation sites which were unlikely to contain alkaline earth cations.

Infra-red data (95) has also been published concerning the adsorption of nitrogen oxides on X type zeolites. The adsorption of nitrogen dioxide resulted in the formation of surface nitrate groups whereas the adsorption of nitric oxide apparently led to dissociation with nitrous oxide and oxygen species being observed.

The adsorption of ammonia on decationated zeolites has been shown (55) to result in bands characteristic of $\text{NH}_4^+$ and it was suggested that reformation of the ammonium zeolite had occurred.

(ii) Organic Molecules

One of the earliest studies of organic molecules on zeolites was reported by Kiselev and co-workers (96) who investigated the adsorption of benzene on sodium and calcium X zeolites which had previously been vacuum dehydrated at 723K. It was considered that benzene was adsorbed on the walls of the large cavities within the zeolite and the changes in the infra-red spectrum of benzene was attributed to changes in electronic distribution caused by the zeolite electrostatic field. It has been confirmed by ultra-violet spectroscopy (97) that/
that adsorption of benzene on zeolites involves the $\pi$ electron system. Angell and Howell (98) have also studied the adsorption of toluene and benzene on a series of ion-exchanged Y zeolites and observed similar results (as the Kiselev group) for both organic molecules. The results were interpreted by assuming the benzene (or toluene) was adsorbed parallel to the zeolite surface, which interacted with the $\pi$ orbital system of the benzenoid species. The adsorption of benzene, cyclohexene and cumene has also been studied on HY zeolites. (99) The spectra of adsorbed cyclohexene resembled that of liquid cyclohexane. Eberly (100) has also observed a loss in double bond character of hex-1-ene adsorbed on DY zeolite. Carter (62) has shown from infra-red studies of ethylene adsorbed on zeolites that weak chemisorptive forces may be involved, the cation interacting directly with the double bond.

Infra-red spectroscopy can also detect surface ionic species where a net transfer of negative charge from an organic substrate to a zeolite framework has taken place. Pyridinium ions have been shown (101) to exist on the surface of decationated X and Y zeolites after pyridine adsorption. Certain features of the spectra of adsorbed molecules such as pyridine, piperidine and ammonia can be identified with either Lewis acid sites and Brønsted acid sites or cations and their hydrogen bonding interactions.

Other techniques can be used to elucidate the surface features of zeolites. Indicators which form stable surface carbonium ions can furnish information regarding surface acidity. (102) Stamires and Turkevich (103) have utilised magnetic resonance spectroscopy to detect aromatic radical cations on dehydroxylated Y faujasites. Kazanskii (77) has used electron paramagnetic resonance spectroscopy to relate the reactivity of copper zeolites, in the ethyl alcohol dehydrogenation, to certain cation positions. The catalytic activity of A, X and Y zeolites for but-1-ene isomerisation has also been related (104) to certain hydroxyl bands observed in the infra-red spectra.

Knowledge/
Knowledge of the surface of zeolites is therefore of importance in considering the reactions catalysed by zeolites.

2.3 Catalytic Properties

Zeolites are known to be active catalysts for a wide range of reactions and detailed reviews of these reactions have been presented by Turkevich (105) and by Venuto and Landis (81). Complete coverage of the reactions catalysed by zeolites is not possible but the following considers aspects of reactions allied to the work carried out in this thesis.

(i) Cracking Reactions

Zeolites have been found to be more active than conventional aluminosilicates for certain cracking reactions (106) and a high cracking activity is observed for molecular sieves with olefinic and paraffinic substrates; virtually no branched chain hydrocarbons being produced. The most active catalysts are those which have been base exchanged with a consequent reduction in their alkali metal content. Cerium, lanthanum and hydrogen zeolites have been found more active than other cracking catalysts in the cracking of n-hexane. (107)

The activity of various zeolites for the cracking of n-hexane and cumene has been studied by several workers (103); the product distributions for the multivalent cation exchanged forms suggested a carbonium ion type of mechanism but there was uncertainty over the nature of the active sites. Wolf and Losse (108) have suggested a correlation of the acidity and the cracking activity of decationated zeolites of differing aluminium content. Boreskova (109) has found that calcium and sodium forms were less active than the decationated forms of synthetic faujasites. He has related the active centres of the decationated forms to tri-coordinated aluminium atoms whereas the active centres of the cationated forms were suggested as being alumina tetrahedra with incompletely compensated negative/
(ii) **Electrophilic Aromatic Substitution Reactions**

Zeolite catalysed reactions of this type are understood to involve attack by an electrophile on an aromatic ring with the formation of a new bond and elimination of proton. The electrophile may be regarded as being generated by protonation of olefinic or carbonyl compounds or by hydride abstraction from a paraffinic or alkyl aromatic compound. The reactions are generally thought of as being acid catalysed, proceeding through carbonium ion intermediates. (110) Features of alkylation reactions catalysed by zeolites are similar to those reported in the presence of strong protonic acids (e.g. liquid HF, liquid H$_2$SO$_4$) or strong Lewis acids.

Quantitative evidence (111) points towards an Eley type mechanism for zeolite alkylation. Alkylation of an olefin can then be regarded as involving fast, reversible and non-competitive adsorption of olefin on catalyst active sites (regarded as surface hydroxyl groups) followed by the slower alkylation step.

Alkylations of alcohols and haloalkanes proceed in a manner analogous to aromatic substrate with heterolysis of carbon-oxygen or carbon-halogen bonds resulting in the formation of carbonium ions which may then associate with the rigid polyanionic lattice. The large amounts of n-alkylate formed during alkylation of primary alcohols and halides are thought to arise by SN$_2$-like Eley processes.

The work of Pickert and co-workers (112) on the activity of zeolites for the propylation of benzene supported the view that the formation of the carbonium ion like species arose through polarisation of reactant hydrocarbons by the cation fields. Consideration of cumene de-alkylation results (63) resulted in similar conclusions concerning the active sites which were ascribed to the cations (carboniogenesis) and not to the 1% of structural OH groups remaining after catalyst activation. However Rabo (59) has suggested that the hydroxyl groups/
groups act as proton donors in similar reactions over trivalent cation exchanged zeolites.

(iii) Hydrogenation/Dehydrogenation

Most crystalline aluminosilicates have little intrinsic activity for hydrogenation/dehydrogenation type reactions. Metal loaded zeolites, prepared by base exchange, followed by reduction in situ, are found to be active for hydrogenation reactions. Galich has observed little activity for dehydrogenation reactions of n-alkanes over sodium and calcium X zeolites although moderate activity was observed for nickel, cobalt, iron or chromium X catalysts. Zinc and cobalt exchanged zeolites show enhanced activity in the presence of ammonia, with the formation of dienes from olefin substrates. It is proposed that ammonia partially poisons acid sites and inhibits coke formation. Non zeolite systems are observed to give similar behaviour as zeolites for reactions of this type and consequently the role of the zeolite structure in such reactions is debatable.

(iv) Olefin Forming Eliminations

Olefin forming eliminations are among the most characteristic reactions observed over zeolite catalysts. Elimination occurs by a $\beta$ type process involving loss of proton from one of the two adjacent ring or chain carbon atoms and loss of a nucleophile from the other carbon atom.

The activity of cation exchanged X zeolites for n-butanol dehydration has been shown to depend on the cation size and valency. Higher activity was observed for zeolites possessing greater cationic charge density and higher calculated electric field strengths. The order of activity at 623K was Li > Na > K > Rb. The water, produced from the alcohol dehydration, which was eliminated, apart from possibly reversing the dehydration, has also been shown to influence zeolite cations and may promote carbonium ion type mechanisms. The activity of CaX for tertiary butanol dehydration was found to increase after pretreatment of the catalyst.
catalyst with small amounts of water.

Mochida and Yoneda (117) have reported different relative isomeric yields of products formed from elimination reactions of 1, 1, 2 trichloroethane over zeolite catalysts. The more acidic sieves (HY, MgX) showed lower (less than equilibrium) $^{1,1}/1,2$ and $\text{trans}/\text{cis}$ ratios (of product dichloroethylenes) than NaX and KX which gave $\text{trans}/\text{cis}$ ratios greater than those expected at equilibrium.

For many zeolite catalyst systems the substrate reactivity parallels the increasing stability of the carbonium ions formed by loss of nucleophile; for alcohols the tertiary alcohols react faster than secondary alcohols which react faster than primary alcohols. Polar or ionic intermediates are generally considered to be involved in reactions of this type, the role of the zeolite being apparently to provide an extensive rigid and ordered polar surface which possibly expedites the ionisation or heterolytic bond cleavage in an adsorbed substrate (alcohol or halide).

(v) Olefin Reactions

The reactions of interest here include isomerisation, polymerisation and isotopic exchange. Acidic sites on the zeolite and carbonium ions are generally thought to be involved in these reactions. A correlation has been observed between catalytic activity and Brønsted acid site concentration for the o-xylene isomerisation reaction. (118, 119) Rare earth exchanged X, and to a lesser extent HY and dehydroxylated Y, zeolites have been found to be the most active catalysts for this class of reactions. Trivalent cation exchanged zeolites have been found to be more active for but-1-ene isomerisation than the divalent forms, with monovalent forms exhibiting little isomerisation activity. (120)

Turkevich (106) has reported that loading of NaX with alkali metals provides catalysts active for double bond isomerisation but inactive for skeletal isomerisation. Norton (121) has found that CuX is more active than NaX for propylene polymerisation and that the polymer products formed were typical of those reported/
reported for conventional acid catalysts. Equilibrium amounts of butanes as major products have been reported \( (81) \) for the dimerisation reaction of ethylene over divalent nickel cation containing zeolites; catalysts containing cobalt or chromium were found to be less effective. Induction periods were reported in this work and these were attributed to formation of intracrystalline polymeric material. Venuto and others \( (111) \) have reported the formation of occluded polyolefins as large as \( C_{30}H_{50} \) from the isomerisation and polymerisation of hex-1-ene over rare earth exchanged X zeolites. Addition of heavy water to these catalysts and subsequent analysis by mass spectrometry showed that extensive transfer of deuterium from catalyst deuteroxy groups to the olefin had occurred resulting in the formation of \( C - D \) bonds. Further evidence for a carbonium ion mechanism involving transfer of hydrogen is presented by Habgood \( (122) \) who studied the isomerisation of cyclopropane over a deuterated Y zeolite. Propane was thought to be formed via a carbonium ion intermediate in a Brönsted type mechanism involving intramolecular hydrogen transfer.

Venuto \( (111) \) has recently emphasised that hydrogen redistribution or transfer is one of the most dominant and recurrent reactions of olefins over acidic zeolite catalysts. The common feature of such reactions is the attack of the hydride ion on an electron deficient carbon atom (carbonium ion). The hydride ion may be formed as a result of intramolecular or intermolecular migration from a carbon atom or possibly from a Lewis acid type catalyst site. The formation of minor quantities of ethane during the ethylation of isobutane \( (123) \) probably occurred via a hydride transfer from isobutane to the carbonium ion generated by the protonation of ethylene.

Various other reactions are also known to be catalysed by crystalline aluminosilicates; these include condensation and cyclisation, acetal and ketal formation, Beckman re-arrangement, epoxide transformations, olefin carbonylation, amination reactions and various inorganic reactions.

2.9 /
2.9 Mechanisms of Zeolite Catalysis

Carbonium ion like intermediates are thought to be involved in certain polymerisation, elimination and aromatic substitution reactions over zeolites. Multivalent and decationated forms of zeolites exhibit the highest activity for such reactions but the function of the zeolite cations in the catalysis is still a subject of some controversy. Pickert (63) has accounted for the observed similarity of the activities of multivalent cation and decationated zeolites by invoking charged sites in the zeolite lattice which polarise hydrocarbons to form semi ion - pair species.

Although electrostatic fields generated by the cations may be involved, current thinking regards acidic protons (formed from hydrolysis of water in an electrostatic field) as the centres of zeolite catalytic activity. These centres are regarded as Brönsted acid sites formed by surface hydroxyl groups although some workers propose that Lewis acid type sites are involved. Turkevich (124) has observed a correlation between catalytic activity and Lewis acid site concentration.

Dehydration, oxidation and cracking reactions over zeolites are generally regarded as being non-carbonium ion in character. For alkali metal zeolites, which exhibit low acidity, radical processes are thought to be involved. The oxidation of hexanes on NaX (125) and the cracking of isomeric hexanes (126) over alkali metal Y zeolites are typical in this respect. Carbenoid and carbene species may also be involved in certain zeolite catalysed dehydration and dehalogenation reactions. The role of the cations for these non-carbonium ion reactions has been suggested as a direct one; interaction between cations in accessible sites and reactant occurs.

Thus present theories concerning the mechanisms of zeolite catalysis clearly show that there is no overall explanation common to all the observed experimental data. Particular models or mechanisms may be favoured for different reactions or for/
for different zeolites, as outlined above, but it is also possible that more than one mechanism may be involved and contribute to the observed catalytic behaviour.

Previous work in this department (127) on the n-butene isomerisation reaction has revealed information about mechanisms and active sites of certain X type zeolites. Similar catalysts have been used in the work described in this thesis. The aim of the study of reactions of mono and dimethyl substituted cyclopropanes was to provide additional evidence concerning the operative reaction mechanisms.
CHAPTER III

ISOMERISATION OF CYCLOPROPANES

3.1. General Properties of Cyclopropane

Cyclopropane and derivatives of this three membered ring compound are of considerable interest as materials to test structural and mechanistic theories.

The bonding in cyclopropane is such that the ring carbon atoms have more 'p' character than sp\(^3\) hybridised carbon atoms. The angle between orbitals lies between that of a sp\(^3\) hybrid (109° 28') and that of an sp\(^2\) hybrid carbon (90°). The electrons of the carbon bonds are thus localised in bent or banana shaped bonds; the regions of high electron density lie outside the triangle formed by the carbon nuclei.

Cyclopropane reacts readily with electrophilic reagents, as is expected from the above; methyl substituted analogues undergo hydrogenation according to the Markovnikov rule. Cyclopropyllium cations stabilised by electron donating groups are known. However it is relatively difficult to form a ring carbanion.

3.2 Reaction Paths/Mechanisms

Methylocyclopropane (MCP), 1,1 dimethylocyclopropane (1,1 DMCP) and 1,2 dimethylocyclopropane (1,2 DMCP) are (STP) stable but these substances can thermally and catalytically isomerise to yield a variety of products. Hydrogenation of these materials (in the presence of catalyst or otherwise) will, depending on the relative reactant pressures, result in saturated and unsaturated/
Figure 3.1  Major Products Arising from Bond Cleavages in Alkylcyclopropane Isomerisation and Hydrogenation Reactions

<table>
<thead>
<tr>
<th>HYDROGENATION</th>
<th>REACTANT</th>
<th>ISOMERISATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 cleavage</td>
<td>n-butane</td>
<td>n-butenes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3 isomers)</td>
</tr>
<tr>
<td>2/3 cleavage</td>
<td>iso-butane</td>
<td>iso-butene</td>
</tr>
<tr>
<td>MCP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/2 cleavage</td>
<td>iso-pentane</td>
<td>methyl-butenes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3 isomers)</td>
</tr>
<tr>
<td>2/3 cleavage</td>
<td>neo-pentane</td>
<td>not allowed</td>
</tr>
<tr>
<td>MCP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/3 cleavage</td>
<td>iso-pentane</td>
<td>methyl-butenes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3 isomers)</td>
</tr>
<tr>
<td>1/2 cleavage</td>
<td>n-pentane</td>
<td>n-pentenes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3 isomers)</td>
</tr>
</tbody>
</table>
unsaturated products. The various types of reaction and the major products which result are presented in Figure 3.1. Complete reactant conversion would yield products as depicted and it is clear that products observed during reaction of such cyclic compounds are a function of the direction of ring cleavage. However an olefinic product will not arise from direct cleavage of a saturated three membered ring and a re-distribution of hydrogen must take place.

It may be supposed that three main types of intermediate are involved in the reactions outlined in Figure 3.1. The products and mechanisms giving rise to these products of reaction of the various alkylcyclopropanes will now be considered in terms of the three main intermediate types (radical, carbanion, carbonium ion).

A simplified general scheme (ignoring the effect of catalyst) for a reaction given in Figure 3.1 would be:

Reactant $\rightarrow$ Intermediate $\rightarrow$ Product

Ionic intermediates would be formed from gain or loss of proton or hydride at various carbon positions in the cyclopropane molecule. Radicals would result from interaction of hydrogen atoms. Formation of cyclic intermediate is not considered. Attack or loss of hydrogen results in ring scission and the stability of intermediate formed determines the product distribution; for carbonium ion and radical the order of stability is tertiary $>$ secondary $>$ primary while for carbanions this is the order of instability. For example loss of hydride ion from C1 in methylcyclopropane would result in formation of iso-butene via a primary carbonium ion whereas loss of hydrogen from C2 would result in n-butene formation via a resonance stabilised intermediate; n-butene formation would be preferred. These products/
<table>
<thead>
<tr>
<th>Type of Mechanism</th>
<th>Centre of Interaction in MCP</th>
<th>Products</th>
<th>Intermediate Type / Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^-\text{Loss} )</td>
<td>1</td>
<td>iso-butene</td>
<td>Primary Carbonium ion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-butenes</td>
<td>Resonance stabilised carbonium ion</td>
</tr>
<tr>
<td></td>
<td>Methyl Carbon</td>
<td>but-1-ene</td>
<td>Primary carbonium ion</td>
</tr>
<tr>
<td>( \text{H}^+\text{Loss} )</td>
<td>1</td>
<td>iso-butene</td>
<td>Primary carbanion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-butenes</td>
<td>( \tau ) allyl type species</td>
</tr>
<tr>
<td></td>
<td>Methyl Carbon</td>
<td>but-1-ene</td>
<td>Primary carbanion</td>
</tr>
<tr>
<td>( \text{H}^-\text{Gain} )</td>
<td>1</td>
<td>but-1-ene</td>
<td>Primary carbanion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>cis ( \text{C}_2 ) ( \text{trans} ) but-2-ene, but-1-ene</td>
<td>Secondary carbanion, but-1-ene formed via methyl group elimination</td>
</tr>
<tr>
<td></td>
<td>iso-butene</td>
<td>Primary carbanion</td>
<td></td>
</tr>
<tr>
<td>( \text{H}^+\text{Gain} )</td>
<td>1</td>
<td>but-1-ene</td>
<td>Primary carbanion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>cis ( \text{or trans} ) but-2-ene, but-1-ene</td>
<td>Secondary carbanion, but-1-ene formed through use of methyl group</td>
</tr>
<tr>
<td></td>
<td>iso-butene</td>
<td>Primary carbanion</td>
<td></td>
</tr>
<tr>
<td>( \text{H}^+\text{Loss} )</td>
<td>1/2</td>
<td>n-butenes</td>
<td>Re-arrangement of primary radical (C2 secondary)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>iso-butene</td>
<td>Primary radical (re-arrangement)</td>
</tr>
<tr>
<td>( \text{H}^+\text{Gain} )</td>
<td>1</td>
<td>but-1-ene</td>
<td>Primary radical</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>cis ( \text{or trans} ) but-2-ene, but-1-ene</td>
<td>Secondary radical, but-1-ene formed via methyl group</td>
</tr>
<tr>
<td></td>
<td>iso-butene</td>
<td>Primary radical</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2

Analysis of Possible Products Arising from Gain/Loss of Hydrogen in 1,1 Dimethylcyclopropane (1,1 DMCP)

<table>
<thead>
<tr>
<th>Type of Mechanism</th>
<th>Centre of Interaction in 1-1, DMCP</th>
<th>Products</th>
<th>Intermediate Type/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^{-}\text{Loss}$</td>
<td>2</td>
<td>3 methyl but-1-ene 2 methyl but-2-ene</td>
<td>resonance stabilised carbonium ion</td>
</tr>
<tr>
<td></td>
<td>Methyl Carbon</td>
<td>2 methyl but-1-ene</td>
<td>primary carbonium ion</td>
</tr>
<tr>
<td>$H^{-}\text{Loss}$</td>
<td>2</td>
<td>3 methyl but-1-ene 2 methyl but-2-ene</td>
<td>$\pi$- allyl species</td>
</tr>
<tr>
<td></td>
<td>Methyl Carbon</td>
<td>2 methyl but-1-ene</td>
<td>primary carbanion</td>
</tr>
<tr>
<td>$H^{+}\text{Gain}$</td>
<td>1</td>
<td>3 methyl but-1-ene</td>
<td>primary carbanion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2 methyl but-2-ene 2 methyl but-1-ene</td>
<td>tertiary carbanion, 2 methyl but-1-ene formed via methyl group</td>
</tr>
<tr>
<td>$H^{+}\text{Gain}$</td>
<td>1</td>
<td>3 methyl but-1-ene</td>
<td>primary carbonium ion</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2 methyl but-2-ene 2 methyl but-1-ene</td>
<td>tertiary carbonium ion, 2 methyl but-1-ene formed via methyl group</td>
</tr>
<tr>
<td>$H^{-}\text{Loss}$</td>
<td>2</td>
<td>2 methyl but-1-ene 2 methyl but-2-ene</td>
<td>tertiary radical</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2 methyl but-1-ene 2 methyl but-2-ene</td>
<td>2 methyl but-1-ene formed via methyl group</td>
</tr>
<tr>
<td>$H^{+}\text{Gain}$</td>
<td>1</td>
<td>3 methyl but-1-ene</td>
<td>primary radical</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2 methyl but-2-ene 2 methyl but-1-ene</td>
<td>tertiary radical, 2 methyl but-1-ene formed via methyl group</td>
</tr>
</tbody>
</table>
### Table 3.3.

**Analysis of Possible Products Arising from Gain/Loss of Hydrogen in 1,2 Dimethylcyclopropane (1,2 DCMP)**

#### A. 1 - 3 Scission

<table>
<thead>
<tr>
<th>Type of Mechanism</th>
<th>Centre of Interaction in 1,2 DMCP</th>
<th>Products</th>
<th>Intermediate/Type Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^-$ Loss</td>
<td>1</td>
<td>2 methyl but-2-ene, 2 methyl but-1-ene</td>
<td>resonance stabilised carbonium ion</td>
</tr>
<tr>
<td></td>
<td>methyl carbon</td>
<td>3 methyl but-1-ene</td>
<td>primary carbonium ion</td>
</tr>
<tr>
<td>$H^+$ Loss</td>
<td>1/3</td>
<td>2 methyl but-2-ene, 2 methyl but-1-ene</td>
<td>allyl species</td>
</tr>
<tr>
<td></td>
<td>methyl carbon</td>
<td>methyl but-1-ene</td>
<td>allyl species</td>
</tr>
<tr>
<td>$H^-$ Gain</td>
<td>1</td>
<td>2 methyl but-1-ene</td>
<td>secondary carbonium, 3 methyl but-1-ene formed via methyl group</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2 methyl but-2-ene, 3 methyl but-1-ene</td>
<td></td>
</tr>
<tr>
<td>$H^+$ Gain</td>
<td>1</td>
<td>2 methyl but-1-ene</td>
<td>primary carbonium ion</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2 methyl but-2-ene, 3 methyl but-1-ene</td>
<td>secondary carbonium ion</td>
</tr>
<tr>
<td>$H^+$ Loss</td>
<td>1</td>
<td>methyl butenes</td>
<td>re-arrangement of primary radical</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>methyl butenes</td>
<td>re-arrangement of secondary radical</td>
</tr>
<tr>
<td>$H^-$ Gain</td>
<td>1</td>
<td>2 methyl but-1-ene</td>
<td>primary radical</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3 methyl but-1-ene, 2 methyl but-2-ene</td>
<td>secondary radical, 3 methyl but-1-ene formed via methyl group</td>
</tr>
</tbody>
</table>
Table 3.3 (continued)

Analysis of Possible Products Arising from Gain/Loss of Hydrogen in 1,2 Dimethylcyclopropane (1,2 DMCP)

B. 1-2 Scission

<table>
<thead>
<tr>
<th>Type of Mechanism</th>
<th>Centre of Interaction in 1,2 DMCP</th>
<th>Products</th>
<th>Intermediate Type/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁻ Loss</td>
<td>1/3</td>
<td>cis and trans pent-2-ene, methyl carbon</td>
<td>resonance stabilised carbonium ion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pent-1-ene</td>
<td>secondary carbonium ion</td>
</tr>
<tr>
<td>H⁺ Loss</td>
<td>3</td>
<td>cis and trans pent-2-ene, methyl carbon</td>
<td>resonance stabilised secondary carbonion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pent-1-ene</td>
<td>secondary carbonion</td>
</tr>
<tr>
<td>H⁻ Gain</td>
<td>1</td>
<td>n-pentenes</td>
<td>secondary carbonion, pent-1-ene formed via methyl group</td>
</tr>
<tr>
<td>H⁺ Gain</td>
<td>1</td>
<td>n-pentenes</td>
<td>secondary carbonium ion, pent-1-ene formed via methyl group</td>
</tr>
<tr>
<td>H⁺ Loss</td>
<td>1</td>
<td>n-pentenes</td>
<td>re-arrangement of secondary radical</td>
</tr>
<tr>
<td>H⁻ Gain</td>
<td>1</td>
<td>n-pentenes</td>
<td>secondary radical, pent-1-ene formed via methyl group</td>
</tr>
<tr>
<td>Reactant/ Mechanism</td>
<td>Methylcyclopropane</td>
<td>1,1 dimethylcyclopropane</td>
<td>1,2 dimethylcyclopropane</td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>H\textsuperscript{-} Loss</td>
<td>( \text{trans but-2-ene} &gt; \text{cis but-2-ene} &gt; \text{but-1-ene} &gt; \text{iso-butene} )</td>
<td>2 methyl but-2-ene, 3 methyl but-1-ene, 2 methyl but-1-ene</td>
<td>2 methyl but-2-ene, ( \text{cis pent-2-ene} ) and ( \text{trans pent-2-ene} )</td>
</tr>
<tr>
<td>H\textsuperscript{+} Loss</td>
<td>( \text{iso-butene} \text{ and but-1-ene} &gt; \text{cis but-2-ene} \text{ and trans but-2-ene} )</td>
<td>3 methyl but-1-ene, 2 methyl but-2-ene</td>
<td>2 methyl but-1-ene, ( \text{cis pent-2-ene} ) and ( \text{trans pent-2-ene} )</td>
</tr>
<tr>
<td>H\textsuperscript{+} Gain</td>
<td>( \text{but-1-ene} \text{ and iso-butene} &gt; \text{cis but-2-ene} \text{ and trans but-2-ene} )</td>
<td>3 methyl but-1-ene, 2 methyl but-2-ene</td>
<td>2 methyl but-1-ene, ( \text{pent-1-ene} &gt; \text{cis pent-2-ene} ) and ( \text{trans pent-2-ene} )</td>
</tr>
<tr>
<td>H\textsuperscript{+} Gain</td>
<td>( \text{cis but-2-ene} \text{ and trans but-2-ene} &gt; \text{but-1-ene} &gt; \text{iso-butene} )</td>
<td>2 methyl but-2-ene, 2 methyl but-1-ene</td>
<td>2 methyl but-2-ene, ( \text{cis pent-2-ene} ) and ( \text{trans pent-2-ene} )</td>
</tr>
<tr>
<td>H\textsuperscript{-} Loss</td>
<td>(products unlikely) \n\text{n-butenes} &gt; \text{iso-butene}</td>
<td>2 methyl but-2-ene, 2 methyl but-1-ene</td>
<td>(products unlikely) \n\text{n-pentenes}</td>
</tr>
<tr>
<td>H\textsuperscript{+} Gain</td>
<td>( \text{cis but-2-ene} \text{ and trans but-2-ene} &gt; \text{but-1-ene} &gt; \text{iso-butene} )</td>
<td>2 methyl but-2-ene, 2 methyl but-1-ene</td>
<td>2 methyl but-2-ene, ( \text{cis pent-2-ene} ) and ( \text{trans pent-2-ene} )</td>
</tr>
</tbody>
</table>
products which form after re-arrangement of an intermediate are considered less likely. The mechanisms are outlined in detail in Appendix I. The products formed and the type of intermediates involved for each of the reactants studied are summarised in Tables 3.1, 3.2 and 3.3. Table 3.4 summarises the preferred product distribution for each of the mechanisms and reactants.

3.3 Influence of Catalyst

Various metals and oxides are known to catalyse the reactions of cyclopropane and mono- and di-methyl derivatives.

Metals Most of the relevant data have been based on experiments with cyclopropane as the reactant. The isomerisation reaction results in the formation of propylene. However certain metals (Fe, Ni) are observed to chemisorb cyclopropane with the formation of ethane and methane from self hydrogenation processes. Hydrogenation of methylcyclopropane over pumice supported group VIII metals resulted in formation of iso-butene, indicative of a 2 - 3 fission, in the ring opening reaction. Catalytic hydrogenolysis of alkylcyclopropane results in ring scission at points remote from the points of substitution; cleavage follows the Markovnikov rule, occurring in that bond where carbon atoms carry the most hydrogen atoms. It has been suggested that the polarising effect of side groups determines the direction of bond cleavage; a carbonyl function gave 1 - 2 cleavage predominantly whereas an alkyl function gave results in accord with previous catalytic work (2 - 3 cleavage).

Mass spectroscopic studies of the metal catalysed deuterolysis of cyclopropane showed that adsorbed hydrocarbon radicals are formed as primary products/
products \textsuperscript{(131)}. The observed exchange could occur via a mono, di or tri
adsorbed species or by a \( \pi \) bonded species utilising delocalised ring
electrons and orbitals of metal atoms on the catalyst surface. Chemisorption
may occur with ring cleavage and such a scheme is thought likely for the
metal catalysed isomerisation of cyclopropane to propylene. \textsuperscript{(131)} An \( \alpha \beta 
\) di-adsorbed species is thought to be involved in the metal catalysed
hydrogenolysis of \( \alpha \) and \( \beta \) \( 1,2 \) dimethylcyclopropane. \textsuperscript{(132)}
Oxides Roberts \textsuperscript{(133)} has studied the isomerisation of cyclopropane
to propylene over various acidic catalysts. Basic molecules were found to
poison the reaction and it was proposed that catalyst proton attached to a
ring carbon atom forming an n-propyl carbonium ion, loss of proton to the
catalyst completing the isomerisation. A protonated cyclopropane intermediate
\textsuperscript{(134)} which yields a primary carbonium ion on ring opening has also been
proposed for the zeolite catalysed reaction. \textsuperscript{(135, 136, 137)}

The results can also be explained in terms of a bimolecular hydride
transfer mechanism as proposed by Hall \textsuperscript{(138, 139)} to explain results of
cyclopropane isomerisation over silica alumina catalysts. In a later paper
Hall \textsuperscript{(140)} proposes that a protonic mechanism, utilising Brønsted catalyst
sites associated with carbonaceous residues, formed by a substrate surface
reaction, is responsible for alkylcyclopropane isomerisation over silica
alumina catalysts. Criteria as given in Appendix I were used to differentiate
between a carbonium ion mechanism based on Lewis or Brønsted type sites.

Carbanions \textsuperscript{(141)} are thought to be involved in hydrocarbon reactions
over basic catalysts such as sodium or lithium on alumina. The catalyst
abstracts proton from olefins to form a carbanion which reacts with another
olefin molecule in a chain reaction.
Cross (127) has proposed that for but-1-ene isomerisation over NiX catalysts a radical mechanism is likely whereas CaX catalysts exhibited a carbonium ion mechanism.

3.4 Summary

Cyclopropane and its alkyl derivatives undergo isomerisation (and hydrogenation) reactions to give a wide variety of products. The type and relative amounts of these products will have an important bearing on the mechanism involved.

Metals generally catalyse these types of reactions through the formation of radical type intermediates, whereas ionic intermediates are generally regarded as being involved in similar reactions over oxides (and zeolites).

Therefore the reactions of alkylcyclopropanes over catalysts will give information about surface species. The properties and scope of zeolites in fundamental studies of this nature has already been outlined (Chapter II).

Ion exchanged X type zeolites were prepared and their activity in alkylcyclopropane test reactions investigated in this work.
CHAPTER IV

EXPERIMENTAL

4.1 Materials

(i) Catalysts

The catalysts prepared in this study were made from a single batch of B.D.H Na13X zeolite obtained from the Linde division of Union Carbide Ltd. This material was in binder free powder form and had a silicon/aluminium ratio of $1.27 \pm 0.02$. Generally a single contact method of exchange was employed in preparation of the zeolites in this thesis. A process of repeated exchange was used for preparation of an ammonium zeolite.

In a typical preparation 10g approx of hydrated NaX (stored over saturated calcium nitrate solution) were slurried with 50 ml of de-ionised water in a conical flask and the desired amount of exchanging salt solution added. The total volume of solution was made up to 150 mls with further addition of de-ionised water as necessary. The flask was then evacuated and shaken from time to time over a period of sixteen hours at room temperature prior to filtration through a sintered glass crucible (porosity 4). The filtrate was washed with de-ionised water till free of salt solution and the catalysts dried in air (1 atmosphere) at 373 K prior to storage over saturated calcium nitrate solution. Copper sulphate and nickel nitrate solutions were used to prepare CuX and NiX zeolites using this method. FeX-1 was made similarly using ferric thiocynate solution. The ammonium zeolite was made by a repeated exchange procedure using ammonia and ammonium chloride solutions.

Analysis/
Analysis of the sieves to determine the amount of sodium replaced was carried out by sodium flame analysis. The method is described elsewhere. (127) In all cases the degree of exchange determined by this method was within 2% of the value quoted in this text and determined by analysis of the exchanging solution after filtration (as described below).

The filtrate and washings obtained from NiX zeolite preparation using nickel nitrate solution was titrated against E.D.T.A. using sodium chloride screened murexide as indicator. Copper sulphate filtrates were analysed by electrodeposition of copper (a). Analysis of residual iron after FeX-I preparation was accomplished by a titrometric method using mercurous nitrate. (146)

(ii) Chemicals

Nitrogen, Oxygen, and Hydrogen were obtained from the British Oxygen Company and used (with no further chemical treatment) for gas chromatographic purposes. For the surface area determinations oxygen free nitrogen was utilised (99.99%) and dried by passage through phosphorous pentoxide and a dehydrated molecular sieve 5Å (Linde) prior to storage.

Isobutane, n-butane, isobutene, but-1-ene, trans but-2-ene and cis but-2-ene (C.P. grade) were obtained from the Matheson Company in small lecture cylinders. These materials were purified and outgassed by vacuum distillation and repeated cycles of freezing, pumping and thawing.

2-methyl but-2-ene, 2-methyl but-1-ene, 3-methyl but-1-ene, pent-1-ene and a mixture of cis and trans pent-2-ones were purchased from Koch-Light and purified and outgassed as for the butenes.

Methylcyclopropane (99% pure) was obtained from K.K. laboratories; 1,1-dimethylcyclopropane (99%) and trans 1,2-dimethylcyclopropane (99%) (Pfaltz and Baur) were purified and outgassed prior to storage and use. Deuterium/

(a) Analysis carried out by M. M. Marshall
Deuterium and hydrogen (Matheson company) were delivered in lecture bottles and purified by diffusion through a palladium thimble (Figure 4.1) prior to usage.

Deuterium Oxide (99.7%) was obtained in 25 g containers from I.C.I. Ltd. This material was outgassed before use.

4.2 Apparatus

(i) Gas Handling and Reaction System

The apparatus was constructed from Pyrex glassware and is depicted in Figure 4.1. The reaction vessels were connected via water cooled ground glass joints to the apparatus. All ground joints were sealed with Apiezon 'L' grease. Evacuation of the system was accomplished by means of mercury diffusion pumps linked to Edwards rotary vacuum pumps (type F.D. 35). Vacuum checks using a McLeod gauge indicated no leaks in the system and similar leak tests were applied before catalytic experiments. Outgassing of the catalysts was accomplished through use of a silica furnace controlled thermostatically through Fielden "Bikini" controllers (Type T C B). Air blown sand-bath furnaces, controlled in a similar manner, (and accurate to within 1 K) were employed for the catalytic reactions. All furnaces and gaseous volumes were calibrated before use. With knowledge of the dosing volumes known quantities of gas were measured on the mercury manometer and admitted to the reaction vessel.

Samples (equivalent to 2½% of total initial gas phase) were then removed as required by means of an evacuable sample loop (Figure 4.1) and analysed by gas chromatography.

(ii) Gas Chromatographic Apparatus

Samples of gas removed from the reaction vessel were admitted to the chromatographic column by means of a Perkin Elmer sampling valve (Figure 4.2 (a)) connected/
Figure 4.1

Gas Handling and Reaction System

To McLeod Gauge M

To Diffusion Pumps and Rotary Pumps

(A) To Diffusion and Rotary Pumps

(F)

To Diffusion Pumps (M)

(from sample loop)

To McLeod Gauge M

To GLC

Analysis

To Sample Loop

Doser

Gas Storage Bulbs

Water Cooled Jacket

Pumps F

Reaction Vessel

Variaq

Supply

Mercury Manometer

Palladium Thimble

Water Cooled Jacket

Reaction Vessel

connected to a 0.2 ml sample loop. Nitrogen was the carrier gas and resolved components were eluted to a hydrogen/air flame ionisation detector maintained at -320 volts potential (Figure 4.2 b.). The resulting signal was amplified by a Vibron electrometer and parallel amplified signals fed to a Kent (chromalog) integrator and Goerz servoscribe recorder. Integrated peak areas were assigned to components of the gaseous mixture as recorded.

Considerable effort was employed to find chromatographic columns capable of resolving the products and reactants of the reactions to be studied. The columns used and the conditions employed are given in Table 4.1.

Table 4.1 Experimental Conditions Relating to Chromatographic Columns Used in Analysis of C4, C5 Hydrocarbons

<table>
<thead>
<tr>
<th>Column (b)</th>
<th>Usage</th>
<th>Air</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Temperature Employed (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inlet Pressure (a)</td>
<td>Flow Rate (a)</td>
<td>Inlet Pressure</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>2</td>
<td>1,2 DMCP Work</td>
<td>69  27.3</td>
<td>69  21.4</td>
<td>138  11.3</td>
<td>298</td>
</tr>
<tr>
<td>1 and 2</td>
<td>1,1 DMCP Work</td>
<td>69  27.3</td>
<td>69  21.4</td>
<td>455  34.8</td>
<td>298</td>
</tr>
<tr>
<td>3</td>
<td>MCP Work</td>
<td>69  27.3</td>
<td>69  21.4</td>
<td>455  16.9</td>
<td>273</td>
</tr>
</tbody>
</table>

(a) Units: Flow rates mls/min
Inlet pressures kN/m2

(b) 1 10 m of 1/8" o.d. polythene tube loaded with 15% silicone oil on 60:80 celite
2 4 m of 1/8" stainless steel loaded with 20% bis - 2 methoxy ethyl adipate on chromosorb P 60:80
3 50' of 1/8" o.d. copper tube loaded with 35% propylene carbonate on P 60:80 chromosorb
The resolution obtained for various hydrocarbon mixtures on these columns is
given in Figures 4.3, 4.4 and 4.5. Standard mixtures of hydrocarbons were
prepared and analysed to determine sensitivity factors so that quantitative
analysis could be accomplished.

4.3 Procedure

Typically 0.1 g of hydrated catalyst was weighed into a clean dry reaction
vessel (volume 150 mls) and outgassed by raising to 673 K over 90 minutes
under vacuum. After outgassing (15 hours) a known quantity (2 x 10^20 molecules)
of reactant was frozen, by means of liquid nitrogen, into the reaction vessel
and then a furnace at a desired temperature raised round the vessel. As
required the gas phase was sampled and analysed by gas chromatography. When
the reaction was complete the gas phase was frozen out of the reaction vessel
and analysed by gas chromatography. The spent catalyst samples were stored
for further investigations and the reaction vessels cleaned by soaking in
chromic acid solution overnight.

4.4 Other Techniques Used

X ray diffraction traces were measured on a Phillips instrument utilising
CuKα radiation. The catalysts were examined before and after catalytic
experiments.

Surface area measurements were carried out on an adsorption balance
described elsewhere. The technique was applied to catalysts before and
sometimes after use.

Mass spectrometry was employed to analyse the effect of using heavy
hydrogen or water in catalytic reactions. An A.E.I. MS 10 unit operated at
10eV/
Figure 4.3

Chromatogram of Methylcyclopropane Isomeric Butenes (Butenes also shown)

(50 ft., 1/8" o.d. copper, 35% w/v propylene carbonate on P50:80 chromosorb)
Chromatogram of 1,2 Dimethylcyclopropane, Isomeric Pentenes and Isomeric Methyl Butenes

(10 m., \(1/8\)" o.d. polythene, 15% silicone oil on 60:80 celite and 4 m.,

\(1/8\)" o.d. stainless steel, 20% bis 2 methoxy ethyl adipate on

P60:80 chromasorb)
Figure 4.5

Chromatogram of 1,2 Dimethylcyclopropane, 1,1 Dimethylcyclopropane, Isomeric Pentanes and Isomeric Methyl Butanes

(4 m., 1/8" o.d. stainless steel, 20% bis-2 methoxy ethyl adipate on PS0:80 chromosorb)
51

100W was used and this was connected via a capillary leak to a Pyrex glassware
gas handling and reaction system. (147)

Carbon analyses were determined for certain used catalyst samples. A
Perkin Elmer 240 elemental analyser, which was operated as a departmental
service, was used.

4.5 Treatment of Data

Knowledge of the peak areas for each resolved chromatographic scan and the
sensitivity factors for the resolved components allowed the percentage composition
of each chromatographic analysis to be determined. This was most conveniently
done by use of a computer. The Fortran programs for calculation of the
percentage composition, percentage products and product ratios for all reactants
and types of observed products are presented in Appendix II.

The reactions generally exhibited first order kinetics. The rate constants
were converted to absolute values from knowledge of catalyst dry weight and
surface area. Values of rate at different temperatures were plotted according
to the Arrhenius equation

\[
\text{rate constant} = A e^{-\frac{E_a}{RT}}
\]

where \( A, R \) are constants.

This allowed calculation of the apparent activation energy term \( E_a \).
Characterisation of the catalysts in this way allowed comparative assessments
of activity to be made.

The product equilibrium data at different temperatures were calculated
assuming a triangular reaction scheme for \( n \) butenes, \( n \) pentenes and methyl
butenes/
butenes i.e.

\[
\begin{array}{c}
\text{but-1-ene} \\
\text{cis but-2-ene} \leftrightarrow \text{trans but-2-ene} \\
\text{pent-1-ene} \\
\text{cis pent-2-ene} \leftrightarrow \text{trans pent-2-ene}
\end{array}
\]

3 methyl but-1-ene

\[
\begin{array}{c}
\text{2 methyl but-1-ene} \\
\text{2 methyl but-2-ene}
\end{array}
\]

The expected equilibrium data at any temperature has been determined for n-butenes by the method of Kallo and Schay (127, 148) and for the other isomers by consideration of free energy values at different temperatures.
CHAPTER V

RESULTS

5.1 Nature of Catalysts

X-ray Measurements

X-ray diffraction analyses were carried out for catalyst samples before and after use. Typical traces are shown in Figure 5.1. These analyses were used qualitatively as a check on the crystallinity of the zeolites. The major peak observed was the $2\theta=6^\circ (111)$ peak; minor differences in the other peaks occurred in different catalyst samples. As can be seen from the NaX sieve examined prior to and after reaction (Figure 5.1) the reacted sample has greater intensities relative to the 111 peak. For the catalysts studied no loss of crystallinity due to structural collapse was observed in the X-ray diffraction analyses. The only exception was NH$_4$X-III outgassed at 823 K for fifteen hours. The 111 peak was still evident but no peaks with $2\theta>20^\circ$ were observed. The CoX samples used in this work have been examined elsewhere.

Surface Areas

Surface area measurements were performed on the zeolites used in this work by a nitrogen adsorption technique. Values of the surface area were determined by the point $B$ method; the zeolite samples studied in this way gave isotherms as in Figure 5.2. Surface area measurements provide a complimentary and more quantitative method than X-ray diffraction of investigation of catalyst crystallinity after normal outgassing and use.
Figure 5.1
X-ray Diffraction Traces

NaX after MCP reaction at 423 K

Hydrated NaX

Hydrated NiX-IV

NiX-IV after MCP reaction at 415 K
Figure 5.2

Surface Area Plot (Point B. Method)

CuX-IV after MCP reaction at 481 K

Area = 676 m$^2$/g
Surface areas were also used to calculate absolute rate constants and A factors. The figures quoted for the surface areas provided in Table 5.1 refer to dry catalyst weight and correspond to those given in the literature. No data for CoX or FeX samples is available and rate constants for these catalysts were calculated on an area of 800 m²/g and a weight loss on outgassing of 25%. Of the zeolites studied no loss of crystallinity, after outgassing and use, was evident. There was a slight reduction in area in those samples examined after reaction and this was attributed to coke formation during reaction. However the \( \text{NH}_4 \text{X-III} \) zeolite outgassed at 823K showed a significant loss in area indicating partial structural collapse.

**Carbon Analysis**

Carbon analyses, utilising a combustion technique, were executed on zeolite catalysts, used in alkylcyclopropane reactions, to investigate possible coke formation during reactions. The results are shown in Table 5.2. The higher ion exchanged zeolites were particularly prone to gas phase loss to an extent unaccountable on the basis of a 2½% sampling loss in the chromatographic analysis system. The samples were degassed after reaction to remove any adsorbed material. From a knowledge of G.L.C. analyses taken and the initial dosage it is possible to calculate how much of the lost gas phase was deposited as carbon. The nickel catalyst examined lost more gas phase as carbon than the corresponding copper zeolite. The reaction in the case of the former was investigated 115 minutes longer than 100% reactant conversion whereas the copper zeolites were only subjected to 100% reactant conversion time.
Table 5.1

Physical Properties of Zeolites Studied

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Na⁺ Exchanged</th>
<th>Surface Area (m²g⁻¹)</th>
<th>% Weight Loss</th>
<th>After Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Area (m²g⁻¹)</td>
</tr>
<tr>
<td>NaX</td>
<td>0</td>
<td>894</td>
<td>25</td>
<td>637</td>
</tr>
<tr>
<td>CuX-I</td>
<td>10</td>
<td>918</td>
<td>26</td>
<td>846</td>
</tr>
<tr>
<td>CuX-II</td>
<td>25</td>
<td>893</td>
<td>27</td>
<td>739</td>
</tr>
<tr>
<td>CuX-III</td>
<td>43</td>
<td>767</td>
<td>27</td>
<td>651</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>56</td>
<td>738</td>
<td>27</td>
<td>691</td>
</tr>
<tr>
<td>CuX-V</td>
<td>63</td>
<td>705</td>
<td>28</td>
<td>610</td>
</tr>
<tr>
<td>NiX-I</td>
<td>9</td>
<td>891</td>
<td>27</td>
<td>683</td>
</tr>
<tr>
<td>NiX-II</td>
<td>25</td>
<td>814</td>
<td>27</td>
<td>780</td>
</tr>
<tr>
<td>NiX-III</td>
<td>38</td>
<td>791</td>
<td>27</td>
<td>737</td>
</tr>
<tr>
<td>NiX-IV</td>
<td>44</td>
<td>754</td>
<td>27</td>
<td>682</td>
</tr>
<tr>
<td>NiX-V</td>
<td>56</td>
<td>792</td>
<td>28</td>
<td>676</td>
</tr>
<tr>
<td>CeX-II⁹</td>
<td>78</td>
<td>823</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>NH₄X-III</td>
<td>75</td>
<td>1026</td>
<td>32</td>
<td>outgassed</td>
</tr>
<tr>
<td>NH₄X-III</td>
<td>75</td>
<td>864</td>
<td>32</td>
<td>outgassed</td>
</tr>
<tr>
<td>NH₄X-III</td>
<td>75</td>
<td>542</td>
<td>32</td>
<td>outgassed</td>
</tr>
</tbody>
</table>

(a) catalyst prepared by N. E. Cross (127)
<table>
<thead>
<tr>
<th>Catalyst (% exchange)</th>
<th>Treatment after reaction</th>
<th>% Carbon (w/w) on catalyst</th>
<th>Unaccountable % Gas phase loss at end of reaction</th>
<th>% of lost gas phase deposited as &quot;carbon&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-V (56%)</td>
<td>degassed 673K/1 hour</td>
<td>2.7</td>
<td>17.8</td>
<td>60</td>
</tr>
<tr>
<td>CuX-IV (56%)</td>
<td>degassed 573K/20 mins</td>
<td>1.0</td>
<td>13.0</td>
<td>37</td>
</tr>
<tr>
<td>CuX-IV (56%)</td>
<td>degassed 673K/1 hour</td>
<td>1.0</td>
<td>19.0</td>
<td>23</td>
</tr>
</tbody>
</table>

**Reactions over X-type Zeolites**

Zeolite catalysts containing nickel, copper and cerium ions, were used as catalysts in the isomerisation reactions of methylcyclopropane, 1,1 dimethylcyclopropane and 1,2 dimethylcyclopropane. A less intense study was carried out on exchanged zeolites containing iron, cobalt and ammonium cations.

For certain catalysts and reactants, experiments were done in which the catalyst was pretreated with hydrogen, at outgassing temperature, prior to admission of reactant. Further experiments, in which water or hydrogen were admitted to the catalyst together with reactant, were also carried out.
The isomerisation reactions were generally kinetically controlled. Complete conversion of reactant to products was observed. Catalyst adsorption studies indicated that the gas phase and adsorbed phase composition were the same.

5.2 Reactions over CuX

Catalysts containing copper at five degrees of exchange were prepared - CuX-I (10%), CuX-II (25%), CuX-III (43%), CuX-IV (56%), CuX-V (63%) and their behaviour with respect to a given reactant examined.

A. Methylcyclopropane

A reaction plot typical of that observed for CuX-I is given on Figure 5.3 (a). The other copper zeolites gave reaction plots as shown by Figure 5.3 (b) which is data for CuX-V. The methylcyclopropane was completely isomerised with only the three n-butenes being detected as products. The equilibrium values for the three n-butenes, at the temperature of the reactions depicted in Figure 5.3 (a) and (b) are also given for comparison. For both CuX-I and CuX-IV the products initially are not near their equilibrium values; for CuX-I initially but-1-ene > trans but-2-ene > cis but-2-ene, for CuX-V initially but-1-ene > cis but-2-ene > trans but-2-ene. By comparison of the data (Figure 5.3 (b)) for the high exchanged copper zeolites with the results of extended reaction on CuX-I (Figure 5.4 (a)) it can be seen that the products of reactant cleavage are closer to the equilibrium values in the case of the higher exchanged catalysts than for CuX-I.

All the catalysts (except CuX-I) displayed the inverted S shaped curve for reactant disappearance, characterised by an initial induction period followed/
Figure 5.3
(a) methylcyclopropane isomerisation over CuX-I at 438 K
(b) methylcyclopropane isomerisation over CuX-V at 361 K

○ = methylcyclopropane (M.C.P.) ○ = but-1-ene △ = trans but-2-ene
□ = cis but-2-ene

(a)

(b)

At 600 mins.
Figure 5.4

(a) extended run on CuX-I at 438 K
(b) derived 1st order plot of methylcyclopropane disappearance on CuX-I at 438 K (using data of Figure 5.3 (a))

○ = M.C.P.  ○ = but-1-ene  △ = trans but-2-ene  □ = cis but-2-ene
followed by more rapid reaction and final reactant disappearance.

The catalysts gave reaction data which fitted zero order kinetics except CuX-I which exhibited first order kinetics in reactant disappearance Figure 5.4 (b). Reaction rates and derived Arrhenius plots for the copper zeolites are presented in Table 5.3 and Figure 5.5 respectively. The temperature ranges of activity recorded for each catalyst in Table 5.3 correspond to the temperature required to give 5% or 100% reactant conversion in 90 minutes and were calculated from the Arrhenius parameters. It is evident (Table 5.3) that the 'A' factors and activation energies for the MCP isomerisation reaction increase with increasing degree of catalyst copper content.

**Induction Period**

The induction period may be regarded as the time in minutes from zero, to the point where the extrapolated zero order portion of the reaction plot intersected with zero per cent conversion line (Figure 5.6 (b)). In this sense induction periods were evident for CuX-III, CuX-IV, and CuX-V catalysts. For these catalysts some degree of correlation was observed between the length of the induction period and the temperature of reaction and the results are given in Table 5.4

Some experiments to investigate the effect of reactant pretreatment on the nature of reaction were also carried out. After a normal experiment the catalyst was outgassed for a short period and a fresh dose of reactant admitted.

For a reaction at 327K on CuX-V the effect of a repeat run after outgassing at 423K for 40 minutes was to reduce the activity, leaving the product type and distribution unchanged and causing removal of the induction period. Further re-use of this catalyst after normal outgassing gave a reduced activity. No induction period was observed and the product distribution/
Figure 5.5
Arrhenius plots for methylcyclopropane isomerisation over CuX catalysts
### Table 5.3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation Energy, (kJ/mole)</th>
<th>$\log_{10}^A$ (Ain mols. min$^{-1}$ m$^{-2}$)</th>
<th>$T(K)$ (5% Conversion in 90 mins.) $\rightarrow T(K)$ (100% conversion in 90 mins.)</th>
<th>Reaction Temperature ($^\circ$C)</th>
<th>Rate MCP disappearance (%/min/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I (10%)</td>
<td>73.5</td>
<td>23.9</td>
<td>305 $\rightarrow$ 418</td>
<td>417</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>420</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>431</td>
<td>6.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>433</td>
<td>7.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>439</td>
<td>7.77</td>
</tr>
<tr>
<td>CuX-II (25%)</td>
<td>60.7</td>
<td>24.7</td>
<td>333 $\rightarrow$ 385</td>
<td>379</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>385</td>
<td>2.04</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td>396</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>419</td>
<td>10.30</td>
</tr>
<tr>
<td>CuX-III (43%)</td>
<td>91.1</td>
<td>30.5</td>
<td>310 $\rightarrow$ 339</td>
<td>332</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>343</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>345</td>
<td>3.85</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>350</td>
<td>5.83</td>
</tr>
<tr>
<td>CuX-IV (56%)</td>
<td>92.1</td>
<td>30.8</td>
<td>309 $\rightarrow$ 338</td>
<td>327</td>
<td>5.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>333</td>
<td>1.64</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>2.36</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>348</td>
<td>5.96</td>
</tr>
<tr>
<td>CuX-V (63%)</td>
<td>91.8</td>
<td>31.5</td>
<td>299 $\rightarrow$ 326</td>
<td>321</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>332</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>341</td>
<td>8.54</td>
</tr>
</tbody>
</table>
Table 5.4

Variation of Induction Period with Degree of Exchange and Temperature of Reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature (K)</th>
<th>Induction Period t(mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-III</td>
<td>343</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>344</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>18</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>327</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>17</td>
</tr>
<tr>
<td>CuX-V</td>
<td>340</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>351</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>421</td>
<td>17</td>
</tr>
</tbody>
</table>

distribution was unchanged. CuX-I exhibited reproducibility in repeat runs after outgassing at reaction temperatures (420K).

Hydrogen Pretreatment

Hydrogen pretreatment experiments were also carried out in order to gain further insight into the processes giving rise to the induction periods observed for the copper zeolites. Typically, 1.3kNm² of purified hydrogen was admitted for 1 hour at 673K over a normally outgassed catalyst. The reaction vessel was then pumped out for 10 minutes at 673K prior to admission of reactant at a selected temperature.

The/
The effect of hydrogen pretreatment on the isomerisation of methylcyclopropane over CuX-I and CuX-IV is presented in Figure 5.6 (a) and (b) and in Table 5.5. On CuX-I the rate of reaction is markedly increased Figure 5.6 (a) when the catalyst is pretreated with hydrogen. The products consisted of n-butenes only and the relative amount of these products remained unchanged. After the reaction on the pretreated catalyst was completed the reaction vessel was pumped out at 673K for five minutes, the pretreatment repeated, and fresh reactant admitted. This procedure was repeated a third time except that the vessel was outgassed for eleven hours at 673K between runs and the hydrogen pretreatment at 673K lasted for 10 hours. These consecutive pretreatment experiments yielded the same results in respect of rate and products as the first experiment. For CuX-IV pretreatment with hydrogen increased the reaction rate and removed the induction period as compared to the non pretreated reaction. The product type and distribution was unchanged.

Table 5.5

Effect of Hydrogen Pretreatment on CuX Zeolites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature (K)</th>
<th>Hydrogen Treatment</th>
<th>Reaction rate (%/min/m^2)</th>
<th>Induction Period (Mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>420</td>
<td></td>
<td>3.56</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>419</td>
<td>Yes</td>
<td>15.80</td>
<td>-</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>327</td>
<td></td>
<td>0.57</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>Yes</td>
<td>2.08</td>
<td>None</td>
</tr>
</tbody>
</table>

Butene/
Figure 5.6  
Effect of Hydrogen Treatment (○) on methylcyclopropane isomerisation  
(○ = normal reaction)  

(a) CuX-I  
(b) CuX-IV

% Composition

\[
\begin{array}{c}
\text{% Composition} \\
\text{time (min)}
\end{array}
\]

Induction Period

\[
\begin{array}{c}
\text{Induction Period} \\
\text{time (min)}
\end{array}
\]

420 K

419 K

328 K

327 K
Butane Isomerisation

Some work on the isomerisation of but-1-ene, which was the major product observed on methylcyclopropane reaction over CuX-I, was carried out to investigate possible secondary reactions.

The reaction was investigated over CuX-I and CuX-IV and the results presented in Table 5.6. Both catalysts gave data which fitted a first order equilibrium law although an induction period was observed for CuX-IV which decreased with increasing temperature. The induction period is taken in the same manner as previously except that the first order plot is extrapolated to zero per cent conversion; no induction period was observed for CuX-I. The isomerisation of but-1-ene produced cis and trans but-2-ene only as products, the relative amounts of these isomers at 10% conversion is presented in Table 5.6.

Table 5.6

Arrhenius Data for But-1-ene Isomerisation on CuX Zeolites

<table>
<thead>
<tr>
<th>Catalyst (% Exchange)</th>
<th>Activation Energy (kJ/mole)</th>
<th>Log$_{10}$A</th>
<th>T(K) (5% Conversion in 90 mins.)</th>
<th>Reaction Temp. (K)</th>
<th>Rate of reaction %/min/m$^2$.10$^2$</th>
<th>Induction Period (Mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I (10%)</td>
<td>85 (a)</td>
<td>25.8</td>
<td>416 - 492</td>
<td>451</td>
<td>20.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>458</td>
<td>49.1</td>
<td>-</td>
</tr>
<tr>
<td>CuX-IV (56%)</td>
<td>70</td>
<td>26.6</td>
<td>326 - 377</td>
<td>328</td>
<td>9.7</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>354</td>
<td>48.7</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>360</td>
<td>81.8</td>
<td>40</td>
</tr>
</tbody>
</table>

(a) based on two points
A reaction was also carried out on CuX-I using methylcyclopropane as reactant and when 90\% conversion was attained the reaction frozen and but-1-ene admitted. The rate of but-1-ene isomerisation was approximately 40 times slower than the methylcyclopropane isomerisation. The product ratios observed in this but-1-ene reaction were similar to those observed on the extended run over CuX-I at 438K (Figure 5.4 (a)).

**Effect of light/heavy water**

Preliminary experiments on one of the more active catalysts (CuX-IV) indicated that admission of large amounts of water, (10 molecules per supercage) prior to reactant, completely poisoned the catalyst for methylcyclopropane isomerisation over the range of temperature in which the dry catalyst was active. The results of experiments, in which 1 molecule per zeolite cage was present, are presented in Table 5.7. In all cases, including a catalyst outgassed at 298K, the reaction rate was reduced for wet catalyst as compared to dry catalyst. Pretreatment with water, apart from reducing catalyst activity, also had the effect of removing the induction period normally found with CuX-IV. This was also true of the sample outgassed at 298K. A typical plot for reactant disappearance is given in Figure 5.7(a). The Arrhenius plot for water pretreated catalysts is given in Figure 5.7(b).

The use of heavy water under identical conditions to that of the light water experiments indicated that a stepwise exchange process was occurring. This exchange reaction was slower than the isomerisation reaction. At 100\% reactant conversion 50\% exchange of one hydrogen atom and 2\% exchange of two hydrogen atoms had occurred (taking into account natural isotopes). A plot of the 57/56 mass ratio, assuming that mass 56 was equivalent to n-butenes only, indicated that the exchange reaction was associated with product/
Figure 5.7

Effect of Water on Methylcyclopropane Reaction over CuX-IV

(a) Exchange and Isomerisation Data

(b) Arrhenius Data

(a) $\square = 57/56$ (56 mass equivalent to products only)

(b) $\log_{10} k$ vs. $\frac{1}{k_B T \times 10^3}$

outgassed 298 K
product formation. This ratio is presented together with the data for the isomerisation reaction in Figure 5.7(a).

Table 5.7

Effect of Water on MCP Isomerisation over CuX-IV

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Molecules Water/Supercage</th>
<th>$\log_{10}$rate water present</th>
<th>$\log_{10}$rate no water</th>
</tr>
</thead>
<tbody>
<tr>
<td>332</td>
<td>0.94</td>
<td>-3.15</td>
<td>-1.86</td>
</tr>
<tr>
<td>344</td>
<td>1.05</td>
<td>-2.28</td>
<td>-1.37</td>
</tr>
<tr>
<td>379</td>
<td>0.64</td>
<td>-2.17</td>
<td>-0.06</td>
</tr>
<tr>
<td>383</td>
<td>0.80</td>
<td>-1.37</td>
<td>+0.07</td>
</tr>
<tr>
<td>338</td>
<td>Degassed at 298K</td>
<td>-2.11</td>
<td>-1.60</td>
</tr>
</tbody>
</table>

Derived data;

$E_a = 67.1$ kJ/mole $\quad A = 10^{27.3}$ molecules/min/m$^2$ $\quad T_{5\%} = 329$ K $\quad T_{100\%} = 374$ K

Product Distribution  The only products formed under any condition of reaction pretreatment were the n-butenes. An assessment of these n-butene product distributions arising from methylcyclopropane isomerisation in the initial stages of reactant conversion was done by consideration of products at 10% reaction. Tangents were drawn to the product curves on the % composition v time plot at 10% conversion and the ratios of products and amounts/
### Table 5.8

**Product Distribution Analysis for MCP Reactions on CuX Sieves**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature (K)</th>
<th>at 10% Conv.</th>
<th>at Equilibrium</th>
<th>Ratios at 10% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C/T</td>
<td>B/T</td>
<td>A/C</td>
</tr>
<tr>
<td>CuX-I</td>
<td>317</td>
<td>6.0</td>
<td>31.0</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>7.0</td>
<td>32.0</td>
<td>61.0</td>
</tr>
<tr>
<td></td>
<td>431</td>
<td>5.0</td>
<td>30.0</td>
<td>65.0</td>
</tr>
<tr>
<td></td>
<td>438</td>
<td>7.0</td>
<td>29.0</td>
<td>64.0</td>
</tr>
<tr>
<td></td>
<td>439</td>
<td>8.0</td>
<td>35.0</td>
<td>57.0</td>
</tr>
<tr>
<td>CuX-II</td>
<td>379</td>
<td>7.0</td>
<td>38.0</td>
<td>55.0</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>7.0</td>
<td>43.0</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>396</td>
<td>9.0</td>
<td>39.0</td>
<td>52.0</td>
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<td></td>
<td>422</td>
<td>6.5</td>
<td>24.0</td>
<td>69.5</td>
</tr>
<tr>
<td>CuX-III</td>
<td>332</td>
<td>9.5</td>
<td>42.0</td>
<td>48.5</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>11.0</td>
<td>39.0</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>12.0</td>
<td>47.0</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>6.0</td>
<td>44.0</td>
<td>50.0</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>327</td>
<td>11.0</td>
<td>41.0</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>15.0</td>
<td>49.0</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>11.0</td>
<td>41.0</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>346</td>
<td>12.0</td>
<td>44.0</td>
<td>44.0</td>
</tr>
<tr>
<td>CuX-V</td>
<td>321</td>
<td>12.0</td>
<td>41.0</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>332</td>
<td>10.0</td>
<td>39.0</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td>341</td>
<td>11.0</td>
<td>46.0</td>
<td>43.0</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>332</td>
<td>14.0</td>
<td>56.0</td>
<td>30.0</td>
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<tr>
<td>Water</td>
<td>344</td>
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<td>47.0</td>
<td>36.0</td>
</tr>
<tr>
<td>Present</td>
<td>379</td>
<td>15.0</td>
<td>57.5</td>
<td>27.5</td>
</tr>
<tr>
<td>298(K) out-</td>
<td>383</td>
<td>4.0</td>
<td>45.0</td>
<td>51.0</td>
</tr>
<tr>
<td>gass</td>
<td></td>
<td>7.5</td>
<td>33.0</td>
<td>59.5</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>327</td>
<td>6.5</td>
<td>36.0</td>
<td>57.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>328</td>
<td>12.0</td>
<td>37.0</td>
<td>51.0</td>
</tr>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuX-I</td>
<td>419</td>
<td>6.0</td>
<td>31.0</td>
<td>63.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>420</td>
<td>13.5</td>
<td>39.0</td>
<td>57.5</td>
</tr>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuX-V</td>
<td>327</td>
<td>9.0</td>
<td>39.0</td>
<td>52.0</td>
</tr>
<tr>
<td>Repeat Runs</td>
<td></td>
<td>10.0</td>
<td>40.0</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>327</td>
<td>16.0</td>
<td>29.0</td>
<td>55.0</td>
</tr>
<tr>
<td>CuX-I Repeat Run</td>
<td></td>
<td>420</td>
<td>8.0</td>
<td>30.0</td>
</tr>
<tr>
<td>n-butene</td>
<td>451</td>
<td>29.0</td>
<td>71.0</td>
<td>6.0</td>
</tr>
<tr>
<td>CuX-I</td>
<td>458</td>
<td>46.0</td>
<td>54.0</td>
<td>-</td>
</tr>
<tr>
<td>n-butene</td>
<td>328</td>
<td>17.5</td>
<td>82.5</td>
<td>-</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>354</td>
<td>21.5</td>
<td>78.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>24.0</td>
<td>76.0</td>
<td>-</td>
</tr>
</tbody>
</table>
amounts determined from gradients of these tangents. The results are presented in Table 5.8. The values expected at equilibrium at the given reaction temperature, under the various normal and pretreated experiments that were undertaken, are also given as is the data for n-butene reactions.

For any given CuX catalyst the product distribution ratios did not vary significantly with reaction temperature. Hydrogen pretreatment of CuX-I did not alter the initial product ratios. With but-1-ene as reactant CuX-I gave initial cis/ trans ratios which were temperature dependent, the values increasing from 0.41 at 441K to 0.86 at 453K. The low temperature values of cis/trans ratios tended towards values expected at equilibrium after 40% reactant conversion. The high temperature cis/trans ratios were constant up to 70% reactant conversion. For CuX-IV the product ratios were not affected by reaction in the presence of water or altered on a hydrogenated catalyst. The reaction on catalyst outgassed at 298K did exhibit some differences. With but-1-ene as reactant CuX-IV gave ratios which were again temperature dependent but constant until over 50% conversion. The cis/trans ratios for the but-1-ene isomerisation were similar to those formed for the MCP isomerisation. Consecutive reactions on CuX-V gave identical results save for the reaction after the catalyst was outgassed at 573K for which a lower amount of trans isomer was produced.

The product ratios observed for each catalyst are summarised in Table 5.9. This lists the average values found over the temperature range used to study the catalyst. The equilibrium values correspond to the mean of this temperature range. Figure 5.8 summarises this data, with equilibrium values being given for the range 323K - 423K. (The results for NaX will be fully presented in a later section).

Further treatment of the data (as in Table 5.9) was undertaken in order to further appraise the product distribution exhibited...
Equilibrium Values over Temperature Range used for Reactions over CuX Sieves

- **trans but-2-one**
- **but-1-one**
- **cis but-2-one**

% Products

% Replacement of Na⁺ by Cu⁺⁺
Table 5.9

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>10% Conversion (a)</th>
<th>Equilibrium Values</th>
<th>Experimental temperature range for reaction (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
<td>trans</td>
<td>but-1</td>
</tr>
<tr>
<td>CuX-I</td>
<td>6.5</td>
<td>28.0</td>
<td>65.5</td>
</tr>
<tr>
<td>CuX-II</td>
<td>7.0</td>
<td>33.0</td>
<td>60.0</td>
</tr>
<tr>
<td>CuX-III</td>
<td>9.0</td>
<td>45.0</td>
<td>46.5</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>12.0</td>
<td>46.0</td>
<td>42.0</td>
</tr>
<tr>
<td>CuX-V</td>
<td>13.0</td>
<td>46.0</td>
<td>41.0</td>
</tr>
</tbody>
</table>

(a) These are average values over the range of temperature of study.

through a reaction. It was found that the product composition was largely independent of reactant conversion and generally the pattern conformed to that shown in Figure 5.9 for low and high copper content catalysts under all experimental conditions used. The cis/trans but-2-ene ratios observed were generally constant and independent of the extent of conversion.

Activity The activity for MCP isomerisation of the copper catalysts studied was expressed in terms of $\log_{10} \text{rate}_{273 \text{K}}$. This data was calculated, for the reactions studied above, from the Arrhenius parameters.
Figure 5.9  Analysis of Product Distribution for CuX catalysts during MCP reaction under various conditions.

CuX-I at 420 K
- but-1-ene
- trans but-2-ene
- cis but-2-ene

CuX-V at 338 K / outgassed 273 K

CuX-IV at 327 K

CuX-IV at 332 K / water present

CuX-I at 419 K / hydrogen pretreatment

CuX-IV at 328 K / hydrogen pretreatment

CuX-IV at 332 K / water present

% conversion
In the case of water and hydrogen pretreatment work the values for CuX-I and CuX-IV were determined assuming the same activation energy as in the normal reaction.

The values are given in Table 5.10 and the catalyst and the activity comparison presented in Figure 5.10. (The results for NaX will be presented later).

Table 5.10

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( \log_{10} \text{rate}_{323 \ K} ) ( (\text{MCP}) )</th>
<th>( \log_{10} \text{rate}_{323 \ K} ) ( (\text{But-1-ene}) )</th>
<th>( \log_{10} \text{rate}_{323 \ K} ) ( (\text{H}_2\text{O}) )</th>
<th>( \log_{10} \text{rate}_{323 \ K} ) ( (\text{Hydrogen Pretreatment}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>-4.20</td>
<td>-6.23</td>
<td>-</td>
<td>-3.51</td>
</tr>
<tr>
<td>CuX-II</td>
<td>-3.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuX-III</td>
<td>-2.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>-2.27</td>
<td>-3.00</td>
<td>-3.29</td>
<td>-1.87</td>
</tr>
<tr>
<td>CuX-V</td>
<td>-1.82</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaX</td>
<td>-6.45</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(rates in \%/\text{min}/m²)

The data of Leach et al., for similar catalysts differing only in the degree of exchange, is compared in Figure 5.11 with the methylcyclopropane and butene work carried out in this thesis. The criterion for activity in this case is the temperature for 5% reactant conversion in 90 minutes.

B. 1,1 Dimethylcyclopropane

The reaction was examined over CuX-I and CuX-IV catalysts. The only products/
Figure 5.10

Copper Zeolite Activity for methylcyclopropane

Isomerisation

- methylcyclopropane
- methylcyclopropane/hydrogen pretreatment
- but-1-ene as reactant
- methylcyclopropane/water

log10 (Rate) vs. % replacement of sodium by copper
Figure 5.11

Comparison of methylcyclopropane and but-1-ene reactivity on CuX zeolites

○ = methylcyclopropane
□ = but-1-ene (data of Dimitrov and Leach (149))
○ = but-1-ene (this work)
products detected were the methyl butenes in the order 2 methyl but-2-ene > 2 methyl but-1-ene > 3 methyl but-1-ene. A typical reaction plot (for both catalysts) is given in Figure 5.12 for CuX-I at 405K. Neither catalyst exhibited an induction period and the product amounts observed were close to the equilibrium values expected at the reaction temperature. The high copper sieve produced marginally greater amounts of 3 methyl but-1-ene than CuX-I which gave trace amounts. The results are presented in Table 5.11 and the product composition in Table 5.12. Data for the CuX-I sieve exhibited first order kinetics Figure 5.12 (b) and CuX-IV zero order kinetics.

Table 5.11

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(E_a) (kJ/mole)</th>
<th>(\log_{10} A)</th>
<th>(T_{5%-T_{100%}}) (K)</th>
<th>Temperature (K)</th>
<th>(\log_{10} 2) Rate</th>
<th>(\log_{10} rate) 323K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>123.3</td>
<td>23.9</td>
<td>337 - 375</td>
<td>368</td>
<td>1.59</td>
<td>-4.25</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>327</td>
<td>29.3</td>
<td>-0.53</td>
</tr>
</tbody>
</table>

\(A\) in molecules/min/m\(^2\), rate in %/min/m\(^2\)

Table 5.12

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(T) (K)</th>
<th>10% Conversion</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>388</td>
<td>11.0</td>
<td>88.5</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>327</td>
<td>8.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>

C. 1,2 Dimethylcyclopropane
Figure 5.12

(a) isomerisation of 1,1 dimethylcyclopropane over CuX-I at 368K

(b) derived 1st order plot of (a)

- ○ = 1,1 dimethylcyclopropane
- ○ = 2 methyl but-1-ene
- □ = 2 methyl but-2-ene
- ▽ = 3 methyl but-1-ene

(a) % Composition vs. t. mins

(b) log(λk) vs. t. mins
C. 1,2 Dimethylcyclopropane

Ring opening of 1,2 dimethylcyclopropane on the CuX-I and CuX-IV catalysts yielded methyl butenes and normal pentenes as products. Typical reaction plots for both catalysts are given in Figures 5.13 (a) and (b).

The Arrhenius and rate data is presented in Table 5.13. Both catalysts exhibited zero order kinetics initially and induction periods were observed. (No further study of these was carried out).

Table 5.13

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation Energy (kJ/mole)</th>
<th>Log$_{10}$A</th>
<th>Log$_{10}$ rate 323K</th>
<th>RT (K)</th>
<th>rate $10^2$</th>
<th>$T_{5%-T_{100%}}$ (K)</th>
<th>IP (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>38.0</td>
<td>26.1</td>
<td>-2.30</td>
<td>371</td>
<td>2.87</td>
<td>273 - 372</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>373</td>
<td>3.99</td>
<td>273 - 372</td>
<td></td>
</tr>
<tr>
<td>CuX-IV</td>
<td></td>
<td>-</td>
<td>-3.49</td>
<td>317</td>
<td>0.03</td>
<td>-</td>
<td>13</td>
</tr>
</tbody>
</table>

RT = reaction temperature

IP = Induction Period

A is in molecules/minute/m²

rate in %/min/m²

The product compositions at 10% conversion and at equilibrium are given in Table 5.14. Each type of product is treated separately i.e. methyl butenes and pentenes. The methyl butenes were the major (greater than 90%) of the products. An extended reaction revealed a slower (approximately 30 times) approach to equilibrium as regards methyl butenes or pentene products compared with reactant isomerisation.

The activity comparison of CuX-I and CuX-IV for the various cyclic reactants studied is presented in Table 5.15.
Figure 5.13

Reaction of 1,2 dimethylcyclopropane over copper zeolites

(a) CuX-I at 383 K
(b) CuX-IV at 317 K
Table 5.14

Product Data for 1,2 Dimethylcyclopropane Reaction over CuX Zeolites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature</th>
<th>(K)</th>
<th>100% Conv.</th>
<th>10% Conv.</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Pentene Products</td>
<td></td>
<td>3MB1</td>
<td>2MB1</td>
<td>2MB2</td>
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<tr>
<td>CuX-I</td>
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<td>7</td>
<td>62.0</td>
<td>4.0</td>
<td>34.0</td>
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<tr>
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<td>383</td>
<td>7</td>
<td>62.5</td>
<td>6.0</td>
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<tr>
<td>CuX-IV</td>
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<td>3</td>
<td>63</td>
<td>3.0</td>
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</tbody>
</table>

Table 5.15

Activity Summary For CuX-I and CuX-IV

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>(E_A^{(c)}) (kJ/mole)</th>
<th>(\log_{10} A^{(d)})</th>
<th>(T_{5%}^{(a)}) (K)</th>
<th>(T_{100%}^{(b)}) (K)</th>
<th>Log_{10} Rate 323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuX-I</td>
<td>MCP</td>
<td>73.5</td>
<td>23.9</td>
<td>345</td>
<td>418</td>
<td>-4.21</td>
</tr>
<tr>
<td></td>
<td>1,1 DMCP</td>
<td>123.3</td>
<td>23.9</td>
<td>337</td>
<td>375</td>
<td>-4.25</td>
</tr>
<tr>
<td></td>
<td>1,2 DMCP</td>
<td>38.0</td>
<td>26.1</td>
<td>0</td>
<td>99</td>
<td>-2.30</td>
</tr>
<tr>
<td>CuX-IV</td>
<td>MCP</td>
<td>92.1</td>
<td>30.8</td>
<td>309</td>
<td>338</td>
<td>-2.27</td>
</tr>
<tr>
<td></td>
<td>1,1 DMCP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-1.53</td>
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<td>1,2 DMCP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-1.48</td>
</tr>
</tbody>
</table>

(a) \(T(K)\) for 5% conversion in 90 minutes
(b) \(T(K)\) for 100% conversion in 90 minutes
(c) \(kJ/mole\)
(d) \(A\) in molecules/min/m^2
5.3 NiX Zeolites

Five catalysts containing nickel were prepared; NiX-I (9% exchange of Na\(^+\)), NiX-II (25%), NiX-III (38%), NiX-IV (43%) and NiX-V (56%). Their catalytic behaviour with respect to alkylcyclopropane isomerisation reactions was investigated.

A. Methylycyclopropane

Results typical of NiX-I, NiX-II and NiX-III are given in Figure 5.14 (a) First order plots were observed for methylycyclopropane disappearance over these catalysts. Nickel sieves NiX-V and NiX-IV gave induction periods in the reaction plot Figure 5.14 (b) and reactant disappearance followed zero order kinetics. There was no apparent correlation between observed induction period and any other parameter for these catalysts.

The nickel catalysts studied gave 100% reactant conversion and the normal butenes, which were the major products, were formed in amounts expected at equilibrium. In addition to the normal butenes NiX-IV and NiX-V catalysts produced n-butane in an amount similar to but-1-ene formation. Formation of n-butane continued with diminution of normal butenes in the gas phase (Figure 5.14 (b). A repeat experiment on NiX-V gave similar rate and product data except that n-butane rate of formation increased especially at a lower extent of reactant conversion. The induction period was not eliminated in this repeat experiment.

After 100% reactant conversion over NiX-I traces (approximately 0.5% of total gas phase in each case) of iso-butene, iso-butane and n-butane were observed. NiX-II gave similar amounts of these side products as well as traces of products (containing 2 or 3 carbon atoms) which were not identified. When followed appreciably beyond 100% conversion NiX-II gave n-butanes/
Reaction of methylicyclopropane over NiX

(a) NiX-I at 365 K  ○ = methylicyclopropane
(b) NiX-V at 398 K  ○ = but-1-ene  △ = trans but-2-ene
                     □ = cis but-2-ene ▽ = n-butane

Figure 5.14

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### Table 5.16

**Extent of C2 - C3 Cleavage in MCP over NiX-III**

<table>
<thead>
<tr>
<th>Reaction Temperature (K)</th>
<th>% C2 - C3 Cleavage 100% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>446</td>
<td>3.5</td>
</tr>
<tr>
<td>453</td>
<td>5.0</td>
</tr>
<tr>
<td>469</td>
<td>4.0</td>
</tr>
<tr>
<td>475</td>
<td>8.0</td>
</tr>
</tbody>
</table>

### Table 5.17

**Rate and Arrhenius Data for NiX Catalysts**

<table>
<thead>
<tr>
<th>Catalyst (% Exchange)</th>
<th>Activation Energy (kJ mol⁻¹)</th>
<th>Log₁₀ A in molecules/min/m²</th>
<th>T(K)(5% Conv. in 90 mins.)</th>
<th>Reaction Temperature T(K)(100% Conv. in 90 mins.)</th>
<th>Rate %/min/m²*10²</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-I (9%)</td>
<td>86.0</td>
<td>26.0</td>
<td>402 - 488</td>
<td>443</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>454</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>465</td>
<td>2.76</td>
</tr>
<tr>
<td>NiX-II (25%)</td>
<td>86.5</td>
<td>26.0</td>
<td>408 - 497</td>
<td>407</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>422</td>
<td>0.18</td>
</tr>
<tr>
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<td></td>
<td>436</td>
<td>0.46</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>442</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>453</td>
<td>1.04</td>
</tr>
<tr>
<td>NiX-III (38%)</td>
<td>106.2</td>
<td>26.0</td>
<td>348 - 521</td>
<td>446</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>453</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>407</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>475</td>
<td>0.74</td>
</tr>
<tr>
<td>NiX-IV (43%)</td>
<td>150.0</td>
<td>37.1</td>
<td>391 - 417</td>
<td>377</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>395</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>404</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>415</td>
<td>2.77</td>
</tr>
<tr>
<td>NiX-V (56%)</td>
<td>142.0</td>
<td>37.1</td>
<td>368 - 394</td>
<td>431</td>
<td>6.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>373</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>381</td>
<td>0.50</td>
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<td></td>
<td></td>
<td></td>
<td>398</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>415</td>
<td>18.70</td>
</tr>
</tbody>
</table>
n-butenes as major product. NiX-III gave similar results to NiX-I and II but this catalyst was the most efficient at C2 - C3 ring cleavage. The extent of C2 - C3 cleavage was apparently temperature dependent as is given in Table 5.16. Traces of butadiene and a species identified as dimethylacetylene were also found after 100% reactant conversion. Rate and Arrhenius data for the nickel zeolites are presented in Table 5.17, and the Arrhenius plots shown in Figure 5.15.

A particular study was made of the effect, on the isomerisation behaviour over NiX-V, of addition of water and hydrogen treatment. The presence of a small quantity of water (pre-adsorbed prior to reactant admission and equivalent to 1 molecule per cage) marginally increased the reaction rate. Hydrogen pretreatment, reaction in the presence of hydrogen and reaction in the presence of hydrogen after hydrogen pretreatment increased the reaction rate as compared to the normal reaction. These results are summarised in Table 5.18. In these experiments with water and hydrogen pretreatment, the induction period was eliminated. Hydrogen pretreatment did not alter the reaction products as compared to the normal reaction;

Table 5.18

Effect of Water and Hydrogen Treatments on Methylcyclopropane Isomerisation on NiX-V

<table>
<thead>
<tr>
<th>Temperature of Reaction (K)</th>
<th>Reactant(s)</th>
<th>$H_2$/ Reactant</th>
<th>Pretreatment</th>
<th>Log$_{10}$ rate Normal</th>
<th>Log$_{10}$ rate MCP Isomerisation</th>
<th>Log$_{10}$ rate 323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>383</td>
<td>MCP</td>
<td>-</td>
<td>Hydrogen</td>
<td>-1.69</td>
<td>-2.21</td>
<td>-5.29</td>
</tr>
<tr>
<td>428</td>
<td>MCP</td>
<td>3.94</td>
<td>Normal</td>
<td>-0.01</td>
<td>-0.21</td>
<td>-5.61</td>
</tr>
<tr>
<td>297</td>
<td>MCP</td>
<td>1.88</td>
<td>Hydrogen</td>
<td>-2.74</td>
<td>-7.81</td>
<td>-0.30</td>
</tr>
<tr>
<td>429</td>
<td>Iso-butene</td>
<td>2.30</td>
<td>Normal</td>
<td>-1.41</td>
<td>-0.21</td>
<td>-</td>
</tr>
<tr>
<td>381</td>
<td>MCP</td>
<td>1.0 $H_2/O$</td>
<td>Normal</td>
<td>-2.04</td>
<td>-2.29</td>
<td>-5.56</td>
</tr>
<tr>
<td>323</td>
<td>MCP</td>
<td>-</td>
<td>Normal</td>
<td>-5.81</td>
<td>-</td>
<td>-5.81</td>
</tr>
</tbody>
</table>

(a) based on activation energy of 142 kJ/mole $^{-1}$

rates in %/min/m$^2$
Figure 5.15

Arrhenius Plots for Disappearance of MCP over NiX

(NiX-I, II and III
$\log_{10}k \cdot 10^2$)
n-butene were the major products (Figure 5.16). However trace amounts of iso-butene were detected after 70% reactant conversion. Reaction in the pressure of hydrogen (Figure 5.16 b) produced n-butane as the final product. About 2% of iso-butene was found and this was resistant to hydrogenation at the reaction conditions. Repetition of this experiment after outgassing at room temperature for one hour with a similar hydrogen/reactant ratio gave a faster rate of n-butane formation. The iso-butene isomerisation and hydrogenation reactions were also investigated over NiX-V and the results are depicted in Figure 5.17 (b). A temperature of 100 K above that normally required for methylcyclopropane reaction was chosen (this was also the temperature at which the 2% iso-butene found in the presence of hydrogen and MCP was resistant to hydrogenation (Figure 5.16 b). At 429 K iso-butene did not react. Associated with this inactivity was a gas phase loss greater than that expected on the basis of sampling alone (Figure 5.17 b). On admission of hydrogen formation of iso-butane was rapid and an increase in total carbon present (gaseous phase) was evident. Reaction in the presence of hydrogen after hydrogen pretreatment was fast compared to the normal isomerisation or isomerisation after hydrogen pretreatment experiments (Figure 5.17 a). The only products formed were n-butane and iso-butane, in the ratio (approx.) 1:1. Traces of but-1-ene and iso-butene were also evident.

Product Distributions

These are derived in the same way as in 5.2 and the graphical treatments are similar. Data summarising the reactions over the temperature range of study of each catalyst is presented in Table 5.19. This data is depicted in Figure 5.18. The range of equilibrium values is presented for comparison as is the data for NaX (NaX data will be presented in detail later). A fuller product distribution analysis for each run on the catalyst and for
Figure 5.16

Isomerisation of methylcyclopropane over NiX-V

(a) hydrogen pretreatment at 383 K
(b) in presence of H₂ at 428 K

○ = MCP  △ = trans but-2-ene  □ = cis but-2-ene
○ = but-1-ene  ▽ = n-butane
Figure 5.17  Reaction over NiX-V

(a) MCP reaction at 298 K - hydrogen present/hydrogen pretreatment

(b) iso-butene at 429 K
Product distribution results for NiX catalysts

- trans-but-2-ene
- cis-but-2-ene
- but-1-ene

Equilibrium values over range of temperatures used for NiX catalysts
the various forms of pretreatment is presented in Table 5.20. Pretreatment with water and hydrogen decreased the rate of n-butane formation.

Table 5.19

Product Composition (n-butenes only) - MCP Isomerisation over NiX Zeolites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Values at 10% Conversion</th>
<th>Equilibrium Values</th>
<th>Experimental Temperature Range For Reaction T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIS  TRANS BUT-1</td>
<td>CIS  TRANS BUT-1</td>
<td></td>
</tr>
<tr>
<td>NiX-I</td>
<td>23.0 53.5 23.5</td>
<td>30.0 58.0 12.0</td>
<td>444 - 463</td>
</tr>
<tr>
<td>NiX-II</td>
<td>27.0 57.0 16.0</td>
<td>29.0 61.0 10.0</td>
<td>403 - 453</td>
</tr>
<tr>
<td>NiX-III</td>
<td>32.0 57.0 11.0</td>
<td>30.0 58.0 12.0</td>
<td>443 - 473</td>
</tr>
<tr>
<td>NiX-IV</td>
<td>32.0 58.0 10.0</td>
<td>28.5 62.5 9.0</td>
<td>373 - 433</td>
</tr>
<tr>
<td>NiX-V</td>
<td>31.0 61.0 8.0</td>
<td>28.5 63.5 8.0</td>
<td>373 - 413</td>
</tr>
</tbody>
</table>

Reaction of but-1-ene over NiX-II and NiX-V produced mainly cis and trans but-2-enes, with traces of iso-butene detected. The major product ratios and the expected equilibrium values are given in Table 5.20. Product and conversion plots for the nickel catalysts (as Figure 5.9) indicated that an n-butene interconversion process was occurring along with the methylcyclopropane reactant conversion. Generally equilibrium butene values were approached before 100% conversion of the methylcyclopropane.

Activity

Activity of the nickel zeolites was determined by consideration of \[ \log_{10} \text{rate} \] at 323 K. This data is presented in Table 5.21 and depicted in Figure 5.19 (the data obtained elsewhere (127) for but-1-ene isomerisation over nickel zeolites differing only in the degree of exchange is also presented).
Figure 5.19
Activity of nickel exchanged X type zeolites for methylcyclopropane and but-1-ene isomerisation
*(data of N. E. Cross (127))*

- Hydrogen present
- Hydrogen pretreatment

- MCP
- but-1-ene

(log to rate 323 K)

% sodium replaced by nickel

- Water present

0 10 20 30 40 50 60 70
Table 5.20
Normal Butene Product Distribution Analysis for MCP
Reactions over NiX Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temp. (K)</th>
<th>at 10% Conv.</th>
<th>at Equilibrium</th>
<th>Ratios at 10% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CIS  TRANS  B1</td>
<td>CIS  TRANS  B1</td>
<td>C/T  B/T  B/C</td>
</tr>
<tr>
<td>NiX-I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>443</td>
<td>14.0 60.0 26.0 30.5 58.5 11.0</td>
<td>0.23 0.43 1.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>454</td>
<td>24.0 61.0 15.0 30.5 58.5 11.0</td>
<td>0.39 0.24 0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>465</td>
<td>20.0 50.0 30.0 31.0 56.5 12.5</td>
<td>0.40 0.60 1.50</td>
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<td>NiX-II</td>
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<td></td>
</tr>
<tr>
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<td>22.0 66.0 12.0 29.0 62.0 9.0</td>
<td>0.33 0.18 0.55</td>
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<td></td>
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<tr>
<td>422</td>
<td>30.0 66.0 4.0 29.0 61.0 10.0</td>
<td>0.45 0.06 0.13</td>
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<td></td>
</tr>
<tr>
<td>436</td>
<td>31.0 58.0 11.0 30.0 59.0 11.0</td>
<td>0.53 0.19 0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>442</td>
<td>26.0 50.0 24.0 30.0 59.0 11.0</td>
<td>0.52 0.48 0.92</td>
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<tr>
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<td>NiX-III</td>
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<td>0.47 0.20 0.43</td>
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<td>0.43 0.21 0.45</td>
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<td></td>
</tr>
<tr>
<td>469</td>
<td>35.0 52.0 13.0 31.0 56.5 12.5</td>
<td>0.66 0.25 0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>475</td>
<td>33.0 55.0 12.0 31.5 56.0 12.5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NiX-IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>395</td>
<td>27.0 67.0 6.0 28.0 63.5 8.5</td>
<td>0.40 0.09 0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>404</td>
<td>28.0 62.0 9.0 29.0 62.0 9.0</td>
<td>0.44 0.14 0.32</td>
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<td></td>
</tr>
<tr>
<td>414</td>
<td>32.5 62.0 7.5 29.5 61.0 9.5</td>
<td>0.49 0.12 0.25</td>
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<td></td>
</tr>
<tr>
<td>431</td>
<td>31.0 60.0 9.0 29.5 60.0 10.5</td>
<td>0.52 0.15 0.29</td>
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<tr>
<td>NiX-V</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>26.0 65.0 9.0 27.5 65.5 7.0</td>
<td>0.40 0.14 0.35</td>
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<td></td>
</tr>
<tr>
<td>381</td>
<td>28.0 64.0 8.0 28.5 64.5 7.5</td>
<td>0.43 0.13 0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>398</td>
<td>27.0 65.0 8.0 28.5 63.0 8.5</td>
<td>0.42 0.12 0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>415</td>
<td>30.0 63.0 7.0 29.0 61.5 9.5</td>
<td>0.48 0.11 0.23</td>
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<td></td>
</tr>
<tr>
<td>Repeat Experiment</td>
<td>381</td>
<td>29.0 65.0 6.0 28.5 64.0 7.5</td>
<td>0.45 0.09 0.20</td>
<td></td>
</tr>
<tr>
<td>In Presence of Water</td>
<td>381</td>
<td>30.0 63.0 7.0 28.5 64.0 7.5</td>
<td>0.48 0.11 0.23</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Pretreatment</td>
<td>383</td>
<td>42.5 50.5 8.0 28.0 64.5 7.5</td>
<td>0.84 0.16 0.19</td>
<td></td>
</tr>
<tr>
<td>In Presence of Hydrogen</td>
<td>428</td>
<td>31.0 59.0 10.0 30.0 60.0 10.0</td>
<td>0.53 0.17 0.32</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Pretreatment In Presence of hydrogen</td>
<td>298</td>
<td>n-butane / iso-butane = 1.12</td>
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<td></td>
</tr>
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</table>

N-Butene As Reactant

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-II</td>
<td>452 30.0 70.0 - 31.0 57.0 - 0.42 10</td>
</tr>
<tr>
<td>NiX-V</td>
<td>381 28.0 56.0 - 28.5 64.0 - 0.50 90</td>
</tr>
</tbody>
</table>
Nickel zeolites appear to be more active for but-1-ene than for methylcyclopropane isomerisation. The temperature range of activity (based on temperature required for 5% - 100% conversion in 90 minutes) for but-1-ene isomerisation over a 40% exchanged nickel zeolite is 308 K - 333 K. The corresponding temperature range for NiX-III (38% exchanged) in the methylcyclopropane isomerisation was 448 K - 521 K. The reactions over NiX-V in the presence of water, hydrogen and after hydrogen pretreatment were faster than the unpretreated catalyst. The greatest increase in activity was observed for the reaction in the presence of hydrogen after hydrogen pretreatment.

Table 5.21

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NiX-I</th>
<th>NiX-II</th>
<th>NiX-III</th>
<th>NiX-IV</th>
<th>NiX-V</th>
</tr>
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<tbody>
<tr>
<td>Log&lt;sub&gt;10&lt;/sub&gt; Rate 323 K</td>
<td>-5.51</td>
<td>-5.94</td>
<td>-7.80</td>
<td>-7.10</td>
<td>-5.81</td>
</tr>
</tbody>
</table>

(a)

But-1-ene Isomerisation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Exchange</th>
<th>(21%)</th>
<th>(40%)</th>
<th>(68%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log&lt;sub&gt;10&lt;/sub&gt; Rate 323 K</td>
<td>-3.20</td>
<td>-2.01</td>
<td>-1.20</td>
<td></td>
</tr>
</tbody>
</table>

(a) data of Cross (127)

8. 1,1 Dimethylcyclopropane

The isomerisation reaction was studied over NiX-I and NiX-V catalysts. First order kinetics were exhibited and there was no indication of an induction period. The only products observed were 2 methyl-but-2-ene and 2/
2 methyl but-1-ene. (3 methyl but-1-ene was detected in trace amounts on NiX-V.) The reaction plot is similar to Figure 5.12 (a).

The results are presented in Table 5.22

Table 5.22
Rate and Product Data for 1,1 DMCP Reaction on NiX-I and NiX-IV

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temp. (K)</th>
<th>rate $10^2$ %/min/m$^2$</th>
<th>log$_{10}$ rate</th>
<th>Products at 10% Conversion</th>
<th>Products at Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-I</td>
<td>368</td>
<td>0.38</td>
<td>-2.42</td>
<td>18.0 82.0 0.0</td>
<td>17.0 82.5 0.5</td>
</tr>
<tr>
<td>NiX-V</td>
<td>323</td>
<td>4.80</td>
<td>-1.32</td>
<td>10.0 88.0 2.0</td>
<td>13.0 86.5 0.5</td>
</tr>
</tbody>
</table>

Reaction in the presence of hydrogen ($H_2$/Reactant = 3.30) on NiX-V at 429K gave 2 methyl but-2-ene and 2 methyl but-1-ene in ratio 1.44:1 respectively. Iso-pentane was detected after 30% reactant conversion and this was the only gaseous species detected at 100% conversion. The rate of reactant disappearance in the presence of hydrogen was slower than the normal isomerisation reaction in the temperature range 323 - 373 K.

C. 1,2 Dimethylcyclopropane

The reaction plots observed over NiX-I and NiX-V are presented in Figure 5.20 and 5.21 respectively. The plot for n-pentene formation is also presented. NiX-I formed 3 methyl but-1-ene as major product. On NiX-V the major product was 2 methyl but-2-ene. Induction periods were observed for NiX-V. The Arrhenius and rate data for the catalysts studied are presented in Table 5.23.

A reaction was studied in the presence of hydrogen and alkylcyclopropane over NiX-V. There was no induction period observed and reaction rate was increased compared with the normal reaction. The results are presented in Figure 5.22 for a reaction in which temperature was raised during reaction.
Figure 5.20

Reaction of 1,2 dimethylcyclopropane over NiX-1 at 384 K

(a) methyl butene products
(b) pentene products
Figure 5.21

1,2 DMCP reaction over NiX-V at 369 K

(a) methyl butene products
(b) pentene products

(a) methyl butene products

(b) pentene products
Figure 5.22

Effect of hydrogen on 1,2 υMCP isomerisation over M1X-Y

(a) reaction plot  (b) products plot

(methyl butenes only)

330 K

2 methyl but-2-ene
3 methyl but-1-ene

330 K

pentene products x10

3 methyl but-1-ene

346 K

2 methyl but-2-ene
trans pent-2-ene

pent-1-ene

346 K

cis pent-2-ene

2 methyl but-1-ene

20 40 60 80 100 120 140 160 180 200 220 240

20 40 60 80 100 120 140 160 180 200 220 240
The Arrhenius and rate data for this single reaction are presented in Table 5.24. No saturated products were detected. In a qualitative study at 429 K with a similar H₂/reactant ratio iso-pentane and n-pentane were formed (in ratio 3:1 respectively) in amounts accounting for 40% of the gas phase after 100% conversion of 1,2-dimethylcyclopropane. In a comparative study employing deuterium and mass spectroscopic analysis of gas phase it was established that exchange occurred with formation of saturated products.

The product data for nickel zeolites are presented in Table 5.25. Reaction in the presence of hydrogen formed more 3 methyl but-1-ene and pent-1-ene than the normal reactions.

Table 5.23

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ea(kJ/mole)</th>
<th>Log₁₀ A</th>
<th>log₁₀(rate)₃₂₃ ²(K)</th>
<th>T5%-T100% (K)</th>
<th>Reaction Temp. (K)</th>
<th>10² rate %/min/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-I</td>
<td>99.7</td>
<td>30.6</td>
<td>-3.75</td>
<td>339 - 375</td>
<td>367</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>384</td>
<td>7.84</td>
</tr>
<tr>
<td>NiX-V</td>
<td>110.0</td>
<td>34.5</td>
<td>-2.59</td>
<td>335 - 362</td>
<td>318</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>369</td>
<td>0.04</td>
</tr>
</tbody>
</table>

(a) A in molecules/min/m²

Table 5.24

<table>
<thead>
<tr>
<th>Ea (kJ/mole)</th>
<th>Log₁₀ A</th>
<th>T5%-T100% (K)</th>
<th>log₁₀(rate)₃₂₃ ²(K)</th>
<th>Reaction Temp. (K)</th>
<th>rate 10²%/min/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.1</td>
<td>28.9</td>
<td>38.75</td>
<td>-2.51</td>
<td>330</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>346</td>
<td>1.79</td>
</tr>
</tbody>
</table>

A in molecules/min/m²  H₂ / reactant = 3.30
Table 5.25

Product Data for NiX Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature (K)</th>
<th>% Cleavage at 100% Conv</th>
<th>10% Conversion</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>3MB1</td>
<td>2MB1</td>
</tr>
<tr>
<td>NiX-I</td>
<td>367</td>
<td>5.0</td>
<td>70.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>384</td>
<td>5.0</td>
<td>66.0</td>
<td>4.0</td>
</tr>
<tr>
<td>NiX-V</td>
<td>318</td>
<td>8.0</td>
<td>3.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>369</td>
<td>9.0</td>
<td>4.0</td>
<td>12.0</td>
</tr>
<tr>
<td>NiX-V</td>
<td>328</td>
<td>9.0</td>
<td>43.0</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂ present</td>
<td></td>
<td></td>
<td>P1</td>
<td>TP2</td>
</tr>
<tr>
<td>NiX-I</td>
<td>56.0</td>
<td>13.0</td>
<td>31.0</td>
<td>3.5</td>
</tr>
<tr>
<td>NiX-V</td>
<td>56.0</td>
<td>13.0</td>
<td>31.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The activity of NiX-I and NiX-V for various reactants is summarised in Table 5.26.

Table 5.26/
Table 5.26

Activity Summary for NiX Catalysts

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Ea kJ/mole</th>
<th>Log$\text{10}A$</th>
<th>T5</th>
<th>T100</th>
<th>Log$\text{10}$ rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiX-I MCP</td>
<td>86.0</td>
<td>26.0</td>
<td>402</td>
<td>488</td>
<td>-4.14</td>
</tr>
<tr>
<td>1,1 DMCP</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>-2.42</td>
</tr>
<tr>
<td>1,2 DMCP</td>
<td>99.7</td>
<td>30.6</td>
<td>339</td>
<td>375</td>
<td>-1.86</td>
</tr>
<tr>
<td>NiX-V MCP</td>
<td>142.0</td>
<td>37.1</td>
<td>369</td>
<td>394</td>
<td>-5.01</td>
</tr>
<tr>
<td>1,1 DMCP</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>-1.32</td>
</tr>
<tr>
<td>1,2 DMCP</td>
<td>11.0</td>
<td>34.5</td>
<td>335</td>
<td>362</td>
<td>-2.59</td>
</tr>
</tbody>
</table>

A in molecules/min/m$^2$ T5 = T(K) for 5% Conversion in 90 mins.
(a) at 368 K (b) at 323 K

5.4 Reactions over CeX-II

A cerium exchanged X zeolite catalyst containing 78% replacement of sodium by cerium was studied.

A. MCP

Reaction of methylcyclopropane over CeX catalyst gave only the normal butenes as products. (Figure 5.23 (a) ) The reactions exhibited zero order kinetics. Typical results and an Arrhenius plot are presented in Table 5.27 and Figure 5.24.

Table 5.27

Rate Data for MCP Disappearance over CeX

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation Energy /kJ/mole</th>
<th>Log$\text{10}A$</th>
<th>T5% (K) Conv in 90 mins.</th>
<th>T100% (K) Conv in 90 mins.</th>
<th>RT (K)</th>
<th>rate $10^4$ %/min/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeX-II</td>
<td>141</td>
<td>43.0</td>
<td>291</td>
<td>307</td>
<td>289</td>
<td>7.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>298</td>
<td>38.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>312</td>
<td>628.00</td>
</tr>
</tbody>
</table>

RT = reaction temperature
Figure 5.23

MCP Reactions over CeX-II

(a) at 298 K
(b) effect of water (28.0 molecules/cage) on activity at 298 K

O = MCP
O = but-1-ene  △ = trans but-2-ene  □ = cis but-2-ene

Composition vs. time (mins.)

(a)

Composition

(b)

Composition

Composition

Composition
Figure 5.24

Arrhenius plot for MCP disappearance over CeX-II
A repeat reaction on a catalyst outgassed at 312K for 40 minutes, after initial use at 312K, exhibited reduced activity. Subsequent outgassing of the catalyst at 673K for 15 hours and admission of reactant resulted in a similar reaction rate as initially observed. When the final reaction mixture was left for 3 weeks at 312K no gas phase products were observed. Cross (127) used a temperature range of 309K - 323K to investigate but-1-ene isomerisation over a similar cerium catalyst.

Effect of Hydrogen

Pretreatment of the catalyst with hydrogen, as described in the section for CuX, enhanced the normally observed isomerisation rate of methylcyclopropane disappearance on CeX. The data is summarised in Table 5.28 together with the results of experiments involving reaction in the presence of hydrogen. In the presence of hydrogen no other products except normal butenes were observed.

When the products of isomerisation after pretreatment with, and in the presence of, deuterium were analysed mass spectrometrically no exchange was observed in unisomerised reactant or products. This analysis was carried out at the start and on completion of reaction.

Table 5.28

<table>
<thead>
<tr>
<th>Type of Pretreatment</th>
<th>H₂/MCP</th>
<th>Reaction Temperature</th>
<th>log₁₀ rate</th>
<th>Normal Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen A *</td>
<td></td>
<td>291</td>
<td>-3.07</td>
<td>-3.07</td>
</tr>
<tr>
<td>Normal B</td>
<td>3.91</td>
<td>298</td>
<td>-2.39</td>
<td>-2.39</td>
</tr>
<tr>
<td>Normal C</td>
<td>2.20</td>
<td>298</td>
<td>-1.85</td>
<td>-2.39</td>
</tr>
</tbody>
</table>

*labels A-F distinguish the various experiments employed as in Table 5.30
Effect of Water

If small amounts of water (equivalent to 1 molecule per supercage) were frozen into the reaction vessel prior to admission of reactant it was found that the reaction rate of the methylcyclopropane isomerisation reaction was enhanced as compared to the normal water free isomerisation rate. Similar admission of larger amounts of water made the rate initially faster but the reaction was soon poisoned as can be seen from Figure 5.23 (b). In this latter experiment water equivalent to 28 molecules per supercage was present.

The isomerisation rate on a catalyst outgassed at 298K was found to be less than that outgassed at 673K. The results in terms of activity for isomerisation of methylcyclopropanes in the presence of water are summarised in Table 5.29 with the normal reaction rate at particular reaction temperatures quoted for comparison.

Experiments using heavy water gave results similar to those observed for CuX-IV in so far as exchange accompanied formation of n-butenes. The process was stepwise and only one hydrogen atom had undergone exchange at 100% reactant conversion.

Table 5.29

<table>
<thead>
<tr>
<th>Temperature of Reaction (K)</th>
<th>Molecules H₂O/cage</th>
<th>Rate Constant %/min/m²</th>
<th>Rate Constant %/min/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 (C)</td>
<td>0.80</td>
<td>9.97 \times 10⁻¹</td>
<td>4.07 \times 10⁻³</td>
</tr>
<tr>
<td>298 (D)</td>
<td>5.81</td>
<td>7.90 \times 10⁻²</td>
<td></td>
</tr>
<tr>
<td>298 (E)</td>
<td>28.0</td>
<td>9.31 \times 10⁻²</td>
<td></td>
</tr>
<tr>
<td>298 (F) Outgassed 298K</td>
<td></td>
<td>9.18 \times 10⁻⁴</td>
<td></td>
</tr>
</tbody>
</table>
Product Distribution

The product distributions were analysed in the manner already described for CuX and NiX catalysts. The data is presented in Table 5.30.

Table 5.30

Product Distributions for MCP Isomerisation over CeX-II

<table>
<thead>
<tr>
<th>Catalyst/Treatment</th>
<th>Reaction Temp.(K)</th>
<th>Temp.(K)</th>
<th>% Products at 10% Conversion</th>
<th>% Products at Equilibrium</th>
<th>Ratios at 10 % Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>289</td>
<td>8.0</td>
<td>36.0</td>
<td>56.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>6.0</td>
<td>33.0</td>
<td>61.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>312</td>
<td>10.0</td>
<td>34.0</td>
<td>56.0</td>
</tr>
<tr>
<td>CeX-II</td>
<td>Consecutive</td>
<td>312</td>
<td>7.0</td>
<td>45.0</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outgass at 312K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outgass at 673K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pretreatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂ Present A</td>
<td>298</td>
<td>11.0</td>
<td>31.0</td>
<td>58.0</td>
</tr>
<tr>
<td></td>
<td>H₂ Present B</td>
<td>298</td>
<td>9.0</td>
<td>28.0</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>Water Present C</td>
<td>298</td>
<td>15.0</td>
<td>45.0</td>
<td>39.0</td>
</tr>
<tr>
<td></td>
<td>Water Present D</td>
<td>298</td>
<td>9.0</td>
<td>35.0</td>
<td>56.0</td>
</tr>
<tr>
<td></td>
<td>Water Present E</td>
<td>298</td>
<td>8.0</td>
<td>47.0</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>Water Present F</td>
<td>301</td>
<td>15.0</td>
<td>32.0</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td>Water Present G</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction in the presence of hydrogen (A) gave a similar composition plot to that observed in the hydrogen pretreated experiment. Repeat experiments at 312 K also resulted in similar product formation as the normal reaction at 312 K.

Activity
The activities of the CeX catalyst in various types of investigation above are summarised in Table 5.31 in order of decreasing activity.

Table 5.31

CeX-II Activity Summary (MCP as reactant)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Reactant</th>
<th>$\log_{10}\text{rate}_{298 \text{ K}}$</th>
<th>$\log_{10}\text{rate}_{323 \text{ K}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>MCP/water</td>
<td>+0.10</td>
<td>+1.90</td>
</tr>
<tr>
<td></td>
<td>Water = 1/cage</td>
<td>+0.10</td>
<td>+1.90</td>
</tr>
<tr>
<td>Normal A</td>
<td>$H_2$/MCP = 3.91</td>
<td>-1.46</td>
<td>+0.44</td>
</tr>
<tr>
<td>Normal B</td>
<td>$H_2$/MCP = 2.20</td>
<td>-1.85</td>
<td>+0.05</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>MCP</td>
<td>-2.32</td>
<td>+0.08</td>
</tr>
<tr>
<td>Normal</td>
<td>MCP</td>
<td>-2.41</td>
<td>-0.05</td>
</tr>
<tr>
<td>Degass</td>
<td>298K MCP</td>
<td>-3.04</td>
<td>-1.14</td>
</tr>
<tr>
<td>Normal</td>
<td>But-1-ene</td>
<td>-</td>
<td>-1.21</td>
</tr>
</tbody>
</table>

(a) rate in %/min/m²

(b) (Results of N. E. Cross [127])

8. 1,1 DMCP

A typical reaction plot is given in Figure 5.25 (a) and Figure 5.25 (b) shows the Arrhenius plot derived from consideration of $k$ values obtained by drawing tangents to the first order plots at the zero conversion level. Data for the CeX-II catalysts are summarised in Table 5.32.

For the reaction at 323K methyl butenes were formed and also iso-pentane to an extent comparable to that of 2 methyl but-1-ene. Reaction in the presence of hydrogen resulted in a small increase in rate compared to normal (Table 5.32)./
Figure 5.25

(a) Reaction of 1,1 dimethylycyclopropane over CeX-II at 292 K

(b) Arrhenius plot for reaction of 1,1 dimethylycyclopropane over CeX-II
Table 5.32

Rate Data for Reaction of 1,1 DMCP

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>rate $10^2$ %/min/m$^2$</th>
<th>Ea $\text{kJ/mole}$</th>
<th>$\log_{10} A$</th>
<th>$T_5 - T_{100}$</th>
<th>$\log_{10} \text{rate}_{323K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>244</td>
<td>4.2</td>
<td>34.0</td>
<td>23.5</td>
<td>236 - 293</td>
<td>-0.29</td>
</tr>
<tr>
<td>292</td>
<td>50.20</td>
<td>34.0</td>
<td>23.5</td>
<td>236 - 293</td>
<td>-0.29</td>
</tr>
<tr>
<td>323</td>
<td>117.00</td>
<td>34.0</td>
<td>23.5</td>
<td>236 - 293</td>
<td>-0.29</td>
</tr>
<tr>
<td>274</td>
<td>4.8</td>
<td>$H_2$/Reactant = 3.71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$A$ in molecules/min $/m^2$

The relative amounts of 2 methyl but-1-ene and of 3 methyl but-1-ene were reversed as compared to a normal run at this temperature although 2 methyl but-1-ene was still the major product. Quantities of iso-pentane, neopentane, hydrocarbons of lesser chain length and small amounts of di-olefins or polymeric material were also detected. These products accounted for about 10% of the gas phase composition at 100% reaction conversion.

The product distributions (for methyl butenes only) are presented in Table 5.33.

Table 5.33

Products for 1,1 DMCP Reaction over CaX-II

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Reaction Temperature</th>
<th>10% Conversion</th>
<th>Equilibrium Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2MB1</td>
<td>2MB2</td>
</tr>
<tr>
<td>Normal</td>
<td>274</td>
<td>18.0</td>
<td>74.0</td>
</tr>
<tr>
<td>Normal</td>
<td>292</td>
<td>6.5</td>
<td>90.0</td>
</tr>
<tr>
<td>Normal</td>
<td>323</td>
<td>7.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>274</td>
<td>3.0</td>
<td>89.0</td>
</tr>
</tbody>
</table>

C. 1,2 DMCP
C. 1,2 DMCP

The observed results of investigation of 1,2 DMCP reaction are illustrated in Figure 5.26(a) and (b). Rate data and derived Arrhenius parameters are presented in Table 5.34.

**Table 5.34**

<table>
<thead>
<tr>
<th>Ea kJ/mole</th>
<th>Log10A</th>
<th>T5%</th>
<th>T100%</th>
<th>Reaction Temperature (K)</th>
<th>10 rate %/min/m²</th>
<th>Pentene Amount at 100% Conversion (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.0</td>
<td>27.0</td>
<td>236</td>
<td>279</td>
<td>274</td>
<td>7.55</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>298</td>
<td>71.60</td>
<td>9%</td>
</tr>
</tbody>
</table>

A in molecules/min/m²

(a) This figure did not alter appreciably after 100% conversion.

The product distributions observed are presented in Table 5.35.

**Table 5.35**

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>10% Conversion</th>
<th>Equilibrium Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2MB1</td>
<td>2MB2</td>
</tr>
<tr>
<td>274</td>
<td>1.0</td>
<td>33.0</td>
</tr>
<tr>
<td>298</td>
<td>2.0</td>
<td>33.0</td>
</tr>
<tr>
<td>CIS to TRANS to P1</td>
<td></td>
<td>CP2</td>
</tr>
<tr>
<td>274</td>
<td>9.0</td>
<td>51.0</td>
</tr>
<tr>
<td>298</td>
<td>10.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>

Consideration of the rate data presented clearly indicates that CeX-II displays comparable activity in the dimethylcyclopropanes isomerisation reactions whereas higher temperatures are necessary for methylcyclopropane reaction.
Figure 5.26

1,2 dimethylcyclopropane reaction on CeX-II at 274 K

(a) methyl butene products
(b) pentene products
5.5 Other Catalysts Studied

(a) NaX

A. Isomerisation of MCP

The results which have been utilised in previous sections for activity comparisons are now detailed below. The isomerisation of MCP over NaX was zero order in reactant disappearance with no induction period being observed. The only products detected were the three normal butenes.

The results are presented in Table 5.36 and the Arrhenius plot in Figure 5.27.

Table 5.36

| Catalyst | Activation Energy (kJ/mole) | Log$_{10}$A | T(K) 5% Conv. | T(K) 100% Conv. | Reaction Temp.(K) | rate $10^4$ %/min/m
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX</td>
<td>61.0</td>
<td>23.0</td>
<td>363</td>
<td>578</td>
<td>466</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>476</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>494</td>
<td>8.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>509</td>
<td>17.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>531</td>
<td>28.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>549</td>
<td>38.80</td>
</tr>
</tbody>
</table>

Log$_{10}$ rate$_{323}$ K$^2$ = -6.46
A in molecules/min$^{-1}$/m$^2$

The product distribution average values have been utilised already but the values observed for experiments in Table 5.36 are presented in Table 5.37.

The product ratios observed during reaction were independent of the extent of conversion. No reaction was examined beyond 100% conversion.

Table 5.37/
Figure 5.27

Arrhenius plot for MCP reaction over NaX

\[ \log_{10} k \] vs. \( \frac{K}{T} \times 10^3 \]
Table 5.37

*n*-Butene Product Distribution for MCP reaction over NaX

<table>
<thead>
<tr>
<th>Reaction Temp. (K)</th>
<th>Values at 10% Conv.</th>
<th>Equilibrium Values</th>
<th>Values at 10% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIS</td>
<td>TRS</td>
<td>B1</td>
</tr>
<tr>
<td>456</td>
<td>29.0</td>
<td>29.0</td>
<td>42.0</td>
</tr>
<tr>
<td>476</td>
<td>22.0</td>
<td>20.0</td>
<td>58.0</td>
</tr>
<tr>
<td>494</td>
<td>23.0</td>
<td>20.0</td>
<td>57.0</td>
</tr>
<tr>
<td>509</td>
<td>15.0</td>
<td>23.0</td>
<td>62.0</td>
</tr>
<tr>
<td>531</td>
<td>13.0</td>
<td>26.0</td>
<td>61.0</td>
</tr>
<tr>
<td>549</td>
<td>16.0</td>
<td>21.0</td>
<td>63.0</td>
</tr>
</tbody>
</table>

B. 1,1 DMCP

The reaction plot is similar to that presented for CuX-I in Figure 5.12. When the reaction was carried out at 366 K on a sample of catalyst outgassed at 298 K the activity was considerably reduced. Pretreatment of catalyst with hydrogen at 673 K for one hour and analysis of gas phase after 30% conversion indicated that the catalyst was reduced in activity as compared to the normal reaction. In all cases no 3 methyl but-1-ene was observed and 2 methyl but-2-ene and 2 methyl but-1-one were the only products detected. The results and product distribution are summarised in Table 5.38 below. The reactions followed zero order kinetics.

<table>
<thead>
<tr>
<th>Catalyst Pretreatment</th>
<th>Reaction (K) Temperature</th>
<th>rate 10^4 %/min/m²</th>
<th>10% Conversion 2MB1</th>
<th>2MB2</th>
<th>3MB1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Outgass</td>
<td>366</td>
<td>126.50</td>
<td>10.0</td>
<td>90.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Outgass 298K</td>
<td>367</td>
<td>0.43</td>
<td>12.0</td>
<td>88.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(Hydrogen 673K)</td>
<td>(for one hour)</td>
<td>366</td>
<td>4.44</td>
<td>18.0</td>
<td>82.0</td>
</tr>
<tr>
<td>Equilibrium Values</td>
<td></td>
<td></td>
<td>17.0</td>
<td>82.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

C. 1,2 DMCP
C. **1,2 DMCP**

An induction period was observed for reaction over NaX at 338 K (Figure 5.28); the data for this reaction are given in Table 5.39. At 10% conversion only 3 methyl but-1-ene was detected. The product composition was unaltered from 40% up to 100% conversion. The products formed from C1 - C2 cleavage were also constant in amount but after following the reaction for five times the period required for reactant conversion, the relative pentene amounts were pent-1-ene: cis pent-2-ene: trans pent-2-ene = 12:4:9 (cis/trans = 0.45; equilibrium value = 0.80)

Table 5.39

<table>
<thead>
<tr>
<th>Reaction (K)</th>
<th>rate $10^3$ %/min/m²</th>
<th>%C1-C2 cleavage at 100% Conv.</th>
<th>40% Conv. methyl butene prod.</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaX</td>
<td>CuX</td>
</tr>
<tr>
<td>338</td>
<td>6.06</td>
<td>10%</td>
<td>67.0 6.0 27.0</td>
<td>0.5 14.5 85.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>@ 50% Conv</td>
<td>P1 TRNS CIS</td>
<td>P1 TRNS CIS</td>
</tr>
<tr>
<td></td>
<td>6.06</td>
<td>10%</td>
<td>56.0 39.0 5.0</td>
<td>3.0 59.5 37.5</td>
</tr>
</tbody>
</table>

The activity of the NaX catalyst has already been utilised in consideration of CuX and NiX catalyst results. From the data the order of activity of the cyclic reactants with respect to NaX is 1,2 DMCP > 1,1 DMCP > MCP.

(b) Other catalysts; a less detailed study was made of alkyl cyclopropane reactions over other ion exchanged X zeolites and these will now be presented in terms of reactant used.

A. **MCP**

A zinc X zeolite exchanged to an extent of 50% and a iron zeolite exchanged to 15% sodium replacement gave results similar in pattern to CuX-IV in respect of an induction period and product distributions. The results/
Figure 5.28

1,2 dimethylcyclopropane reaction on NaX (330 K)

(a) methyl butenes and reactant

(b) pentenes
results are summarised in Table 5.40. In the case of ZnX-II, but-1-ene was the major product, but for FeX-I, the butane isomerisation was occurring to a greater extent giving \( \text{trans} \) but-2-ene as major product. In the comparable work (127) on but-1-ene isomerisation over ZnX-II, reaction at a temperature of the order of 448 K was necessary to obtain good rate plots, this being 50 K higher than required for MCP isomerisation.

**Table 5.40**

Summary of Catalyst Reactivities (MCP Reaction)

<table>
<thead>
<tr>
<th>Catalyst (% Exchange)</th>
<th>Reaction (K) Temperature</th>
<th>rate ( \times 10^{-3} ) %/min/m²</th>
<th>Induction Period (minutes)</th>
<th>Products 10% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CIS</td>
</tr>
<tr>
<td>ZnX-II (b)</td>
<td>395</td>
<td>4.2</td>
<td>8</td>
<td>8.0</td>
</tr>
<tr>
<td>FeX-I (15)</td>
<td>299</td>
<td>5.6 (a)</td>
<td>68</td>
<td>19.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Products @ Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIS</td>
</tr>
<tr>
<td>ZnX-II (b)</td>
<td>26.0</td>
</tr>
<tr>
<td>FeX-I (15)</td>
<td>23.5</td>
</tr>
</tbody>
</table>

(a) based on a surface area of 800 m²/g
(b) prepared by N.E. Cross (127)

8. **1,1 DMCP**

An ammonium zeolite and a series of cobalt zeolites were examined in this reaction. The results are given in Table 5.41. For the ammonium zeolite no induction period was observed and reactant disappearance followed first order kinetics resulting in formation of 2 methyl but-2-ene > 2 methyl but-1-ene only. The ammonium zeolite was activated by vacuum outgassing at 423 K/
423 K for 15 hours. The cobalt catalysts were activated in the normal way by outgassing at 673 K. These catalysts did not exhibit an induction period and followed first order kinetics the products being 2 methyl but-2-ene > 2 methyl but-1-ene with a trace of 3 methyl but-1-ene formed. Surface area figures for the cobalt catalysts are not available but an activity comparison for these sieves and the other catalysts is based on a surface area of 800 m²/g. Reaction with CoX-I was preceded by hydrogen pretreatment for one hour at 673 K.

Table 5.41

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction (K)</th>
<th>temperature</th>
<th>rate 10³/min/m²</th>
<th>Products 10% Conv.</th>
<th>Products at Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄X-III</td>
<td>289</td>
<td>21.3</td>
<td>4.0</td>
<td>96.0 Nil</td>
<td>9.5 90.0 0.5</td>
</tr>
<tr>
<td>(75)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoX-I *</td>
<td>328</td>
<td>2.1</td>
<td>10.0</td>
<td>90.0 Nil</td>
<td>13.5 86.0 0.5</td>
</tr>
<tr>
<td>(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoX-II</td>
<td>328</td>
<td>4.7</td>
<td>10.0</td>
<td>90.0 Nil</td>
<td>13.5 86.0 0.5</td>
</tr>
<tr>
<td>(36)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoX-III</td>
<td>328</td>
<td>41.2</td>
<td>9.0</td>
<td>90.0 1.0</td>
<td>13.5 86.0 0.5</td>
</tr>
<tr>
<td>(52)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* after hydrogen pretreatment

C. 1,2 DMCP

This isomerisation reaction was studied over CoX-I and a NH₄X-III catalyst which had been outgassed at 423, 573 and 823 K respectively. Surface area values at the temperature of outgassing have been presented earlier. For both catalysts disappearance of reactant exhibited zero order kinetics and no induction periods were observed. The ammonium catalysts were reacted at /

(a) prepared by R.M Cosh (142)
at 285 K.

The activity of the NH$_4$X-III catalyst is plotted as a function of the activation temperature in Figure 5.29. The rate and product results are summarised in Table 5.42.

Reaction over CoX-I gave a 7% 1,2 scission at 100% conversion; the composition plot was similar to that of CuX-I in respect of 3 methyl but-1-ene as major product. 2 methyl but-1-ene was found also and the pentene products gave pent-1-ene $>$ Trans pent-2-ene $>$ cis pent-2-ene.

Table 5.42

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction (K) Temperature</th>
<th>rate $10^3$ %/min/m$^2$</th>
<th>Products 10% Conv.</th>
<th>Products at Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoX-I</td>
<td>369</td>
<td>20.8</td>
<td>3.0</td>
<td>30.0</td>
</tr>
<tr>
<td>NH$_4$X-III (Outgassed)</td>
<td>423</td>
<td>295</td>
<td>2.2</td>
<td>trace</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>293</td>
<td>238.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>823</td>
<td>296</td>
<td>242.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

On the NH$_4$X-III catalyst outgassed at 423 and 823 K respectively only 3 methyl but-1-ene and 2 methyl but-2-ene were observed. After 40% conversion on NH$_4$X-III outgassed at 423 K traces of n-pentenes and 2 methyl but-1-ene were observed. At 100% conversion on NH$_4$X-III outgassed at 823 K these products accounted for less than 2% of the gas phase composition (Trans pent-2-ene $>$ 2 methyl but-1-ene $>$ pent-1-ene $>$ cis pent-2-ene). The results for an ammonium catalyst outgassed at 573 K are presented in Figure 5.30. For this catalyst n-pentene formation continued after 100% reactant conversion.
Figure 5.29

1,2 dimethylcyclopropane reaction at 295 K over NdX-III as a function of outgassing
Figure 5.30

1,2 dimethylcyclopropane reaction at 293 K on NK₄X-III
outpased at 573 K

(a) methyl butene products

(b) pentene products
6.1 Catalyst Properties

Yates (150) has employed X ray diffraction techniques to determine surface area changes in X zeolites. However thermogravimetric (151) and infra-red data (89) indicate that zeolites contain water even after outgassing at 873 K. The presence of water can markedly influence the relative peak intensities of the X ray diffraction analyses (64, 152). Therefore it seems unlikely that X ray diffraction analyses alone are sensitive enough to determine the extent of zeolite crystallinity. All samples used in this study (except NH₄X-III outgassed at 823 K) yielded X ray diffraction data which indicated crystallinity.

For NH₄X-III it was evident that the zeolite structure had partially collapsed after outgassing at 823 K. This was confirmed by surface area measurements which showed that a 50% loss in surface area had occurred after outgassing at 823 K. Smaller reductions (about 10%) were noted for other zeolites after reaction (Table 5.1); these are attributed to strongly adsorbed intermediates (cokes) or occluded material. Gas phase losses attributable to polymer formation have been observed in similar work on X zeolites (153).

The total peak area as determined from chromatographic scans during reaction indicated that the highest exchanged catalysts exhibited the most significant gas phase losses. Carbon analyses of these catalysts showed that NiX-V gave higher gas phase losses than CuX-IV. Prolonged reaction (3 days) on CsX-II resulted in no gas phase and in this case it seems likely that a high/
high proportion of the lost gas phase formed coke and/or occluded polymeric material. Venuto\textsuperscript{(154)} has observed the formation of occluded intracrystallinic polyolefins on reacting ethylene over rare earth exchanged zeolites. The accountable gas phase loss consists of adsorbed hydrocarbons (reactants and products). For the nickel and copper catalysts studied the occluded material was formed to the extent of 10\%, at 100\% conversion, of the total gas phase. No detailed adsorption studies were done in this work although desorption of products at the end of reaction generally resulted in the same gaseous composition as observed over the catalyst. However for methylocyclopropane reaction over NiX-IV and NiX-V n-butane will be desorbed faster than the n-butenes\textsuperscript{(155)}. Cross\textsuperscript{(127)} observed little difference in sorption strengths of n-butenes on X type zeolites and it was regarded as unlikely that observed products were a function of sorption - desorption equilibrium. However for the higher exchanged zeolites the gas phase composition might be affected by preferential adsorption processes on the catalyst surface.

6.2 CuX Results

Both the $A$ factors and apparent activation energies (Table 5.3) found for CuX zeolites increased with increase in catalyst copper content. This may be rationalised in terms of the compensation effect. The increase in activation energy that was observed on replacement of sodium by copper may be attributed to an increase in the heat of adsorption component of the apparent activation energy term\textsuperscript{(156)}. Sorption of reactant was greatest for those catalysts which were most active (functioned at lower temperatures), they being the highest exchanged catalysts studied. From the catalyst activity pattern observed for methylocyclopropane isomerisation (Figure 5.10) it is clear that initial replacement of sodium by copper greatly increases catalyst activity. Further increase/
increase in catalyst copper content results in a lessened increase in activity. CuX III, IV and V are of the same order of activity. The shape of the activity plot in relation to the position at which $S_1$ and $S_{II}$ sites would be fully populated would rule against stepwise filling of cation sites on replacement of sodium ions by copper. Dimitrov and Leach (147) observed an increase in CuX zeolite activity for but-1-ene isomerisation after 30\% sodium replacement indicating a stepwise replacement. Such behaviour is not apparent in this work.

If catalyst activity is regarded as arising mainly through reactant interaction with cations in accessible sites it is therefore evident that in this work copper ions are to be found in surface sites even at low levels of cation replacement.

Infra red (69) and E.S.R. (70) spectra of divalent ions in X zeolites indicate $S_1$ (or $S_1'$) site preference. Recent E.S.R. data on CuY (77) show that after the aqueous exchange preparation procedures copper ions exist as non-localised hexaquo complexes in the supercage. Subsequent dehydration at 473 K resulted in removal of water ligands and localisation in the zeolite cavities ($S_{II}$ sites were proposed). The presence of reversibly formed (depending on the extent of hydration) hexaquo complexes in CuA and CuX zeolites has been confirmed by U.V. techniques (157). In this work copper ions were placed in $S_{II}$ sites in a partially dehydrated zeolite but on more rigorous hydration an unassigned band appeared. This may be attributable to copper ions in the $S_1'$ sites as has been suggested by Leith and co-workers (158) for E.S.R. data on CuX zeolites vacuum dehydrated at 673 K. It was proposed that migration of copper to these sites occurred on dehydration. Further migration to more exposed sites took place on admission of hydrocarbon vapours to a dehydrated catalyst. This latter process occurred at temperatures associated with the hydrocarbon isomerisation reaction over the zeolite and a reduction of Cu$^{++}$ to Cu$^+$ in surface sites was thought to be operative. Hydrogen pretreatment at 423 K caused a similar reduction/
reduction process for ions in $S_{11}'$ and $S_1'$ sites. Yates $^{(159)}$ has reported reduction processes for ion exchanged zeolites after hydrogen pretreatment at 673 K.

On the basis of the available physical evidence the observed results relating to induction periods and effect of hydrogen and water can be understood. It is thought likely that interaction with zeolite cation (as was suggested by the activity pattern (Figure 5.10)) together with an associated reduction process take place during catalysis. Depending on the degree of hydration three types of cation population are proposed. The cation distribution after preparation and storage is different to that after dehydration and the two are distinct to that after admission of reactant. Admission of reactant to dehydrated CuX-I will result in reduction of cations in relatively exposed sites (e.g. $S_{11}'$) and possible migration and reduction of a much smaller number of cations from less exposed positions. The observed reproducibility of isomerisation rate and characteristics suggest that the reduction process is reversible. The increase in catalyst activity observed after hydrogen pretreatment at 673 K and the reproducibility of this data in consecutive pretreatment and isomerisation experiments support this view. The enhanced activity presumably arises as a result of an increase in the number of cations reduced and situated in surface sites due to the more rigorous conditions of reduction.

The observed results for CuX-III, IV and V are in accord with the suggestion $^{(127, 149)}$ that induction periods are a function of reduction processes associated with the catalysis. It has been proposed $^{(149)}$ that hydrogen formed in trace amounts from self hydrogenation and cracking type reactions facilitates the reduction of ions. Increasing the reaction temperature would further facilitate/
facilitate this process and hence decrease the induction period. For the higher dehydrated copper catalysts the relative amounts of ions in inaccessible sites must be greater than for dehydrated CuX-I. The irreproducibility of repeat reactions for CuX-V together with the levelling off in activity pattern suggests that the surface site population during catalysis does not continuously increase as ion replacement. Sites inaccessible to reactant are involved to a greater extent for CuX-V than for CuX-I. For these hidden cations reduction by trace hydrogen and subsequent migration to positions more exposed to reactant must occur for catalysis to ensue. Recent X-ray work on CuY zeolites has indicated that a similar cation migration occurs under influence of hydrocarbon reactants. It is considered unlikely for reactant to penetrate to positions or that increasing temperature, as was employed in the range used, would facilitate entry of reactant to such hidden positions as a result of increased port size. The formation of trace hydrogen species as indicated above would yield strongly adsorbed cokes, residues or polymeric material on the zeolite channel walls. Such species appear to be particularly important for higher exchanged catalysts (6,1) and would result in a reduction in catalytic activity on catalyst re-use through blockage of active catalyst sites. Since cation reduction has already occurred no induction period would be expected on catalyst re-use, as was found. These results imply that a mechanism in which Brønsted protons are furnished by carbon residues, as was suggested for alkylcyclopropane isomerisation over silica alumina (140), is unlikely in this work.

The enhanced activity observed after hydrogen pretreatment of CuX-IV arises through reduction and migration of more cations than would be accomplished through reactant - catalyst interaction. The lack of induction period in these experiments/
experiments can also be rationalised in this manner.

The colour of the copper zeolites after outgassing was pale blue grey and after contact with atmosphere this reverted to pale blue green. After reaction the colour observed was a dark blue grey which changed to pale blue green on contact with air. After hydrogen pretreatment both CuX-I and CuX-IV were a pale sand-brown colour and on contact with air both catalysts exhibited a similar pale blue hue. Similar colour changes have been reported elsewhere (149, 158) for copper zeolites and a cationic reduction was proposed. For certain hydrogen treated catalysts formation of copper metal has been suggested. The general similarities in reaction characteristics observed for normally outgassed and hydrogen pretreated catalysts must rule against this idea since metal formation would presumably result in changes in reaction mechanism which would be manifest in the product distributions. These showed no major differences.

Therefore it would appear likely that a cationic reduction process is associated with the catalysis and that the observed induction periods are a function of this reduction. The cation site populations during reaction and after dehydration prior to admission of reactant are similar for CuX-I and CuX-II; mainly surface sites are involved. For the other copper zeolites studied cations in more inaccessible sites are involved. The number of ions in such inaccessible sites is greater for the dehydrated catalyst than for the catalyst with reactant present. Migration of ions in such inaccessible sites must occur for catalysis.

The reduction in rate observed in the presence of water on CuX-IV can also be rationalised in terms of the cation population in the dehydrated zeolite. On adsorption of water the cation distribution normally associated with/
with dehydrated CuX-IV reverts to the hydrated catalyst distribution. The degree of reversion depends on the degree of hydration so induced. The reversibly formed aquo copper complexes observed in the E.S.R. (77) and UV spectra (157) may be responsible for the rate reduction observed for reaction with water present. For CuX-IV there are 28 copper ions to be distributed between the various sites in one unit cell consisting of eight \( \beta \) or supercages. Addition of water equivalent to 80 molecules per unit cell poisoned the catalyst whereas addition of 8 water molecules per unit cell gave a slower rate of reaction in comparison to dehydrated catalyst. In these latter types of experiments presumably surface sites are hydrated whereas the former treatment would hydrate all copper ions. The absence of induction periods for catalysts reacted in the presence of water implies that catalysis involves use of surface sites mainly with little migration occurring. Reduction of copper ions could arise as follows:

\[
\text{Cu}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}^{+}\text{OH} + \text{H}^+
\]

The proton is associated with the catalyst to preserve electrical neutrality. The experimental data suggests that a proton addition scheme of this type is inoperative since rate enhancement would result on addition of water.

Alternatively if hydrated copper cations in CuX-IV formed in \( S_1 \) sites preferentially then rate reduction (compared to normal) would result through use of surface sites only and absence of induction periods would be observed. Although this is a possibility the notion (77) of supercage complex formation is favoured.

Such complex formation may stabilise ions in hidden sites against migration to more exposed catalyst positions. If migration took place then little or no reduction in activity would be expected. It appears that addition of water to CuX-IV results in partial hydration of ions in accessible sites and that catalysis takes place at these sites. This implies that a reduced copper species and its hydrated counterpart are mechanistically equivalent although the latter may not react/
react as quickly possibly through a steric effect or else due to stabilisation of the zeolite against migration of ions from inaccessible site positions.

When heavy water was used the results showed that initially (up to 100% conversion) only one hydrogen atom in the products had undergone exchange. A mechanism based on sec butyl carbonium ion as intermediate was proposed for similar exchange data observed during but-1-ene reaction over NiX catalysts (153). In the present study no exchange was observed in the unisomerised methylcyclopropane and such evidence supports the view that the reactant ring opening step is irreversible. Attack on the cyclic reactant followed by ring opening probably takes place.

The n-butenes which were the only products observed in the methylcyclopropane isomerisation reaction can only arise via a 1-3 scission reaction. It is clear from the reaction composition plots given for high and low copper content catalysts (Figure 5.3(a) and (b) ) that secondary isomerisation of but-1-ene to cis and trans but-2-enes was occurring. This secondary isomerisation reaction becomes more evident as the copper content of the zeolite increases.

Comparison of the results of copper zeolite activity for methylcyclopropane and but-1-ene isomerisation (Figure 5.10 and 5.11) indicates that the higher exchanged copper zeolites are equally active for both reactants whereas the lower copper content sieves are more active for methylcyclopropane isomerisation. This may be explained by steric factors since a cyclic reactant is presumably less able to influence cation migration processes from inaccessible sites than is but-1-ene. This idea would support the view that inaccessible site cations are more (indirectly) involved in the catalysis for higher copper content zeolites. Furthermore the similarity in activity for CuX-III, IV and V may also be rationalised in terms of a geometrical effect which limits the amount of cations/
cations that are activated for use in catalysis. The observed increase in the rate of the secondary isomerisation as copper exchange increase also accounts for the product distribution analyses (Figure 5.8).

Further information regarding the secondary isomerisation may be obtained by consideration of plots as in Figure 5.9. The linear nature of these percentage products versus percentage composition plots indicating an overall constant rate of formation of products. However, towards 100% conversion product interconversion became more pronounced and the linear shape of the plots was lost. Both CuX-I and CuX-II gave plots which did not vary (in product relative amounts) as the temperature of reaction was increased.

The other copper catalysts studied gave plots indicating a faster rate of secondary reaction as temperature increased. Two reactions may be said to be occurring; these are the reactant isomerisation (X) and the secondary isomerisation of product butenes (Y). Reaction Y is suggested as mainly being reaction of but-1-ene to cis and trans but-2-enes. The product data would support this view. Reactions X and Y must be such that linear nature of the plots in Figure 5.9 are obtained.

Factors which influence X do not necessarily influence Y although Y depends on X. Increasing the rate of X by hydrogen pretreatment does not increase the rate of Y as would be manifested by n-but-ene amounts further displaced toward equilibrium values. Reducing the rate of X by water adsorption gives a product distribution further toward equilibrium than normal. These comments apply to both CuX-I and CuX-IV catalysts and it seems that in these cases the rate of X is affected while the rate of Y is altered very little. It is therefore likely that the sites responsible for reaction X are not for the most part associated/
associated with reaction Y. Cations situated in the β cages are thought to be responsible for reaction X and for high exchanged zeolites some Si or S' cations which migrate to accessible positions are involved. It is suggested in view of the discussion on cation distribution and activity patterns given above that the latter type of cations are mostly responsible for reaction Y.

The apparently anomalous results observed for CuX-IV outgassed at 298 K which give reduced rates for both X and Y can be rationalised in terms of the relatively high amounts of water left after mild outgassing affecting both types of cation in a manner already described.

Previous workers in this department (127, 149) have related the initial product ratios observed for but-1-ene isomerisation over X zeolites to the type of mechanism thought to be operative. Consideration of the stabilities of various conformers allowed these workers to conclude:

\[
\begin{align*}
\text{cis but-2-ene} / \text{trans but-2-ene} &< 1 \quad \text{implied a radical mechanism,} \\
\text{cis but-2-ene} / \text{trans but-2-ene} &> 1 \quad \text{implied a carbanion mechanism,} \\
\text{cis but-2-ene} / \text{trans but-2-ene} &> 1 \quad \text{implied a carbonium mechanism.}
\end{align*}
\]

Using these criteria all the data in this thesis would be explained by radical mechanisms for both but-1-ene and methylcyclopropane isomerisation. An approach of this type cannot explain the results over catalysts generally regarded as functioning differently from this; Dimitrov and Leach (149) proposed a radical mechanism for but-1-ene reaction over copper catalysts with less than 40% replacement of sodium whereas catalysts with a greater degree of exchange functioned via carbonium ion mechanisms.

Methylcyclopropane isomerisation is suggested as proceeding via a ring opened intermediate which isomerises to normal butene products through an equilibrium/
equilibrium reaction scheme in which each butene isomer can react to form any other (161). The results suggest preferential but-1-ene formation.

Reaction of 1,2 dimethylcyclopropane gave methyl butenenes and n-pentenes in the ratio 19:1. Preferential formation of 3 methyl but-1-ene occurred and the data indicated secondary isomerisation of this product to the other methyl butene isomers as would be expected on the basis of equilibrium data.

Pent-1-ene was the major product of the n-pentene products and this was clearly isomerising under the experimental conditions to cis and trans pent-2-enes. Generally the secondary reactions were faster on CuX-IV than on CuX-I.

The only products observed from 1,1 dimethylcyclopropane isomerisation were the methyl butenenes which were formed in amounts close to the expected equilibrium values. The major product was 2 methyl but-2-ene. Apparently the observed product distribution was a function of secondary methyl butene isomerisation since higher temperatures were required to isomerise 1,1 dimethylcyclopropane compared to 1,2 dimethylcyclopropane; 3 methyl but-1-ene being the major product for the latter reaction.

The data suggests that a reversibly formed reduced copper ion is responsible for and associated with the ring opening step of the alkylcyclopropane reactants studied. For olefinic reactants the ionic reduction step has been suggested (149) as the rate determining step. Similar conclusions regarding the reduction or related ring scission reaction apply here on the basis of the former being an activated process (Table 5.4).

It is also postulated that ring opening is irreversible and that no stable cyclopropane intermediate is formed. Such species have been proposed for n-propyl systems (162) and for certain ionic re-arrangements which are induced/
induced under electron impact (163). The relatively high energies required in the latter work together with the absence of unisomerised and exchanged reactant in exchange experiments must rule against such species in the present study. Copper is known to form olefin complexes (164); no stable cyclopropane -transition metal complexes are known although a platinum cyclopropane complex in solution was proposed (165, 166). If such a complex were to be formed in this work it would be short lived and readily ring open to form products.

The reduction of copper ions which is associated with the catalysis would involve an electron transfer to the copper cation. Such a process could result in formation of different intermediate types. Homolytic fission of a C-H bond would result in formation of a radical and generation of Cu+. Simultaneous ring cleavage of the radical intermediate followed by oxidation of copper completes the isomerisation reaction. For ionic mechanisms loss of hydride ion would yield carbonium ion and a reduced copper species. Alternatively loss of proton yields a carbanion or allylic species capable of reduction and association with the copper ion.

On the basis of the water pretreatment experiments a proton addition mechanism is considered unlikely. Except for the hydrogen pretreatment experiments it is regarded that the isomerisation mechanism does not involve addition by hydride ions or radicals present on the catalyst. Only in the former case would such species be likely to be present although the overall similarity of the isomerisation data indicates that the non pretreated and hydrogen pretreated mechanisms are the same. Comparison of the observed products from the alkylcyclopropane isomerisation with those predicted for different mechanisms (Chapter III) would indicate that no one mechanism exclusively/
exclusively accounts for the observed products for various reactants.

Clearly the predicted product distributions for each mechanism as given in Chapter III (Table 3.4) can only be considered as a guide. Secondary reactions have as far as is possible been accounted for but allowance has to be made for the electronic properties of the cycloparaffin reactants and the polyanionic nature of the catalysts. A simple approach to the latter point would suggest presence of carbonium ion, to preserve electrical neutrality, in a zeolite containing reduced copper (possibly Cu\(^+\)) ions. The inductive effect of alkyl groups on the cyclopropane ring would stabilise formation of a transient (instantaneously cleaved) cyclic carbonium ion; thus 1,2 and 1,1 dimethylcyclopropanes would be more reactive than methylcyclopropane, as was observed. Loss of hydrogen atom in a radical type reaction is considered unlikely in view of the relatively unstable intermediates that are formed; such species subsequently undergo re-arrangement to give products. It is generally thought that zeolite catalysts undergo hydrocarbon transformations through ionic processes (77, 101, 103, 122) and it is proposed that such mechanisms are operative in this work.

The absence of isobutene from the products of methylcyclopropane isomerisation indicate the proton loss or hydride gain to be less likely. However, these two mechanisms can account for preferential formation of 3 methyl but-1-ene from 1,1 dimethylcyclopropane isomerisation. However, secondary isomerisation may not be responsible for the observed 1,1 dimethylcyclopropane isomerisation products and preferential formation of 2 methyl but-2-ene may be a function of either hydride loss or proton gain mechanisms. Preferential formation of 3 methyl but-1-ene from 1 - 3 scission of 1,2 dimethylcyclopropane could occur via/
via any of the four ionic mechanisms as could pent-1-ene formation in the
1 - 2 scission of this reactant.

However it is suggested that carbonium rather than allylic or radical
species are more likely and in view of this either proton gain or hydride loss
mechanisms would apply with formation of carbonium (162) ions respectively.

Those schemes which result in formation of carbonium ions at points
initially associated with methyl side groups may be more favoured due to the
inductive stabilisation effects of methyl groups at that point prior to ring
opening.

On this basis the hydride loss mechanism effectively accounts for but-1-ene
formation from methylcyclopropane isomerisation and 3 methyl but-1-ene
formation from 1,1, dimethylcyclopropane isomerisation (secondary isomerisation
to 2 methyl but-2-ene occurring). However, the proton gain mechanism is most
suited to explain 1,2 dimethylcyclopropane results on this basis. Although it
has been reported (153) that zeolite reaction mechanisms depend on the reagent
used it is felt unlikely that different mechanisms are operative for the alkyl-
cyclopropane reactants over copper zeolites.

The proton addition mechanism does not explain the observed data as well
as the hydride loss mechanism and indeed the former mechanism would require
use of a greater number of relatively unstable intermediates.

In view of this and the preceding discussion it is proposed that a
hydride loss mechanism is operative in the alkylcyclopropane isomerisation
reactions over copper zeolites.

The/
The mechanism is illustrated below for methylocyclopropane isomerisation.

Copper (II) ions are reduced to copper (I) ions either by reactant or by hydrogen, and migration of ions may precede this reversible reduction. Preferential formation of but-1-ene may arise due to presence of positive charge at a carbon atom formerly attached to a ring substituent.

Loss of hydride ion from C2 is probably the most dominant reaction since loss of hydride ion at C1 would result in iso-butene formation whereas loss of methyl carbon hydrogen would result in but-1-ene formation or resonance stabilised cyclobutonium ion as has been suggested by other workers (140).
6.3 NiX Zeolites

As is evident from Table 5.17 the $A$ factors and apparent activation energy both increase as the degree of sodium replaced by nickel increases. This may in fact be due to the compensation effect discussed for similar behaviour observed for copper zeolites in reaction 6.2. A heat of adsorption term may also contribute to the increase in activation energy observed through NiX-I to NiX-V since generally adsorption would be greatest for NiX-V which reacts at relatively lower temperatures than the other catalysts.

The X-ray data regarding the site occupancy of nickel in nickel faujasite (outgassed at 673 K for nine hours) indicated that nickel ions were mainly in $S_1$ and $S_{II}$ positions. Proportionately less ions were said to be situated at $S_1$ or $S_{II}'$ sites (Table 2.1). Angell and Schaffer found nickel to have no preference for site I occupation in NiY zeolites although similar work by Egerton on NiY demonstrated that in zeolites with less than 50% replacement that $S_1$ sites rather than surface sites were populated. On X zeolites surface sites were occupied after 20% replacement. E.S.R. studies on the NiX catalyst used for n-butene work (Figure 5.19) indicated that nickel ions were found in $S_1$ sites at lower levels of exchange but that nickel ions were present in surface sites for all the sieves. In a re-examination of the X-ray data Dempsey and Olsen proposed that nickel ions occupied two types of $S_1'$ sites.

Exchange of the sodium ions in NaX for nickel ions increases the zeolite activity for methylcyclopropane isomerisation (Figure 5.19). However unlike the activity pattern observed for CuX catalysts (Figure 5.10) the nickel zeolite activity was approximately constant except for NiX-III and NiX-IV which/
which were less active. Consideration of temperature values (Table 5.19 and 5.36) required to give 5% conversion in 90 minutes agrees with this observation although NaX has a similar activity to NiX-V in this respect. The NiX sieves do not seem to be so active in the isomerisation of MCP as are the CuX zeolites.

If the cation distribution in the dehydrated zeolites was such that inaccessible sites were filled primarily then presence of active centres would arise after about 64% sodium replacement (for Si sites). However the absence of observed induction periods until about 43% sodium exchange would indicate that inaccessible cations do not influence the catalysis at lower levels of cation exchange. Surface sites in the dehydrated zeolites must be involved even at low levels of catalyst exchange; perhaps the cation population for the dehydrated catalyst is in proportion with respect to site positions, to that given in Table 2.1 for a nickel faujasite containing approximately 22 Ni ions per unit cell (152).

The relative inactivity of the nickel zeolites in the methylocyclopropane isomerisation may be explained in terms of contribution from metal in the catalysts. Each catalyst examined gave slightly different types of side products. The formation of saturated products (n-butane), of di-olefins and of cracking products are typical of the behaviour of hydrocarbon isomerisation reactions over metals (128). Quantities of nickel metal have been proposed to exist in Ni\textsuperscript{++} Y zeolites (169). Flame photometric analysis results indicated no leaching out of sodium or of excess sodium in the structure as would result if exchange did not occur to the extent indicated by titrometric determinations on the exchanging solutions. Reaction of methylocyclopropane on an/
an alumina supported nickel catalyst prepared in this department (147) was negligible at 450 K (the α alumina support was unreactive at 523 K). Qualitative comparison of the data suggests that supported nickel metal is less active than nickel zeolites in methylcyclopropane isomerisation.

The presence of metallic nickel in the zeolite can be envisaged as arising after the exchange preparation of the zeolite or after outgassing or as a result of interaction of hydrocarbons with the zeolite.

In an allied study in this department Cross (127) reported that for a 20% exchanged nickel zeolite E.S.R. data indicated that a reduction of Ni²⁺ ions to either Ni⁺ or Ni⁰ species occurred on outgassing. The effect of reactant on the Ni⁰ and Ni⁺ population will also have to be considered.

The colour changes observed on outgassing and after hydrogen pretreatment support the view that a reduction process was occurring. The fact that the induction period was eliminated after hydrogen pretreatment and partially eliminated on catalyst re-use (NiX-V) also suggests that the induction periods reported for NiX-IV and V are a function of a reduction process associated with ions in relatively inaccessible sites (6.2.). This reduction process may involve reduction to Ni⁺ and Ni⁰ species but it is proposed that only that component to obtain Ni⁺ is linked to the induction period since this is probably the active centre responsible for isomerisation activity. Similar conclusions were arrived at for but-1-ene isomerisation over NiX catalysts (127).

The hydrogenation data which is to be discussed later rules against the possibility of a metallic mechanism to explain the results. (exclusively)

The metallic nature of the nickel catalysts is apparently responsible for the lower relative activity of the nickel zeolites. NiX-III and NiX-IV must have/
have a relatively higher $\text{Ni}^0 / \text{Ni}^+$ ratio especially in sites which are exposed to reactant. It is interesting to note at this point that the catalyst which is least active for C1 - C2 exchange of reactant is most active for C2 - C3 cleavage and this latter reaction has a higher apparent activation energy than the former. The factors influencing the $\text{Ni}^0 / \text{Ni}^+$ ratio include the outgassing procedure, cation distribution and reactant. No explanation is offered for the higher $\text{Ni}^0 / \text{Ni}^+$ ratio for NiX-III and NiX-IV unless the degree of nickel loading and presence of species necessary to stabilise $\text{Ni}^0$ or $\text{Ni}^+$ in the zeolite are such as to bring this about.

The effect of reactant on NiX-V catalyst re-use can now be rationalised in terms of a higher $\text{Ni}^0 / \text{Ni}^+$ ratio. Only $\text{Ni}^0$ is suggested as being formed by reactant or on pumping off prior to admission of reactant. This would result in an increased rate of n-butane formation, which is formed as a result of self hydrogenation on metallic centres, whilst the rate of isomerisation remains unchanged. The induction period would also be reduced for reasons outlined in 6.2. Thus although the reproducibility of the reduction process generating species responsible for the isomerisation reaction is established conclusions regarding the reversibility of $\text{Ni}^0$ formation are much less certain.

For further evidence on this point it is worthwhile considering what happens to the zeolite after hydrogen pretreatment and reactions in the presence of hydrogen with or without hydrogen pretreatment. Yates (150) reported that hydrogen treatment of various zeolites at 673 K resulted in ionic reduction (formation of $\text{Ni}^0$ was reported) and Pope and Kemball (156, 170) reported reversible reduction of $\text{Ni}^{2+}$ ions after initial hydrogen treatment at 573 K and outgassing. In these experiments formation of $\text{Ni}^+$ or $\text{Ni}^0$ was generally regarded as having taken place. Yates (150) has suggested that metal ions formed after/
after hydrogen reduction at 673 K are loosely held to the lattice and migrate and irreversibly form metallic agglomerates on the zeolite surface. An increase in nickel crystal size for a series of nickel X and A zeolites with increase in nickel content has been proposed (151) to explain the reduction in specific activity observed in cyclohexane dehydrogenation, after reduction of the catalysts with hydrogen at 673 K.

It is possible that such an irreversible agglomeration process occurred to an extent which affected those centres most likely to isomerise methylcyclopropane. The reducing medium would be the reactant itself and for NiX-III and NiX-IV the Ni$^0$/Ni$^+$ ratio would still be such that Ni$^0$ ions were in or formed in surface sites more so than for the other zeolites. However the colour change observed on re-oxidation after hydrogen treatment indicates that a reversible process was occurring.

Furthermore the evidence on hydrogen treatment suggested that the presence of hydrogen in activated form or otherwise is necessary to maintain the effect of bulk metal - this will be discussed in detail shortly.

The isomerisation activity of NiX-V was increased after hydrogen pretreatment with loss of induction period. Such behaviour can be understood in terms of a process affecting a reduction to Ni$^+$ rather than Ni$^0$ species. There must apparently be a limit to the Ni$^0$/Ni$^+$ ratio in the zeolite providing no agglomeration occurs and this can be a function of those species required to preserve neutrality in the zeolites. Ni$^0$ would require more charge stabilising entities than Ni$^+$.

By comparison (Table 5.18) reaction over NiX-V in the presence of hydrogen after/
after normal outgassing gave a similar rate enhancement as in the hydrogen pretreatment reaction. The rate of hydrogenation was slightly slower (Figure 5.16 b) than the reactant disappearance and the final product was n-butane. Presumably the effect of reaction mixture at 428 K is the same as hydrogen pretreatment at 673 K in respect of the formation of Ni⁺ species in the zeolites. Although the causes are not apparently similar the effect on reaction rate is the same.

The greatest increase in rate was evident for the reaction carried out in the presence of hydrogen after hydrogen pretreatment. Hydrogenation of methylcyclopropane generally results in predominantly C2 – C3 cleavage over nickel and supported nickel catalysts (128, 129, 131). The hydrogenation reaction is faster than the isomerisation reaction as no unsaturated products appear. Most noteworthy, however, is the change in direction of reactant cleavage. Formation of isobutene is presumably a function of metallic character in the zeolite.

It is evident that the reaction conditions are such that not only is a very fast MCP disappearance reaction obtained but also that the catalyst has a more metallic character. What is perhaps even more surprising is the relative super activity of apparently metallic centres in the catalyst by comparison with reaction in the presence of hydrogen above (particularly in view of what has been said about the relative inactivity of nickel metal zeolites). The hydrogen in the reaction mixture may stabilise the active centres formed on hydrogen reduction at 673 K with the formation of extremely active nickel metal centres.

The factors that make these different types of reaction distinct are (i)/
(i) the effect of hydrogen in generation of Ni\(^+\) species after pretreatment
(ii) the effect of hydrogen in the reaction mixture to form and stabilise a
superactive metallic centre (as well as a Ni\(^+\) centre) after hydrogen reduction
at 673 K
(iii) the effect of reactant and hydrogen in generation of metallic centres
which are less active than (ii).

The evidence suggests that for (ii) the reactant may be ring opened
and hydrogenated simultaneously whereas for (iii) formation of butenes and
subsequent hydrogenation of the products occurs. The experiments using
iso-butene as reactant indicated that an iso-butene \(\rightarrow\) n-butane reaction was
not taking place under the conditions used.

Thus it would appear that nickel metal formation contributes to the
generally observed inactivity of the zeolite. The catalyst (NiX-III) with
the most metallic character in methylcyclopropane isomerisation was the least
active catalyst to be examined.

The effect of water on methylcyclopropane isomerisation was to generate
a marginally faster rate of reaction while leaving the product distribution
unchanged (Table 5.20). Such effects have been noted elsewhere (110, 115) and
have been ascribed to the interaction of water with zeolite cation to yield
species which act as protonic acid centres. This suggests that a protonic
mechanism for methylcyclopropane isomerisation on the ionic centres may be
important.

For all the nickel catalysts studied particularly at higher levels of exchange
but-1-ene isomerisation was faster than methylcyclopropane isomerisation
(Table 5.19). When but-1-ene isomerisation was carried out on NiX-II and NiX-V
at temperatures within the range required to give good rate plots for
methylcyclopropane/
methylcyclopropane isomerisation, the rate of but-1-ene reaction was so fast that equilibrium was approached within fifteen minutes. A qualitative appraisal of these reactions in terms of product data is presented in Table 5.20. It is evident by comparison with the remainder of the values in the table that even at low levels of methylcyclopropane conversion (the values were taken at 10\% conversion) that the normal butene products are in amounts corresponding to those expected at equilibrium.

Comparison of the average product values for the nickel zeolites (Figure 5.18) and extrapolation to the values at zero exchange (NaX) suggests that but-1-ene may be a major product (as in the CuX work) and that the observed data are a consequence of a relatively faster secondary isomerisation process.

Reaction of 1,1 dimethylcyclopropane over NiX-I and NiX-V gave 2 methyl but-2-ene and 2 methyl but-1-ene in amounts close to values expected at equilibrium at the particular reaction temperature used.

The main product formed as a result of 1,2 dimethylcyclopropane reaction over NiX-I was 3 methyl but-1-ene whereas NiX-I formed 2 methyl but-2-ene as major product. It seems likely that in this instance isomerisation of 3 methyl but-1-ene is a relatively fast reaction on NiX-V. However it is interesting to note that NiX-I does not apparently form 3 methyl but-1-ene as major product from 1,1 dimethylcyclopropane isomerisation since this product was stable under similar reaction conditions (367 K) from 1,2 dimethylcyclopropane reaction. Thus for 1,1 dimethylcyclopropane the observed products are probably not a function of 3 methyl but-1-ene secondary isomerisation.

Reaction of 1,2 dimethylcyclopropane over NiX-V gave more C1 - C2 cleavage than did NiX-I. The data for the pentenes formed over each catalyst (Table 5.25) clearly indicates that a pent-1-ene isomerisation reaction to cis and trans pent-2-enes/
pent-2-enes was occurring and on NiX-V the n-pentene products were close to values expected at equilibrium.

The effect of hydrogen on the reactions of both dimethylcyclopropane reactants is considered in terms of the active centre in the zeolite and the possible catalysis mechanisms involved for nickel zeolites. A slower rate of 1,1 dimethylcyclopropane disappearance over NiX-V was observed when the reaction was carried out in the presence of hydrogen and the relative amount of 2 methyl but-1-ene formed during reaction was greater. The rate of hydrogenation was as fast as the reactant disappearance. Such facts contrast to the methylcyclopropane data; possibly increased metallic character in the catalyst would account for the observed behaviour. Reaction of 1,2 dimethylcyclopropane in the presence of hydrogen on NiX-V resulted in an increase in the rate of reactant disappearance and absence of saturated products. The induction period normally associated with the reaction was also removed. It seems that there is less contribution from metallic centres in this case. Indeed a temperature of 100 K above that in which rate enhancement was observed was necessary to form saturated products. In this qualitative study although a relatively slow hydrogenation rate compared to isomerisation rate was observed it was apparent that the extent of C1 - C2 cleavage had increased. Reaction of 1,1 2,2 tetra methylcyclopropane over supported nickel metal catalysts has been reported to (131) result in 50% C1 - C2 cleavage. Thus the contribution of metallic nickel is important in considering the results of alkylcyclopropane isomerisation reactions over nickel zeolites.

Apart from the influence of metallic centres in the nickel zeolites there is a general similarity between the nickel and copper zeolites in terms of products/
products and hence possible mechanisms involved. The remarks, which applied to the type of mechanism involved over CuX zeolites, are also applicable in this section.

The activity of the nickel catalysts for alkylcyclopropane reactions suggests that a carbonium ion intermediate is involved. The observed order of activity for NiX-I and NiX-V was 1,2 dimethylcyclopropane ≈ 1,1 dimethylcyclopropane > methylcyclopropane. Although secondary isomerisations occur with reactant isomerisation the products formed were similar to those of 5.2. The main type of mechanisms to be considered are the $\text{H}^+$ loss or $\text{H}^+$ gain mechanisms. The rate enhancement observed after the addition of water to NiX-V favours the latter type of mechanism. Only a limited study (with 1,2 dimethylcyclopropane and hydrogen) was made of the possibility of cyclic intermediates being involved. However the available evidence suggests that ring opening occurs irreversibly.

Presence of Ni$^+$ and Ni$^0$ species or indeed formation of these entities in the zeolite can only result if sufficient positively charged species are present in the zeolite to preserve electrical neutrality. The carbonium ions postulated for alkylcyclopropane isomerisation are suggested as satisfying this criterion in respect of Ni$^+$ and apparently to a lesser extent Ni$^0$. Residual water molecules and possibly hydrogen could also split heterolytically in the electrostatic field surrounding the nickel ions to form species which satisfy the charge requirements of the lattice. Hydrogen increased the metallic nature of the catalysis observed and apparently is most suited to stabilising Ni$^0$ in the zeolite especially for the reaction in which iso-butane was observed. Thus the observed catalytic behaviour relating to metallic centres may/
may be rationalised in terms of radical mechanism involving addition from such a centre. The product based on hydrogen loss from reactant alone would be unlikely to form since relatively unstable radical intermediates involving re-arrangement would be involved (Table 3.4).

The metallic behaviour observed for nickel zeolites in alkylcyclopropane isomerisation reactions is explained in terms of a radical type mechanism involving addition from a Ni\(^0\) centre. The rate enhancement observed for methylcyclopropane isomerisation in the presence of water is accountable in terms of a Brønsted mechanism involving proton addition to the reactant. A carbonium ion mechanism of this type is suggested as being responsible for the isomerisation activity of the nickel zeolites.

6.4 CeX-II

No comparative assessment of site occupancies is possible on the basis of study on one catalyst. However in the allied work on n-butene isomerisation over CeX catalysts it was proposed that inaccessible sites are filled primarily in the dehydrated catalyst (127). X-ray data on Ce-faujasite supports this view (68). After dehydration at 623 K the cerium ions in such a zeolite were found in the \(\beta\) cage at site I' position where co-ordination with three oxygen atoms of the six membered oxygen ring occurred and co-ordination with water molecules occurred. In the hydrated catalyst cerium ions preferred surface sites (Table 2.1). However the effect of bonding of trivalent ions to residual water molecules in the zeolite and subsequent reduction of the cation electrostatic field may be important (78).

The catalyst used in this study has 26 Ce\(^{++}\) ions per unit cell and conceivably full S.I' site occupation can occur. Such a site population scheme/
scheme is proposed for a lanthanum X catalyst calcined at 623 K with $S_1$ position filled by water molecules yielding a stable structure (64). However, Cross (127) has proposed some degree of surface site occupancy for a cerium X catalyst with 77% sodium replacement. Comparison of the data for but-1-ene isomerisation over this catalyst with methylcyclopropane isomerisation over CeX-II indicates that at a high level of exchange the cerium catalyst is more reactive for methylcyclopropane isomerisation than but-1-ene isomerisation. The product distributions observed (Table 5.30) already reflect this; but-1-ene was the major product.

The reduced activity observed in consecutive reactions may be due to partial poisoning due to adsorbed species since more rigorous outgassing restored catalyst activity. The total gas phase loss observed at long contact times may arise as a result of adsorption or formation of occluded polymeric material (111).

The catalytically active centres in rare earth exchanged X zeolites are considered to be acidic hydroxyl groups formed by hydrolysis of water molecules associated with the cerium cation. The following scheme has been proposed (154).

$$\text{Ce}^{3+} \cdot \text{O}^\text{H} \quad \text{O}^\text{Zeo} \quad \text{Ce}^{2+} \cdot \text{O}^\text{H} \quad \text{Ce}^{2+} \cdot \text{O}^\text{H}$$

Depending/
Depending on the calcination temperature both Brönsted and Lewis acid centres arise, the latter being formed by dehydroxylation \(^{(171)}\). It is likely that Brönsted type centres are involved in this study.

This is evidently true since in the presence of water significant increase in reaction rate was observed. None of the other catalysts studied gave such appreciable rate enhancement in this respect.

Thus protons appear to be associated with the isomerisation activity of CeX-II. The poisoning effect (Figure 5.23.b), observed when larger amounts of water are admitted, may arise due to shielding of the electrostatic fields surrounding the cerium ions so inhibiting formation of protonic acid centres. It is interesting that for this reaction a greater cis/trans but-2-ene ratio is observed and this may be regarded as an increase in the carbonium ion character of the reaction. When heavy water was used exchange occurred in the products only, indicating a non reversible ring opening step.

In contrast reaction in the presence of deuterium and after deuterium pretreatment resulted in no exchange. However it is surprising that rate enhancement was observed for reactions (Table 5.28) after hydrogen pretreatment.

Similar rate enhancement in the presence of hydrogen was observed for the 1,1 dimethylcyclopropane reaction. The presence of saturated products together with the side products detected indicates some degree of hydrogenation activity for CeX-II. It is difficult to envisage a rate enhancement as a result of polarisation of hydrogen via cation electrostatic field without exchange being observed in the reaction products of methylcyclopropane reaction discussed above.

Both 1,1 dimethylcyclopropane and 1,2 dimethylcyclopropane reacted at similar temperatures over CeX-II. Secondary isomerisations were not dominant for/
for these types of reactant as is evident from Table 5.33 and 5.35. For 1,2 dimethylcyclopropane the C1 - C2 ring scission reaction has a higher apparent activation energy than C2 - C3 cleavage although 3 methyl but-1-ene is the major product. A proton gain mechanism fits the observed data and this can clearly be related to the Brønsted acidity of the catalyst.

5.5 Other Catalysts

Apart from the HX work, it is proposed only to give a comparative account of the data obtained for the other catalysts studied. It is evident that experiments on these catalysts did not yield results markedly different from the nickel or copper catalysts already discussed. This is surprising since other workers have ascribed the activity of NaX and zeolites containing monovalent ions to radical type processes (125, 126).

However, higher temperatures were in general required for reactions to proceed over NaX and the degree of ionic activity of this catalyst is less than CuX zeolites or CeX-II. It seems that for but-1-ene (127) and methylcyclopropane isomerisation reactions NaX exhibits ionic activity with the latter reactant being more active. These facts are reflected in the products observed from these reactions. Under similar conditions of dehydration as used in this work NaX is reported to exhibit OH bands in the infra-red (69, 90). Other data (171) suggest that such groups are present as a result of siliceous impurities or partial hydrolysis in the zeolite. Such effects may result in hydroxyl groups which account for the observed ionic activity for NaX in this work.

Brønsted sites are also thought to be responsible for but-1-ene isomerisation over ZnX zeolites (127) with no supporting evidence for a reduction of Zn\textsuperscript{++} ions.
ions being involved. For the iron zeolites studied such a reduction process may be important (76).

The cobalt results for 1,1 dimethylcyclopropane and 1,2 dimethylcyclopropane reactions are similar to those described for CuX. The activity of CoX zeolites for hydrogen – deuterium exchange has been related to removal of water with hydrogen pretreatment enhancing activity as a result (153).

Several workers have related the effect of calcination temperature of ammonium zeolites to formation of infra-red hydroxyl frequencies (55,56,68,101). Outgassing conditions of 423 and 573K would result in loss of ammonia and water and in formation of NaHX zeolite (decationisation) whereas outgassing at 823 K would result in the formation of tri co-ordinated aluminium sites (dehydroxylation) through further loss of water. These processes are represented schematically below;

**Decationisation**

$$\begin{align*}
2 \text{Al}_2\text{Si}_2 \text{O}_{10}^{\text{NH}_4} & \rightleftharpoons 2\text{NH}_3 + 2 \text{Al}_2\text{Si}_2\text{O}_{10} \\
\end{align*}$$

**Dehydroxylation**

$$\begin{align*}
\text{Al}_2\text{Si}_2\text{O}_{10}^{\text{OH}} & + \text{Al}_2\text{Si}_2\text{O}_{10}^{+} + \text{H}_2\text{O} \\
\end{align*}$$

Beaumont/
Beaumont and co-workers (172) reported that structural collapse occurred if sodium X was exchanged for ammonia to a degree greater than 50%. A different reported exchange procedure was utilised in this work and X-ray and surface area work indicated no structural collapse before or after calcination except for the sample outgassed at 823 K. This showed 50% loss of crystallinity and may be due to the dehydroxylation process featured above. Inspection of the activity plot (Figure 5.30) for NK₄X-III for 1,2 dimethylcyclopropane reaction outgassed at various temperatures indicates the relative inactivity of the dehydroxylated form. This may be related to an incomplete dehydroxylation process or to reduced activity of the dehydroxylated catalyst which operates through Lewis acid centres.

However the fact that no overall change in reaction products was observed may rule against the latter possibility. The relative inactivity of the sample outgassed at 423 K is suggested as being due to incomplete decationisation process. However by comparison this catalyst is still many more times more active than NaX.

The location of hydroxyl groups in hydrogen faujasite zeolites has been elucidated by infra-red studies (55,56) and by X-ray determinations (173). However the effect of interacting piperidene indicated proton delocalisation in hydrogen zeolites. A proton addition mechanism would be considered likely for such catalysts. This scheme fits the observed results both for 1,1 dimethylcyclopropane and 1,2 dimethylcyclopropane reactions. Other workers (174) have observed a further peak of activity due to Lewis sites for HY catalysts outgassed at 933 K. Some contribution of Lewis sites to the observed activity for 1,2 dimethylcyclopropane reaction as a result of carbonium ion formation through H⁻ ion abstraction may occur.
The n-pentene formation which was observed, for NH₄X-III outgassed at 573 K, after 100% conversion may be due to slow reaction of occluded reactant (not desorbed on freezing out reaction mixture) or a methyl butene → n-pentene reaction.

6.6 Conclusion

The activity observed for alkylcyclopropane isomerisation over ion exchanged X zeolites was found to depend on the cation present; trivalent cation exchanged X zeolite was more active than the divalent exchange sieve whereas the monovalent form was the least active. This is probably a function of the extent of ionic character associated with the zeolite cations in such isomerisation reactions; the order of activity being CeX > CuX > NiX > NaX.

Zeolite activity is suggested as arising either as a result of hydroxyl group proton addition, as a result of heterolytic fission of water molecules in the electrostatic fields around the cations, or by a cationic reduction process.

As a result of the latter charge transfer reaction a hydrocarbon intermediate may be formed in the proximity of the reduced cation. Similar charge transfer reactions have been reported for the adsorption of acetylene on CoX, NaX and NiX catalysts (175) and for anthracene adsorbed on CuY (176). The induction periods observed at high levels of cation exchange for CuX and NiX catalysts are regarded as being linked to the cation reduction process associated with the catalysis. Cobalt, zinc and iron catalysts appear to function in the same manner as the nickel and copper zeolites in as much as the cation is directly involved in the reaction.

Brønsted protons are thought to account for the isomerisation activity of the cerium and hydrogen (and sodium) zeolites studied. The relatively high protonic activity observed for CeX-II and NH₄X-III outgassed at 673 K is attributable/
attributable to the high charge density on the cerium ion and the decationisation process which formed the hydrogen zeolite.

The rate enhancement observed for reaction in the presence of water over CeX-II can then be clearly understood. The small activity increase exhibited after addition of water to NiX-V probably arises through generation of Brönsted protons in the same manner. For CuX zeolites formation of copper aquo complexes results in rate inhibition.

Zeolite activation also resulted after hydrogen pretreatment. While this behaviour can be rationalised in terms of cation reduction and migration for nickel, cobalt and copper catalysts the reason for the activity increase observed on hydrogen pretreatment of CeX-II and NaX is less certain. Although ion migration may account for this behaviour it is suggested that some degree of hydrogenation and Brönsted activity is associated with each catalyst. An extreme example is the high amount of hydrogenation activity found for nickel zeolites for which some extent of metallic character is proposed.

Isomerisation of the alkylcyclopropane reactants over the zeolites studied is suggested as proceeding via an irreversible ring opening reaction with the formation of a carbonium ion. Although secondary isomerisation reactions made interpretation of the data difficult it was possible to make certain conclusions regarding the operative mechanisms. The direction of ring cleavage was also apparently a function of mechanism; the high amount of C2 - C3 cleavage noted on hydrogenation of methylcyclopropane after hydrogen pretreatment of NiX-V implied a metallic behaviour for the reaction. Over copper, cobalt, iron, zinc and nickel (to a lesser extent a radical addition mechanism is proposed for nickel catalysts) catalysts, hydride loss from reactant is proposed whereas a proton addition mechanism is more likely for cerium, hydrogen (and sodium) zeolites.
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APPENDIX I

MECHANISTIC SCHEMES FOR ALKYL CYCLOPROPANE ISOMERISATION

(A) \( H^- \) Loss

(i) MCP

[@ C1] 

[@ C2] 

[@ methyl carbon] 

(a) or (b) 

n-butenes 

but-I-ene
(A) $H^-$ Loss (Continued)

(ii) 1,1 DMCP

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \\
\text{H}_2 & \quad \text{CH} \\
\end{align*}
\]
\[\xleftarrow{-H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \\
\text{H}_2 & \quad \text{CH} \\
\end{align*}
\]
\[\xrightarrow{+H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \\
\text{H}_2 & \quad \text{CH} \\
\end{align*}
\]

(c2)

\[\xleftarrow{-H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \\
\text{H}_2 & \quad \text{CH} \\
\end{align*}
\]
\[\xrightarrow{+H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \\
\text{H}_2 & \quad \text{CH} \\
\end{align*}
\]

(a) or (b)

(© methyl carbon)

(iii) 1,2 DMCP

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
\[\xleftarrow{-H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
\[\xrightarrow{+H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

(©1)

\[\xleftarrow{-H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{CH}_2 \\
\end{align*}
\]
\[\xrightarrow{+H^-} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

cis and trans pent-2-enes

(a) or (b)
(A) $H^-$ Loss (Continued)

(iii) 1,2 DMCP (Continued)

($\Theta \Theta 3$)

\[
\text{H-C} - C-H \overset{\text{H}^-(\text{CH}_3)}{\rightleftharpoons} \text{CH}_3 - \text{CH} = \text{CH} - \text{CH} - \text{CH}_3 \overset{\text{H}^+}{\rightleftharpoons} \text{cis and trans pent-2-ones}
\]

($\Theta$ methyl carbon)

\[
\text{H-C} - C-H \overset{\text{H}^-(\text{CH}_2)}{\rightleftharpoons} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 \overset{\text{H}^+}{\rightleftharpoons} \text{pent-1-ene}
\]

\[
\text{H-C} - C-H \overset{\text{H}^-(\text{CH}_2)}{\rightleftharpoons} \text{CH}_2 - \text{CH} - \text{CH} = \text{CH}_2 \overset{\text{H}^+}{\rightleftharpoons} \text{3 methyl but-1-ene}
\]
(B) H⁺ Loss

(1) MCP

\[ \begin{align*}
\text{CH}_3 & \quad \text{(ac1)} \\
\text{H} & \quad \text{C} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*} \]

\[ \begin{align*}
\text{(ac1)} & \quad \text{CH}_2 - \text{C} - \text{CH}_3 \\
& \quad \text{+H⁺} \\
& \quad \text{iso-butene}
\end{align*} \]

(2) MCP

\[ \begin{align*}
\text{CH}_3 & \quad \text{(ac2)} \\
\text{CH} & \quad \text{C} \\
\text{CH}_2 & \quad \text{H} \\
\text{CH} & \quad \text{CH}_2
\end{align*} \]

\[ \begin{align*}
\text{(ac2)} & \quad \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_3 \\
& \quad \text{+H⁺} \\
& \quad \text{n-butene}
\end{align*} \]

(3) methyl carbon

\[ \begin{align*}
\text{H} & \quad \text{C} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*} \]

\[ \begin{align*}
\text{(methyl carbon)} & \quad \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 \\
& \quad \text{+H⁺} \\
& \quad \text{but-1-ene}
\end{align*} \]
(B) \( H^+ \) Loss (Continued)

(ii) 1,1 DMCP

\[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{CH} \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \text{3 methyl but-1-ene}
\]

\[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{CH} \\
\text{CH}_3
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \begin{array}{c}
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \text{2 methyl but-2-ene}
\]

(\( \text{o methyl carbon} \))

(iii) 1,2 DMCP

\[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \begin{array}{c}
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \text{2 methyl but-1-ene}
\]

\[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \begin{array}{c}
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \text{2 methyl but-2-ene}
\]

(\( \text{o methyl carbon} \))

\[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \begin{array}{c}
\text{CH}_2 \\
\text{H}
\end{array} \quad \xrightleftharpoons{\text{H}^+} \quad \text{cis and trans pent-2-enes}
\]
(B) H⁺ Loss (Continued)

(iii) 1,2 DMCP (Continued)

(C) methyl carbon

2 methyl but-1-ene
2 methyl but-2-ene
pent-1-ene
3 methyl but-1-ene
(C) $H^-$ Gain

(i) MCP

\[
\begin{align*}
&\text{CH}_3 &+ H^- \\
&\text{CH} &\text{CH}_2 \\
&\text{H} &\text{CH}_2 \\
\rightarrow &\text{CH}_2\text{CH}_2\text{CH}_3 \\
\rightarrow &\text{but-1-ene}
\end{align*}
\]

(ii) MCP

\[
\begin{align*}
&\text{CH}_3 &+ H^- \\
&\text{CH} &\text{CH}_2 \\
&\text{H} &\text{CH}_2 \\
\rightarrow &\text{CH}_3\text{CH}_2\text{CH}_3 \\
\rightarrow &\text{n-butene}
\end{align*}
\]

(iii) MCP

\[
\begin{align*}
&\text{CH}_3 &+ H^- \\
&\text{CH} &\text{CH}_2 \\
&\text{H} &\text{CH}_2 \\
\rightarrow &\text{CH}_3\text{CH}_2\text{CH}_3 \\
\rightarrow &\text{iso-butene}
\end{align*}
\]
(ii) 1,1 DMCP

\[ \text{CH}_3 \text{CH} = \text{CH} - \text{CH}_2 \text{CH}_3 \xrightarrow{+ \text{H}^-} \text{CH}_3 \text{CH} - \text{CH}_2 \text{CH}_3 \xrightarrow{- \text{H}^-} \text{3 methyl but-1-ene} \]

(iii) 1,2 DMCP

\[ \text{CH}_3 \text{CH} = \text{CH} - \text{CH}_2 \text{CH}_3 \xrightarrow{+ \text{H}^-} \text{CH}_3 \text{CH} - \text{CH}_2 \text{CH}_3 \xrightarrow{- \text{H}^-} \text{2 methyl but-2-ene} \]

\[ \text{H}^- \text{C} = \text{CH} \xrightarrow{+ \text{H}^-} \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \xrightarrow{- \text{H}^-} \text{n-pentenes} \]
(C) H⁻ Gain (continued)

1,2 DMCP (continued)

(©C1)

H⁻ \[\text{CH₂} \quad +H⁻ \rightarrow \text{CH₃}\text{CH₂CH}_2\text{CH₂} \quad -H⁻ \rightarrow 2 \text{methyl but-1-ene}\]

(©C3)

H⁻ \[\text{CH₂} \quad +H⁻ \rightarrow \text{CH₃}\text{CHCHCHCHCH}_3 \quad -H⁻ \rightarrow 2 \text{methyl but-2-ene} \quad 3 \text{methyl but-1-ene}\]
(D) $\text{H}^+$ Gain

(1) MCP

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[\text{H}^+ \rightleftharpoons \text{CH}_3 \quad \text{CH}_2 \quad \text{H}^+ \quad \text{CH}_2 \quad \text{H}^+ \rightleftharpoons \text{but-1-ene}
\]

(C1)

(C2)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[\text{H}^+ \rightleftharpoons \text{CH}_3 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{H}^+ \rightleftharpoons \text{n-butanes}
\]

(C2)

(C2)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[\text{H}^+ \rightleftharpoons \text{CH}_3 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{H}^+ \rightleftharpoons \text{iso-butene}
\]
(ii) 1,1 DMCP

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[+ \text{H}^+ \Leftrightarrow \begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{H}^+ & \quad \text{H}^+
\end{align*}\]

\(\Rightarrow 3\text{ methyl but-1-ene}\)

(iii) 1,2 DMCP

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[+ \text{H}^+ \Leftrightarrow \begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{H}^+ & \quad \text{H}^+
\end{align*}\]

\(\Rightarrow 2\text{ methyl but-1-ene}\)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[+ \text{H}^+ \Leftrightarrow \begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{H}^+ & \quad \text{H}^+
\end{align*}\]

\(\Rightarrow \text{n-pentenes}\)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[+ \text{H}^+ \Leftrightarrow \begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{H}^+ & \quad \text{H}^+
\end{align*}\]

\(\Rightarrow 2\text{ methyl but-1-ene}\)
(0) $H^+$ Gain (continued)

(iii) 1,2 DMCIP (continued)

(c3)

$$\begin{align*}
\text{H} & \quad \text{H} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}$$

$$\begin{align*}
\text{H}^{+} & \quad +\text{H}^{+} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}$$

$$\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}$$

2 methyl but-2-ene

3 methyl but-1-ene
(E) H⁺ Loss

(i) MCP

\[
\begin{align*}
\text{CH}_3 & \text{CH} & \text{H} \\
\text{CH} & \text{CH}_2 & \text{CH}_2
\end{align*}
\]

\[\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 \rightarrow n\text{-butenes}\]

(ii) 1,1 DMCPP

\[
\begin{align*}
\text{CH}_3 & \text{CH} & \text{H} \\
\text{CH} & \text{CH}_2 & \text{CH}_2
\end{align*}
\]

\[\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_3 \rightarrow \text{iso}-\text{butene}\]
(E) **H⁺ Loss** (continued)

(iii) **1,2 DMCP**

\[ \begin{align*}
\text{(C1)} \\
&\text{CH}_2 \quad \text{-H⁺} \quad \text{+H⁺} \\
&\text{CH}_3 \quad \text{CH}-\text{CH}_2 \quad \text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{n-pentenes} \\
\text{CH}_2 \quad \text{-H⁺} \quad \text{+H⁺} \\
&\text{CH}_3 \quad \text{CH}-\text{CH}_2 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{methyl butenes} \\
\end{align*} \]
(F) \( H^* \) Gain

(i) MCP

\[
\begin{align*}
H^* & \quad \text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}
\]

\( \rightarrow \)

\( \text{but-1-ene} \)

(ii) 1,1 DMCP

\[
\begin{align*}
H^* & \quad \text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 & \quad \text{CH} & \quad \text{CH}_3 \\
\end{align*}
\]

\( \rightarrow \)

\( \text{iso-butene} \)

\( \rightarrow \)

\( \text{3 methyl but-1-ene} \)
(ii) 1,1 DMCP

\[
\begin{align*}
+H^+ & \quad \text{H}^+ & \\
\text{CH}_3 & \quad \text{CH}_3 & \\
\text{CH}_2 & \quad \text{CH}_2 & \\
\text{C} & \quad \text{CH}_3 & \\
\text{H}^+ & \quad \text{H}^+ & \\
\text{CH}_3 & \quad \text{CH}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 & \\
2 \text{methyl but-1-ene} & \\
2 \text{methyl but-2-ene} & \\
\end{align*}
\]

(iii) 1,2 DMCP

\[
\begin{align*}
+H^+ & \quad -H^+ & \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 & \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 & \\
\text{C} & \quad \text{CH}_3 & \\
\text{H}^+ & \quad \text{H}^+ & \\
\text{CH}_3 & \quad \text{CH}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 & \\
n\text{pentene} & \\
\text{2 methyl but-2-ene} & \\
3 \text{methyl but-1-ene} & \\
\end{align*}
\]
The following programs were written in Fortran IV language for a Watfor compiler in use on an IBM (series 360/50) computer.

**1.** Methylcyclopropane as reactant

(a) n-butane products

```fortran
COMPILE CHED09/0000,TIME=60,PAGES=20

PRODUCTS/COMPOSITION/CONVERSION    RESULTS

REAL MCP,T2,C2,B1,TOTAL,SUM,BUT1,TRANS2,CIS2,CONV,TIME,CTRAT,BTRAT,
BCRAT
INTEGER N,J,I,L

1000 FORMAT(I1)
1001 FORMAT(I2)
1002 FORMAT(1X,'TIME',4X,'TOTAL',5X,'SUM',5X,'T2',6X,'C2',6X,'B1',5X,
'BUT1',4X,'TRANS2',3X,'CIS2',4X,'CONV',4X,'MCP',5X,'CTRAT',3X,'BTRAT',
3X,'BCRAT')
1003 FORMAT(5(F10.3))
1004 FORMAT('0',14(F8.2))
1005 FORMAT('1',I1)

DO 8888 I=1,L
WRITE(6,1005) I
WRITE(6,1002)
READ (5,1003) MCP,T2,C2,B1,TIME
T2=T2*1.11
C2=C2*1.09
B1=B1*1.06
CTRAT=(C2/T2)
BTRAT=(B1/T2)
BCRAT=(B1/C2)
TOTAL=T2+C2+B1+MCP
SUM=T2+C2+B1
BUT1=(B1/SUM)*100
TRANS2=(T2/SUM)*100
CIS2=(C2/SUM)*100
MCP=(MCP/TOTAL)*100
T2=(T2/TOTAL)*100
C2=(C2/TOTAL)*100
B1=(B1/TOTAL)*100
CONV=T2+C2+B1

9999 WRITE(6,1004) TIME,TOTAL,SUM,T2,C2,B1,BUT1,TRANS2,CIS2,CONV,MCP,
CTRAT,BTRAT,BCRAT
8888 CONTINUE
CONTINUE
STOP
END
```
(b) n-butene and n-butane products

```fortran
LCOfPILC 	 CHEDO8/162,TIRE=60,PAGES=20
C PRODUCTS/COMPOSITION/CONVERSION RESULTS
C REAL MCP,T2,C2,B1,TOTAL,SUM,BUT1,TRANS2,CIS2,CONV,TIME,CTRAT,BTRAT,
1000 BCRAT,NBTAN,NBU
1001 INTEGER N,J,I,L
1002 FORAT(I1)
1003 FOR1'AT(' 1 ,2X,'TIFIE',4X,'NBTAN',5X,'NBU',5X,'T2',6X,'C2',6X,'B1',
1004 5X,'BUT1',4X,'TRANS2',3X,'CIS2',4X,'CONV',4X,'MCP',5X,'CTRAT',3X,
1005 'BTRAT',3X,'BCRAT',2X,'TOTAL')
1006 FORMAT(6(F10.3))
1007 FORMAT('0',15(F8.2))
1008 FORMAT('1',I1)
1009 READ (5,1000) L
1010 DO 8888 I=1,L
1011 WRITE (6,1005) I
1012 WRITE (6,1002)
1013 READ (5,1001) J
1014 DO 9999 N=1,3
1015 READ (5,1003) IICP,T2,C2,81,NBU,11RE
1016 T2=T2*1.11
1017 C2=C2*1.09
1018 B1=B1*1.06
1019 NBU=NBU*1.02
1020 CTRAT=(C2/T2)
1021 BTRAT=(B1/B2)
1022 BCRAT=(B1/C2)
1023 TOTAL=T2+C2+B1+MCP+NBU
1024 SUM=T2+C2+B1+NBU
1025 BUT1=(B1/SUM)*100
1026 TRANS2=(T2/SUM)*100
1027 CIS2=(C2/SUM)*100
1028 NBTAN=NBU/SUM)*100
1029 MCP=(MCP/TOTAL)*100
1030 T2=(T2/TOTAL)*100
1031 C2=(C2/TOTAL)*100
1032 B1=(B1/TOTAL)*100
1033 NBU=(NBU/TOTAL)*100
1034 CONV=T2+C2+B1+NBU
9999 WRITE(6,1004) TIME,NBTAN,NBU,T2C2,B1,BUT1,TRANS2,CIS2,CONV,MCP,CTRAT,
1000 BTRAT,BCRAT,TOTAL
8888 CONTINUE
CONTINUE
STOP
END
```
(c) Isomeric butenes as products

!COMPILE CHE008/1162,TIME=60,PAGES=20

C \PRODUCTS/COMPOSITION/CONVERSION RESULTS

REAL MCP,T2,C2,B1,TOTAL,SUM,BUT1,TRANS2,CIS2,CONV,TIME,CTRAT,BTRAT,
BCRAT,ISO01,ISO
INTEGER N,J,I,L
1000 FORMAT(I1)
1001 FORMAT(I2)
1002 FORMAT(' ',2X,'TIME',4X,'ISO01',5X,'ISO',5X,'T2',6X,'C2',6X,'B1',
      5X'BUT1',4X,'TRANS2',3X,'CIS2',4X,'CONV',4X,'MCP',5X,'CTRAT',3X,
      'BTRAT',3X,'BCRAT',2X,'TOTAL')
1003 FORMAT(6(F10.3))
1004 FORMAT('0',15(F8.2))
1005 FORMAT('1',I1)
READ (5,1000) L
DO 8888 I=1,L
WRITE (6,1005) I
WRITE (6,1002)
READ (5,1001) J
DO 9999 N=1,J
READ (5,1003) MCP,T2,C2,B1,ISO,TIME
T2=T2*1.11
C2=C2*1.09
B1=B1*1.06
ISO=ISO*0.96
CTRAT=(C2/T2)
BTRAT=(B1/T2)
BCRAT=(B1/C2)
TOTAL=T2+C2+B1+MCP+ISO
SUM=T2+C2+B1+ISO
BUT1=(B1/SUM)*100
TRANS2=(T2/SUM)*100
CIS2=(C2/SUM)*100
ISO01=(ISO/SUM)*100
MCP=(MCP/TOTAL)*100
T2=(T2/TOTAL)*100
C2=(C2/TOTAL)*100
B1=(B1/TOTAL)*100
ISO=(ISO/TOTAL)*100
CONV=T2+C2+B1+ISO
9999 WRITE(6,1004) TIME,ISO01,ISO,T2,C2,B1,BUT1,TRANS2,CIS2,CONV,MCP,
CTRAT,BTRAT,BCRAT,TOTAL
8888 CONTINUE
CONTINUE
STOP
END
(2) 1,1 dimethylcyclopropane as reactant

```
ECOMPILE CHE009/0000,TIME=60,PAGES=20

PRODUCTS/COMPOSITION/CONVERSION RESULTS

REAL DMCP11,M381,M2B1,M2B2,CP2,TP2,P1,TOTAL,SUM,M3BU1,M2BU1,M2BU2,
CPEN2,TPEN2,PENT1,TIE
INTEGER N,J,I,L
1000 FORMAT(I2)
1001 FORMAT(I2)
1002 FORMAT(1 ',2X,'TIME',2X,'TOTAL',3X,'SUM',3X,'M381',3X,'M2B1',3X,
'M2B2',4X,'CP2',4X,'TP2',4X,'P1',4X,'M3BU1',2X,'M2BU1',2X,'M2BU2',
2X,'CPEN2',2X,'TPEN2',2X,'PENT1',2X,'DMCP11')
1003 FORMAT(10.3)
1004 FORMAT('0',16(F7.2))
1005 FORMAT(1 ',I1)
READ (5,1000) L
DO 6688 I=1,L
WRITE(6,1005) I
WRITE (6,1002)
READ (5,1001) J
DO 9999 N=1,J
READ (5,1003) M381,DMCP11,P1,M2B1,TP2,CP2,M2B2,TIE
DMCP11=DMCP11*0.58
M381=M381*0.76
M2B2=M2B2*1.09
CP2=CP2*0.95
TP2=TP2*1.02
P1=P1*1.15
TOTAL=M381+M2B1+M2B2+CP2+TP2+P1+DMCP11
SUM=M381+M2B1+M2B2+CP2+TP2+P1
M3BU1=(M381/SUM)*100
M2BU1=(M2B1/SUM)*100
M2BU2=(M2B2/SUM)*100
CPEN2=(CP2/SUM)*100
TPEN2=(TP2/SUM)*100
DMCP11=(DMCP11/TOTAL)*100
M381=(M381/TOTAL)*100
M2B2=(M2B2/TOTAL)*100
M2B1=(M2B1/TOTAL)*100
CP2=(CP2/TOTAL)*100
TP2=(TP2/TOTAL)*100
P1=(P1/TOTAL)*100
9999 WRITE(6,1004) TIME,TOTAL,SUM,M381,M2B1,M2B2,CP2,TP2,P1,M3BU1,M2BU1,
M2BU2,CPEN2,TPEN2,PENT1,DMCP11
6688 CONTINUE
CONTINUE
STOP
END
```
(3) 1,2 dimethylcyclopropane as reactant

```fortran
INTEGER N,J,I,L
READ (5,1000) L
DO 8880 I=1,L
WRITE (6,1001) I
WRITE (6,1002)
READ (5,1003) M3B1,DMCP12,P1,M2B1,TP2,CP2,M2B2,TIME
M3B1=M3B1*0.74
M2B1=M2B1*1.07
CP2=CP2*1.22
TP2=TP2*1.08
TOTAL=M3B1+M2B1+M2B2+CP2+TP2+P1+DMCP12
SUM=M3B1+M2B1+M2B2+CP2+TP2+P1
M3BU1=(M3B1/SUM)*100
M2B1U1=(M2B1/SUM)*100
M2B2U2=(M2B2/SUM)*100
CPEN2=(CP2/SUM)*100
TPEN2=(TP2/SUM)*100
PENT1=(P1/SUM)*100
DMCP12=(DMCP12/TOTAL)*100
M3B1=(M3B1/TOTAL)*100
M2B1=(M2B1/TOTAL)*100
M2B2=(M2B2/TOTAL)*100
CP2=(CP2/TOTAL)*100
TP2=(TP2/TOTAL)*100
P1=(P1/TOTAL)*100
9999 WRITE (6,1004) TIME,TOTAL,SUM,M3B1,M2B1,M2B2,CP2,TP2,P1,M3BU1,
M2B1U1,M2B2U2,CPEN2,TPEN2,PENT1,DMCP12
8880 CONTINUE
CONTINUE
STOP
END
```