THE ROLE OF THE SUPPORT IN HETEROGENEOUS CATALYSIS.

THESIS

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Douglas A. Buchanan

ABSTRACT.

The catalysed hydrogenation of buta-1,3-diene has been studied using deuterium as a tracer over alumina- and boehmite-supported gold and silica-supported copper catalysts. The physical nature of the gold catalysts were examined by ultra-violet spectrocopy, electron microscopy and X-ray diffraction techniques.

The kinetics and variation of the butene distribution with i) conversion, ii) inital 'hydrogen' pressure and iii) temperature have been investigated over each catalyst and mechanisms are proposed which are consistent with the experimental results. Preferential formation of but-1-ene is observed but the trans-but-2-ene : cis-but-2-ene ratio is 1 : 2 over the supported gold catalysts whereas over the silica-supported copper the ratio is 1 : 1. It is concluded that butadiene adsorbs as a mono-π-bonded complex which rapidly undergoes further adsorption to the di-π-bonded species. The resonance energy of stabilisation associated with the anti di-π-adsorbed complex is thought to be important in determining the trans : cis ratio over the supported gold catalysts.

In the initial stages of reaction separate 1,2- and 1,4-addition processes are thought to be responsible for the formation of but-1-ene and the but-2-ene , respectively, although at high conversion it is suggested that isomerisation, over the supported gold catalysts, occurs by an abstraction-addition mechanism.

The variation of the deuterium distribution with i) conversion, ii) initial deuterium pressure and iii) temperature was determined mass spectrometrically. Over Au/Boehmite the d_0-species is most abundant whereas over Au/γ-alumina the predominant product is the d_1-species. It is postulated that hydrogen migrates

from the support to active sites on the metal and hence the nature of the support is reflected in the deutero-content of the butenes. The source of this hydrogen is believed to be water associated with the lattice of the support.

Over silica-supported copper the surface coverage of adsorbed deuterium is shown to be greater than over the supported gold catalysts. From the results obtained it appears that the support does not play a significant role in the hydrogenation reaction over supported copper catalysts.

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CHAPTER 1

INTRODUCTION.

1.1 General introduction.

Supported metal systems occupy an important place in the field of catalysis and such catalysts find considerable application in a wide variety of industrial processes. They have certain definite advantages over other forms of metal catalysts such as films, wires, or unsupported powders for the use of a support leads to a high dispersion of the metal in the form of very small crystallites. As a result, the metal has a high surface area and shows a resistance to sintering (1). This latter point is particularly important for catalytic applications at high temperatures, where loss of surface by sintering can severely limit the useful life of a metal catalyst (2,3).

1.2 Adsorption and surface heterogeneity.

The reaction in heterogeneous catalysis occurs at the interface of two phases, with reactions at the gas-solid interface most important. The concept of adsorption of gaseous atoms or molecules on a metal surface was developed by Langmuir (4). Two distinct types of adsorption have been recognised and these were first explained in a semi-quantitative manner by Lennard-Jones (5) in terms of potential energy diagrams.

Physical adsorption is caused by weak van der Waals forces between the adsorbent and adsorbate and the process is random, non-activated and usually occurs at temperatures near to the boiling point of the gas. The heat of adsorption is generally similar to the heat of liquefaction, the values usually being in the range 1 - 5 kcal mol $^{-1}$.

Chemical adsorption, or chemisorption, however, involves the formation of chemical bonds between the adsorbate and adsorbent. Such a process involves an energy of activation and leads to reaction in heterogeneous catalysis (6). The bond lengths are of the order 1.5 to 3 Å, comparable to the bond lengths in chemical compounds, and the heat of adsorption is in the range 10 - 150 kcal mol $^{-1}$. Since reaction occurs at a particular surface site there will be a limiting, monolayer coverage, the extent of chemisorption depending on the number of surface sites available. In physical adsorption, however, multilayer adsorption is possible. For chemisorption, both covalent and ionic bonding have been recognised (7).

The concept of surface heterogeneity has been established from studies of the fall of the heat of adsorption with increasing surface coverage (8), and appears to arise due to point imperfections, dislocations and impurities. Adsorption will thus occur preferentially on the sites which are energetically most favourable.

The migration of adsorbed molecules on surfaces, first reviewed by Volmer (9), may be regarded as a partial desorption process. This is an activated process, dependent on the heat of adsorption. Thus mobility will increase with temperature and surface coverage and cause the most active adsorption sites to become saturated. Sites which have a low activation energy for desorption tend to be the most "catalytically active", but it is significant that sites which are active for one reaction may be inactive for another (10).

1.3 Geometric and electronic factors.

Although many attempts have been made to distinguish a geometric from an electronic factor in catalysis, it is important to note that the d-character of a metal is related to interatomic spacing (11). Thus one cannot clearly distinguish the two concepts, when the electronic factor is expressed in terms of d-character.

The correlation of interatomic distances on metal surfaces with catalytic activity was first reviewed by Balandin (12) in his Multiplet Theory, which postulated that the catalytic decomposition of a relatively large molecule could only take place by simultaneous adsorption at several points. With cyclohexane, for example, attachment at six centres was postulated to be necessary before benzene could be formed by the loss of three hydrogen molecules. Calculations for nickel and platinum catalysts, which have a close-packed structure and a surface co-ordination of six for every atom in the surface, indicated that the distances between metal atoms were of the same order of magnitude as those of the C-C distances in benzene.

More recently, single crystals have been used as catalysts and many workers (13, 14) have shown that both physical and chemical adsorption occur preferentially on certain crystal planes. Similar studies by Gwathmey, Rhodin and others (15,16,17) show that for any one catalyst the activity depends on the crystal face exposed at the surface.

This is interpreted in terms of metal - metal bond lengths, which are determined by two factors, (i) the atomic radius, and (ii) the crystal plane. Reactions will occur most readily on interatomic spacings which allow adsorbed intermediates to be relatively strain free. The adsorption of acetylene, for example, on f.c.c. metals is expected to occur only on the 100 and 101 faces, and not on the 111 face, which has shorter interatomic spacings (18.)

An early contribution to the electronic theory was made by Schwab and his co-workers (19) in studies based on the catalytic decomposition of formic acid on Hume-Rothery alloys. It was found that the electron concentration in the d-bond of such alloys was related to the activation energy. For example, on pure gold the activation energy was about 11 kcal mol $^{-1}$ but increased to about 27 kcal mol $^{-1}$ on alloying 20% of cadmium with the gold. Schwab concluded that the catalytic activation consists in an entrance of substrate electrons into empty levels of the first Brillouin zone of the metal.

Similar results have been obtained on Transition metal alloys. Couper and Eley (20) showed that the activation energy of the para-hydrogen conversion on palladium-gold alloys increased abruptly when the holes in the d-band of palladium were filled with electrons from gold. Reports, however, varied as to the degree of electron transfer from substrate to metal. While Dowden (21) supported Schwab's idea that the activated complex in formic acid decomposition should bear a positive charge, Eley (22), without actually postulating a mechanism involving electron transfer, proposed that the holes in the d-band of the alloy were responsible for the catalytic activity.

An alternative to electron theories, which use the concepts of bands of allowed energies, was the correlation noted by Boudart (23). This involved the concept of the d-character of the metallic bond which was introduced in Pauling's Valence Bond Theory (11). Boudart showed a correlation between the d-character of a series of metals and their catalytic activity for the hydrogenation of ethylene.

In spite of the many suggested relationships, attempts to correlate bulk electron and surface properties have not been entirely successful. Whereas Schwab (19) found a decrease in the activation energy with increasing number of empty electronic levels in binary alloys, Sachtler and co-workers showed that there is no question of electron transfer (24) towards the adsorbent metal, but that conversely the adsorbate attracted electrons from the metal and thus became negatively charged.

1.4 Hydrogenation of unsaturated hydrocarbons.

1.4.1 Introduction.

The hydrogenation of unsaturated hydrocarbons has been for many years one of the most intensely investigated catalytic reactions. In spite of the work done in this field, however, there is still a great deal of controversy concerning the actual mechanisms. Much information has come from three sources; kinetics, distribution of reaction products, and the use of isotopic tracers, especially deuterium.

Kinetic studies may yield information on the adsorption coefficients and consequently the relative surface coverages of the reactants. They may also give some indication as to whether the reaction is proceeding by a Rideal-Eley mechanism(25) which envisages a reaction between a chemisorbed species and molecules which are weakly adsorbed, or a Langmuir-Hinshelwood mechanism (26), which postulates that both the reactants are adsorbed and that the rate is controlled by the reaction of adjacently adsorbed molecules.

Where more than one reaction product may be formed, analyses of the reaction products may lead to valuable mechanistic information. This consideration would apply to the interaction of hydrogen and diunsaturated hydrocarbons at metal surfaces. First, a diunsaturated hydrocarbon may be hydrogenated to both a monoolefin and a paraffin; second, for hydrocarbons containing four or more carbon atoms, the olefin may be produced in more than one isomeric form. Thus for example, in the hydrogenation of buta-1,3-diene (27), the reaction products may comprise of a mixture of butene isomers and n-butane and from the relative yields of each, important conclusions regarding the stereochemistry of the reaction may be obtained.

The use of isotopic tracers have provided much valuable information regarding the mechanism of the hydrogenation of unsaturated hydrocarbons. Initial studies with deuterium involved the thermal conductivity technique to measure the extent of dilution of deuterium by hydrogen (28) but it was not until after the application of mass spectrometry to the exchange of saturated hydrocarbons (29) that really significant advances in the understanding of the various reactions were made. If, for example, deuterium is employed in the hydrogenation of acetylene (30), as well as the expected dideuteroethylene, ethylene with zero, one, three and four deuterium atoms are found in the reaction products. Also, analysis of the residual acetylene and deuterium shows deuterated acetylene and hydrogen deuteride respectively. It is clear, then, that direct addition across the unsaturated linkage is complicated by the occurrence of other reactions such as hydrocarbon exchange, i.e. substitution of H-atoms of the unsaturated hydrocarbon by D-atoms, and hydrogen exchange, i.e. the formation of HD and H_2. It is important to realise that reactions over supported metal catalysts may be further complicated due to the presence of the carrier (30).

1.4.2 Nature of the adsorbed species.

The establishment of the mechanism of a heterogeneous reaction is a more difficult task than for a homogeneous reaction. The main cause of the greater complexity of heterogeneous reactions is that the surface is an active partner in the reaction and thus must be regarded in any mechanistic considerations. As a consequence much attention has been focussed on the nature of the chemisorbed molecule.

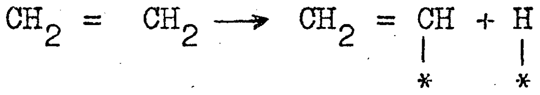
There are two possible avenues to this information. A number of very useful direct physical methods have been employed to establish the nature of the adsorbed hydrocarbon species; the principle ones are infrared spectroscopy (31,32), first developed by Eischens and Pliskin (33,34), and the technique of magnetochemistry (35). Ultraviolet and visible spectroscopy (36) have been applied in a similar manner to infrared spectroscopy. Other methods used include the measurement of changes in nuclear magnetic resonance (37,38), electron spin resonance (39), work fuhction (40), and the conductivity of solids (41). Unfortunately, many of these studies were carried out on "clean" surfaces and therefore most of the information so obtained is of doubtful relevance to the problem of the adsorbed state of the hydrocarbon <u>during its hydrogenation</u>.

There are two reasons for this. First, a clean metal is highly reactive and becomes progressively less so as surface coverage increases: thus on energetic and steric grounds we may expect certain processes to occur on a nearly "clean" surface, while these processes would be unable to proceed on a highly covered surface. Second, in the presence of reactant hydrogen it might be expected that the extent of the dissociative adsorption of hydrocarbon e.g.

$$C_2H_4(g) \longrightarrow C_2H_3(a) + H(a)$$

would occur to a smaller extent than on "clean" surfaces. Infrared spectroscopic studies (31) suggest that this is in fact the case. However, although infrared spectroscopy can provide definite information as to the nature of the adsorbed species, there is no assurance that any species seen by this method is in fact active in catalysis. The most valuable information on the adsorbed state of hydrocarbons relevant to their hydrogenation has been deduced almost entirely by the indirect approach of interpreting observed kinetics and product distributions.

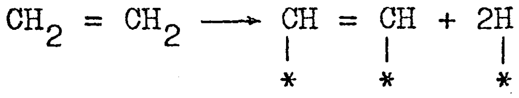
Two types of adsorption have been identified. Farkas, Farkas and Rideal (42,43) in 1934 suggested that ethylene was dissociately adsorbed on nickel and platinum with loss of a hydrogen atom;



$$\mathrm{CH_2 = CH_2 \longrightarrow CH_2 = \underset{*}{\underset{|}{CH}} + \underset{*}{\underset{|}{H}}}$$

Olefin exchange was thereby explained by the incorporation of deuterium in the reverse step, while hydrogenation was assumed to proceed by further addition of a hydrogen atom to the adsorbed molecule.

From studies of ethylene hydrogenation on metal films, Beeck (14,44) postulated a form of dissociative adsorption requiring four adjacent surface sites;



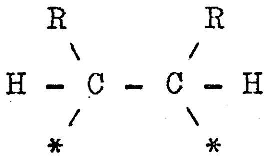
$$\mathrm{CH_2 = CH_2 \longrightarrow \underset{*}{\underset{|}{CH}} = \underset{*}{\underset{|}{CH}} + \underset{*}{\underset{|}{2H}}}$$

Conclusive evidence for the dissociative adsorption of saturated hydrocarbons was given by H.S. Taylor (45) who showed that exchange occurred between deuterium and methane at 140°C on nickel, while more recently T.I. Taylor (46) obtained similar results with platinum at temperatures above 20°C. Douglas and

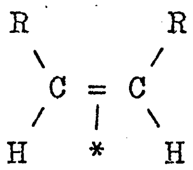
Rabinovitch (47) showed that olefins underwent dissociative adsorption by observing hydrogen exchange between ethylene and deutero-ethylene over supported nickel and nickel wire catalysts.

An alternative mechanism whereby unsaturated hydrocarbons may chemisorb on a metal surface is by associative adsorption. It is generally agreed that this is the important interaction in the hydrogenation of unsaturated hydrocarbons.

Two possible structures for the associatively adsorbed olefin may be postulated, namely (1) σ -diadsorbed olefin and (2) π -adsorbed olefin



structure (A)



structure (B)

In structure (A) it is supposed that the σ-diadsorbed olefin is formed by the rupture of the carbon-carbon π-bond, sp^3 hybridisation of the carbon atoms followed by the formation of two σ -bonds between the carbons and two metal atoms. It was first postulated by Horiuti and Polanyi et al. (48,49) in a proposed mechanism for the hydrogenation and exchange of ethylene.

Since two neighbouring metal atoms are involved, it might be expected that a geometrical factor is involved in the formation of structure (A). Bond (18), however, showed that contrary to expectation, acetylene generally inhibits the reaction of ethylene, implying that the same sites may adsorb both acetylene and ethylene.

Also, the results of certain exchange reactions of cycloalkanes (50) were inexplicable in the conventional terms. This led Rooney et al. (50-52) to the alternative postulate of a π-adsorbed olefin (structure (B)), envisaging the same type of bonding as that found in the olefin complexes of palladium, platinum and silver (53,54). The nature of the bonding is shown in Fig. 1.1. In this structure the atoms and groups attached to the carbon atoms are almost coplanar in a plane parallel to the surface: only one metal atom is directly involved, although others may be obscured by the adsorbed molecule.

Although π-bonded intermediates explained many otherwise unexplicable reaction mechanisms (51), there is little direct evidence in favour of either structure (A) or structure (B). However, some similarities appear to exist between the organometallic chemistry of the transition metals and their behaviour as catalysts. π-olefin complexes are formed by virtually all of the Group VIII metals, the strength of the olefin-metal bond depending on the other ligands present in the complex (53,54). All of these metals adsorb olefins and are active in olefin hydrogenation. As a result of the correlations, recent discussions of olefin hydrogenation have assumed that structure (B) is the relevant species.

There is also the possibility of an adsorbed species involving attachment at more than two consecutive carbon atoms with delocalisation over the carbon atoms involved (structure (C)).

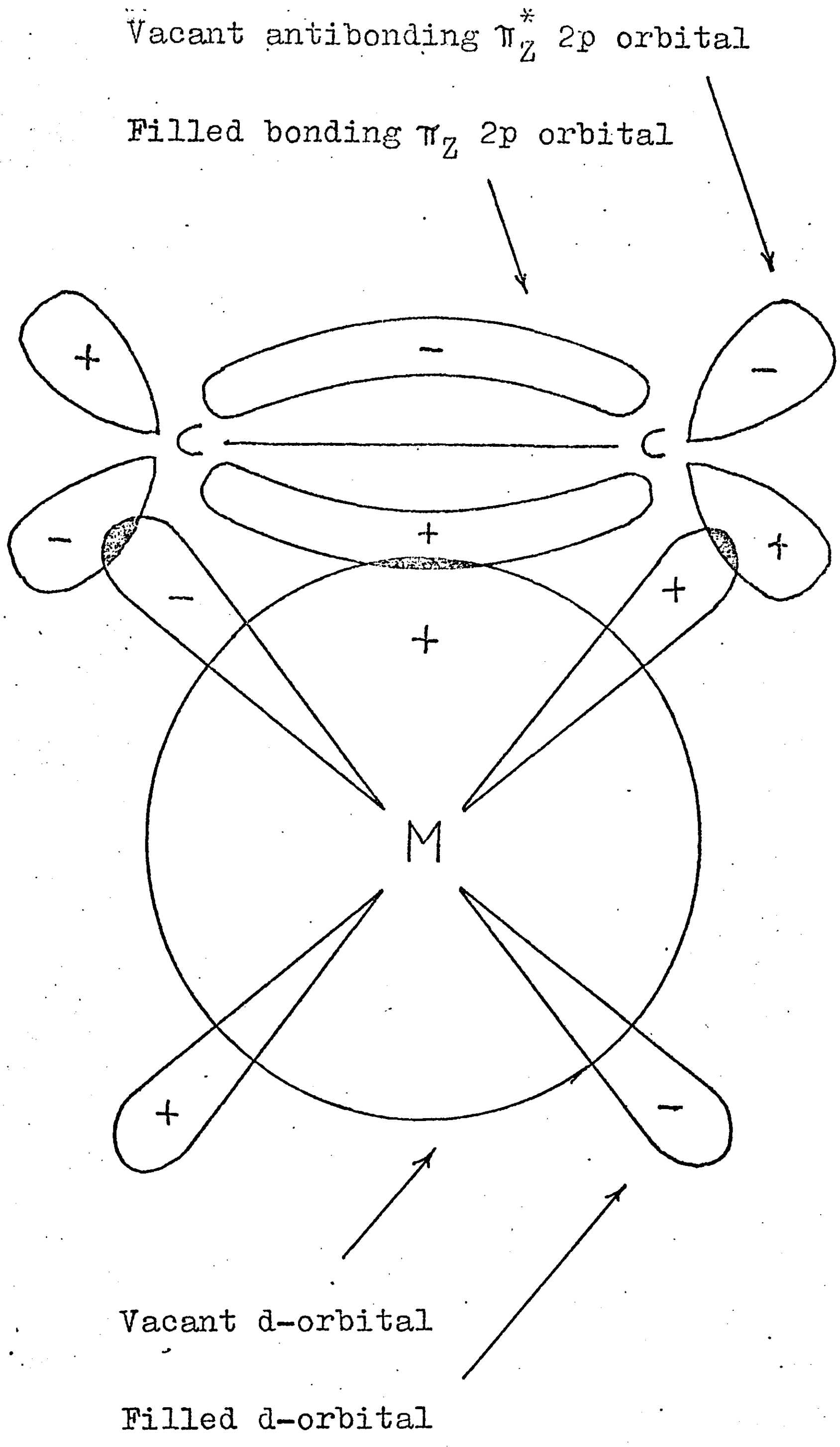
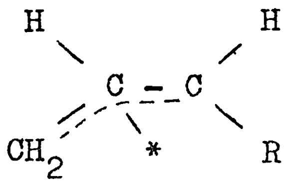
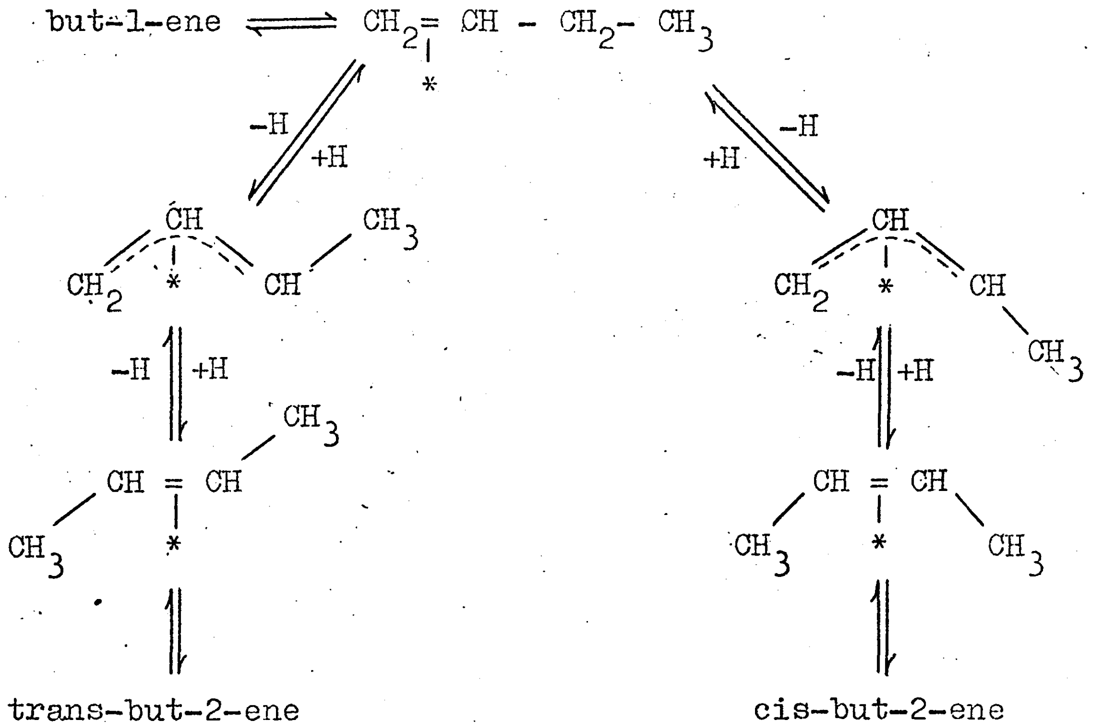


Fig.1.1 Diagramatic representation of the π-bonding of an olefin to a metal atom having a vacant d-orbital.

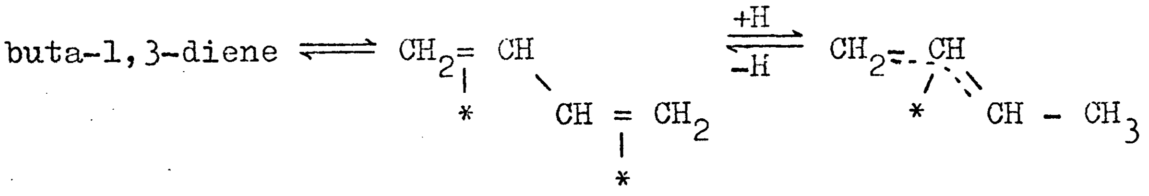


structure (C) (syn-1-methyl- π -allyl)

The type of bonding postulated is therefore closely similar to that found in ferrocene and related organometallic compounds and several π-allylic compounds have been described in the literature (55). Very good evidence for the participation of π-allylic complexes has been presented in the exchange of cycloalkanes with deuterium (50), and now the occurrence of such intermediates is generally accepted in the butene isomerisation reaction (51).



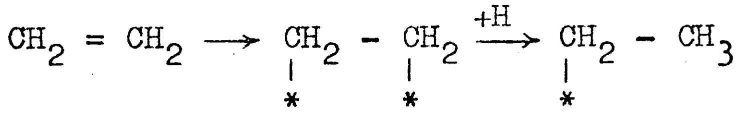
Addition of a hydrogen atom to an adsorbed buta-1,3-diene molecule can also result in a π-allyl intermediate (51).



1.4.3 The hydrogenation of olefins.

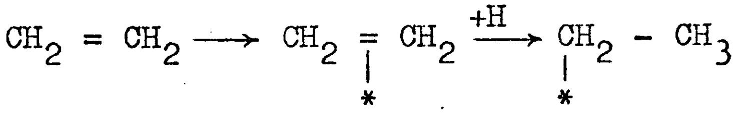
Although the hydrogenation of ethylene has attracted the attention of a great many workers for over thirty years, it is only comparatively recently that significant advances in the understanding of the mechanism have been made. It is now generally agreed that the transformation of an adsorbed olefin into a saturated hydrocarbon occurs principally in two stages, and that a "half-hydrogenated state", i.e., an adsorbed alkyl radical, is a relatively stable intermediate. The most impressive evidence for this point of view is the identity of products obtained when equilibrated and non-equilibrated hydrogen-deuterium mixtures are employed (47,56,57). Addition of a second hydrogen atom completes the process. The possibility of a part of the reaction proceeding through the addition of a molecule of hydrogen cannot be ruled out (58).

What is still less certain is the manner of formation of the alkyl radicals. Horiuti and Polanyi (48,49) assumed that ethylene was adsorbed as structure (A) (section 1.4.2)



$$CH_2 = CH_2 \longrightarrow \underset{*}{\underset{|}{CH_2}} - \underset{*}{\underset{|}{CH_2}} \xrightarrow{+H} \underset{*}{\underset{|}{CH_2}} - CH_3$$

but observations on the homogeneous reduction of co-ordinated olefins (59,60) confirm the possibility of addition of H to structure (B), as



$$CH_2 = CH_2 \longrightarrow CH_2 \underset{*}{\underset{|}{=}} CH_2 \xrightarrow{+H} \underset{*}{\underset{|}{CH_2}} - CH_3$$

Further addition in both cases produces ethane.

Although precise mechanistic information is unavailable, the general picture of the hydrogenation of ethylene over the metals of Group VIII is fairly clear. There are present on the surface adsorbed ethylene, ethyl radicals, hydrogen atoms and probably no other species. The order in hydrogen is usually 1.0 or 0.5 on most metals; thus the olefin is more strongly adsorbed than the hydrogen. Most striking are the differences between the strengths of adsorption of ethylene on the various metals, and these determine whether exchange reactions will be detected.

With the higher olefins there is a shortage of results, but what information that is available points to reaction schemes and adsorbed species, similar to that found in the hydrogenation of ethylene.

1.4.4 The hydrogenation of diolefins.

The gas phase hydrogenation of buta-1,3-diene (subsequently referred to as butadiene) was first reported in 1963 by Meyer and Burwell (61) who, using deuterium as a tracer, proposed that 1:2- and 1:4-addition of hydrogen to the diolefin takes place at room temperature over a palladium-alumina catalyst. This was followed by a more detailed study by Bond, Wells et al. (62-67) of the catalytic activities of each of the Group VIII metals and copper for the gas phase reaction of butadiene with hydrogen; deuterium was also used when examining cobalt, nickel, copper, palladium and platinum (65,67). These reactions, apart from the hydrogenation over metal wires and films (66), were studied over supported metal catalysts.

A summary of the results for the gas phase hydrogenation of butadiene catalysed by the noble Group VIII metals (63,67) is shown in Tables 1.1 and 1.2.

Information on the hydrogenation in the liquid phase is very much more sparse. Ethanol was used as a solvent in studies over the Group VIII metals (68-71), but the only mechanistic discussion is that of Rieche, Grimm and Albrecht (70) who assumed an ionic mechanism. More recently the homogeneous hydrogenation of butadiene and other dienes, catalysed by some transition metal complexes has been studied by several workers (72,73).

The hydrogenation of multiply unsaturated hydrocarbons illustrate many features described in section 1.4.3 for olefins but in addition pose many problems of a kind essentially different from those encountered in monoolefin hydrogenation. Thus a diolefin will generally hydrogenate to give both monoolefin and paraffin, and the system may show a degree of preference for either product depending upon the catalyst and the conditions used. In consequence of this, the term "selectivity" is used to denote the extent to which a diunsaturated hydrocarbon will yield alkene as opposed to alkane; thus;

$$\text{Selectivity, S} = \frac{\text{yield of olefin}}{\text{yield of olefin + paraffin}}$$

So defined, S may take values between zero and unity.

Selectivity is governed by two factors. Consider the following reaction scheme.

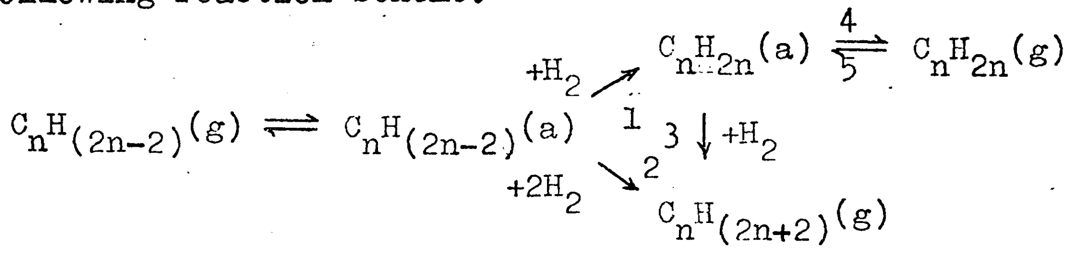


TABLE 1.1

Orders of reaction and activation energies.

Metal	Order in Hydrogen	Order in Butadiene	Temp. (^{o}C)	Activation Energy kcal mol^{-1}	Temp. Range (^{o}C)
Ru	1.0	0.0	14	12.5	0-48
Rh	1.0	0.1	0	11.1	16-82
Pd	1.7	-0.7	16	16.7	20-42
Os	1.0	0.0	70	10.2	24-70
Ir	0.8	0.0	0	4.5	0-62
Pt	0.3	-0.5	16	19.5	0-152
Fe				11.1	200-260
Co-I	1.5	-0.5	148	12.2	94-153
Co-II	1.0	0.0	111	10.3	76-132
Co-III	1.0	0.0	140	8.6	107-184
Ni	1.0	-0.2	78	15.0	84-110
Cu	1.0	0.0	105	13.1	82-130

TABLE 1.2

The dependence of butene distribution and selectivity upon temperature.

		% Butene Distribution				
Metal	Temp.(^{o}C)	1-BUT	TRANS	CIS	T/C	Selectivity
Pd	0	64	33	2	13.8	1.000
"	43	59	37	4	9.7	1.000
Ru	0	69	19	12	1.6	0.736
"	49	61	23	16	1.4	0.835
Rh	16	51	32	17	1.9	0.743
"	82	48	32	20	1.6	0.906

TABLE 1.2 (continued)

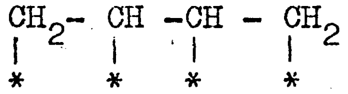
Metal	Temp.(°C)	1-BUT	TRANS	CIS	T/C	Selectivity
Os	24	65	19	16	1.2	0.431
"	70	57	21	22	0.9	0.630
Ir	24	59	19	22	0.9	0.251
"	75	32	34	34	1.0	0.384
Pt-I	0	72	18	10	1.8	0.501
"	45	64	17	19	0.9	0.625
Pt-II	107	61	22	17	1.3	0.800
"	152	38	36	26	1.4	0.920
Fe	198	23	45	32		0.980
"	259	27	41	32		0.994
Co-I	94	53	32	15		0.968
"	152	50	33	17		0.980
Co-II	75	28	64	8		1.000
"	130	22	70	8		1.000
Ni-I	45	44	38	18		0.988
"	110	55	30	15		0.998
Cu	60	87	6	7		1.000
"	130	83	8	9		1.000

(1-BUT = but-1-ene ; TRANS = trans-but-2-ene ; CIS = cis-but-2-ene ; T/C = trans-but-2-ene/cis-but-2-ene)

If the sole route to the paraffin is via adsorbed olefin (step 1 followed by step 3), the chance of paraffin formation will depend on the ability of the olefin to adsorb, or remain adsorbed in competition with the diolefin. The extent to which this happens and the olefin undergoes further hydrogenation depends on the relative strengths of adsorption of the diene and olefin, and this is termed the "thermodynamic factor", denoted by S_t. The "mechanistic factor" is operative if the alkane can be formed by two distinct routes (step 1 followed by step 3 or alternatively step 2). In all systems studied to date, diolefins are adsorbed more strongly than monoolefins (63), thus variations in the observed selectivity are due to variations in the mechanistic factor (74).

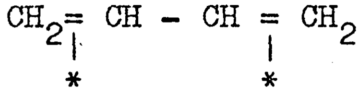
Matters are further complicated in the case of diolefins other than allene since a distribution of isomeric olefins is generally obtained. Thus the stereoselectivity exhibited by a catalyst is a further peremeter to be considered.

The strong adsorption of butadiene relative to monoolefins (63) suggests that both olefinic linkages interact with the surface. Thus, by analogy with section 1.4.2, two possible structures may be postulated for the adsorbed state, one involving the formation of four carbon-metal bonds (structure I) and the other involving two metal-olefin interactions (structure II)



$\underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH}}-\underset{*}{\underset{|}{CH}}-\underset{*}{\underset{|}{CH_2}}$

structure I

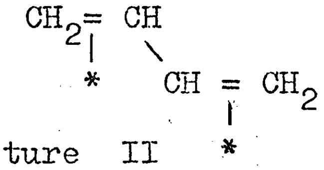


$\underset{*}{\underset{|}{CH_2}}=CH-CH=\underset{*}{\underset{|}{CH_2}}$

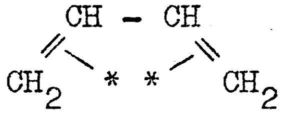
structure II

The increased stability of structure I relative to an adsorbed olefin with only two carbon-metal σ-bonds would be offset, however, by the considerable internal strain inherent in this structure due to the sp^3 hybridisation of all of the carbon atoms and the geometrical requirement of four metal sites at a suitable interatomic spacing. Considering structure II, the interaction of both olefin linkages with the surface would certainly cause butadiene to be more strongly held to the surface than a monoolefin. Moreover the sp^2 hybridisation of the free molecule is not likely to be greatly disturbed by the interaction with the surface and hence little strain will be present in the adsorbate.

A second source of evidence of the adsorbed state of butadiene lies in information obtained from the examination of the products of the hydrogenation reaction. In the diadsorbed state a butadiene molecule may take up one of two possible conformations.

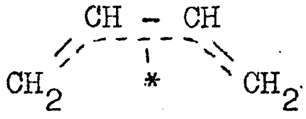


structure II



structure III

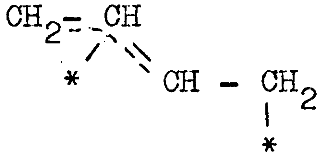
Geometrical considerations require conformation II to be adsorbed to two metal atoms. However, in the alternative conformation the double bonds may interact with one metal atom although others may be obscured, and where this occurs the π-electrons may become delocalised over all four carbon atoms (structure IV).



structure IV

Conformational interconversion may possible occur via a mono- π -adsorbed species or via the half-hydrogenated state, i.e., the adsorbed C_4H_7 species. For butadiene molecules in the gas phase, rotation about the central carbon-carbon bond takes place but is hindered by steric repulsion of the vinyl groups of the anti-conformation. Smith and Massingill (75) have estimated the ratio of gas phase transoid:cisoid butadiene to be approximately 95:5 at ambient temperatures. Thus, at the instant that adsorption occurs the population of II is expected to exceed III on the surface.

Results obtained using palladium catalysts (63,65) yielded trans:cis ratios in the but-2-ene of 10-20 which would signify virtually non-interconvertability of the conformations on this metal. To account for this, it was necessary to invoke an adsorbed species which would prevent conformational interconversion due to the nature of the chemisorption bonds (structure V).



structure V

Similar results over cobalt catalysts (67) suggest strongly that π-allylic complexes are formed readily on palladium and cobalt surfaces. This concurs with the organometallic properties of these metals (53,54) and with the finding that palladium has a high ability for the formation of π-allylic complexes during the catalysed exchange of cycloalkanes with deuterium (50,52).

The following features are common to the hydrogenation of butadiene catalysed by the noble Group VIII metals:

a) orders of reaction are ca. unity in hydrogen, and zero or slightly negative in butadiene;

b) activation energies are in the range 8-20 kcal mol^{-1};

c) all three n-butenes are formed under all conditions but not in thermodynamic equilibrium proportions;

d) for each metal (except iron) the butene composition was independent of the initial hydrogen pressure;

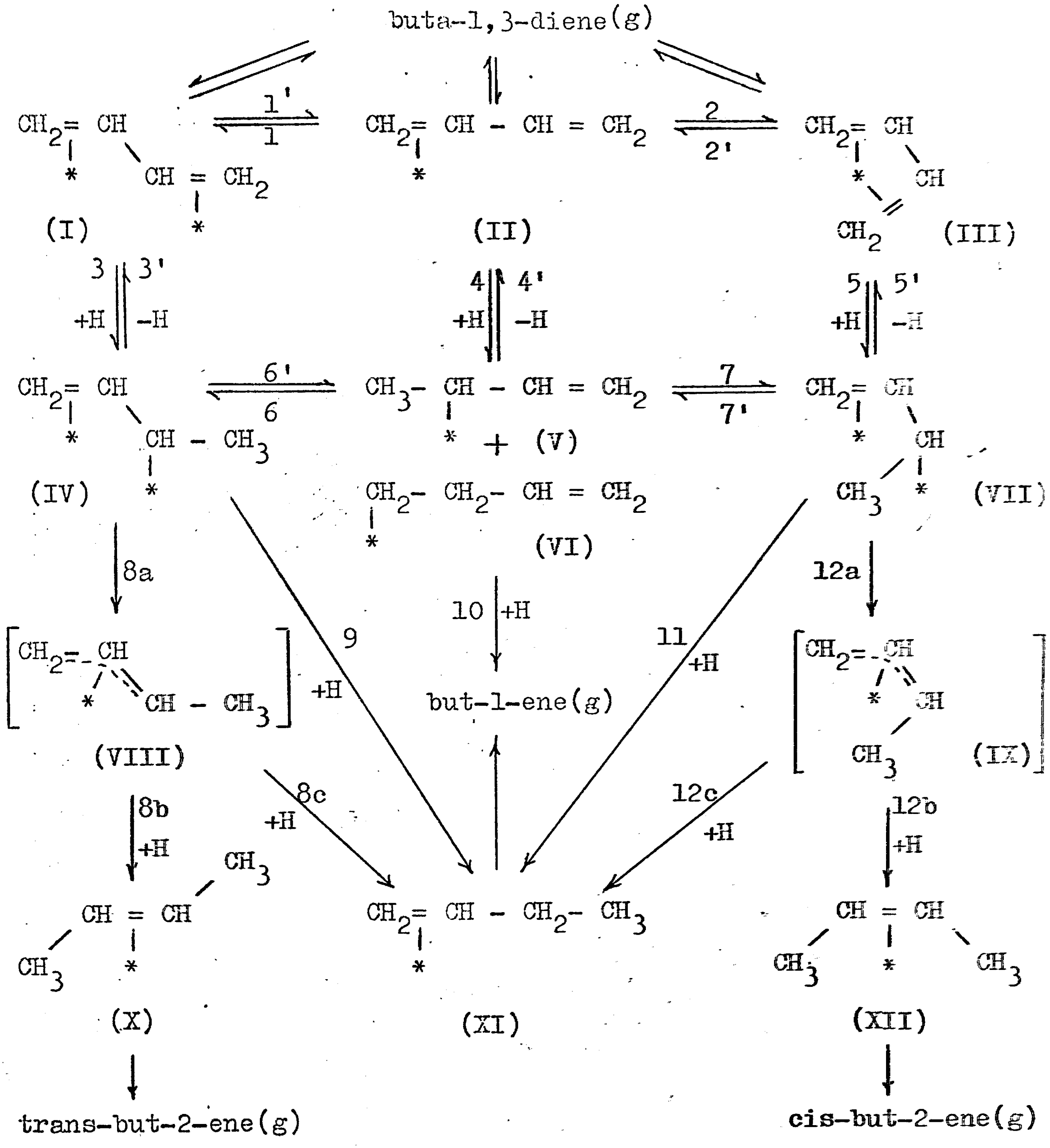
e) where n-butane is formed, the selectivity for butene formation decreased slightly with increasing conversion (except over Co-I), increasing initial hydrogen pressure, and decreasing temperature.

As far as selectivity is concerned, a pattern emerges, in that the selectivity for butene formation decreases under comparable conditions as each of the vertical triads of elements in Group VIII is descended;

e.g. $S_{Fe} > S_{Ru} > S_{Os}$

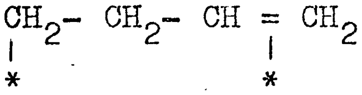
No single mechanism satisfactorily accounts for the different results obtained over the various metals and one is forced to invoke two reaction mechanisms (67).

In mechanism A, gaseous butadiene is considered to chemisorb as a mono-π-bonded species (II), and as di-π-bonded

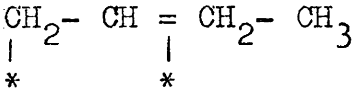


Scheme 1. Reaction mechanism A

species which can exist in conformations (I) and (III). Hydrogen atom addition converts chemisorbed butadiene into the half hydrogenated states (IV), (V), (VI), and (VII), together with a further species



$\underset{\substack{|\\ *}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\substack{|\\ *}}{\mathrm{CH}}=\mathrm{CH_2}$ (XIII) which is not shown in the scheme. Each of these species may give but-1-ene after the addition of a further hydrogen atom and this completes the 1:2- addition process. 1:4- addition is achieved when (IV) and (VII) are converted by further hydrogen atom addition, via the π-allylic species (VIII) and (IX) respectively, into trans- and cis-but-2-ene respectively. The π-allylic species may play one of three roles: (a) they may be transient species, (b) they may be true intermediates in equilibrium with (IV) and (VII), or (c) they may simply allow bonding rearrangement to occur such that (IV) and (VII) are converted into trans- and cis-forms of the species

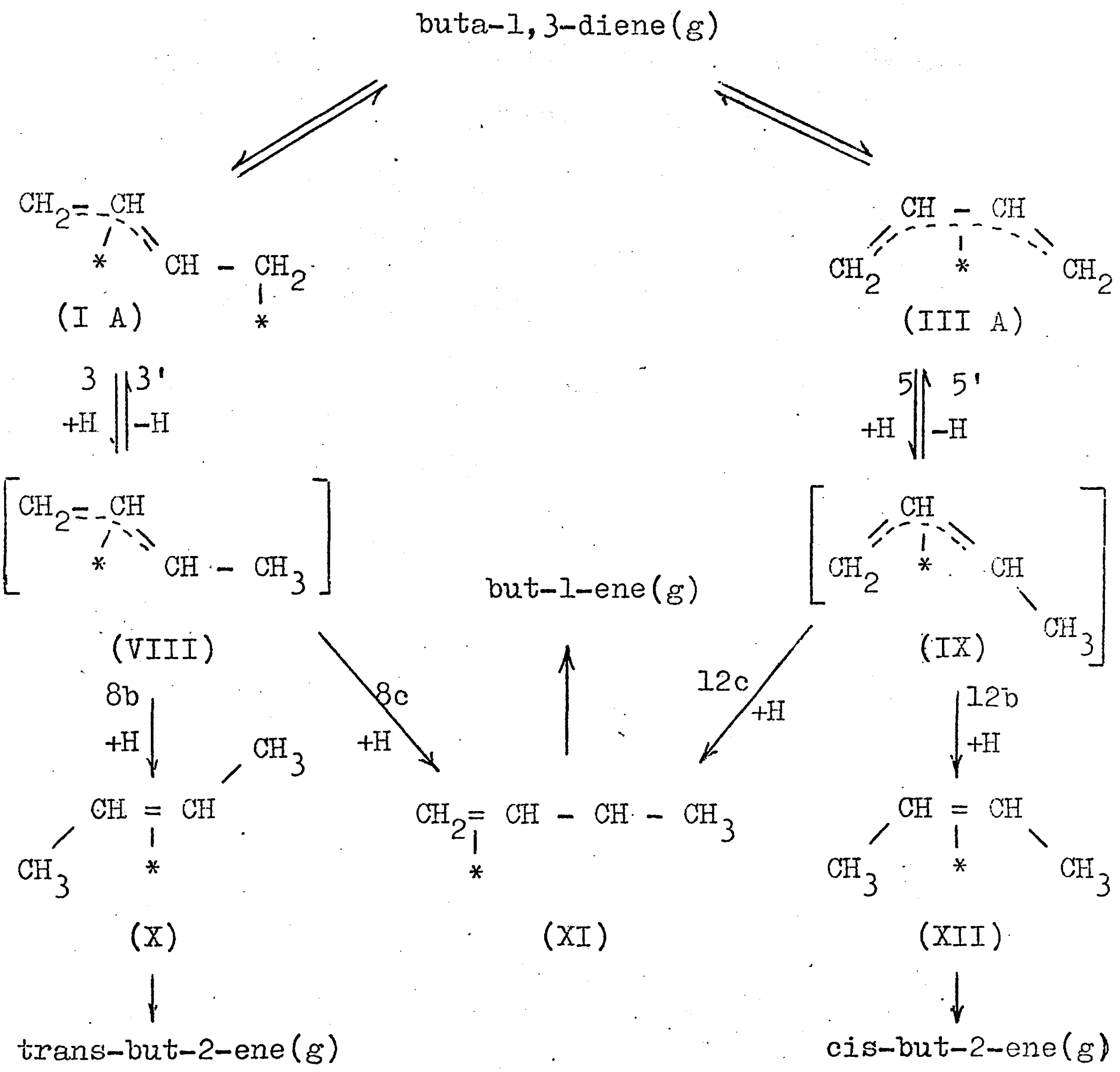


$\underset{\substack{|\\ *}}{\mathrm{CH_2}}-\underset{\substack{|\\ *}}{\mathrm{CH}}=\mathrm{CH_2}-\mathrm{CH_3}$ (XIV). According to alternative (c) but-2-ene would be formed from (XIV) only, and but-1-ene would be the sole product of the hydrogenation of (IV) and (VII). A choice between these alternatives cannot be made at present. Mechanism A shows (VIII) and (IX) participating as described in alternative (a). Mechanism A was developed by Bond et al. (63) to interpret reactions catalysed by ruthenium, rhodium, osmium, iridium and platinum in which the trans:cis ratio in the but-2-ene was about unity. There it was proposed in the absence of tracer evidence that the interconversion of (I) and (III), or of (IV) and (VII) was rapid compared with the process of hydrogenation, so that (IV) and (VII) were present in comparable concentrations.

Further work (67) using deuterium as a tracer and involving N-profile calculations demonstrate that this is not in fact true i.e. conformational interconversion is slow compared with hydrogenation. The problem is resolved if it is supposed that butadiene is not chemisorbed directly as species (I) and (III) but only as species (II) and that (I) and (III) are formed rapidly and in similar proportions from (II).

According to mechanism B, butadiene is adsorbed in such a manner that the two conformations (IA) and (IIIA) cannot interconvert because of the nature of the chemisorption bonds (63,65) Hydrogenation proceeds by the formation of methyl-π-allylic species, and conformational interconversion of these half-hydrogenated states is also prohibited. Since the relative concentrations of (IA) and (IIIA) may be in the ratio 1:15 (63,75), this mechanism interprets a high trans:cis ratio in the but-2-ene. This concept of non-interconvertibility of conformations was developed to account for the palladium-catalysed reaction in which the trans:cis ratio was in the range 10-17, depending on the conditions.

There is a possibility that butene, once formed by these 1:2 and 1:4- addition processes, may isomerise before desorption. Such isomerisation may take place in principle



Scheme 1. Reaction mechanism B

either by an addition-abstraction mechanism which involves adsorbed C_4H_9 as an intermediate, or by an abstraction-addition mechanism which involves C_4H_7 (47,61,75,76). At the moment however, there is little evidence to suggest that but-2-ene is formed in the butadiene hydrogenation reaction by but-1-ene isomerisation.

The general features of butadiene hydrogenation catalysed by rhodium, palladium and platinum wires (66) resemble in many respects those reported for the corresponding metal-alumina catalysts (63). Similarities between the catalytic behaviour of iridium wire and iridium-alumina are less evident although fewer results are available for comparison.

Over each metal the butene isomers were formed in non-equilibrium proportions, the thermodynamically least stable isomer, but-1-ene, being the major product of most reactions. The butene composition was independent of the initial hydrogen pressure.

The temperature-dependence of the trans:cis ratio suggests that conformational interconversion of the transoid and cisoid adsorbed species becomes progressively more important as the temperature is raised. There should therefore be a tendancy for the yield of but-1- ene to increase with increasing temperature, as a result of 1:2- addition of hydrogen to the increasingly important mono-adsorbed species. However, previous results (63) suggest that the activation energy for 1:4- addition is higher than 1:2- addition. Together, these two opposing factors determine the manner in which the but-1-ene yield varies with temperature. Selectivity resembles the sequence observed for alumina-supported metals (63).

1.5 The role of the support.

For some time now, there has been a growing body of evidence to suggest that the support plays a very much more important part in catalysis than merely providing a structural framework for the catalytic component and increasing the surface area per unit weight of metal above that of the unsupported metal. If the carrier is a variable perameter differences in the reactivity of catalysts would be expected in view of the varying structure and behaviour of the supports employed.

In 1956, Bond (58) reported a detailed study of the reaction of ethylene with deuterium over various types of platinum catalysts in which he concluded that the support may provide some chemical action although he did not draw any conclusions as to its cause. Since then many workers (10, 30,34,78-85) have postulated that the support may play a significant role in determining the catalytic activity and the idea of migration of active intermediates (10,83-86) between the metal and the support has been widely accepted. A change of the support from silica to alumina has been shown to cause differences in the infrared spectrum of carbon monoxide on platinum (34) and in the activation energy for the hydrogenolysis of ethane (80). Platinum on α-alumina or silica was found by Shephard and Rooney (81) to be much less active than platinum on γ-alumina in catalysing reactions of C_9 alkyl aromatics.

The exchange of the hydrogen atoms in p-xylene with deuterium and the deuteration of p-xylene were used by Kemball and Hightower (82) to examine the role which supports play in determining the catalytic properties of platinum. The rates of the reactions at 100°C on all catalysts followed the order: exchange of ring atoms $\geq$ exchange of methyl hydrogen atoms $>$ deuteration, but the relative rates varied as the support was changed from γ-alumina to α-alumina or to silica. It was postulated that the acidities of the supports which are affected by strongly held water (87) may work in conjunction with the platinum to modify the catalytic properties of the metal.

Sinfelt and Lucchesi (83) measured the rates of ethylene hydrogenation on a Pt/SiO_2 catalyst mixed with Al_2O_3 and SiO_2. The rate of ethylene hydrogenation, under comparable conditions, was much greater when the Pt/SiO_2 catalyst was mixed with Al_2O_3. It was postulated that the metal centres on the Pt/SiO_2 catalyst activated the hydrogen which then migrated to other centres to react with ethylene. The fact that Al_2O_3 chemisorbs ethylene to a much greater extent than does SiO_2 (88) offered a reasonable explanation for the much higher activity of the $(Pt/SiO_2+Al_2O_3)$. In view of the lack of reaction on alumina itself in the absence of metal (10), a more likely explanation would appear to be that the hydrocarbon is adsorbed on the metal and that hydrogen migrates from the alumina support to the metal before reaction takes place. Furthermore, it was shown (84) that an alumina support is an essential constituent to a catalyst if butene isomerisation is to be achieved in the absence of molecular hydrogen over the Group VIII metals. It appears likely that hydrogen atoms which migrate from the support to the metal initiate butene isomerisation at the metal surface.

Recently, impressive evidence for the support effect has come from radiochemical studies carried out by Thomson et al. (10) and Webb et al. (85). Results showed that for alumina and silica supported platinum catalysts, the reactivity of the adsorbed species is dependent on the nature of the support and on these catalysts, hydrogen migration between metal and support readily occurs. This observation together with the observation that alumina, and to a lesser extent silica, itself is active in hydrogen exchange suggests that in reactions involving hydrogen and hydrocarbons, the support may play a very important rôle in determining the catalytic activity.

The migration of stable intermediates hasbeen recognised in bifunctional catalysis (89-92) which is most important industrially for the reforming of hydrocarbon molecules in petroleum napthas. Such catalysts have a dehydrogenation function (D.F.),which is usually platinum, and an acid function (A.F.),which is inherent in or added to the support (usually alumina). Some of the over-all reactions occurring in reforming involve several consecutive steps over the different catalyst functions; for example, the conversion of methycyclopentane to benzene is believed to proceed by the mechanism

$$\begin{tikzcd}
\text{Methylcyclopentane} \arrow[r, shift left, "\text{D.F.}"] & \text{Methylcyclopentene} \arrow[l, shift left] \arrow[r, shift left, "\text{A.F.}"] & \text{Cyclohexene} \arrow[l, shift left] \arrow[dl, shift left, "\text{D.F.}"] \\
 & \text{Benzene (89)} \arrow[ur, shift left] &
\end{tikzcd}$$

For this reaction, the dehydrogenation function and the acid function need not be present at the same adsorption site, nor even on the same catalyst surface (90). In this case, the intermediate reaction products, methylcyclopentene and cyclohexene, must be of sufficient stability to diffuse through the gas phase from one type of catalytic site to the other.

1.6 Reactions over gold.

The low activity of gold for most catalytic reactions has been generally attributed to its lack of a partially filled d-band at the usual experimental temperature, and its consequent inability to chemisorb simple molecules. Thus, Trapnell (93) reported that gold was the only metal which did not chemisorb oxygen or hydrogen. Carbon monoxide and ethylene were weakly chemisorbed, however, with heats of adsorption of 8.7 and 20.8 kcal mol^{-1}. There is, however, evidence that oxygen must chemisorb on gold (94-98), especially during oxidation reactions (95,96). Kul 'Kova and Levchenko (97) observed that chemisorption occurred in the temperature range 50 - 400°C with an activation energy of

3.2 kcal mol^{-1}. More recently, MacDonald and Hayes (98) produced results that are indicative of a firmly chemisorbed oxygen species even at low temperatures. Gold has also been briefly studied as the end member of the palladium-gold alloy system in the catalysis of the oxidation of carbon monoxide (95), methane (99) and ethylene (100).

Recently, Cha and Parravano reported that considerable reactivity towards carbon monoxide-carbon dioxide (101)and benzene-cyclohexane (102) mixtures can be developed at the surface of gold dispersed upon magnesium oxide and alumina. In both studies rate constants of the order of 10^{-6} (mole/g (Au)sec) were calculated but the two transfer steps had a large difference in the apparent activation energies:- 24 kcal mol^{-1} for oxygen and $\sim$ o kcal mol^{-1} for hydrogen. This is related to the variation in affinity of the surface for oxygen and for hydrogen, and to the different energy of the C-O bond in CO_2 and C-H bond in cyclohexane.

Also, Boudart and Ptak (103) found that gold catalysed the isomerisation and hydrogenolysis of neopentane. It is postulated that the exceptional activity of gold to isomerise neopentane is related to its high electronegativity and to a readily shifted surface valency as a result of promotion of d electrons to empty s levels.

The heterogeneous oxidation of ethylene and propylene has been extensively studied over several gold catalysts (104). The principal products from ethylene were carbon dioxide and water, but small amounts of acetic acid and acetaldehyde were also found. In addition to these products, up to 3% acetone and 50% acrolein were obtained from propylene.

An extensive investigation of the catalytic decomposition of formic acid vapour on gold has been carried out by Sachtler et al. (24,105,106). It was reported that the initial reaction step is a dissociative chemisorption of the HCOOH molecule, yielding a formate and adsorbed hydrogen, with the rate-determining step being the adsorption process. The activation energy is 14.3 kcal mol^{-1}, in perfect agreement with the result obtained by Eley and Luetic (22) for the same reaction on a gold wire, and the reaction order is near unity. Isotopic tracers have been employed to measure the isotopic composition of the hydrogen formed when deuterated formic acids decompose. There is no exchange of either formic acid or hydrogen with deuterium over silica supported gold. However, when mixtures of HCOOH and HCOOD are allowed to decompose, the three molecular isotopes of hydrogen are formed in their equilibrium proportions (24,105,106).

Although the transition metals are generally superior as hydrogenation catalysts compared with those outside that group, studies (107) of the kinetics of hydrogen atom recombination on surfaces showed that many non-transition metals were better catalysts than transition metals. Furthermore, it was found that the rate of hydrogen-deuterium equilibration on gold at moderate temperatures was promoted by the preadsorption of hydrogen on the gold surface (108). The common aspect of both of these systems appeared to be the existence of a surface layer of chemisorbed hydrogen on the metal. These observations led Wood and Wise (109,110) to examine the gas-phase hydrogenation of but-1-ene and cyclohexene on a gold surface. Since molecular hydrogen for the hydrogenation reaction does not adsorb on gold at this temperature (105), it was supplied to the gold surface by diffusing it through a palladium-silver alloy membrane on which a gold layer was electroplated. Table 1.3 summarises the results of a number of experiments carried out to measure the individual and combined hydrogenation rates of but-1-ene and cyclohexene. To elucidate the order of the kinetics with respect to alkene concentration, the hydrogenation rate of cyclohexene was measured as a function of its initial pressure (Table 1.4). The data suggest that the process is first order in alkene concentration, since the ratio of the normalised hydrogenation coefficient to the initial alkene pressure is constant.

The study also shows that (a) the catalytic activity is nearly the same for the two structurally different alkenes used in the work and (b) the two alkenes are hydrogenated in admixture as the sum of the individual rates. In addition, the results demonstrate that the hydrogenation of olefins does not require special surface-hydrocarbon interactions but only the

TABLE 1.3

Catalytic hydrogenation of but-1-ene and cyclohexene on gold at 383°C.

Reactants present	Hydrogen diffusion rate R_d (mole/min) × 10^6	Hydrogenation rate (initial) (mol/min) × 10^6 R_h		R_h/R_d	
		C_4H_{10}	C_6H_{12}	C_4H_{10}	C_6H_{12}
C_4H_8	29	0.34	-	0.012	-
C_4H_8	24	0.43	-	0.018	-
C_4H_8	35	0.44	-	0.013	-
				0.014	
				±0.002	
C_6H_{10}	13	-	0.13	-	0.010
C_6H_{10}	18	-	0.38	-	0.021
C_6H_{10}	24	-	0.20	-	0.008
					0.013
					±0.003
C_4H_8, C_6H_{10}	11	0.20	0.19	0.018	0.017
	38	0.45	0.43	0.012	0.011
				0.013	0.014
				±0.004	±0.003

TABLE 1.4

Effect of initial pressure of cyclohexene on the hydrogenation rate at 383°C.

Initial pressure of C_6H_{10} (torr)	23	53	83
Hydrogen diffusion rate R_d (moles/min) × 10^6	22	18	33
Hydrogenation (initial) rate R_h (moles/min) × 10^6	0.12	0.24	0.59
Normalized hydrogenation coefficient R_h/R_d	0.005	0.013	0.018
$\frac{R_h/R_d}{P_{C_6H_{10}}}$ (torr^{-1}) 10^4	2.2	2.5	2.2

presence of a sufficient quantity of adsorbed H atoms, which serve as sites for the production of the intermediate.

1.7 Reactions over copper.

Much of the early catalytic research involving copper has been concerned with the elucidation of the influence of the electronic properties of the solid state on the surface reactivity of metals. Since the alloy system copper-nickel forms a continuous series of solid solutions with a phase diagram that shows little deviation from ideality (111), the series has been frequently chosen in studies which utilise the technique of alloying metals in Group VIII and IB in the periodic table to decrease their d-band vacancies and hence control their catalytic activity.

The hydrogenation of ethylene has been studied over alloy powders (112,113) and foils (114). It was shown (112, 114), that the activation energies are essentially constant, and the activity differences are thus chiefly caused by differences in the pre-exponential factor in the Power Rate Law. Especially striking in the studies using Ni-Cu foils is the very abrupt decrease in activity between 80.2 and 80.8 per cent copper, but while this is above the normal critical composition (60 atom % copper), it is not impossible that thermal excitation will create additional d-band holes, and hence will raise the critical copper concentration. Less extensive studies of olefin hydrogenation have been carried out using styrene over nickel-copper foils (115), and cinnamic acid over Kieselguhr-supported alloys and unsupported alloy powders (116).

The activity of nickel-copper alloys for the hydrogenation of benzene has been reported by several workers (117-119). Although quantitatively the results are not in complete agreement, a comparison indicates a similar trend in the variation of specific activity and apparent activation energy with composition. The activity at first increases with increasing copper content, and passes through a maximum at 25% copper, subsequently falling smoothly, and the apparent activation energies remain essentially constant in the 30-90 atom % nickel compositional range.

Bond and Mann (120) reported that the hydrogenation of acetylene over pumice-supported copper and copper powder exhibited kinetics which correspond to a rate expression containing two rate constants of the type described for nickel (121). However, in contradiction to nickel, the activation energy of the process operating at low hydrogen pressures(20 kcal mol^{-1}) is greater than that for the additional process at high hydrogen pressures (4 kcal mol^{-1}).

The hydrogenation of but-2-yne has been examined over alumina-supported copper catalysts (122). At all temperatures, the catalysts were completely selective for cis-2-butene formation (Selectivity=1) and the activation energy was 13.4 kcal mol^{-1}).

The high catalytic activity exhibited by copper for the hydrogenation of but-2-yne led Wells et al.(67) to study the alumina-supported copper-catalysed hydrogenation of buta-1, 3-diene. As reported in section 1.4.4, the order in hydrogen was unity, the order in butadiene was zero and the activation energy, measured in the temperature range 82-130°C was 13.1 kcal mol^{-1}. During the initial stages the reaction was completely selective for butene formation and the onset of butene hydrogenation was marked by a much diminished rate of pressure fall.

The relative yields of the three butenes under all conditions were:

$$\text{but-1-ene} \gg \text{cis-but-2-ene} \sim \text{trans-but-2-ene}$$

The yield of but-1-ene was higher in the initial stages and it declined slowly and continuously thereafter. While the butene composition was strictly independent of initial reactant pressures (Table 1.5), the yield of but-1-ene decreased with a rise in temperature (Table 1.6). The trans:cis ratio in the but-2-ene was not markedly affected.

Studies using deuterium as a tracer indicated that the deuterium content of the butenes increased with increasing conversion. This was a result of the hydrogen atoms of butadiene being exchanged for deuterium atoms and the butadiene subsequently being readsorbed and hydrogenated. Throughout the series of reactions the deuterium numbers of all butenes were closely similar; cis-but-2-ene contained slightly less deuterium than the trans isomer, but slightly more than but-1-ene. Table 1.7 and Table 1.8 give results for the butadiene/hydrogen exchange reaction and the distribution of deuterium in the butenes respectively.

The small differences in deuterium number between

TABLE 1.5

The dependence of the product distribution upon initial reactant pressures.

Temp. (°C)	Initial hydrogen pressure (mm.)	Initial butadiene pressure (mm.)	Pressure fall before analysis (mm.)	% Butene Distribution 1-BUT	TRANS	CIS
105	50-250	50	13	83	7	10
	100	25-200	12	84	7	9

TABLE 1.6

The dependence of the product distribution upon temperature.

Initial butadiene pressure = 50 mm. ; initial hydrogen pressure = 100 mm. ; pressure fall before analysis = 10 mm.

	% Butene Distribution		
Temp. (°C)	1-BUT	TRANS	CIS
60	87	6	7
130	83	8	9

(1-BUT = but-1-ene ; TRANS = trans-but-2-ene ; CIS = cis-but-2-ene)

TABLE 1.7

Butadiene and hydrogen exchange at 120°C.

Initial butadiene pressure = 50 mm. ; initial deuterium pressure = 100 mm.

Pressure fall before analysis (mm.)	Deuterium distribution in butadiene (%) d_0	d_1	d_2	d_3	d_4	d_5	d_6	D.N.	H.N.
5	83.4	14.4	2.0	0.2	0.0	0.0	0.0	0.19	0.009
12	62.6	29.2	7.0	1.1	0.1	0.0	0.0	0.47	0.025
25	38.6	39.5	16.5	4.5	0.5	0.4	0.0	0.96	0.042
40	11.0	27.8	34.9	20.5	5.2	0.1	0.1	1.83	0.067

TABLE 1.8

Distribution of deuterium in butenes obtained by reaction at 120°C.

Initial butadiene pressure = 50 mm. ; initial deuterium pressure = 100 mm. ; pressure fall before analysis = 40 mm.

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
1-BUT	30.6	29.8	21.6	12.0	4.8	1.1	0.1	0.0	0.0	1.35
TRANS	26.6	28.8	23.8	13.4	5.8	1.5	0.1	0.0	0.0	1.48
CIS	27.4	29.4	23.4	13.1	5.3	1.3	0.1	0.0	0.0	1.44

(1-BUT = but-1-ene ; TRANS = trans-but-2-ene ; CIS = cis-but-2-ene) butenes produced at the same conversion arise as a result of very small differences in the yields of multiply exchanged products i.e. those species which contain three or more deuterium atoms. Thus the adsorbed species which give rise to these products must show very small differences in reactivity.

The effect of varying the initial deuterium pressure (over the range 50-200 mm.) and temperature (100-140°C) on the distribution of deuterium in the butenes was also studied. Deuterium numbers of the butenes increased slightly as the initial deuterium pressure was increased, and as the temperature was raised. These effects however were not marked.

Data from Table 1.7 indicates that considerable exchange occurs between butadiene and deuterium and the isotopic composition of the adsorbed 'hydrogen' changed greatly with increasing conversion. Nevertheless, formation of HD in the gas phase was slow. Equilibration of 1:1 hydrogen-deuterium mixtures was rapid. It is therefore concluded that the surface coverage of atomic hydrogen was low; this conclusion is confirmed by the low values of the reaction orders.

The activity of copper for but-1-ene isomerisation was far too low to account even for the small yields of cis- and trans-but-2-ene, and hence but-2-ene was formed by the 1:4-addition of hydrogen as shown in mechanism A (scheme 1, section 1.4.4). This conclusion is supported by almost identical distributions of deuterium formed after 80% conversion (Table 1.8).

Exchange of butadiene with hydrogen is considered to occur via diolefin chemisorption as species II (scheme 1, mechanism A, section 1.4.4), exchange followed by desorption. This process was rapid and caused the deuterium in the vicinity of such reaction sites to become hydrogen-rich. Subsequent hydrogenation at such sites would give a product with a lower deuterium number than a butene formed at 'normal' sites. Since hydrogenation at these special sites will give only but-1-ene, the relatively low deuterium number of this isomer is interpreted. Very selective formation of but-1-ene would also result if the major route of formation was via species II, V and VI in mechanism A.

The considerable activity of copper, illustrated in this study, is remarkable as the d-band of the metal is nominally filled. The enhanced reactivity of the supported catalyst compared to the bulk metal indicates that the surface atoms of the small copper crystallites in the supported catalyst have properties which differ considerably from those of surface atoms in the bulk metal.

CHAPTER 2

THE AIMS OF THE PRESENT WORK.

The hydrogenation of unsaturated hydrocarbons over supported metal catalysts has been extensively reported throughout the literature. Reaction orders, activation energies and possible mechanisms have been well defined although most studies haveassumed that the support has no catalytic influence upon the reaction. Recent work, however, including radiochemical studies of chemisorption and catalysis suggest that the nature of the support may definitely influence the behaviour of supported metal catalysts in hydrogenation reactions.

In an attempt to further the understanding of the role of the support in metal catalysed hydrogenation reactions it was decided to investigate the catalytic hydrogenation of an unsaturated hydrocarbon over a supported metal catalyst on which the population of chemisorbed hydrogen was extremely low. Gold is such a metal for at temperatures below 200°C its rate of chemisorption of hydrogen from the moleculor state is immeasurably slow (93) relative to its rate of desorption (40).

The effect of the support was examined by investigating the interaction of buta-1,3-diene with deuterium over silica, α- and γ- alumina and hydrated alumina supported gold with the following aims:

(1) to study the kinetic features of the hydrogenation reaction;

(2) to determine the distribution of reaction products;

(3) to determine the distribution of deuterium in the product hydrocarbons and exchanged 'hydrogen', and thus investigate the influence of the support upon the mechanism and reaction products;

(4) to elucidate mechanisms for the hydrogenation reaction.

These studies were extended to include an investigation of the hydrogenation of buta-1,3-diene over silica supported copper catalysts in order to allow comparisons to be made with

(i) the results obtained for the supported gold catalysts, and,

(ii) results obtained by other workers (67) for the hydrogenation of butadiene over alumina supported copper catalysts.

CHAPTER 3

EXPERIMENTAL.

3.1 Materials.

3.1.1 Catalysts.

The gold catalysts consisted of 1% (w/w) metal supported on γ-alumina (Degussa Ltd.), α-alumina (I.C.I. Ltd.) 'Aerosil' silica (Degussa Ltd.) or boehmite (Cawood Wharton Refectories). They were prepared by mixing an aqueous solution containing the required weight of gold chloride ($AuCl_3 3H_2O$) with a slurry of support in distilled water. After evaporation to dryness the catalysts were dried in an oven at 150°C.

In the course of the work it was shown that boehmite could be prepared by refluxing 2-3g. of γ-alumina in 1M. base, e.g. sodium acetate, for 24 hours. The product was filtered, washed in distilled water and dried in the oven. The X-ray powder photographs showed a structure identical to that of boehmite.

The copper catalyst consisted of 5% (w/w) metal supported on 'Aerosil' silica (Degussa Ltd.) and was prepared from an aqueous solution of cupric nitrate. The nitrate was converted to the oxide by calcination at 400°C for 3 hours. This was followed by reduction of the supported oxide in hydrogen at 250°C for 18 hours.

3.1.2 Gases.

Hydrogen. Cylinder hydrogen (British Oxygen Co. Ltd.) was purified by diffusion through a palladium/silver alloy thimble into a degassed storage vessel.

Deuterium. (Norsk Hydro Ltd.) was examined by mass spectrometry and shown to be at least 97.8 atom% pure. The oxygen content was $<$ 10p.p.m., and hence no further purification was carried out.

Buta-1,3-diene. This was supplied by Matheson Co. Inc. and contained no impurities detectable by gas chromatography and was merely degassed before use.

3.2 The vacuum system.

The apparatus used for carrying out all reactions is shown in Fig. 3.1. A vacuum of 10^{-4} torr or better was obtained by an oil-diffusion pump backed by a rotary oil-pump. Reactions were followed by use of the mercury manometer M. All taps were greased with Apiezon N grease as this is inert to the gases used. The reaction vessels employed for all experiments were made from "Pyrex" glass and consisted of cylindrical vessels of ~120cc. capacity. Temperature control was effected by surrounding the reaction vessel by an electric furnace, the current being controlled by the use of a Variac transformer. Temperatures were measured to ± 1°C using a Pt-Pt/Rh thermocouple in contact with the base of the reaction vessel.

Before each reaction series, the catalyst vessel was thoroughly washed with a mixture of equal volumes of concentrated hydrochloric and nitric acids, after which it was rinsed with distilled water and dried. The required weight of catalyst was sealed in the vessel, which was then attached to the system by the B 10 socket B_1 and evacuated while the

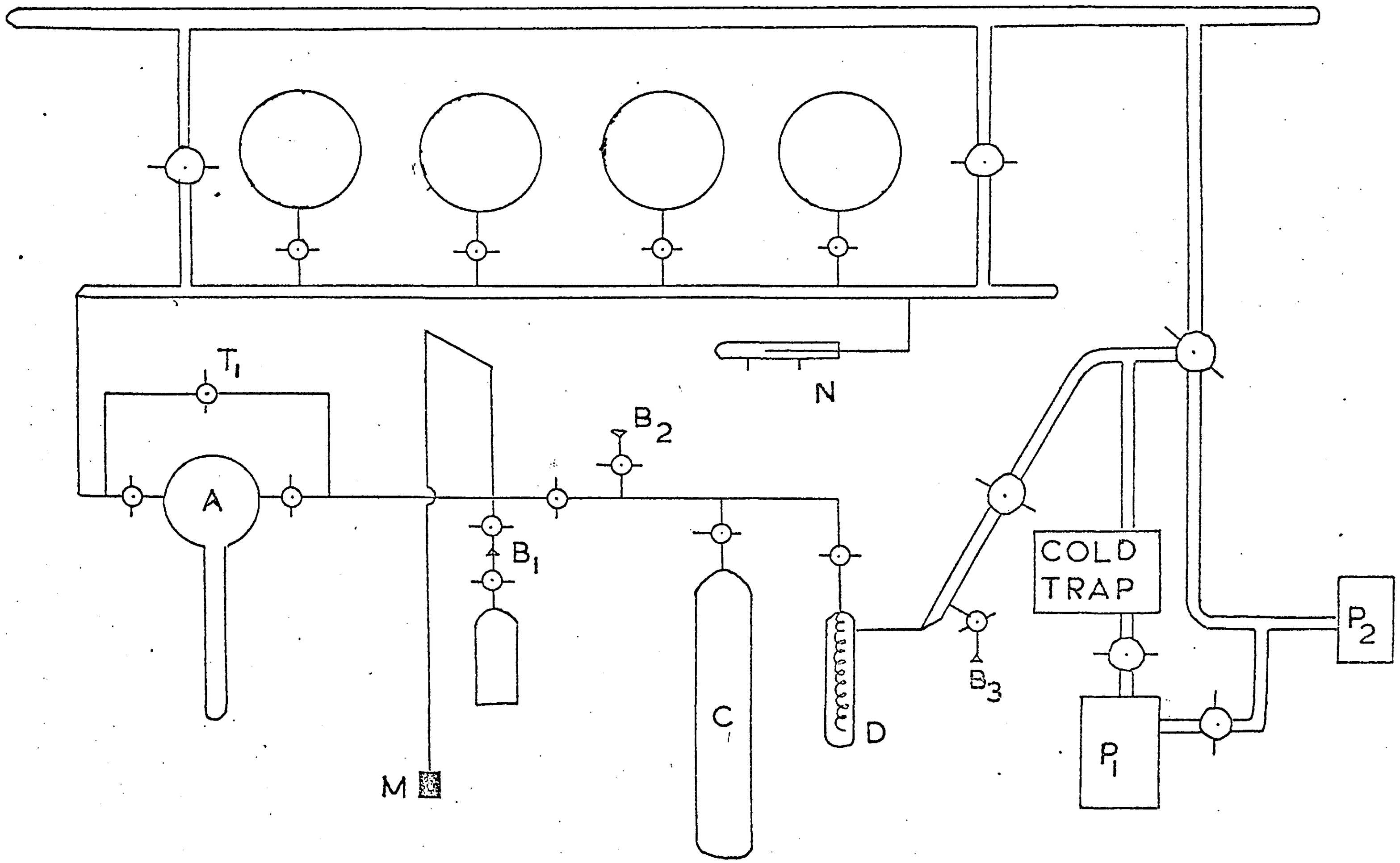


FIG.3.1. THE VACUUM SYSTEM.

P_1 = DIFFUSION PUMP
P_2 = ROTARY PUMP
M = MANOMETER
N = PALLADIUM THIMBLE

temperature was raised to 250°C. The catalyst was then activated in 200 mm. of deuterium for 12 hours at 250°C. Finally, the vessel was evacuated for 30 minutes and allowed to cool under vacuum to the reaction temperature.

Gas mixtures consisting of one volume of butadiene to two volumes of deuterium were pre-mixed in the cold finger A. This was done by condensing a known volume of hydrocarbon in the cold finger, then admitting deuterium to the required pressure. The vessel was allowed to warm up to ambient temperature and left to stand for 30 minutes to ensure complete mixing. For other ratios of reactant gases, butadiene was admitted to the catalyst vessel from the cold finger A followed by deuterium by way of tap T_1. No significant variation in product distribution was noticed between this method and that using pre-mixed reactants.

Reactions were carried out by admitting the required pressure of the reaction mixture to the catalyst vessel, and measuring the pressure fall on the mercury manometer. At the required pressure fall, the reaction products were expanded into vessel C and a sample of the residual 'deuterium' removed for mass spectroscopic analysis to an evacuated sample vessel connected to the apparatus at the B 14 socket B_2. The hydrocarbon products were condensed into the spiral trap D, the unreacted hydrogen pumped away and then the products collected by allowing the spiral to come to ambient temperature, after which the hydrocarbon products were condensed in an evacuated sample vessel at the B 14 socket B_3. Between successive reactions the catalyst vessel was evacuated for 30 minutes.

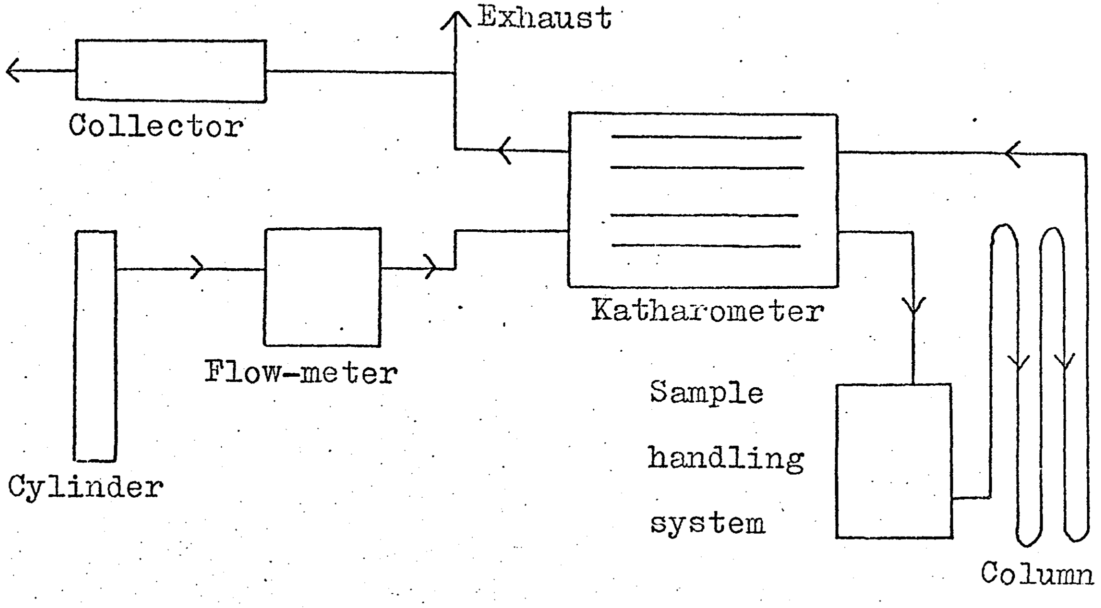
For exchange reactions in the absence of butadiene the catalyst was activated in 200 mm. hydrogen for 12 hours at either 250 or 400°C. The vessel was then evacuated for 1 hour at the reduction temperature. Three successive pressures of 100 mm. deuterium were admitted to the catalyst vessel for 1 hour at 200°C, after which the samples were collected in an evacuated sample vessel at the B 14 socket B_2 for mass spectroscopic analysis. The vessel was pumped for 30 minutes between the exchange reactions.

3.3 The gas chromatography system.

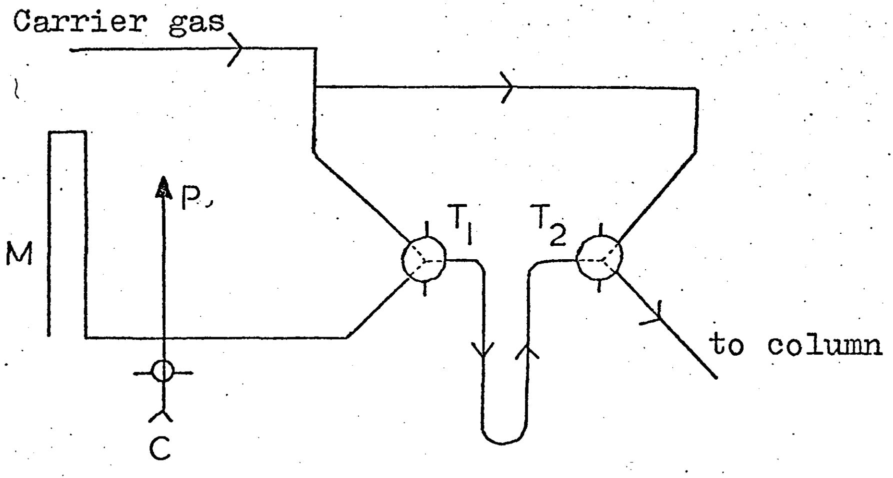
Quantatitive analysis of the reaction products was achieved by gas chromatography.

A block diagram of the chromatography system is shown in Fig. 3.2(a). The sampling system was designed to accept gas samples transferred from the main reaction system (Fig. 3.2(b)). The U-tube between the three-way taps T_1 and T_2 formed a fixed sample volume of $\sim$ 14 ml., which, with the manometer M, was evacuated by a rotary oil-pump P. Samples were admitted to the system from sample vessels via the B 10 socket C, the pressure being read from the manometer. If necessary, the whole sample could be condensed in the U-tube. During this operation the carrier gas flowed through the by-pass B, and by simultaneously turning both T_1 and T_2, the gas was diverted through the U-tube, thus carrying the sample on to the column.

For most of the work, nitrogen (British Oxygen Co. Ltd.) was used as the carrier gas. This was of sufficient purity



(a) Block diagram of apparatus.



(b) The sampling system.

Fig.3.2 The chromatography system.

to be used direct from the cylinder. In order to achieve a more stable baseline in the output from the detector and to ensure reproducibility of peak sizes, variation in the carrier gas flow rate was controlled by a Crawford Swagelock needle valve. The flow rate was measured by means of a bubble flowmeter.

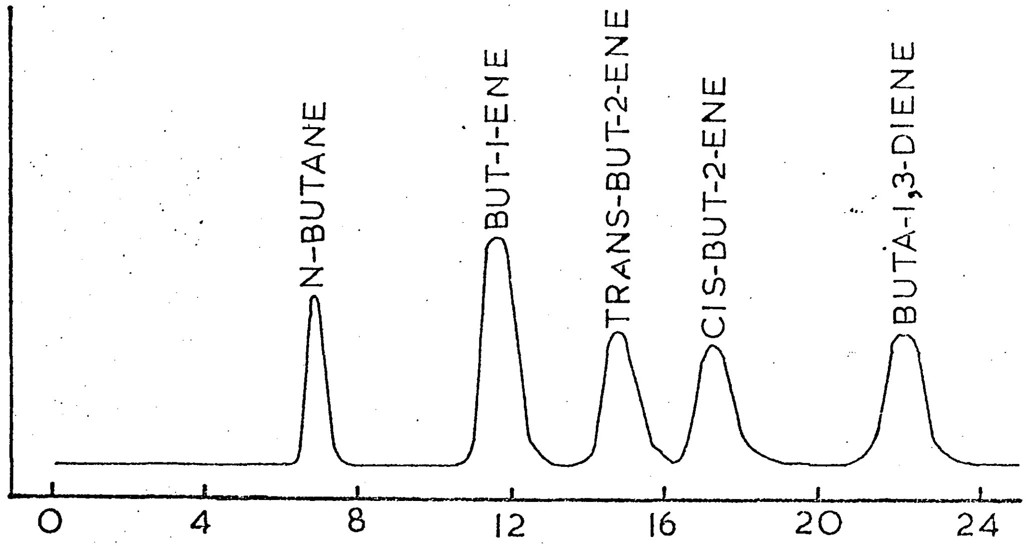
The analytical requirements necessitated a column which would separate the products of the hydrogenation of buta-1,3-diene, these being n-butane, but-1-ene, trans-but-2-ene, cis-but-2-ene, and buta-1,3-diene. A 40% (w/w) hexa-2,5-dione (acetonyl acetone) on firebrick column was found to be suitable. This was prepared by dissolving 40g. acetonyl acetone in 250 ml. acetone and stirring in 103g. 60-80 mesh Silocel firebrick. The mixture was evaporated to partial dryness and left to dry completely at room temperature until a free-running powder was left.

A 20ft. column gave corrected retention volumes for n-butane, but-1-ene, trans-but-2-ene, cis-but-2-ene, and buta-1,3-diene of 200,385,525,650 and 990ml. respectively. These values decreased with use and the column had to be repacked at fairly regular intervals. A typical trace is shown in Fig. 3.3.

TABLE 3.1

Operating conditions for acetonyl acetone column.

Carrier gas	Nitrogen
Input pressure	1.6 atmos.
Flow rate	50 ± 1.5 ml./min.
Temperature	$20^{\circ} \pm 3^{\circ}$C.



Separation on acetonyl acetone column.

Fig.3.3 Typical trace obtained from chromatography column.

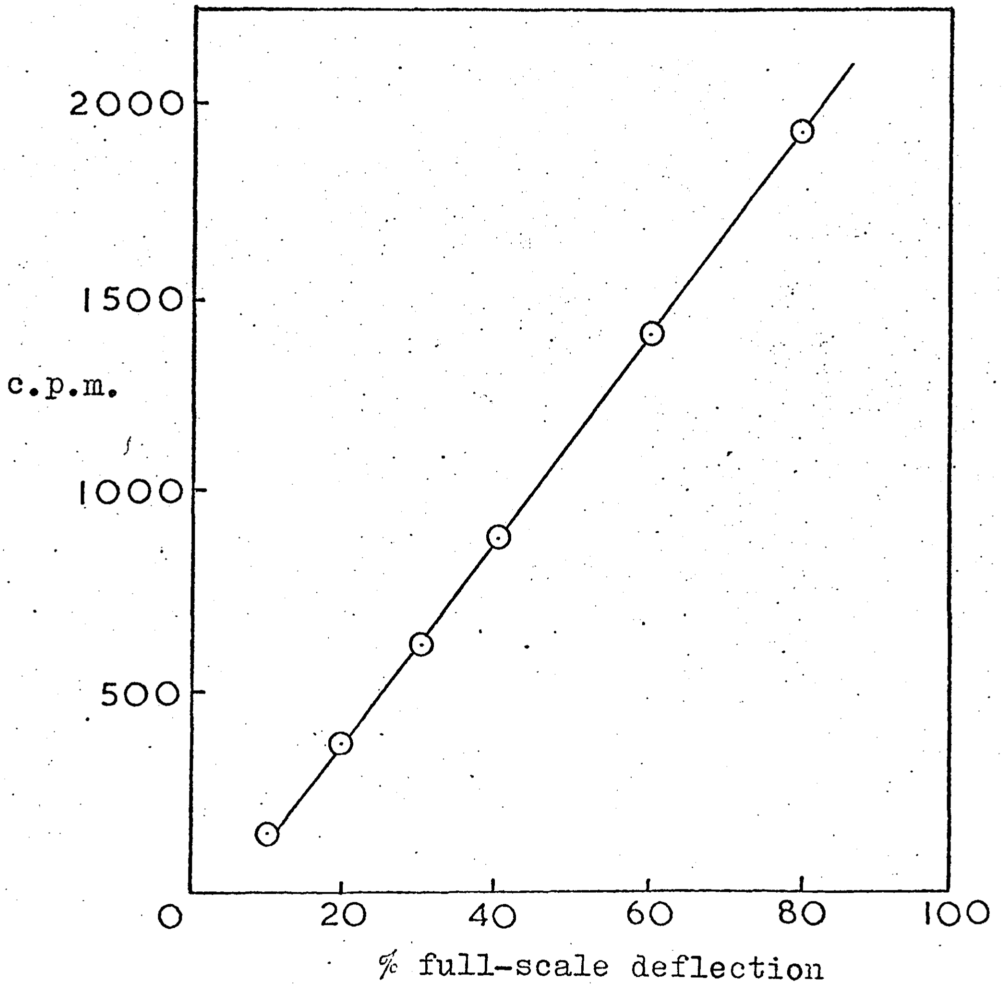


Fig.3.4 Increase in integrator count with % deflection.

The detector used was a Gow-Mac hot-wire katharometer, fitted with four tungsten-rhenium filaments. Each wire formed one arm of a Wheatstone-bridge circuit and was heated by a bridge current of 150 mA. supplied by a 12v. battery.

The output from the detector bridge circuit was fed directly to an analogue to digital converter and the digitised output measured on an Echo scaler. A continuous output was also taken from the integrating unit to a Servoscribe potentiometric chart recorder operated in most cases at 5 mv. full scale deflection. Where small partial pressures were being measured, however, it was operated on the 2 mv. range to give greater recorder response. A plot of count rate against % deflection for the 5 mv. range (Fig. 3.4) shows a linear relationship above 100c.p.m. The rate controlling potentiometer on the integrator was therefore adjusted so that 3% deflection on the recorder, normally used as the baseline, corresponded to a count rate of 100c.p.m.. The baseline count rate was measured before and after each peak was eluted, and by noting the total counts and the time for which it was counted, the net counts were obtained, corresponding to the peak area in arbitrary units.

An attempt was made to replace the integrator and scaler with a modified integrator with automatic print-out. This would dispense with the procedure of correcting the peak area for the baseline count rate but would directly print out the area under each peak. In order to increase sensitivity, it was necessary to change the carrier gas from nitrogen to helium which has a higher thermal conductivity. Under these conditions it was necessary to increase the bridge current to 300 mA.; a stable base-line was obtained and sensitivity increased by a factor of ~ 5 over that obtained using nitrogen as carrier gas.

3.4 Mass spectrometric analysis.

The use of a non-destructive detector such as a katharometer allows each fraction of the chromatograph eluant to be collected for analysis of the deuterium content by mass spectrometry after elution from the chromatograph. This was achieved by passing the eluant through a collector (Fig. 3.2(a)). This consisted of five traps tightly packed with glass wool, placed in series. Each was surrounded by a Dewar vessel containing liquid nitrogen, and by directing the gas flow through a U-tube or by-pass, as appropriate, samples of each hydrocarbon in turn could be condensed out of the carrier gas stream. The traps were evacuated and allowed to warm up, and the samples removed for analysis by condensing them into evacuated sample vessels. Mass spectrometeric analysis made of (i) the hydrocarbon products of the reaction of buta-1,3-diene with deuterium, and (ii) the residual hydrogen/deuterium from the same reactions.

These were carried out using A.E.I. MS 10 mass spectrometer.

TABLE 3.2

Mass spectrometer operating conditions.

	Hydrocarbons	Hydrogen/Deuterium
Ionising voltage	12ev.	70ev.
Trap current	50A.	50A.
Ion repeller	-1v.	-1v.

CHAPTER 4

TREATMENT OF RESULTS.

4.1 The hydrogenation reaction.

The pressure fall, measured on the mercury manometer was plotted against time; the gradient of the tangent to the curve at the origin, or the gradient of the line itself if it was linear, was measured and taken to be the initial rate of hydrogenation.

4.2 Determination of the reaction orders.

To determine the order with respect to one of the reactants, the initial pressure of that reactant was varied and the inital pressure of the other reactant kept constant in a series of experiments at constant temperature. By this method, orders in the hydrocarbon and in hydrogen could both be determined.

During the kinetic studies it was observed that the catalyst activity decreased slightly from reaction to reaction. To minimise this variation it was necessary to standardise carefully conditions between reactions. Slight variations were then corrected by adopting a "standard run" technique in which the activity was recorded by carrying out alternate reactions with a standard mixture comprising 50 mm. butadiene and 100 mm. deuterium.

By this means, a plot could be obtained of the change of "standard" activity with reaction number, and hence by interpolation the rate r_{sn} of a hypothetical standard reaction number n could be estimated. The measured rate r_n of reaction n was converted to the corrected rate R_n by multiplying by the activity correction factor f, where $f = \frac{R_0}{r_{sn}}$, R_0 being the standard rate for the series, and generally equal to the measured rate of the first (standard) reaction of the series. Thus $R_n = \frac{R_0}{r_{sn}} \cdot r_n$.

4.3 Determination of activation energies.

Initial rates were measured as a function of temperature in a series of experiments in which the same reactant pressure ratio was used. The relationship between reaction rates and temperature is expressed by the Arrhenius equation,

$$\text{rate} = Ae^{-Ea/RT}$$

and thus by plotting $\log_{10}$ (initial rate) against the reciprocal of the absolute temperature the activation energy could be calculated since the gradient of the line is equal to $^{Ea}/2.303R$ (where Ea is the activation energy and R = 1.986 cals/mol/deg.). As with the determination of reaction orders, a standard run technique was adopted, the standard temperature being 200°C.

4.4 The interpretation of gas chromatography traces.

The area under a peak in the chromatography traces was found to be proportional to the partial pressure being termed the sensitivity coefficient for that gas. The columns were calibrated using samples of a standard mixture of all the gases to be encountered in the reaction analyses; a high degree of reproducibility was achieved, and the respective sensitivity coefficients were determined as the mean ratio obtained for each gas. A calibration check was carried out at regular intervals to allow for any changes with usage. The partial pressure of each reaction product was calculated and hence the distribution as a percentage of the total was obtained. The distribution of each butene was also expressed as a percentage of the total butene pressure.

4.5 The interpretation of mass spectra.

At a beam voltage of 12.0ev. each of the hydrocarbons undergo both ionisation and fragmentation. The parent ion was always the most abundant, while the fragments were denoted by f-values (fractions relative to parent ion intensity equal to unity). With butene, for example, the relevant species are:

$C_4H_8^+$	$C_4H_7^+$	$C_4H_6^+$
1	f_1	f_2

It is therefore apparent that in calculating the deutero-butene distribution allowance must be made for the fragments. It was assumed that the fragmentation pattern of a deuterated butene is the same as for the light butene. A set of simultaneous equations may therefore be derived to enable the true intensity of each deutero-butene parent ion to be calculated. The ion current of a given mass is produced by (i) the parent ion of the same mass, and (ii) fragments from species of higher mass. The latter contribution is dependent upon (a) the f-values, which are determined by experiment, and (b) a statistical factor to account for the probability of the formation of the given species from each ion of higher mass, assuming no preferential splitting of C-H or C-D bonds. The intensities of each parent ion after correction for fragmentation are thus calculated. If the scheme is valid, it is apparent that the corrected intensities of the first and second fragments of the d_o-butene should each be zero. A check on this showed they were generally less than 2% of the highest intensity, which is acceptable within experimental error. The full equations used in the analysis of each hydrocarbon are given in Appendix A.

The parent ion intensities obtained from these equations were then corrected for the C^{13} content of each hydrocarbon by subtracting 4.4% of the intensity of the d_o-species from that of the d_1-species, then subtracting 4.4% of the C^{13}-corrected d_1-intensity from that of the d_2-species, and so on.

The deuterium distributions were calculated by expressing each of the final corrected intensities as a percentage of the total. The mean number of deuterium atoms contained in the molecule, known as the deuterium number, was calculated from the expression

$$D.N = \sum_{i=1}^{n} id_i$$

where d_i is the fractional abundance of the species containing i deuterium atoms.

By this method the mass spectrum of, say, a butene sample was given as a series of species d_0-, d_1- ....d_8-butene. Burwell (123) has pointed out that, for a consideration of the mechanisms of catalytic reactions, the quantities of fundamental importance are not the fractions of the sample which contain 0,1,2 ....n deuterium atoms, but the fractions of the sample which contain 0,1,2......n 'hydrogen' positions which have equilibrated with the chemisorbed protium and deuterium atoms. These fractions are denoted as N_0, N_1, N_2 ....N_n and a whole series of such numbers is called an "N-profile". Burwell (123) has described a method for calculating the N-profile which requires that trial values be assigned to N_0,N_1,N_2 ....N_n and to the effective ratio (D(ads):H(ads)) (denoted a:b). A calculated distribution in the given hydrocarbon can then be derived and compared with the observed mass spectrum. The effective hydrogen:deuterium ratio on the surface is determined when unique N-profiles are obtained.

The analysis of the hydrogen content of the residual deuterium was carried out at 70ev. The ion current attributable to H_2^+ was corrected for D_2^+ fragmentation and along with D_2^+ and HD^+ used to calculate the atom per cent deuterium, assuming the ionisation cross-sections were the same. Under these conditions, the hydrocarbons present in the sample gave no interference and thus the isotopic purity of the 'deuterium' after reaction could be determined from the spectra of the mixtures. The deuterium number of the sample was simply obtained by multiplying the atom per cent deuterium by two; the hydrogen number was given by

$$H.N. = 2 - D.N.$$

CHAPTER 5

PHYSICAL CHARACTERISATION OF THE GOLD CATALYSTS.

5.1 Ultra violet spectroscopy.

A series of experiments were carried out in order to discover the cause of the strong pink or purple colouration exhibited by the gold catalysts after reduction at 250°C. The spectrometer used was a Unicam SP 800 B ultraviolet spectrophotometer together with a pair of Spectrosil Precision Cells for use in the far ultraviolet spectral range. The reference cell contained distilled water.

A spectrum of gold chloride ($AuCl_3 3H_2O$), yellow in a distilled water solution, was recorded in the range 190-850 millimicrons. Two absorption bands were observed; one very intense band at 215 and a second at 292 millimicrons which was considerably weaker (Fig. 5.1).

A sample of $Au/\gamma-Al_2O_3$ catalyst which had been reduced for 12 hours at 265°C was boiled in distilled water for 30 minutes, the mixture was centrifuged and the spectrum of the gold solution recorded. It can be seen from Fig. 5.2 that no bands are observed below 500 but at 530 millimicrons a weak band is observed.

Particle size distributions obtained from electron micrographs (section 5.2) indicated that the diameter of the metal crystallites was in the range 200-300 Å. This observation, together with the pink colour of the reduced catalysts, suggested the presence of colloidal gold. In order to test this postulate colloidal gold was prepared by dissolving

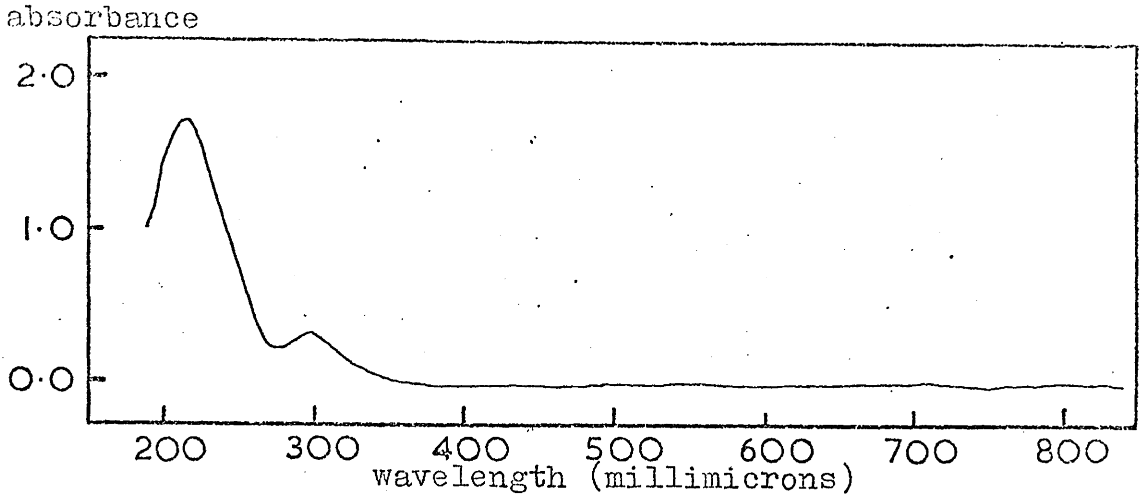


Fig.5.1. The ultra-violet absorption spectrum of gold chloride solution.

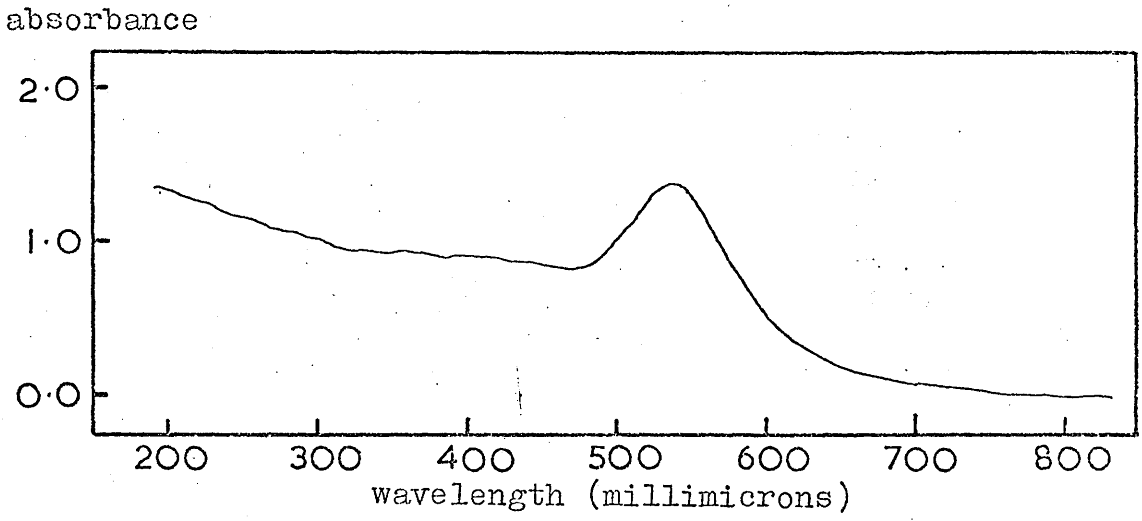


Fig.5.2. The ultra-violet absorption spectrum of the gold solution extracted from a reduced catalyst.

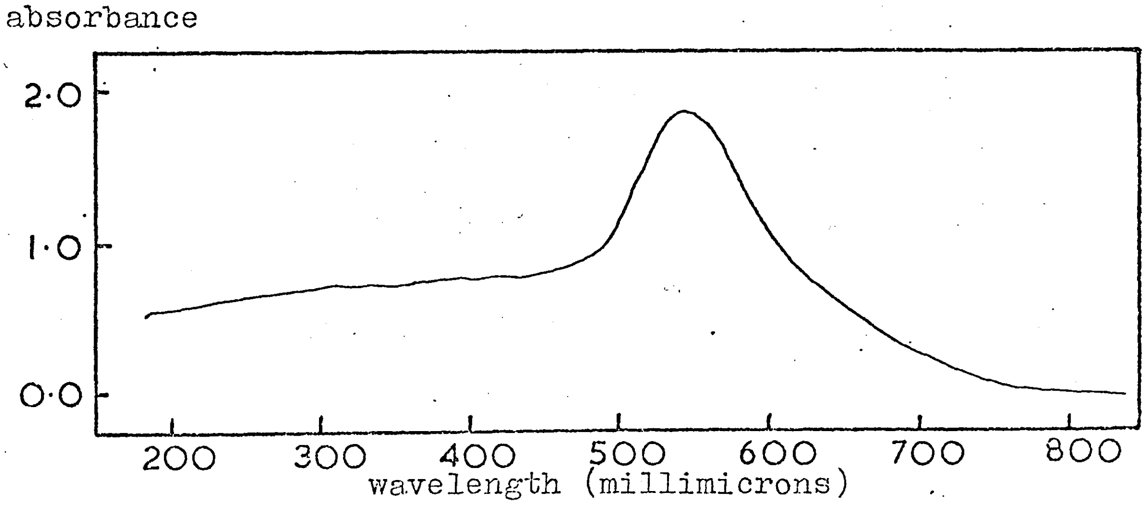


Fig.5.3. The ultra-violet absorption spectrum of a colloidal gold solution.

1ml. of gold chloride in 200 ml. of distilled water and the gold precipitated with formaldehyde solution. A small amount of sodium carbonate was used to stabilise the solution. This was centrifuged and the resulting spectrum of the solution corresponded to that of the reduced metal in the catalyst (Fig.5.3).

It is therefore concluded that the gold in the catalyst is present as colloidal particles. This is in agreement with the results obtained from a study of the oxidation state of the gold by the electron-spin resonance technique. The spectra indicated the absence of bands corresponding to spinfree electrons.

5.2 Electron microscopy.

The supported metal catalysts were prepared for examination by two methods : (a) samples were mixed with distilled cyclohexane in a test tube and dispersed in a 80 K cycle/sec. ultrasonic bath (b) samples were mixed with a few drops of araldite resin and placed in the bottom of an embedding capsule. The sample was then centrifuged to compact the sample in the tip, topped up with resin and placed in an oven at 60 to 80°C for 12 hours. When the capsule was removed from the oven it was allowed to cool and then cut away leaving the sample located in the tip. Thin sections of about 300Å were cut in an L.K.B. ultra-microtome, using a glass knife.

Catalyst samples were examined using a Siemens Elmiscope 1 Electron Microscope at 80 KV. with double condenser illumination. Particle size distributions (Fig. 5.4) were obtained from the micrographs. The results are listed in Table 5.1.
Sections of the micrographs are shown in Figs. 5.5 - 5.9.

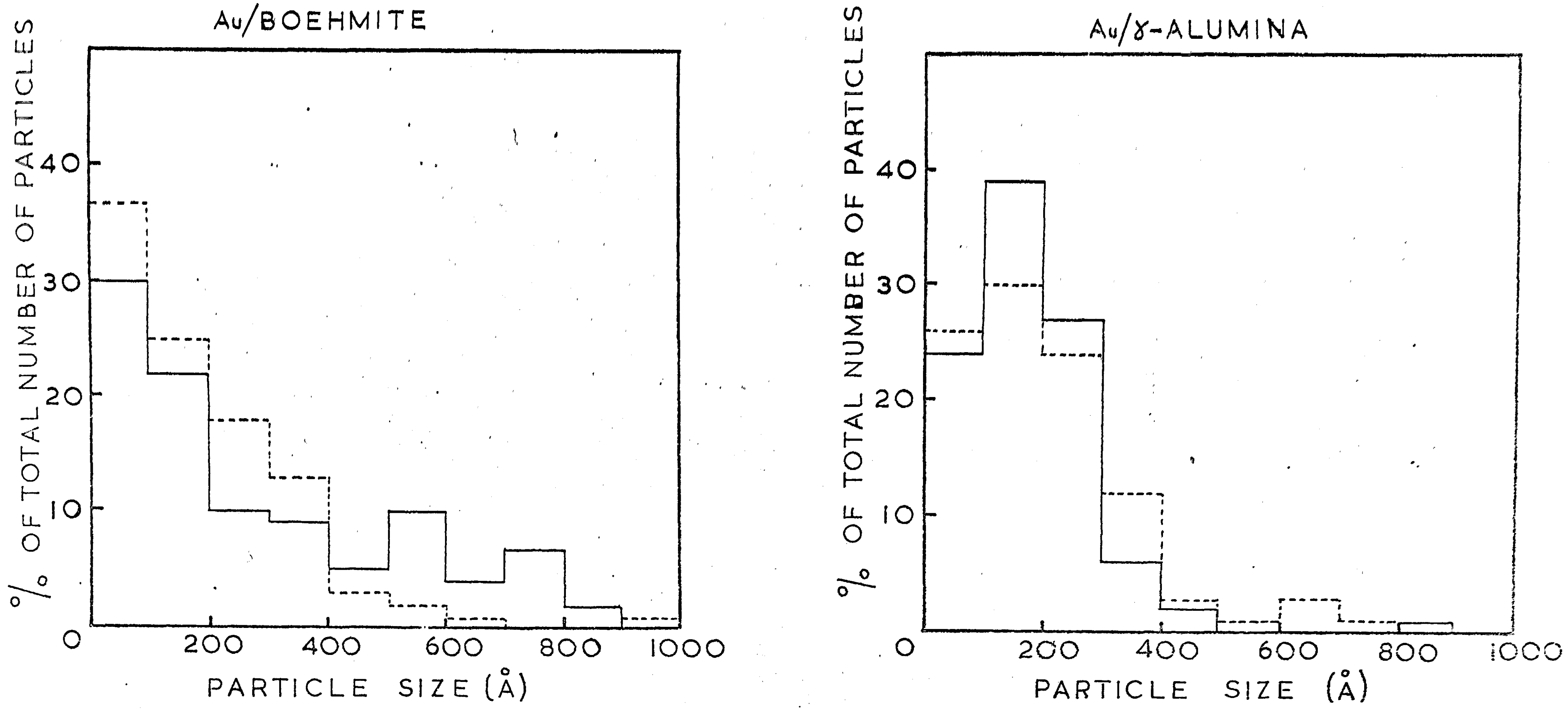


FIG.5.4. PARTICLE SIZE DISTRIBUTIONS.

LEGEND : — ULTRASONICS ; ---THIN SECTION .

TABLE 5.1

Metal particle size distribution in gold supported catalysts.

Au/Boehmite : ultrasonics Average diameter = 200 Å ; ~ 2% particles > 500 Å ; largest particle ~ 1100 Å

: sections Average diameter = 240 Å ~5% particles > 500 Å; largest particle ~ 750 Å

Au/γ-Al_2O_3 : ultrasonics Average diameter = 320 Å ; ~ 5% particles > 1000 Å ; largest particle ~ 4000 Å

: sections Average diameter = 220 Å ; no particles > 1000 Å

5.3 X-ray diffraction.

X-ray specimens were prepared by mixing samples with "Durofix" to make a thin "rod" of material. This was mounted in a Derbye-Scherrer camera and exposed to copper K_α radiation of wavelength 1.5418 Å. The exposure was through a nickel filter for approximately 6 hours and the tube conditions were 35 KV. and 15 mA. The calculated d-spacings for γ-alumina treated with sodium acetate, pure γ-alumina and boehmite are listed in Table 5.2 along with the theoretical values for γ-alumina and boehmite. The X-ray diffraction photographs are shown in Fig 5.10.

TABLE 5.2

The calculated and theoretical d-spacings.

		boehmite		γ-alumina
Specimen 1	Specimen 2	(theoretical)	Specimen 3	(theoretical)
6.237	6.237	6.110	4.520	4.550
3.165	3.165	3.160	2.789	2.782
2.338	2.334	2.347	2.430	2.387
1.981	1.981	1.983	2.280	2.283
1.852	1.852	1.856	1.981	1.977
1.766	1.764	1.771	1.395	1.398
1.661	1.664	1.662		
1.533	1.455	1.528		
1.455	1.433	1.454		
1.431	1.310	1.435		
1.386		1.384		
1.251		1.223		
1.135		1.135		

Specimen 1. Sodium acetate treated γ-alumina.

Specimen 2. Pure boehmite.

Specimen 3. Pure γ-alumina.

Fig. 5.5 Au/γ-alumina x 80,000 ; ultrasonics

Fig. 5.6 Au/γ-alumina x 80,000 ; thin section

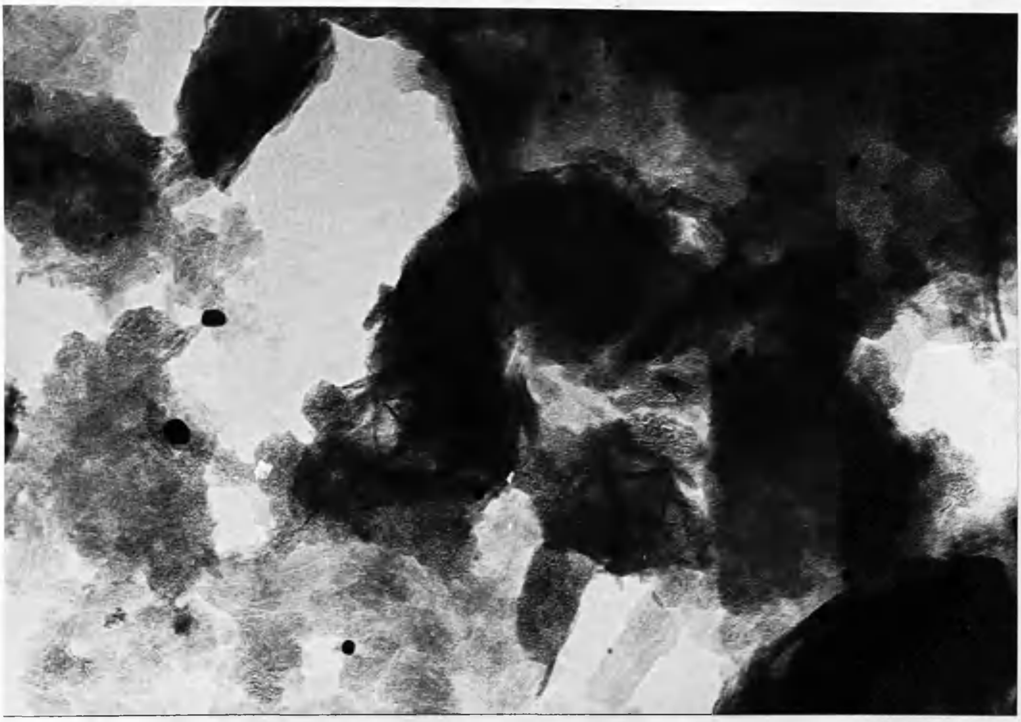


Fig. 5.7 Au/γ-alumina treated with sodium acetate × 80,000 ; ultrasonics

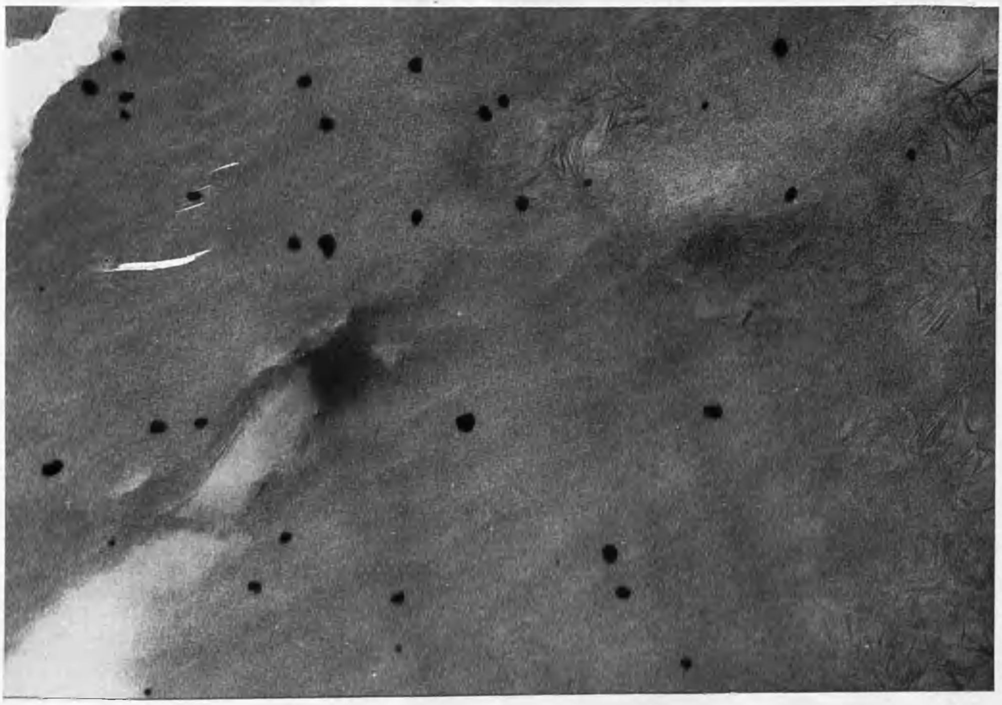


Fig. 5.8 Au/γ-alumina treated with sodium acetate × 80,000 ; thin section

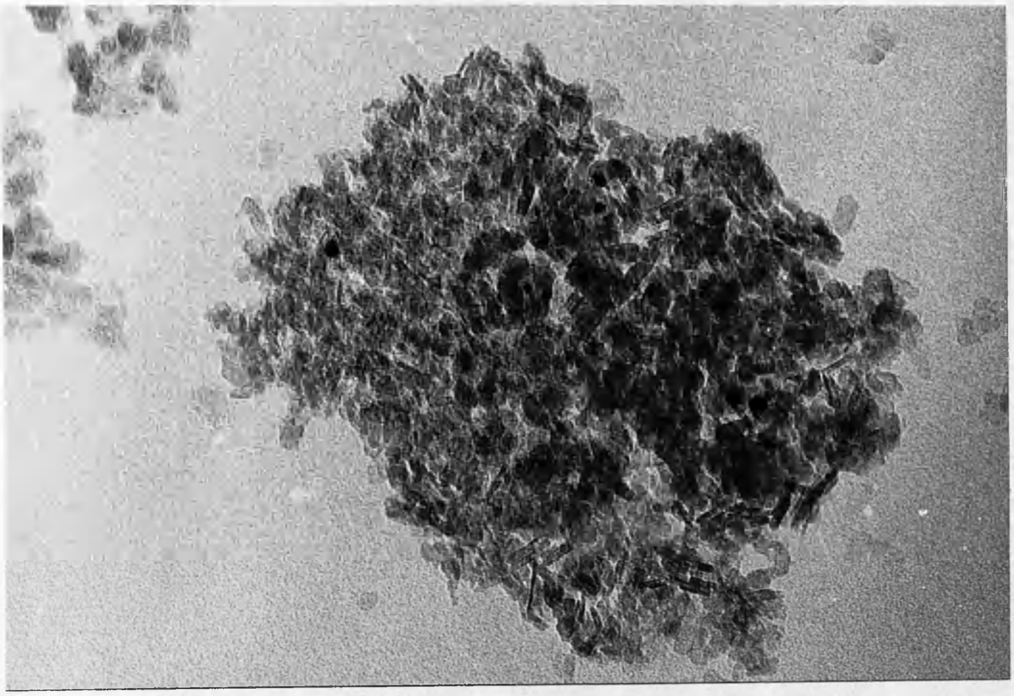


Fig 5.9 Au/Boehmite × 160,000 ; ultrasonics

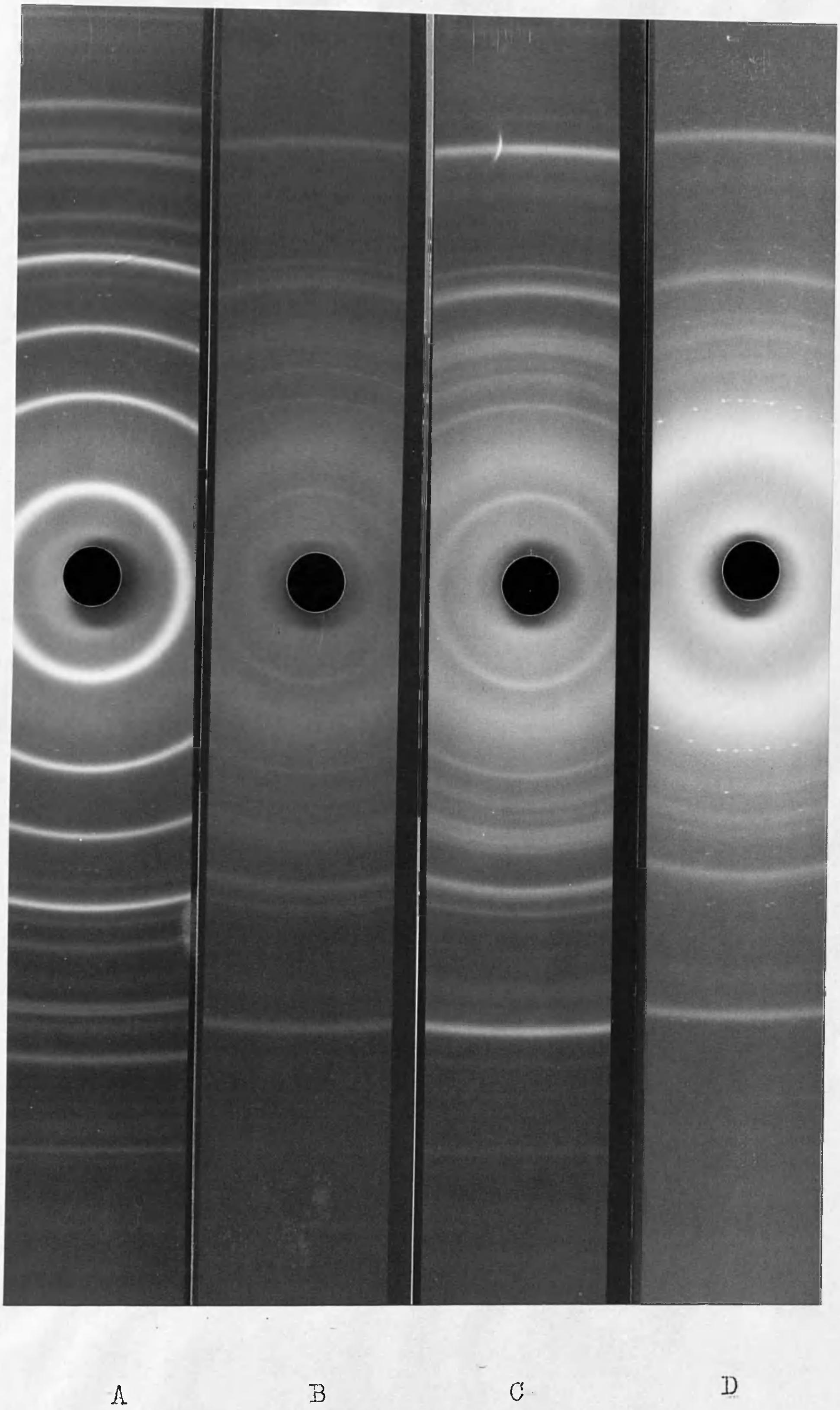


Fig. 5.10 X-ray diffraction photographs.

A. Boehmite

B. γ-alumina treated with sodium hydroxide

C. γ-alumina treated with sodium acetate

D. γ-alumina

CHAPTER 6

REACTIONS OF BUTA-1,3-DIENE WITH DEUTERIUM OVER ALUMINA-SUPPORTED GOLD.

6.1 Introduction.

The reaction of buta-1,3-diene, from henceforth referred to as butadiene, with deuterium over Au/ γ-Al_2O_3 was studied at temperatures between 200 and 260°C using samples of catalyst weighing 0.75g. A different sample was used to study the series of reactions A,B,C,D and E. This was necessary as the catalyst decreased in activity with each succeeding run, until eventually becoming totally inactive. Storage under a hydrogen pressure of 200mm. at 250°C did not reactivate the catalyst. Thus, in investigations of initial rates, the "standard reaction" technique was adopted and the activity corrected as described in section 4.2. The use of deuterium instead of hydrogen was found to make no difference to the activity of the catalyst or the initial rates.

The dominant feature to emerge from the product analysis is the complete selectivity of the catalyst for butene formation. This allowed the reaction to be investigated without the further complication of butene hydrogenation.

A typical pressure fall against time curve is shown in Fig. 6.1, along with plots to test for first and second order. The curve shows a continuous decrease in rate.

6.2 The dependence of the butene distribution upon conversion.

Two series of reactions, A and B, were carried out at

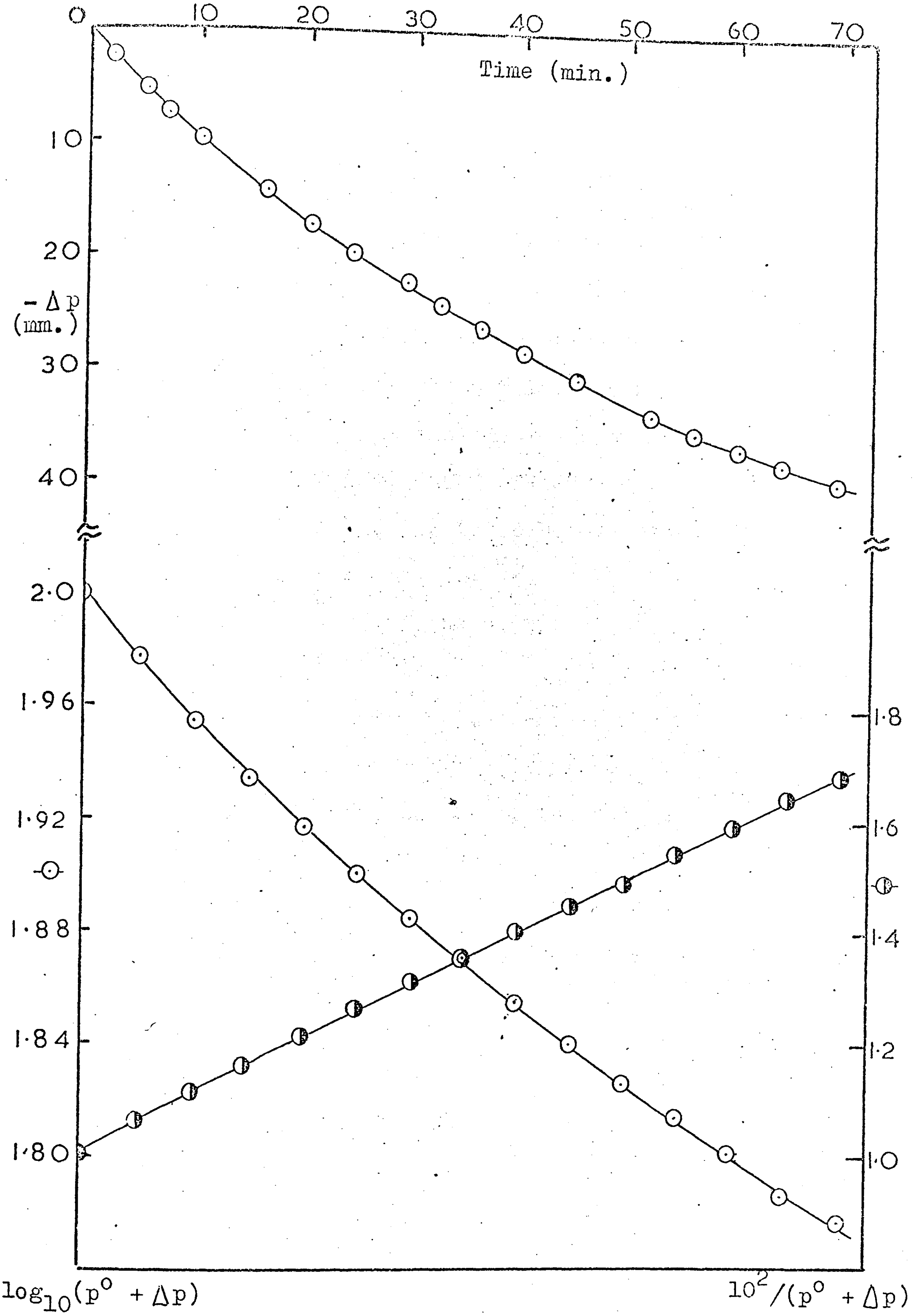


Fig.6.1. A typical pressure fall against time curve for the reaction of 50 mm. buta-1,3-diene with 100 mm. deuterium at 200°C over Au/γ-alumina. Also shown are the plots to test for first and second order.

$200^{\circ}C$ using 50mm. of butadiene and 100mm. deuterium. The principal reason for carrying out two series of reactions was that samples of catalyst from the same batch exhibited remarkably different activities. The analysis figures and the time (t) in minutes at which the products were extracted for analysis, are shown in Tables 6.1 and 6.2. The terms buta-1,3-diene, but-1-ene, trans-but-2-ene and cis-but-2-ene are abbreviated to 1-3 BUT, 1-BUT, TRANS and CIS respectively for use in all tables, and the trans-but-2-ene: cis-but-2-ene ratio, where given, is denoted by $^{T}/_{C}$. The conversion is expressed as a percentage of the number of moles of hydrogen taken up per mole of butadiene. Thus, for complete reaction to any distribution of butenes, the conversion is 100%. The results are illustrated graphically in Figs. 6.2 and 6.3, with the equilibrium distribution of the butenes at the right hand side of the plot.

It is interesting to note that the two catalysts, although from the same batch, showed remarkably different activity. Reaction A/1 to 64% conversion took 60 minutes whereas reaction B/1 to 68% conversion lasted only 18 minutes. This difference in activity, however, was not reflected in the distribution of products. The decrease in activity was quite markable; for example, reaction A/1 to 64% conversion lasted for 60 minutes whereas reaction A/4 to 67% conversion took 114 minutes. The variation of initial rate of reaction with reaction number for series A is shown in Fig. 6.4.

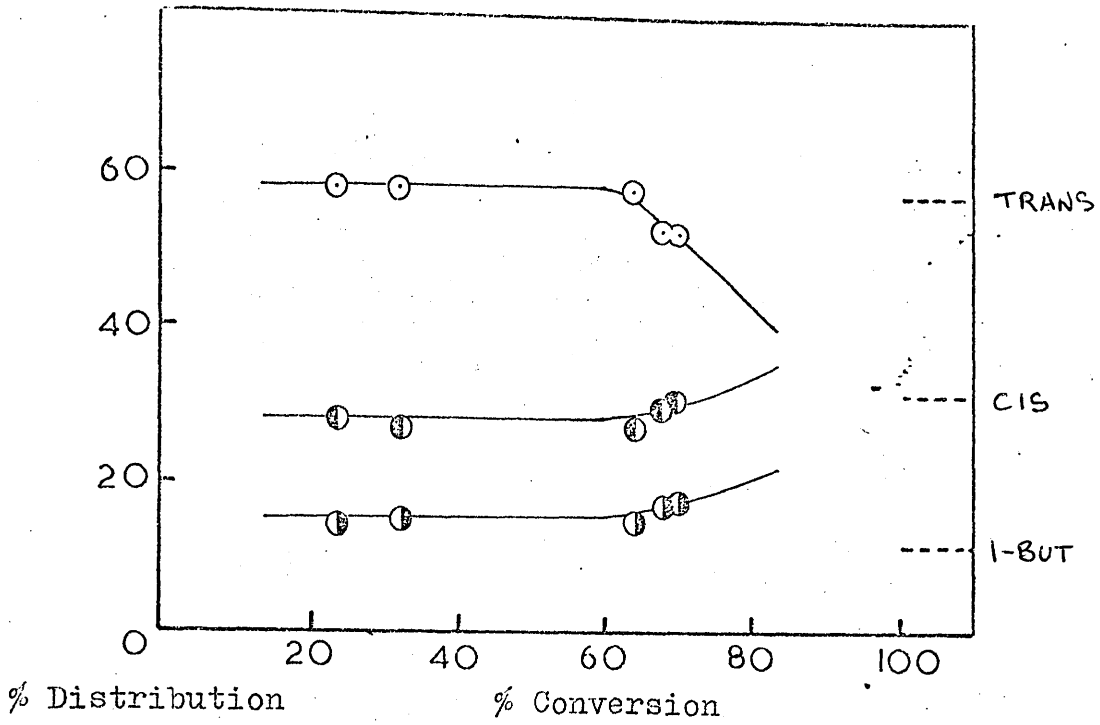


Fig. 6.2. The variation of butene distribution with increasing conversion (Series A).

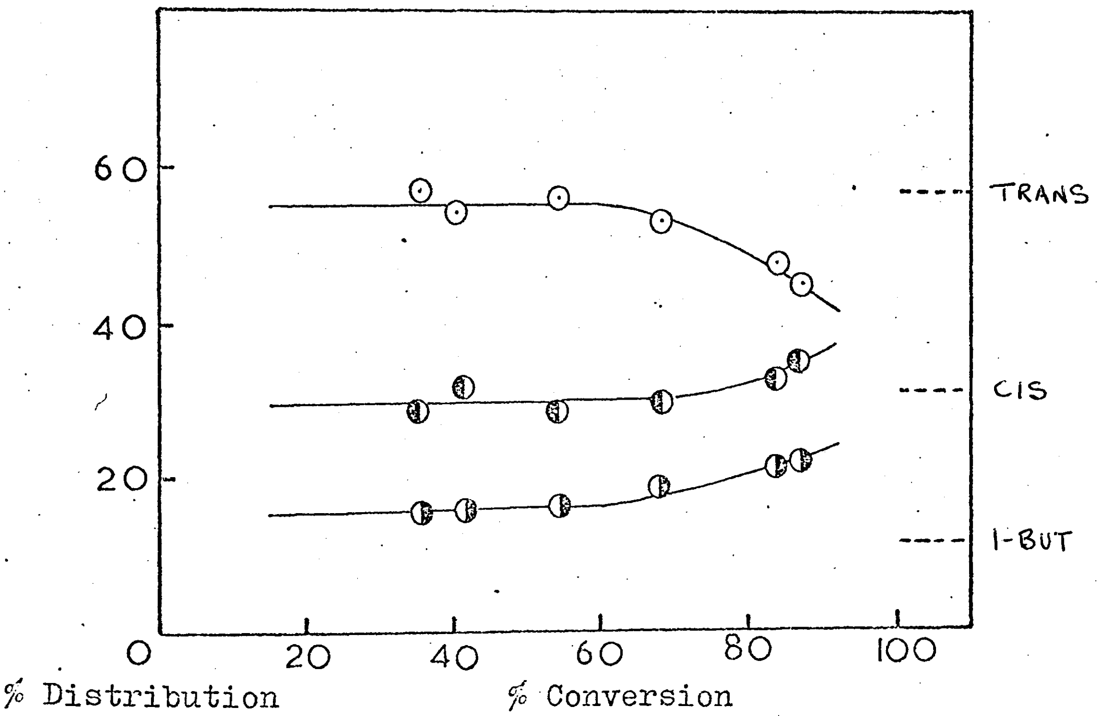


Fig. 6.3. The variation of butene distribution with increasing conversion over Au/γ-alumina at 200°C (Series B). Legend to Figs. 6.2 and 6.3 : -⊙- but-1-ene ; -◑- trans-but-2-ene ; -◐- cis-but-2-ene ; Broken lines show thermodynamic equilibrium values.

TABLE 6.1

Variation of the butene distribution with conversion (Series A).

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm. ; Tp. = 200°C.

Reaction	% Conversion	Butene Distribution			t(min.)
		1-BUT	TRANS	CIS	
A/3	23.8	58.3	14.2	27.5	34
A/5	32.0	57.8	15.3	26.9	65
A/1	64.2	57.9	15.1	27.0	60
A/4	68.6	52.8	17.3	29.9	114
A/2	69.9	51.7	17.9	30.4	100
A/6	100	11.4	57.3	31.3	1080

TABLE 6.2

Variation of the butene distribution with conversion (Series B).

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm. ; Tp. = 200°C.

Reaction	% Conversion	Butene Distribution			t(min.)
		1-BUT	TRANS	CIS	
B/6	35.4	57.1	15.1	27.8	11
B/4	40.9	53.7	15.1	31.2	16
B/3	53.9	56.4	15.9	27.7	22
B/1	68.0	52.9	18.1	29.0	18
B/7	84.4	46.7	20.9	32.4	55
B/5	87.2	44.3	21.6	34.1	50

The butene distribution, initially independent of conversion, shows a but-1-ene:but-2-ene ratio of a little greater than 1:1 and a trans-but-2-ene: cis-but-2-ene ratio of ~ 1:2. At about 65% conversion the proportion of but-1-ene becomes lower and there is a corresponding increase in the trans-but-2-ene and cis-but-2-ene percentages. This can be attributed to isomerisation; reaction A/6 left over the catalyst for 18 hours isomerised to thermodynamic equilibrium proportions. Only a trace quantity of n-butane was observed in the product analysis.

In series B, reaction B/2 was lost during separation and reaction B/7 was carried out the next day after the catalyst had been stored in 100mm. deuterium for 12 hours at 250°C. The catalyst however did not exhibit enhanced activity.

6.3 The order with respect to deuterium and the dependence of the butene distribution upon initial deuterium pressure.

The study of the order with respect to deuterium was carried out at 200°C and the results are shown in Table 6.3. The initial rate in this and all subsequent tables has been corrected using the "standard reaction" technique and is denoted by R_i. All reaction rates are quoted in units of $mm.min^{-1}$.

TABLE 6.3

Variation of initial rate with increasing deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm. ; Temp. = 200 °C

Initial deuterium pressure (mm.)	25	50	100	150	200
R_i	0.22	0.35	0.50	0.64	0.84

It was found that the initial rate was directly proportional to the initial deuterium pressure (Fig. 6.5); hence an order of 1.0 ± 0.1 in deuterium was obtained.

Reactions were extracted and analysed at pressure falls between 11 and 13 mm. and the distribution of butenes is shown in Table 6.4. The standard reactions C/3 and C/6 were not analysed and no figures are available for the reaction with 25 mm. deuterium as the sample was lost in separation. No definite trends are readily discernible and changes in the distribution fall within the limits of experimental error.

6.4 The order with respect to butadiene.

The results of the series at 200°C to determine the dependence on initial butadiene pressure are shown in Table 6.5 and from these it can be seen that increasing the butadiene pressure had no effect upon the initial rate.

TABLE 6.5

Variation of initial rate with increasing butadiene pressure.

Initial deuterium pressure = 200 ± 1.0 mm. ; Temp. = 200°C

Initial butadiene pressure (mm.)	25	50	75	100
R_i	0.95	0.90	0.98	0.86

6.5 Temperature dependence of the butene distribution and the activation energy.

The variation of the butene distribution was studied

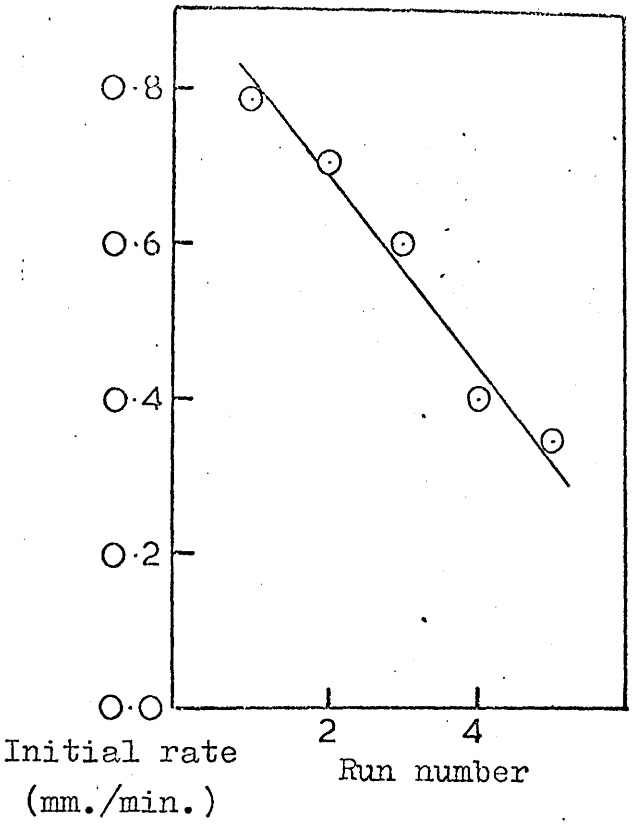
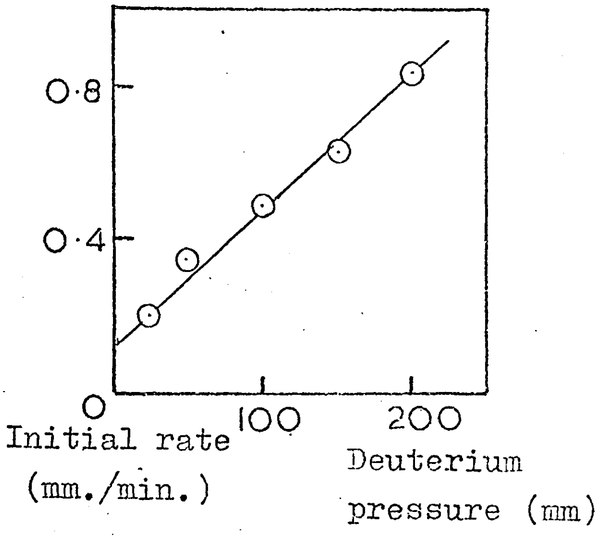


Fig.6.4. Variation of initial rate of reaction with run number over Au/γ-alumina at 200°C.

Fig.6.5. Variation of the initial rate of reaction with increasing deuterium pressure over Au/γ-alumina at 200°C.



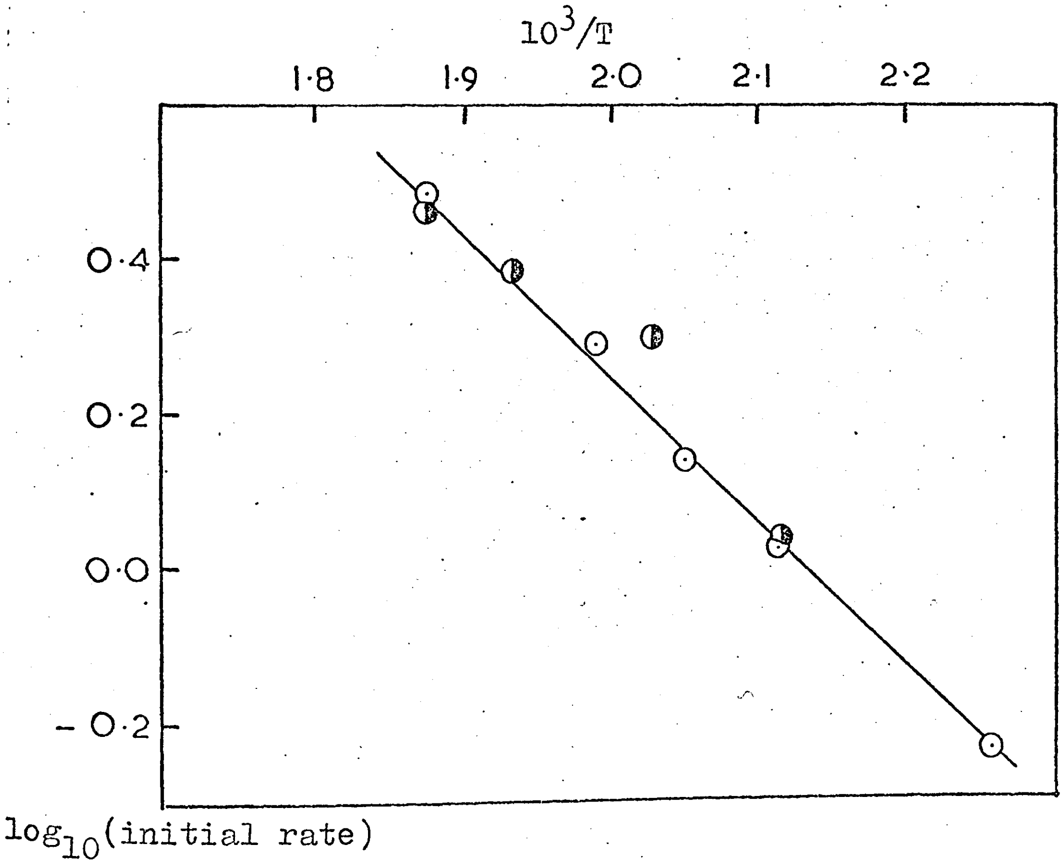


Fig.6.6. Variation of $\log_{10}$(initial rate) with the reciprocal of absolute temperature over Au/γ-alumina (◑) and Au/Boehmite (⊙).

TABLE 6.4

Variation of the butene distribution with initial deuterium pressure

Initial butadiene pressure = 50 ± 0.5 mm. ; Tp. = 200°C; pressure fall at extraction = 12 ± 1.0 mm.

Reaction	P_{D_2}(mm.)	Butene Distribution			T/C	t(min.)
		1-BUT	TRANS	CIS		
C/5	50	59.7	15.2	25.1	0.61	120
C/1	100	51.7	16.0	32.3	0.50	36
C/4	150	61.0	11.8	27.2	0.41	59
C/2	200	56.1	16.8	27.1	0.62	31

TABLE 6.7

Variation of the butene distribution with temperature.

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm. ; pressure fall at extraction = 15 ± 1.0 mm.

Reaction	Tp.(°C)	Butene Distribution			T/C	t(min.)
		1-BUT	TRANS	CIS		
D/2	200	50.5	17.6	31.9	0.55	25
D/1	220	51.3	16.8	31.9	0.53	9.5
D/5	245	59.9	15.2	24.9	0.61	10
D/3	260	51.9	20.6	27.5	0.75	7

over the temperature range 200 to 260°C, using an initial butadiene pressure of 50 mm. and an initial deuterium pressure of 100 mm. The products were extracted for analysis after pressure falls of between 14 and 16 mm. The results are shown in Tables 6.6 and 6.7.

TABLE 6.6

Variation of initial rate with temperature.

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm.

Temp. (°C)	200	220	245	260
R_i	1.01	2.00	2.46	2.90

The plot of $\log_{10}$ (initial rate) against the reciprocal of absolute temperature (Fig. 6.6) produced a straight line from which an activation energy of 8.7 ± 0.5 kcal mol^{-1} was calculated. While there are changes in the butene distribution they are nevertheless very slight. ~~and fall within the experimental precision of the chromatograph~~.

6.6 Dependence of deuterated product distributions upon conversion.

The experimental conditions and distributions of butenes for the two series of reactions are described in section 6.2. Tables 6.8 and 6.9 give the deuterated product distributions for series A and B respectively along with the hydrogen numbers of the residual deuterium.

In series A, the most significant feature of the deuterobutene distribution is the high proportion of d_0- and d_1-species. All reactions except A/1 show that the most abundant

TABLE 6.8

Variation of deuterated product distributions with conversion (Series A).

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm. ; Tp. = 200°C.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
A/3	Conversion = 23.8%				Final H.N. = 0.23					
1-BUT	25.6	44.2	25.7	3.9	0.6	0.1	0.0	0.0	0.0	1.10
TRANS	25.2	46.6	26.4	4.2	1.2	0.4	0.0	0.0	0.0	1.15
CIS	24.8	44.3	24.6	4.7	1.2	0.4	0.0	0.0	0.0	1.14
1-3BUT	82.9	14.7	1.8	0.6	0.0	0.0	0.0	-	-	0.20
A/5	Conversion = 32.0%				Final H.N. = 0.22					
1-BUT	19.5	42.0	31.7	5.9	0.9	0.0	0.0	0.0	0.0	1.27
TRANS	19.2	39.3	33.5	6.4	1.2	0.3	0.0	0.0	0.0	1.32
CIS	19.7	40.7	31.5	6.3	1.7	0.2	0.0	0.0	0.0	1.30
1-3BUT	75.2	20.3	3.5	0.7	0.3	0.0	0.0	-	-	0.30
A/1	Conversion = 64.2%				Final H.N. = 0.27					
1-BUT	42.0	39.6	15.7	2.4	0.4	0.0	0.0	0.0	0.0	0.79
TRANS	39.6	38.5	18.5	3.0	0.5	0.0	0.0	0.0	0.0	0.86
CIS	42.9	38.7	15.1	2.8	0.5	0.0	0.0	0.0	0.0	0.79
1-3BUT	77.1	17.4	3.9	1.1	0.5	0.0	0.0	-	-	0.30
A/4	Conversion = 68.6%				Final H.N. = 0.33					
1-BUT	20.5	41.3	28.6	7.4	1.9	0.3	0.0	0.0	0.0	1.30
TRANS	19.9	38.4	30.5	8.5	2.1	0.5	0.0	0.0	0.0	1.36
CIS	19.7	40.1	28.7	8.2	2.7	0.7	0.0	0.0	0.0	1.36
1-3BUT	64.0	25.7	7.2	2.0	1.0	0.2	0.0	-	-	0.51

TABLE 6.8 (Continued)

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
A/2	Conversion = 69.9%				Final H.N. = 0.44					
1-BUT	31.1	40.9	21.6	5.2	1.1	0.1	0.0	0.0	0.0	1.05
TRANS	29.6	39.9	22.9	6.0	1.3	0.2	0.0	0.0	0.0	1.10
CIS	30.8	39.8	22.4	5.6	1.1	0.3	0.0	0.0	0.0	1.07
1-3BUT	71.2	9.9	7.8	6.9	3.3	0.9	0.0	-	-	0.65

TABLE 6.9

Variation of deuterated product distributions with conversion (Series B).

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
B/6	Conversion = 35.4%				Final H.N. = 0.24					
1-BUT	16.0	39.3	32.8	9.6	2.1	0.3	0.0	0.0	0.0	1.43
TRANS	14.6	38.3	33.2	10.5	2.7	0.8	0.0	0.0	0.0	1.51
CIS	17.5	39.9	30.1	9.9	2.0	0.6	0.0	0.0	0.0	1.41
1-3BUT	62.5	28.0	7.6	1.7	0.3	0.0	0.0	-	-	0.49
B/4	Conversion = 40.9%				Final H.N. = 0.24					
1-BUT	18.9	38.0	31.8	9.3	1.8	0.2	0.0	0.0	0.0	1.38
TRANS	15.3	35.1	32.9	12.7	3.4	0.5	0.1	0.0	0.0	1.56
CIS	21.0	40.0	28.4	8.6	1.7	0.3	0.0	0.0	0.0	1.31
1-3BUT	59.3	30.0	8.6	1.7	0.3	0.0	0.0	-	-	0.54
B/3	Conversion = 53.9%				Final H.N. = 0.26					
1-BUT	25.7	41.1	22.2	8.5	1.9	0.7	0.0	0.0	0.0	1.22
TRANS	22.9	37.6	24.5	10.2	3.5	0.5	0.3	0.0	0.0	1.39
CIS	25.8	35.0	26.3	10.0	2.5	0.4	0.0	0.0	0.0	1.30
1-3BUT	54.9	26.8	13.1	4.5	0.8	0.0	0.0	-	-	0.69

TABLE 6.9 (Continued)

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
B/1	Conversion = 68.0%					Final H.N. = 0.46				
1-BUT	22.9	37.4	26.7	10.1	2.5	0.4	0.0	0.0	0.0	1.33
TRANS	21.8	37.1	27.8	9.9	2.8	0.6	0.0	0.0	0.0	1.36
CIS	24.6	39.0	25.2	8.8	2.2	0.3	0.0	0.0	0.0	1.26
1-3BUT	57.6	27.0	11.3	3.1	0.8	0.2	0.0	-	-	0.63
B/7	Conversion = 84.4%									
1-BUT	5.6	20.9	31.4	24.7	12.3	4.2	0.9	0.1	0.0	2.34
TRANS	5.8	21.8	32.3	23.3	11.5	4.2	1.2	0.0	0.0	2.30
CIS	6.0	23.3	30.4	24.0	11.4	4.0	1.0	0.0	0.0	2.27
1-3BUT	64.7	12.4	11.5	6.9	2.9	1.2	0.5	-	-	0.77
B/5	Conversion = 87.2%					Final H.N. = 0.52				
1-BUT	11.7	31.3	32.1	17.0	6.5	1.5	0.1	0.0	0.0	1.80
TRANS	13.1	31.0	32.6	15.7	6.0	1.4	0.3	0.0	0.0	1.76
CIS	14.2	33.2	31.3	14.1	5.8	1.3	0.1	0.0	0.0	1.68
1-3BUT	87.7	5.1	2.7	2.2	1.5	0.8	0.0	-	-	0.27

deutero-butene is the d_1- species; for reaction A/1, it is the d_0- species which is the most abundant. With the more active catalyst used in series B, the proportion of the d_0- species is lower, the main increase being in the d_2- species. This leads to corresponding samples having butenes with higher deuterium numbers. However, the most abundant deutero-butene is still the d_1- species, except at very high conversion. This unexpectedly low deuterium incorporation indicates that there must be a ready supply of hydrogen atoms present in the system. In none of the butenes obtained in series A did the incorporation of deuterium extend beyond the d_5- species, while in series B there is a small fraction containing up to six deuterium atoms.

Reaction B/7 carried out after storage for 18 hours in deuterium at 250°C yields butenes which have the d_2- species most abundant and an abnormally high deuterium number. The hydrogen content of the residual deuterium was not determined. The reaction is therefore ignored in plots involving deuterium distributions.

Although the deuterium numbers of the three butenes obtained in any one reaction were closely similar, the trans-but-2-ene almost always exhibited a higher deuterium content than did the but-1-ene or cis-but-2-ene. For this reason the small differences are considered to be significant.

Considerable exchange occurred between deuterium and butadiene, the deuterium number of the hydrocarbon increasing with increasing conversion. However, no obvious relationship is apparent. The low deuterium number in the butadiene obtained in reaction B/5 can perhaps be attributed to the remoteness of the catalyst surface from the small pressure of unreacted butadiene and the consequent inability of the hydrocarbon to undergo exchange.

The variation of the hydrogen content of the residual deuterium with conversion is illustrated in Fig. 6.7. The hydrogen number, which appears to be independent of the catalyst activity, remains almost constant until a conversion approximately corresponding to the onset of isomerisation. Thereafter the hydrogen number increases rapidly. The only point which does not lie on the curve is B/5 but this reaction was carried out to somewhat higher conversion.

No regular trend in the deutero-butene distribution with conversion is readily discernible. However, a plot of deuterium number against run number (Fig. 6.8) produces a quite definite pattern; initially at least the deuterium content increases with each succeeding run. The deuterium number used is that of the trans-but-2-ene.

The relationship between the deuterium number and the number of reaction for series B is not quite so clear; the deuterium number of the trans-but-2-ene obtained from reaction B/6 being very much lower than that from B/5. This however could be a result of the extreme differences in conversion - 35% for B/6, 87% for B/5. If the deuterium content is

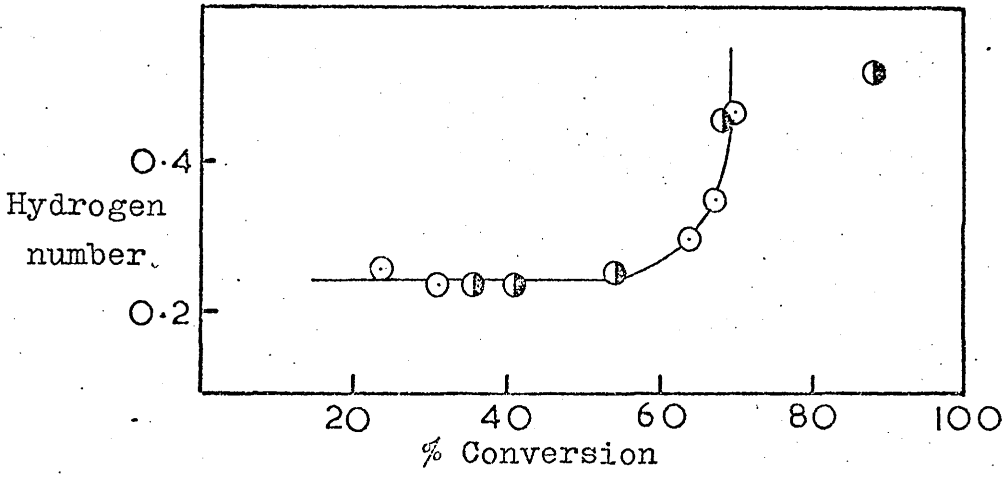


Fig.6.7. The variation of the hydrogen number of the residual deuterium with conversion over Au/γ-alumina at 200°C.

Legend : -⊙- series A ; -◐- series B.

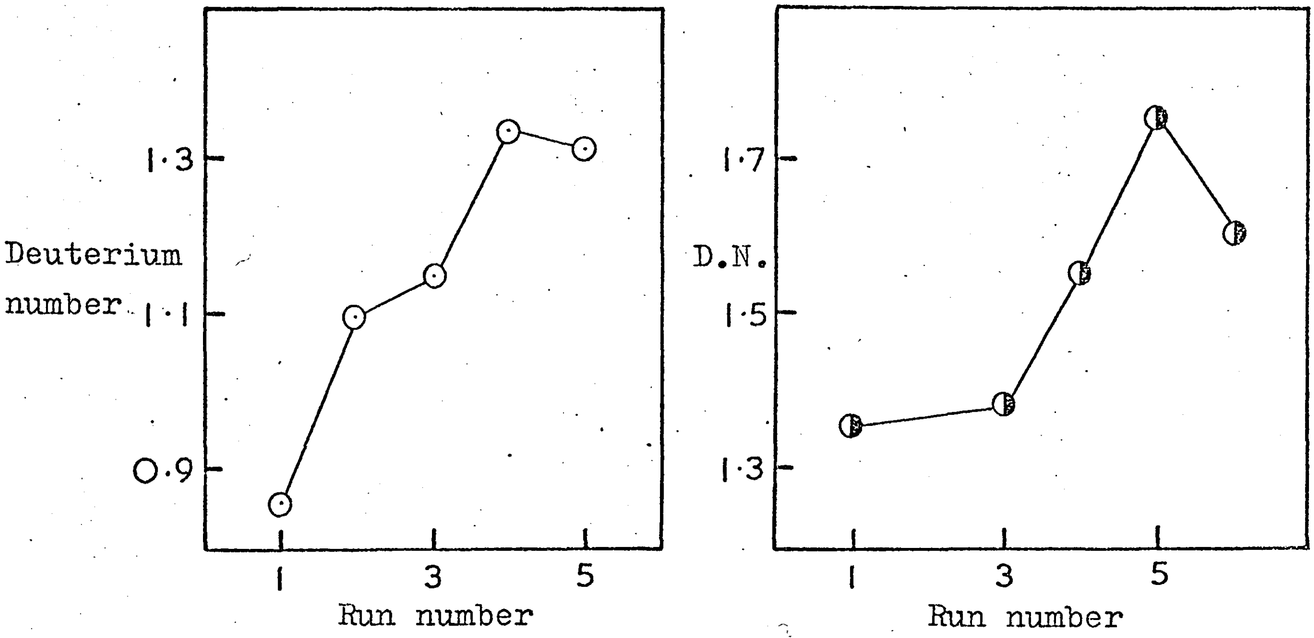


Fig.6.8. The variation of deuterium number of trans-but-2-ene with reaction number over Au/γ-alumina at 200°C.

Legend : -⊙- series A ; -◐- series B.

related to pressure fall, it would be expected that the deuterium numbers of the butenes would increase with increasing conversion because the hydrogen atoms of the butadiene would be able to exchange with deuterium before the hydrogenation reaction (67). If this effect was operating, products from reaction B/5 would be deuterium rich while reaction B/6 would yield butenes with correspondingly lower deuterium numbers than predicted by the simple run number/deuterium number plot.

In order to investigate more fully the effect of the run number on the deutero-butene distributions, a series of reactions was carried out at 200°C to approximately the same pressure fall - 40% conversion. The distribution of butenes is shown in Table 6.10 and the deuterated product distributions are shown in Table 6.11, along with the hydrogen numbers of the residual deuterium.

It is observed that although the distribution of butenes is independent of the run number, the deuterium numbers of the reaction products increase linearly with successive reactions. Fig. 6.9 illustrates the relationship between the deuterium number of a) the trans-but-2-ene and b) butadiene and run number. There is a very small but steady increase in the hydrogen content of the residual deuterium from one reaction tothe following (Fig. 6.10).

It is therefore apparent that in all investigations of deuterium distributions the run number effect will have

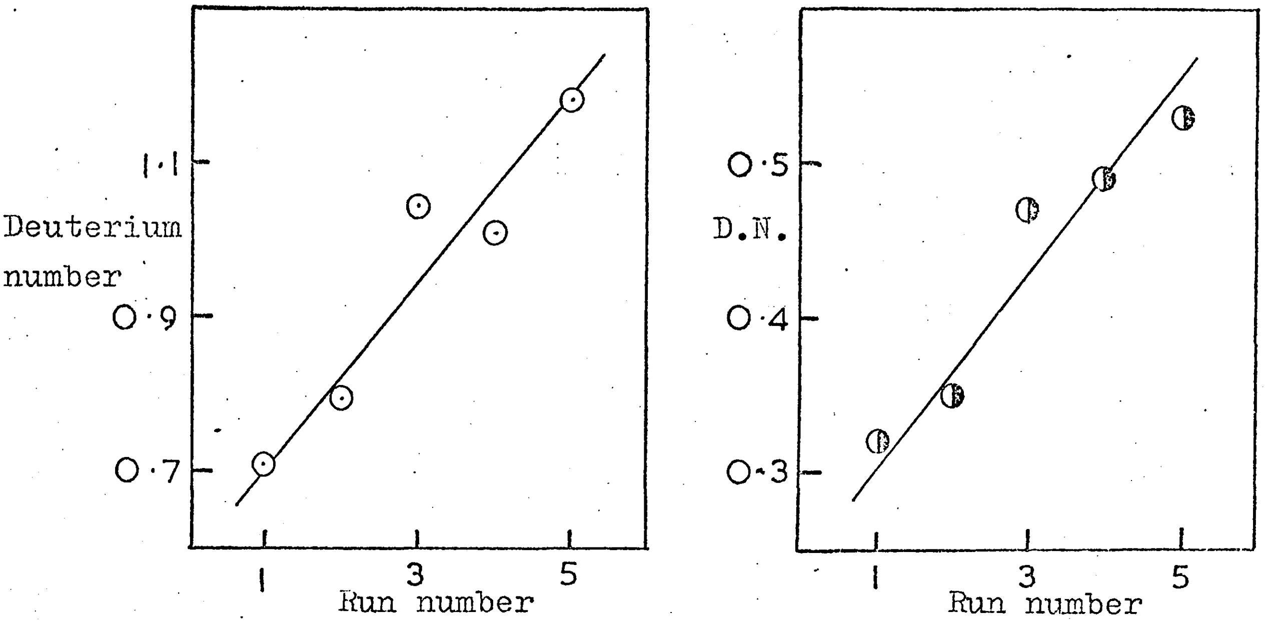


Fig.6.9. The variation of the trans-but-2-ene (-⊙-) and butadiene (-◐-) deuterium number with run number for reactions to constant conversion over Au/γ-alumina at 200°C.

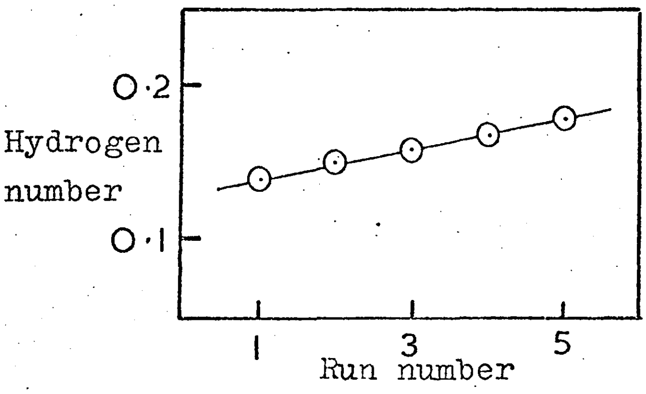


Fig.6.10. The variation of the hydrogen content of the residual deuterium with run number for reactions to constant conversion over Au/γ-alumina at 200°C.

TABLE 6.10

Variation of the butene distribution with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 20 ± 1.0 mm.

Reaction	Butene Distribution			T/C	t(min.)
	1-BUT	TRANS	CIS		
E/1	59.4	15.0	25.6	0.59	26
E/2	57.3	16.0	26.7	0.60	32
E/3	57.0	13.8	29.2	0.47	33
E/4	56.4	16.6	27.0	0.61	37
E/5	58.3	14.1	27.6	0.51	40

TABLE 6.11

Variation of deuterated product distributions with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 20 ± 1.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
E/1	Final H.N. = 0.14									
1-BUT	48.5	37.4	12.0	1.8	0.3	0.0	0.0	0.0	0.0	0.68
TRANS	47.2	37.8	12.6	1.7	0.7	0.0	0.0	0.0	0.0	0.71
CIS	49.9	37.4	10.8	1.5	0.4	0.0	0.0	0.0	0.0	0.65
1-3BUT	74.4	20.3	4.3	0.8	0.2	0.0	0.0	-	-	0.32
E/2	Final H.N. = 0.15									
1-BUT	44.8	37.5	14.9	2.5	0.3	0.0	0.0	0.0	0.0	0.76
TRANS	43.9	37.4	15.4	2.8	0.5	0.0	0.0	0.0	0.0	0.79
CIS	44.1	40.8	13.4	1.2	0.6	0.0	0.0	0.0	0.0	0.73
1-3BUT	70.9	23.7	4.4	0.9	0.0	0.0	0.0	-	-	0.35

TABLE 6.11 (Continued)

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
E/3	Final H.N. = 0.16									
1-BUT	35.4	41.9	17.7	4.3	0.7	0.0	0.0	0.0	0.0	0.92
TRANS	32.5	39.6	20.6	5.8	1.6	0.0	0.0	0.0	0.0	1.04
CIS	35.4	42.1	17.6	4.1	0.7	0.0	0.0	0.0	0.0	0.92
1-3BUT	63.5	28.0	6.7	1.6	0.2	0.0	0.0	-	-	0.47
E/4	Final H.N. = 0.17									
1-BUT	34.6	39.8	19.6	5.1	0.9	0.0	0.0	0.0	0.0	0.98
TRANS	32.9	40.3	20.7	4.9	1.3	0.0	0.0	0.0	0.0	1.01
CIS	34.3	39.5	20.0	5.2	1.0	0.0	0.0	0.0	0.0	0.99
1-3BUT	63.0	27.9	7.0	1.5	0.6	0.0	0.0	-	-	0.49
E/5	Final H.N. = 0.18									
1-BUT	30.1	38.7	23.4	6.4	1.5	0.0	0.0	0.0	0.0	1.10
TRANS	26.4	40.7	23.4	7.9	1.7	0.0	0.0	0.0	0.0	1.18
CIS	28.6	39.8	22.5	7.4	1.6	0.0	0.0	0.0	0.0	1.14
1-3BUT	60.8	28.8	8.1	1.6	0.7	0.0	0.0	-	-	0.53

to be taken into consideration.

6.7 Dependence of deuterated product distributions upon initial deuterium pressure.

The conditions and butene distributions for thisseries of reactions are described in section 6.3. The dependence of the deuterated product distributions upon initial deuterium pressure is shown in Table 6.12. The hydrogen number of the residual deuterium is seen to decrease with increasing deuterium pressure, as does the amount of exchange in the butadiene. The trend with regard to the deuterium content of the butenes is less clear. However, it may be noted that with regard to reactions C/1 and C/2, the deuterium number of the butenes increases with increasing deuterium pressure. Similarly with regard to run numbers C/4 and C/5. It may therefore be assumed that the reverse trend with regard to reactions C/2 and C/4 is a direct result of the run number effect increasing the deuterium content of the butenes obtained in reactions C/4 and C/5.

6.8 Dependence of deuterated product distributions upon temperature.

The analysis results shown in Table 6.13 were obtained from the series of reactions described in section 6.5. It is apparent that consideration ofthe series as two pairs of reactions, D/1 and D/2, and D/3 and D/5 suggests that the deuterium content of the butenes decreases with increasing temperature. The influence of the reaction number may again

TABLE 6.12

Variation of deuterated product distributions with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 12 ± 1.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
C/5	Initial D_2 pressure = 50 ± 0.5 mm. Final H.N. = 0.53									
1-BUT	26.5	40.8	24.9	5.9	1.4	0.4	0.0	0.0	0.0	1.16
TRANS	23.8	39.0	27.5	7.0	1.9	0.6	0.3	0.0	0.0	1.27
CIS	24.8	39.5	25.4	7.5	2.1	0.5	0.2	0.0	0.0	1.25
1-3BUT	69.7	25.2	4.5	0.7	0.0	0.0	0.0	-	-	0.36
C/1	Initial D_2 pressure = 100 ± 0.5 mm. Final H.N. = 0.35									
1-BUT	35.5	41.2	19.3	3.0	0.7	0.3	0.0	0.0	0.0	0.93
TRANS	31.4	37.5	24.0	5.1	1.5	0.5	0.0	0.0	0.0	1.09
CIS	34.9	40.9	19.4	3.7	0.9	0.2	0.0	0.0	0.0	0.96
1-3BUT	78.1	18.8	2.6	0.5	0.0	0.0	0.0	-	-	0.25
C/4	Initial D_2 pressure = 150 ± 1.0 mm. Final H.N. = 0.31									
1-BUT	23.2	40.6	28.1	5.8	1.5	0.5	0.3	0.0	0.0	1.24
TRANS	19.1	36.8	33.2	7.0	2.2	0.8	0.5	0.0	0.0	1.42
CIS	23.3	41.0	27.4	5.9	1.6	0.6	0.3	0.0	0.0	1.24
1-3BUT	81.9	16.0	2.2	0.0	0.0	0.0	0.0	-	-	0.20
C/2	Initial D_2 pressure = 200 ± 1.0 mm. Final H.N. = 0.20									
1-BUT	28.0	38.2	27.4	4.5	1.3	0.5	0.0	0.0	0.0	1.14
TRANS	22.1	37.4	30.7	6.5	2.1	0.8	0.5	0.0	0.0	1.33
CIS	27.2	40.4	24.4	5.4	2.0	0.7	0.0	0.0	0.0	1.16
1-3BUT	82.7	15.1	1.8	0.4	0.0	0.0	0.0	-	-	0.20

TABLE 6.13

Variation of deuterated product distributions with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 15 ± 1.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
D/2	Temperature = 200°C					Final H.N. = 0.18				
1-BUT	28.7	45.1	22.5	3.2	0.6	0.0	0.0	0.0	0.0	1.02
TRANS	27.7	44.1	23.8	4.0	0.5	0.0	0.0	0.0	0.0	1.05
CIS	28.4	45.7	22.2	3.5	0.2	0.0	0.0	0.0	0.0	1.02
1-3BUT	80.4	17.1	2.2	0.2	0.0	0.0	0.0	-	-	0.22
D/1	Temperature = 220°C					Final H.N. = 0.18				
1-BUT	34.8	42.9	19.5	2.6	0.2	0.0	0.0	0.0	0.0	0.91
TRANS	32.9	43.8	20.1	2.9	0.3	0.0	0.0	0.0	0.0	0.94
CIS	34.0	44.9	18.3	2.6	0.3	0.0	0.0	0.0	0.0	0.90
1-3BUT	81.1	16.7	2.0	0.2	0.0	0.0	0.0	-	-	0.21
D/5	Temperature = 245°C					Final H.N. = 0.25				
1-BUT	26.0	43.1	25.1	5.0	0.7	0.2	0.0	0.0	0.0	1.12
TRANS	24.6	42.8	25.9	5.5	0.9	0.3	0.0	0.0	0.0	1.16
CIS	23.8	42.4	26.2	6.1	1.2	0.2	0.1	0.0	0.0	1.19
1-3BUT	75.3	20.6	3.8	0.3	0.0	0.0	0.0	-	-	0.29
D/3	Temperature = 260°C					Final H.N. = 0.28				
1-BUT	33.8	43.3	19.1	3.2	0.5	0.1	0.0	0.0	0.0	0.94
TRANS	33.1	43.2	19.7	3.3	0.7	0.0	0.0	0.0	0.0	0.95
CIS	31.3	44.2	19.6	3.8	0.8	0.3	0.0	0.0	0.0	0.99
1-3BUT	79.7	17.6	2.5	0.1	0.0	0.0	0.0	-	-	0.23

be responsible for the high deuterium numbers of the butenes obtained in reactions D/3 and D/5.

The hydrogen content of the residual deuterium was found to rise with temperature and the exchange of the butadiene to be virtually unaffected.

6.9 The hydrogen exchange reaction in the absence of buta-1,3-diene.

Three successive pressures of 100 mm. deuterium were exposed to the catalyst for one hour at 200°C after pre-treatment in 200 mm. of hydrogen at 250 and 400°C for 12 hours. After the initial reduction, the catalyst vessel was pumped for one hour at the reduction temperature and between additions of deuterium it was pumped for 30 minutes at the temperature of the exchange. The results are shown in Table 6.14. Two series of reactions were carried out on different samples of catalyst at a reduction temperature of 250°C due to the varying activity of the catalyst for the hydrogenation reaction.

TABLE 6.14

The hydrogen exchange reaction in the absence of butadiene.

Initial deuterium pressure = 100 ± 1.0 mm.; Temp. = 200°C

	Hydrogen number		
Reduction Temp. (°C)	Reaction 1	Reaction 2	Reaction 3
250	1.30	0.98	0.68
250	0.65	0.47	0.35
400	0.35	0.29	0.22

Although there was a wide difference in the exchange of corresponding samples in reactions reduced at 200°C, both exhibited a decrease in hydrogen content with succeeding exchange. Reduction and pumping at 400°C resulted in a drop in hydrogen number.

6.10 The mass balance

The absolute amounts of deuterium and hydrogen in the reaction products were calculated from the partial pressure and hydrogen and deuterium numbers of each product. The final totals in units of mm. atoms, were compared with the initial amounts of each in order to obtain the balance of hydrogen and deuterium over the reaction. ~~The calculation for reaction A/1 is shown in detail.~~ The results are shown in Tables 6.15 - 6.19. It can be seen that good mass balance was not obtained for any of the reactions.

TABLE 6.15

Variation of mass balance with conversion (series A).

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C.

Initial hydrogen (mm. atoms) = 305.20

Initial deuterium (mm. atoms) = 194.80

Reaction	% Conversion	Final hydrogen	Final deuterium
A/3	23.8	323.14	176.87
A/5	32.0	319.71	180.29
A/1	64.2	351.57	148.53
A/4	68.6	336.47	163.28
A/2	69.9	351.42	148.39

TABLE 6.16

Variation of mass balance with conversion (series B).

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C.

Initial hydrogen (mm. atoms) = 305.20

Initial deuterium (mm. atoms) = 194.80

Reaction	% Conversion	Final hydrogen	Final deuterium
B/6	35.4	313.89	186.11
B/4	40.9	315.75	184.25
B/3	53.9	322.84	177.16
B/1	68.0	344.10	156.44
B/5	87.2	338.49	161.51

It can be seen that the best mass balance was obtained when the reaction number was high and the conversion was low.

TABLE 6.17

Variation of mass balance with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 12 ± 1.0 mm.

Initial hydrogen (mm. atoms) = 305.20

Initial deuterium (mm. atoms) = 194.80

Reaction	P_{D_2} (mm.)	Final hydrogen	Final deuterium
C/5	50	341.59	158.42
C/1	100	333.59	166.42
C/4	150	328.71	170.49
C/2	200	318.48	181.52

As the deuterium pressure was increased, the mass balance became progressively better.

TABLE 6.18

Variation of mass balance with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 15 ± 1.0 mm.

Initial hydrogen (mm. atoms) = 304.80

Initial deuterium (mm. atoms) = 195.20

Reaction	Temperature (°C)	Final hydrogen	Final deuterium
D/2	200	321.21	178.80
D/1	220	322.82	177.18
D/5	245	322.97	177.04
D/3	260	332.41	167.60

Results show that better mass balance was obtained as the temperature was decreased.

TABLE 6.19

Variation of mass balance with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 20 ± 1.0 mm.

Initial hydrogen (mm. atoms) = 305.40

Initial deuterium (mm. atoms) = 194.60

Reaction	Final hydrogen	Final deuterium
E/1	327.02	172.99
E/2	325.65	174.37
E/3	321.56	178.38
E/4	317.94	182.06
E/5	314.22	185.79

It is found that better mass balance was obtained with each succeeding reaction.

CHAPTER 7

REACTIONS OF BUTA-1,3-DIENE WITH DEUTERIUM OVER BOEHMITE-SUPPORTED GOLD.

7.1 Introduction.

The reaction of buta-1,3-diene with deuterium over Au/Boehmite was studied at temperatures between 170 and 260°C using samples of catalyst weighing 0.5g. As with Au/ γ-Al_2O_3 the catalyst was changed after any one study due to the decrease in activity, and in the investigation of trends dependent on the initial rate the "standard reaction" technique was employed. When hydrogen was used instead of deuterium, no variation in the rate of reaction was noticed.

Gas chromatographic analysis showed that the catalyst was also completely selective for butene formation. A typical pressure fall against time curve is shown in Fig. 7.1, along with the plots to test for first and second order.

7.2 The dependence of the butene distribution upon conversion.

In a series of six reactions at 200°C using 50 mm. of butadiene and 100 mm. of deuterium, the conversion was varied between 27.5% and 88.5% The analysis of the products and the time (t) at which the products were extracted are shown in Table 7.1, the notation for the products being the same as applied in section 6.2. Fig. 7.2 shows the graphical variation of butenes with conversion, with the equilibrium distribution of the butenes at the right hand side of the plot. Using a fresh sample of catalyst reaction F/7 was

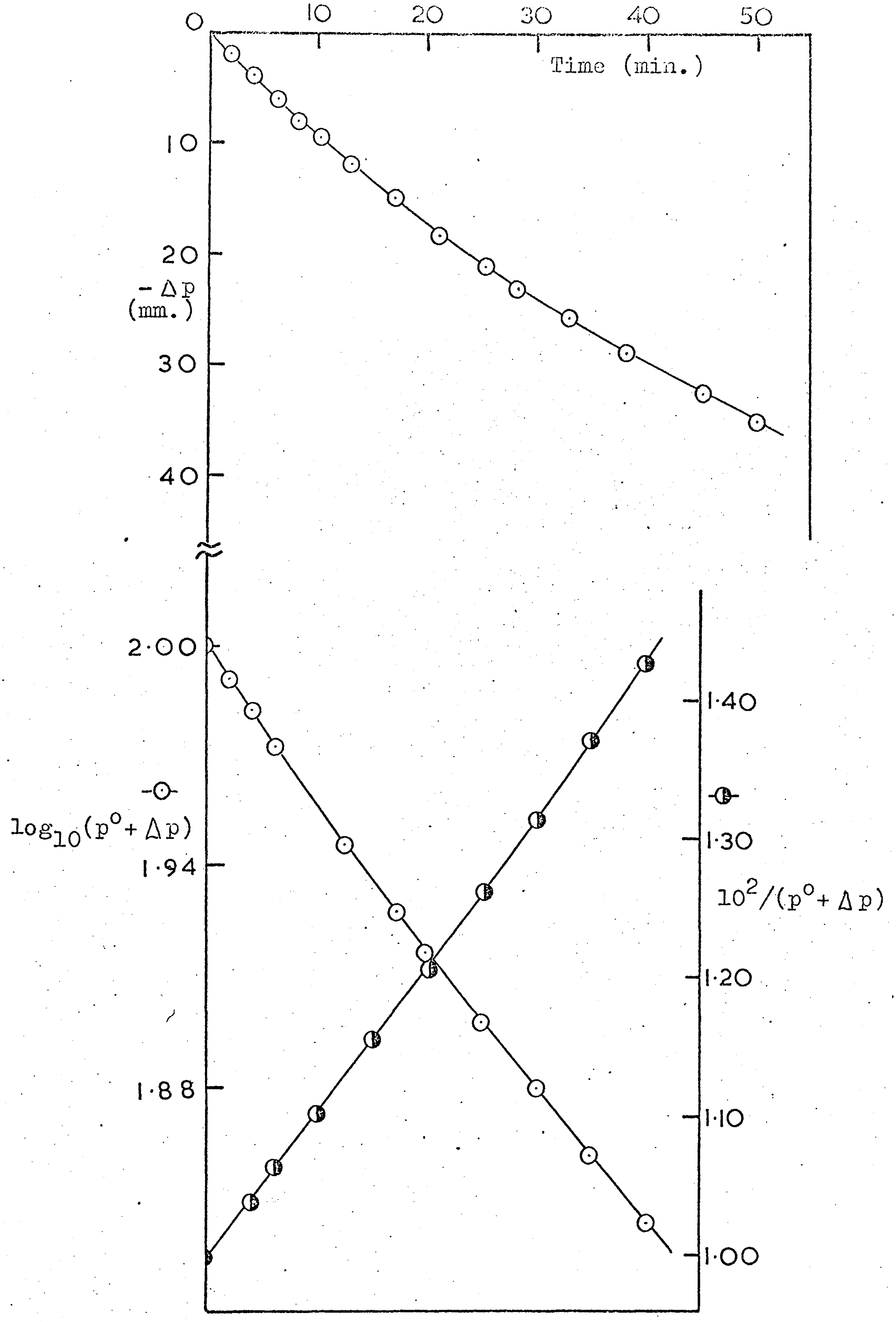


Fig.7.1. A typical pressure fall against time curve for the reaction of 50 mm. of buta-1,3-diene with 100 mm. of deuterium at 200°C over Au/Boehmite. Also shown are the plots to test for first and second order.

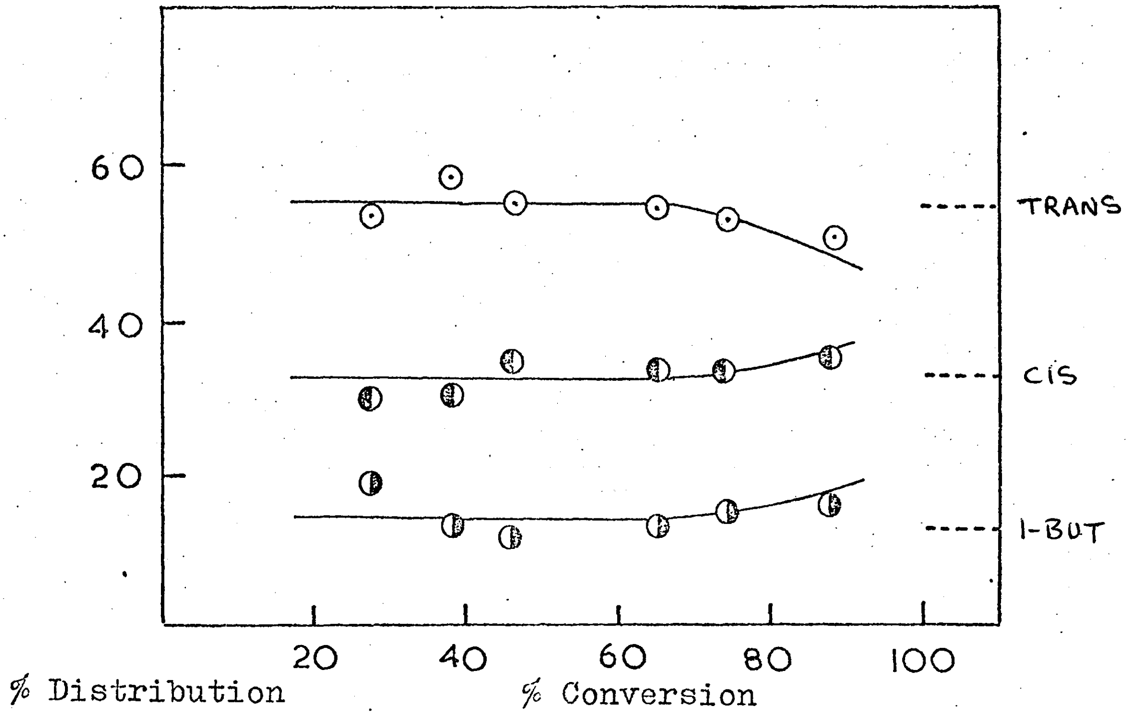


Fig.7.2. The variation of butene distribution with increasing conversion over Au/Boehmite at 200°C.
Legend : -⊙- but-1-ene ; -◑- trans-but-2-ene ; -◐- cis-but-2-ene ; Broken lines show thermodynamic equilibrium values.

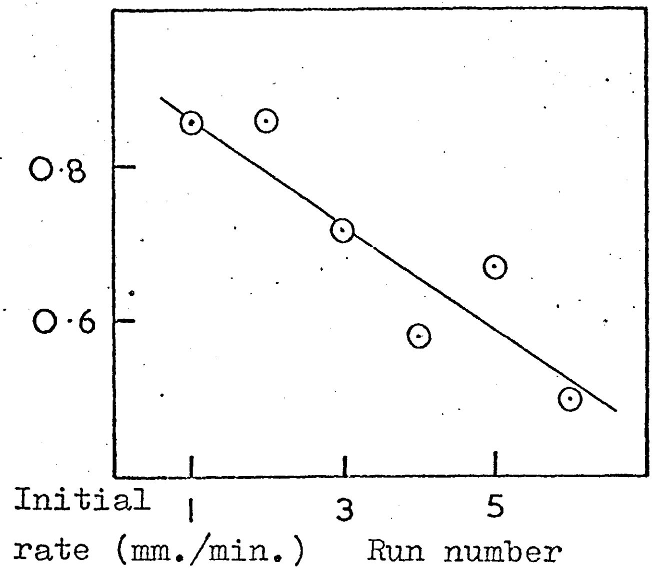


Fig.7.3. The variation of initial rate of reaction with run number over Au/Boehmite at 200°C.

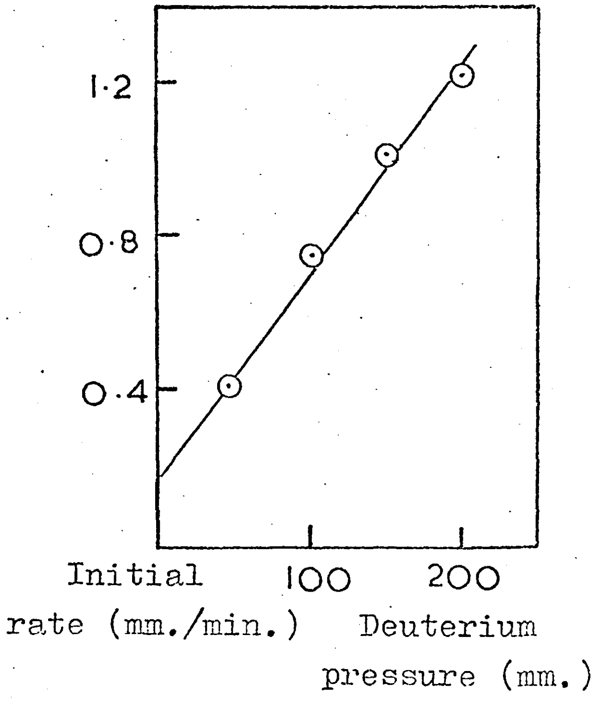


Fig.7.4. Variation of initial rate of reaction with increasing deuterium pressure over Au/Boehmite at 200°C.

TABLE 7.1

Variation of the butene distribution with conversion.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C

Reaction	% Conversion	Butene Distribution			t(min.)
		1-BUT	TRANS	CIS	
F/6	27.5	52.8	18.5	28.7	34
F/5	38.1	58.0	13.1	28.9	43
F/3	45.8	54.5	11.4	34.1	52
F/4	64.7	54.1	12.9	33.0	77
F/2	74.0	52.3	15.0	32.7	64
F/1	88.5	50.5	15.4	34.1	75
F/7	100	12.8	54.7	32.5	1080

left over the catalyst for 18 hours. Complete hydrogenation was achieved and the products isomerised to thermodynamic equilibrium proportions with only a trace yield of n-butane.

The variation of initial rate with number of reaction is shown in Fig. 7.3. Although a linear relationship is not clearly shown, it can be seen that the trend is toward decreasing inital rates with succeeding reactions. This decrease in activity of the catalyst is reflected in the times of reaction; for example reaction F/1 to 89% conversion took 75 minutes while reaction F/4 to 65% conversion lasted 77 minutes.

The butene composition was independent of conversion until a pressure fall of approximately 35 mm. At this conversion isomerisation resulted in enhanced yields of the but-2-ene. The initial ratio of but-1-ene:but-2-ene was a little greater than 1:1 and cis:trans ratio was ~ 2:1, almost identical to the results obtained over Au/γ-Al_2O_3.

7.3 The order with respect to deuterium and the dependence of the butene distribution upon initial deuterium pressure.

The initial rate order with respect to deuterium was determined at 200°C from a series of reactions in which a constant butadiene pressure of 50 mm. was used and the deuterium pressure was varied between 50 and 200 mm. The results are shown in Table 7.2. Activity corrections were applied as described in the previous section and units of R_i

are mm. min^{-1}.

TABLE 7.2

Variation of initial rate with increasing deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm. ; Temp. = 200°C

Initial deuterium pressure (mm.)	50	100	150	200
R_i	0.42	0.75	1.01	1.29

Fig. 7.4 exhibits the linear relationship between the initial rate and pressure, from which an order of 1.0 ± 0.1 in deuterium was derived.

Differences in the product distribution, obtained after extraction at pressure falls between 13 and 15 mm., fall within the limits of the efficiency of the chromatograph and it is therefore concluded that the butene composition was independent of initial deuterium pressure (Table 7.3).

7.4 The order with respect to butadiene.

The initial rate was found to be independent of the initial butadiene pressure. The results are shown in Table 7.4.

TABLE 7.4

Variation of initial rate with increasing butadiene pressure.

Initial deuterium pressure = 200 ± 1.0 mm. ; Temp. = 200°C

Initial butadiene pressure (mm.)	25	50	75	100
R_i	1.16	1.21	1.24	1.16

7.5 Temperature dependence of the butene distribution and the activation energy.

The temperature dependence of the butene distribution was studied over the temperature range 170 to 260°C, using

TABLE 7.3

Variation of the butene distribution with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 14 ± 1.0 mm.

Reaction	P_{D_2} (mm.)	Butene Distribution			T/C	t(min).
		1-BUT	TRANS	CIS		
G/5	50	55.1	12.9	32.0	0.40	58
G/1	100	58.8	14.9	26.3	0.57	24
G/2	150	58.3	14.4	27.3	0.53	22
G/3	200	56.5	11.3	32.2	0.35	20

TABLE 7.6

Variation of the butene distribution with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 14 ± 2.0 mm.

Reaction	Tp.(°C)	Butene Distribution			T/C	t(min.)
		1-BUT	TRANS	CIS		
H/3	170	53.4	15.8	30.8	0.51	69
H/1	200	58.1	14.3	27.6	0.52	16
H/6	215	53.7	11.5	34.8	0.33	24
H/2	230	49.2	17.7	33.1	0.53	9
H/5	260	59.7	15.4	24.9	0.62	7

an initial butadiene pressure of 50 mm. and an initial deuterium pressure of 100 mm. Reactions were extracted at pressure falls between 12 and 16 mm. and analysed. The results are shown in Table 7.5 and 7.6.

TABLE 7.5

Variation of initial rate with temperature.

Initial butadiene pressure = 50 ± 0.5 mm. ; initial deuterium pressure = 100 ± 0.5 mm.

Tp.(°C)	170	200	215	230	260
R_i	0.58	1.08	1.40	1.97	3.07

The Arrhenius plots for the hydrogenation lay on the same straight line as those over Au/γ-Al_2O_3 (Fig. 6.6). The activation energy is thus also 8.7 ± 0.5 kcal mol^{-1}. The spread in butene composition is fairly wide but it is not markedly dependent on temperature.

7.6 Dependence of deuterated product distributions upon conversion.

The reactions correspond to the series described in section 7.2. The distribution of deutero-butenes and deutero-butadienes in the products of the reactions and the hydrogen content of the residual deuterium are shown in Table 7.7.

The dominant feature of the deutero-butene distribution is again the high proportion of d_o- and d_1-species. In products obtained over Au/Boehmite, the d_o-species is most abundant and this leads to butenes with very low deuterium numbers. Multiple exchange occurred as far as the d_4-species. The small but significant differences in the deuterium numbers of the three butenes obtained in any one reaction was maintained; the deuterium content of trans-but-2-ene was always a little greater than that of the but-1-ene or cis-but-2-ene.

Exchange of the butadiene increases with conversion. This trend however is slight since the rate of exchange is very low.

The hydrogen content of the residual deuterium was found to rise with conversion (Fig. 7.5), and to be virtually independent of any run number effect.

At first sight it appears that the deuterium content of the butenes is to some extent dependent on the degree of conversion. The deuterium number remains almost constant up to 65% conversion; thereafter it falls steadily. Initially this was assumed to be a result of the isomerisation process. However, it may be noticed that the reactions were carried out in a uniform order; with the exception of reactions F/3 and F/4 each succeeding reaction was extracted at a lower conversion. This procedure was adopted as deactivation of the catalyst led to later reactions to high conversion proceeding at a very slow rate.

In order to ascertain whether a run number effect was wholly or at least partly responsible for the low deuterium content of the butenes obtained in reactions F/1 and F/2, a series of five reactions was carried out at 200°C to a

TABLE 7.7

Variation of deuterated product distributions with conversion.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
F/6	Conversion = 27.5%				Final H.N. = 0.24					
1-BUT	48.3	40.4	10.4	0.7	0.2	0.0	0.0	0.0	0.0	0.64
TRANS	45.9	39.5	12.8	1.2	0.6	0.0	0.0	0.0	0.0	0.71
CIS	45.8	42.2	11.3	0.5	0.2	0.0	0.0	0.0	0.0	0.67
1-3BUT	97.3	2.1	0.6	0.0	0.0	0.0	0.0	-	-	0.03
F/5	Conversion = 38.1%				Final H.N. = 0.25					
1-BUT	47.3	40.6	11.6	0.6	0.0	0.0	0.0	0.0	0.0	0.65
TRANS	46.3	39.6	13.0	0.8	0.3	0.0	0.0	0.0	0.0	0.69
CIS	48.4	40.4	10.7	0.5	0.0	0.0	0.0	0.0	0.0	0.63
1-3BUT	98.2	0.7	0.9	0.2	0.0	0.0	0.0	-	-	0.03
F/3	Conversion = 45.8%				Final H.N. = 0.30					
1-BUT	52.6	37.7	9.1	0.5	0.0	0.0	0.0	0.0	0.0	0.57
TRANS	51.0	36.5	11.2	1.2	0.0	0.0	0.0	0.0	0.0	0.63
CIS	53.7	37.6	8.2	0.6	0.0	0.0	0.0	0.0	0.0	0.56
1-3BUT	95.1	4.0	0.7	0.2	0.0	0.0	0.0	-	-	0.06
F/4	Conversion = 64.7%				Final H.N. = 0.34					
1-BUT	49.1	39.4	10.8	0.7	0.1	0.0	0.0	0.0	0.0	0.63
TRANS	47.1	38.9	12.6	1.1	0.2	0.0	0.0	0.0	0.0	0.69
CIS	51.2	39.0	9.2	0.5	0.1	0.0	0.0	0.0	0.0	0.59
1-3BUT	94.3	4.4	1.0	0.4	0.0	0.0	0.0	-	-	0.07

TABLE 7.7 (Continued)

Reaction	d_o	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
F/2	Conversion = 74.0%					Final H.N. = 0.41				
1-BUT	61.6	31.1	7.0	0.3	0.0	0.0	0.0	0.0	0.0	0.46
TRANS	59.3	31.2	8.5	0.7	0.2	0.1	0.0	0.0	0.0	0.52
CIS	62.7	31.3	5.7	0.3	0.0	0.0	0.0	0.0	0.0	0.44
1-3BUT	94.1	4.3	1.2	0.3	0.0	0.0	0.0	-	-	0.08
F/1	Conversion = 88.5%					Final H.N. = 0.51				
1-BUT	64.5	29.6	5.6	0.4	0.0	0.0	0.0	0.0	0.0	0.42
TRANS	61.0	30.8	7.5	0.7	0.0	0.0	0.0	0.0	0.0	0.48
CIS	65.1	29.8	4.7	0.5	0.0	0.0	0.0	0.0	0.0	0.41
1-3BUT	93.1	4.0	2.2	0.8	0.0	0.0	0.0	-	-	0.11
F/7	Conversion = 100%					Final H.N. = 1.29				
1-BUT	37.5	40.0	17.8	3.8	0.9	0.0	0.0	0.0	0.0	0.91
TRANS	40.5	40.3	15.9	3.0	0.5	0.0	0.0	0.0	0.0	0.83
CIS	40.6	40.2	15.8	2.9	0.6	0.0	0.0	0.0	0.0	0.83

TABLE 7.8

Variation of the butene distribution with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C ; pressure fall at extraction = 16 ± 1.0 mm.

Reaction	Butene Distribution			T/C	t(min.)
	1-BUT	TRANS	CIS		
I/1	53.5	15.6	30.9	0.50	26
I/2	57.8	15.8	26.4	0.60	30
I/3	53.9	12.9	33.2	0.39	44
I/4	55.0	16.4	28.6	0.57	45
I/5	58.6	12.5	28.9	0.43	48

TABLE 7.9

Variation of deuterated product distributions with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200°C ; pressure fall at extraction = 16 ± 1.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
I/1	Final H.N. = 0.26									
1-BUT	69.2	24.8	4.5	0.9	0.5	0.0	0.0	0.0	0.0	0.39
TRANS	63.7	27.4	7.3	1.2	0.5	0.0	0.0	0.0	0.0	0.47
CIS	73.1	22.9	3.5	0.4	0.0	0.0	0.0	0.0	0.0	0.31
1-3BUT	96.9	1.2	1.4	0.5	0.0	0.0	0.0	-	-	0.06
I/2	Final H.N. = 0.28									
1-BUT	64.5	27.8	6.0	1.0	0.4	0.3	0.0	0.0	0.0	0.46
TRANS	57.4	29.5	10.5	1.6	0.6	0.3	0.0	0.0	0.0	0.60
CIS	66.2	28.2	4.7	0.6	0.3	0.0	0.0	0.0	0.0	0.41
1-3BUT	96.5	2.2	1.1	0.3	0.0	0.0	0.0	-	-	0.05
I/3	Final H.N. = 0.32									
1-BUT	60.5	29.3	8.0	1.3	0.6	0.3	0.0	0.0	0.0	0.53
TRANS	52.6	32.0	12.5	1.5	1.0	0.5	0.0	0.0	0.0	0.68
CIS	57.7	32.1	8.5	1.2	0.5	0.0	0.0	0.0	0.0	0.55
1-3BUT	96.1	3.1	0.9	0.0	0.0	0.0	0.0	-	-	0.05
I/4	Final H.N. = 0.38									
1-BUT	58.0	32.8	7.3	1.2	0.8	0.0	0.0	0.0	0.0	0.54
TRANS	50.7	34.0	13.1	1.7	0.6	0.0	0.0	0.0	0.0	0.68
CIS	62.5	33.3	3.5	0.5	0.3	0.0	0.0	0.0	0.0	0.43
1-3BUT	96.4	2.4	1.3	0.0	0.0	0.0	0.0	-	-	0.05
I/5	Final H.N. = 0.40									
1-BUT	57.9	32.5	8.3	0.9	0.4	0.0	0.0	0.0	0.0	0.53
TRANS	52.0	34.1	12.2	1.2	0.5	0.0	0.0	0.0	0.0	0.64
CIS	60.0	32.7	6.6	0.5	0.3	0.0	0.0	0.0	0.0	0.48
1-3BUT	96.4	2.4	1.3	0.0	0.0	0.0	0.0	-	-	0.05

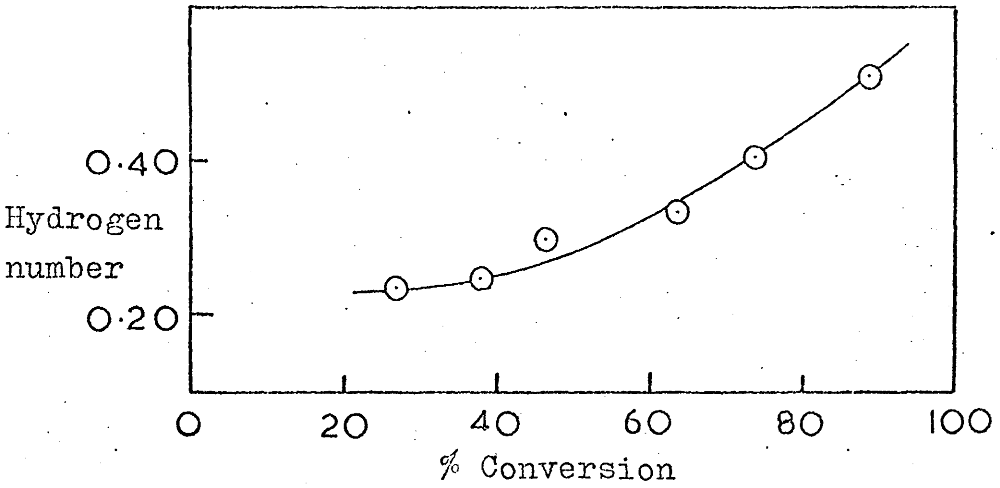


Fig.7.5. The variation of the hydrogen content of the residual deuterium with conversion over Au/Boehmite at 200°C.

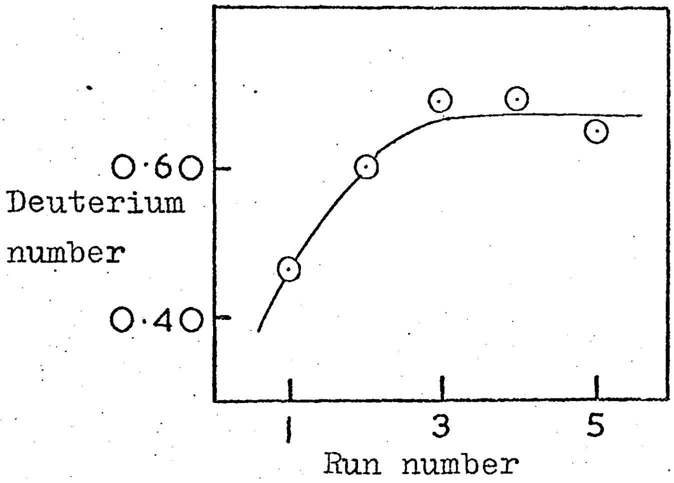


Fig.7.6. The variation of the deuterium number of the trans-but-2-ene with run number for reactions to constant conversion over Au/Boehmite at 200°C.

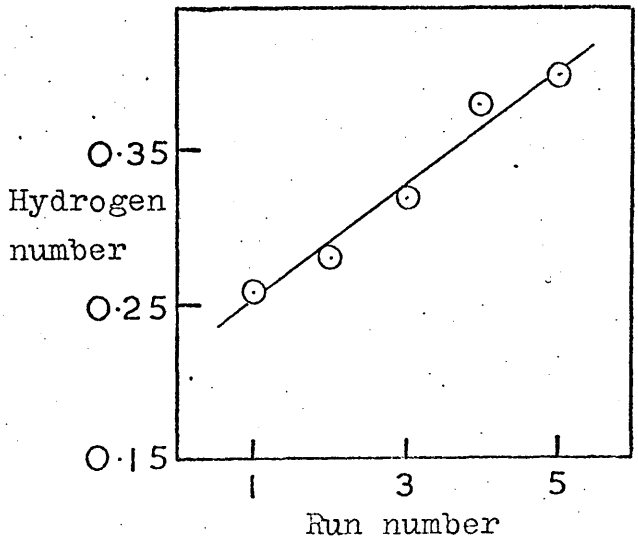


Fig.7.7. The variation of the hydrogen content of the residual deuterium with run number for reactions to constant conversion over Au/Boehmite at 200°C.

constant pressure fall. The pressure of butadiene used was 50mm., that of hydrogen 100mm., and all reactions were carried out to ~ 33% conversion. The distribution of products is shown in Table 7.8 and the deuterated product distributions are shown in Table 7.9, along with the hydrogen content of the residual deuterium.

While the variation in butene composition is not significant, the deuterium number of the butenes increases until reaction I/3 and thereafter shows little variation (Fig. 7.6). The distribution of deuterium in the butadiene remains virtually constant while the amount of exchanged hydrogen increases with run number (Fig. 7.7).

Thus the low deuterium number of the butenes extracted at high conversion is to some extent due to the variation in the deutero-butene distributions with the number of reaction, and the effect of temperature and initial deuterium pressure on the deuterated product distribution is more difficult to estimate.

7.7 Dependence of deuterated product distributions upon initial deuterium pressure.

The conditions and butene distribution for this series of reactions are described in section 7.3. The distributions of deuterium in the butenes and thebutadiene are shown in Table 7.10.

The deuterium content of the butenes rises with increasing initial deuterium pressure, while the hydrogen number of the residual deuterium is found to decrease. Variation in the

TABLE 7.10

Variation of deuterated product distributions with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 200°C; pressure fall at extraction = 14 ± 1.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
G/5	Initial D_2 pressure = 50 ± 0.5 mm. Final H.N. = 0.53									
1-BUT	70.9	25.4	3.6	0.1	0.0	0.0	0.0	0.0	0.0	0.33
TRANS	67.7	27.3	4.8	0.3	0.0	0.0	0.0	0.0	0.0	0.38
CIS	71.7	25.1	3.0	0.2	0.0	0.0	0.0	0.0	0.0	0.32
1-3BUT	98.5	1.0	0.5	0.0	0.0	0.0	0.0	-	-	0.02
G/1	Initial D_2 pressure = 100 ± 0.5 mm. Final H.N. = 0.29									
1-BUT	65.6	29.8	4.3	0.2	0.0	0.0	0.0	0.0	0.0	0.39
TRANS	65.1	29.0	5.6	0.3	0.0	0.0	0.0	0.0	0.0	0.41
CIS	67.6	28.8	3.6	0.1	0.0	0.0	0.0	0.0	0.0	0.36
1-3BUT	97.6	1.7	0.6	0.2	0.0	0.0	0.0	-	-	0.03
G/2	Initial D_2 pressure = 150 ± 1.0 mm. Final H.N. = 0.23									
1-BUT	67.8	27.2	4.6	0.4	0.0	0.0	0.0	0.0	0.0	0.38
TRANS	64.8	28.3	6.5	0.5	0.0	0.0	0.0	0.0	0.0	0.43
CIS	68.5	27.5	3.9	0.2	0.0	0.0	0.0	0.0	0.0	0.36
1-3BUT	97.5	1.5	1.1	0.1	0.0	0.0	0.0	-	-	0.04
G/3	Initial D_2 pressure = 200 ± 1.0 mm. Final H.N. = 0.19									
1-BUT	64.0	30.0	5.8	0.3	0.0	0.0	0.0	0.0	0.0	0.42
TRANS	59.1	32.0	7.9	0.5	0.6	0.0	0.0	0.0	0.0	0.51
CIS	67.3	27.8	4.5	0.4	0.0	0.0	0.0	0.0	0.0	0.38
1-3BUT	98.2	1.1	0.8	0.0	0.0	0.0	0.0	-	-	0.03

exchange of butadiene is neglible. These trends are discernible without examination of the characteristics of the run number effect.

7.8 Dependence of deuterated product distributions upon temperature.

The deuterated product distributions shown in Table 7.11 correspond to the distribution of butenes in section 7.5. From these results it can been seen that the deuterium numbers of the butenes generally decrease with increasing temperature, while the content of the butadiene is steady. The exchange of the deuterium tends to increase with temperature. If the effect of the run number is taken into consideration, the trend in the deutero-butenes becomes clearer : butenes from reactions H/5 and H/6 would exhibit lower deuterium numbers with respect to the other reactions if they had been carried out at the beginning of the series.

7.9 The hydrogen exchange reaction in the absence of buta-1,3-diene.

Three successive pressures of 100 mm. deuterium were exposed to the catalyst for one hour at 200°C after pretreatment in 200 mm. of hydrogen at 250 and 400°C for 12 hours. After the initial reduction, the catalyst vessel was pumped for one hour at the reduction temperature and between additions of deuterium it was evacuated for 30 minutes at the temperature of the exchange. The results

TABLE 7.11

Variation of the deuterated product distributions with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 14 ± 2.0 mm.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
H/3	Temperature = 170°C					Final H.N. = 0.22				
1-BUT	48.0	39.3	11.4	0.0	0.6	0.0	0.0	0.0	0.0	0.67
TRANS	43.4	37.4	15.0	2.0	1.2	0.6	0.4	0.0	0.0	0.83
CIS	49.8	39.5	9.5	0.6	0.2	0.2	0.0	0.0	0.0	0.63
1-3BUT	98.0	1.5	0.4	0.1	0.0	0.0	0.0	-	-	0.03
H/1	Temperature = 200°C					Final H.N. = 0.22				
1-BUT	56.1	34.0	8.6	1.3	0.0	0.0	0.0	0.0	0.0	0.55
TRANS	53.3	33.7	10.7	1.5	0.9	0.0	0.0	0.0	0.0	0.63
CIS	58.5	34.3	6.5	0.4	0.3	0.0	0.0	0.0	0.0	0.50
1-3BUT	97.5	1.9	0.7	0.0	0.0	0.0	0.0	-	-	0.03
H/6	Temperature = 215°C					Final H.N. = 0.38				
1-BUT	56.1	35.1	7.5	0.7	0.4	0.2	0.0	0.0	0.0	0.55
TRANS	52.5	35.4	9.6	1.2	1.0	0.4	0.0	0.0	0.0	0.64
CIS	56.0	35.0	7.9	0.6	0.4	0.2	0.0	0.0	0.0	0.55
1-3BUT	98.3	1.4	0.3	0.0	0.0	0.0	0.0	-	-	0.02
H/2	Temperature = 230°C					Final H.N. = 0.38				
1-BUT	65.2	29.4	4.7	0.5	0.1	0.0	0.0	0.0	0.0	0.41
TRANS	63.3	28.9	6.8	0.9	0.0	0.0	0.0	0.0	0.0	0.45
CIS	65.9	29.3	4.6	0.3	0.0	0.0	0.0	0.0	0.0	0.40
1-3BUT	97.6	1.9	0.5	0.0	0.0	0.0	0.0	-	-	0.03
H/5	Temperature = 260°C					Final H.N. = 0.54				
1-BUT	64.3	31.0	4.4	0.3	0.0	0.0	0.0	0.0	0.0	0.41
TRANS	63.0	31.2	5.2	0.3	0.4	0.0	0.0	0.0	0.0	0.33
CIS	63.4	30.9	4.9	0.5	0.4	0.0	0.0	0.0	0.0	0.43
1-3BUT	97.8	1.6	0.6	0.0	0.0	0.0	0.0	-	-	0.03

are shown in Table 7.12.

TABLE 7.12

The hydrogen exchange reaction in the absence of butadiene.

Initial deuterium pressure = 100 ± 1.0 mm. ; Temp. = 200°C

	Hydrogen number		
Reduction Temp.(°C)	Reaction 1	Reaction 2	Reaction 3
250	0.82	0.65	0.60
250	0.24	0.17	0.10
400	0.14	0.10	0.08

The degree of exchange varied over the two samples of catalyst, but both exhibited a decrease in hydrogen number with succeeding reaction. Lowest exchange was observed after reduction and evacuation at 400°C.

7.10 The mass balance.

The calculations were carried out as in section 6.10. Good mass balances were unable to be obtained for all the reactions.

TABLE 7.13

Variation of mass balance with conversion.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200 °C.

Initial hydrogen (mm. atoms) = 305.60

Initial deuterium (mm. atoms) = 194.40

Reaction	% Conversion	Final hydrogen	Final deuterium
F/6	27.5	338.70	162.11
F/5	38.1	344.99	155.03
F/3	45.8	354.17	145.87
F/4	64.7	366.32	133.69
F/2	74.0	381.68	118.32
F/1	88.5	397.40	102.60

Better mass balance was obtained at low conversion and high reaction number. The results also show that for corresponding reactions, better mass balance was obtained over Au/γ-Al_2O_3.

TABLE 7.14

Variation of mass balance with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 200 °C; pressure fall at extraction = 14 ± 1.0 mm.

Initial hydrogen (mm. atoms) = 305.60

Initial deuterium (mm. atoms) = 194.40

Reaction	P_{D_2} (mm.)	Final hydrogen	Final deuterium
G/5	50	367.05	132.95
G/1	100	347.89	152.11
G/2	150	341.77	158.24
G/3	200	339.03	160.96

As with Au/γ-Al_2O_3, better mass balance was obtained as the deuterium pressure was increased.

TABLE 7.15

Variation of mass balance with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 14 ± 2.0 mm.

Initial hydrogen (mm. atoms) = 305.60

Initial deuterium (mm. atoms) = 194.40

Reaction	Temperature (°C)	Final hydrogen	Final deuterium
H/3	170	333,70	166.30
H/1	200	339.57	160.43
H/6	125	350.70	149.30
H/2	230	355.93	144.89
H/5	260	369.20	130.80

With increase in temperature the degree of unbalance becomes greate

TABLE 7.16

Variation of mass balance with run number.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Tp. = 200 °C; pressure fall at extraction = 16 ± 1.0 mm.

Initial hydrogen (mm. atoms) = 305.20

Initial deuterium (mm. atoms) = 194.80

Reaction	Final hydrogen	Final deuterium
I/1	344.33	155.67
I/2	351.99	148.02
I/3	346.42	153.57
I/4	354.41	145.59
I/5	353.86	146.14

No trend with regard to variation of mass balance with run number is discernible.

CHAPTER 8

REACTIONS OF BUTA-1,3-DIENE WITH DEUTERIUM OVER SILICA-SUPPORTED COPPER.

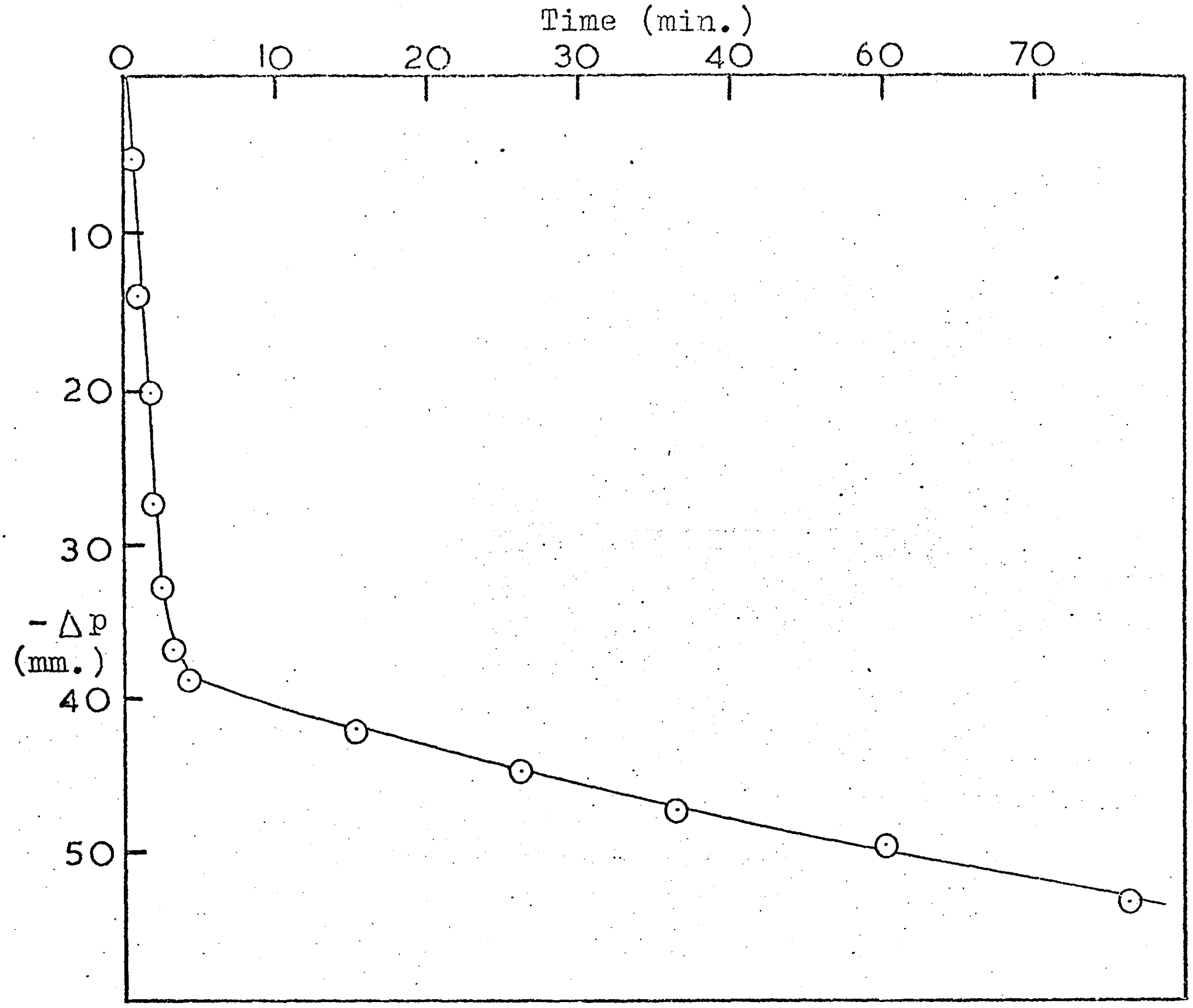
8.1 Introduction.

The interaction between buta-1,3-diene and deuterium over Cu/SiO_2 catalysts was studied in a series of reactions between 140 and 230°C. The reaction took place in two stages. In the first stage the diolefin was hydrogenated to give the three butenes. The second stage commenced when all butadiene had been removed and was accompanied by an abrupt decrease in the rate of pressure fall because of the low activity of the catalyst for butene hydrogenation; a typical curve is shown in Fig. 8.1, along with the first order test plot derived from the first stage of the reaction. Since the latter plot is linear, the overall order of reaction for hydrogenation is unity.

8.2 The dependence of the butene distribution on conversion.

Two series of reactions were carried out at temperatures of 157 and 200°C, using catalyst samples weighing 0.25g. and 0.10g. respectively. All reactions used a butadiene pressure of 43 mm. and a pressure of deuterium of 107 mm. The results for the distribution of butenes are shown in Tables 8.1 and 8.2, the notation being the same as applied in section 6.2; they are also illustrated graphically in Figs. 8.2 and 8.3.

It can be seen that the butene distribution is independent of conversion for both series of reactions. The yields of the three butenes were but-1-ene $\gg$ trans-but-2-ene $\sim$ cis-but-2-ene. As the temperature of reaction decreased, the yield of but-1-ene increased.



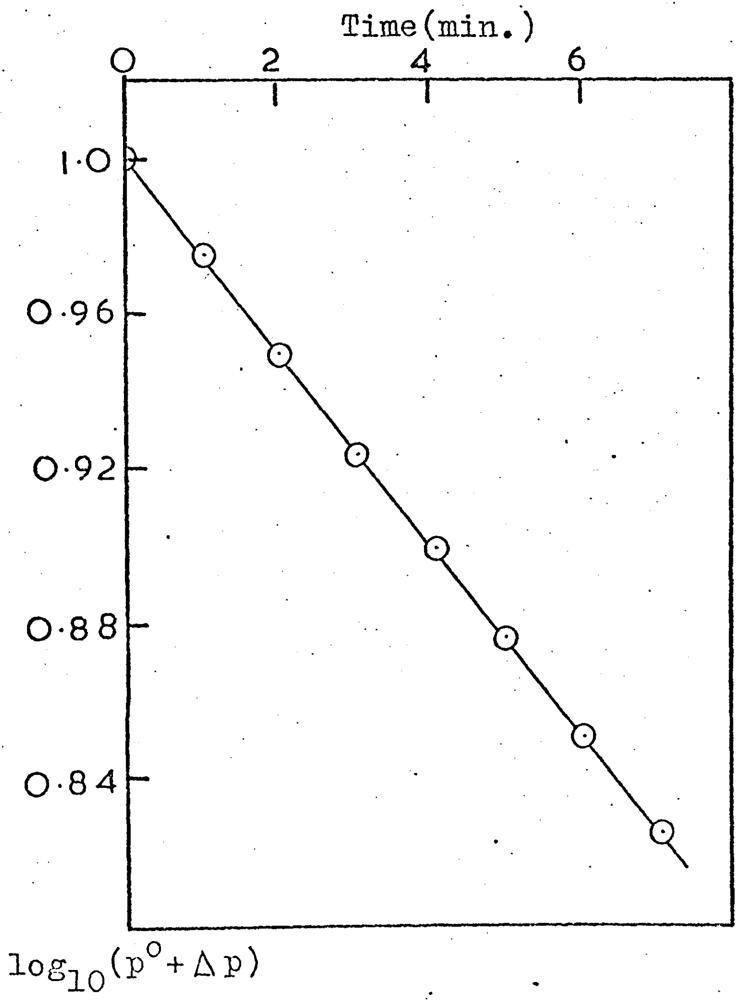


Fig.8.1. Pressure fall against time curve and first order plot for a typical reaction of 43 mm. buta-1,3-diene and 107 mm. deuterium over Cu/silica at 200°C.

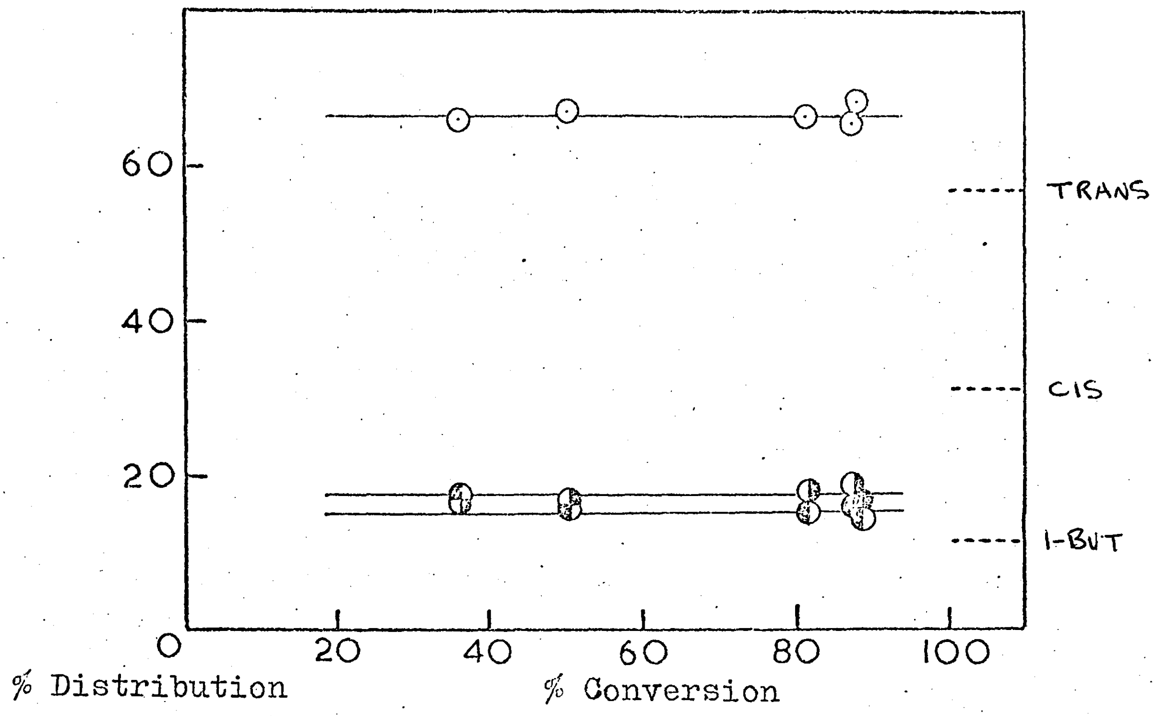


Fig.8.2. The variation of butene distribution with increasing conversion over Cu/silica at 200°C.

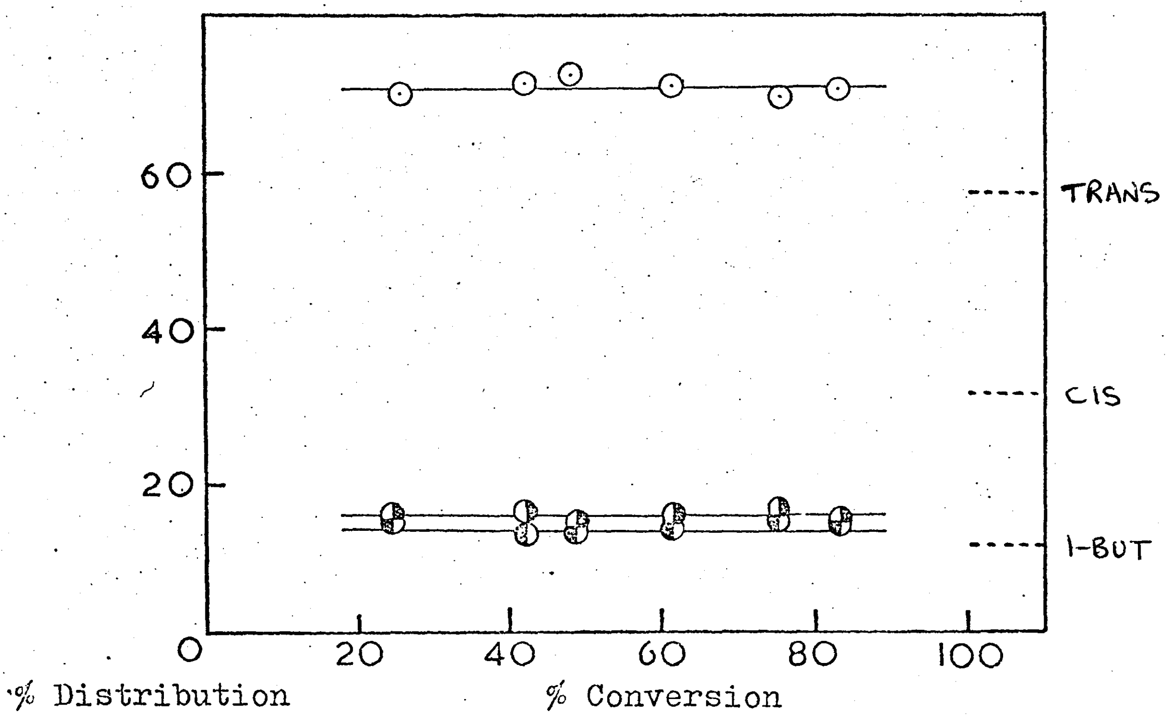


Fig.8.3. The variation of butene distribution with increasing conversion over Cu/silica at 157°C.

Legend to Figs.8.2 and 8.3 : -⊙- but-1-ene ; -◑- trans-but-2-ene ; -◐- cis-but-2-ene ; Broken lines show thermodynamic equilibrium values.

TABLE 8.1

Variation of the butene distribution with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; initial deuterium pressure = 107 ± 0.5 mm.; Tp. = 200°C; wt. of catalyst = 0.10 g.

Reaction	% Conversion	Butene Distribution		
		1-BUT	TRANS	CIS
K/4	35.8	66.1	16.6	17.3
K/2	48.6	67.4	17.2	15.4
K/5	81.2	66.5	18.0	15.5
K/3	86.8	65.5	18.5	16.0
K/1	87.1	68.5	16.9	14.6
K/6	127.6	6.4	58.4	35.2

TABLE 8.2

Variation of butene distribution with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; inital deuterium pressure = 107 ± 0.5 mm.; Tp. = 157°C; wt. of catalyst = 0.25 g.

Reaction	% Conversion	Butene Distribution		
		1-BUT	TRANS	CIS
L/6	24.5	69.7	15.4	14.9
L/2	42.0	71.2	15.7	13.1
L/4	48.0	72.4	14.2	13.4
L/1	62.4	70.8	15.2	14.0
L/5	75.0	69.4	15.8	14.8
L/3	83.1	70.9	15.0	14.1

8.3 The order with respect to deuterium and the dependence of the butene distribution upon initial deuterium pressure.

The effect of varying the deuterium pressure was studied in a series of reactions at 157°C, in which the deuterium pressure was varied between 50 and 200 mm. at a constant butadiene pressure of 50 mm. The results are shown in Tables 8.3 and 8.4.

TABLE 8.3

Variation of initial rate with increasing deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Temp. = 157°C;

Wt. of catalyst = 0.10g.

Initial deuterium pressure (mm.)	50	100	150	200
Initial rate (mm./min.)	0.81	1.50	2.00	2.68

Fig. 8.4 exhibits the linear relationship between the initial rate and butadiene pressure, from which an order of 1.0 ± 0.1 in deuterium is derived.

The butene composition, obtained after extraction at pressure falls between 13 and 16 mm., is seen to be independent of initial deuterium pressure.

8.4 The order with respect to butadiene.

The initial rate was found to be independent of the initial butadiene pressure; this confirms that the order for the diolefin is zero. The results are shown in Table 8.5.

TABLE 8.5

Variation of initial rate with increasing butadiene pressure.

Initial deuterium pressure = 200 ± 1.0 mm.; Temp. = 157°C;

Wt. of catalyst = 0.10g.

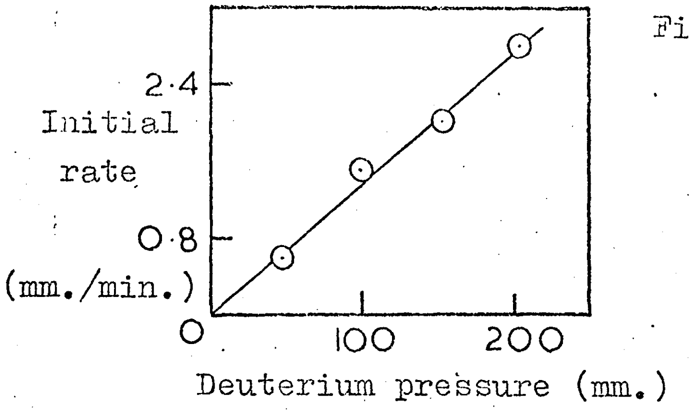


Fig.8.4. The variation of the initial rate of reaction with increasing deuterium pressure over Au/Boehmite at 200°C.

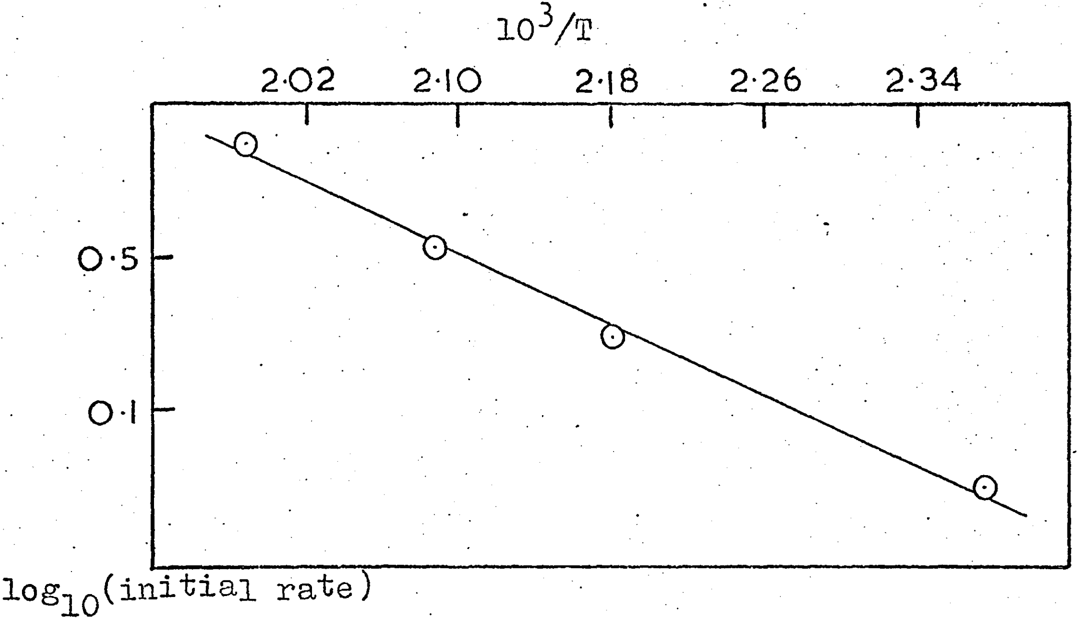


Fig.8.5. The variation of $\log_{10}$(initial rate) with the reciprocal of absolute temperature over Cu/silica.

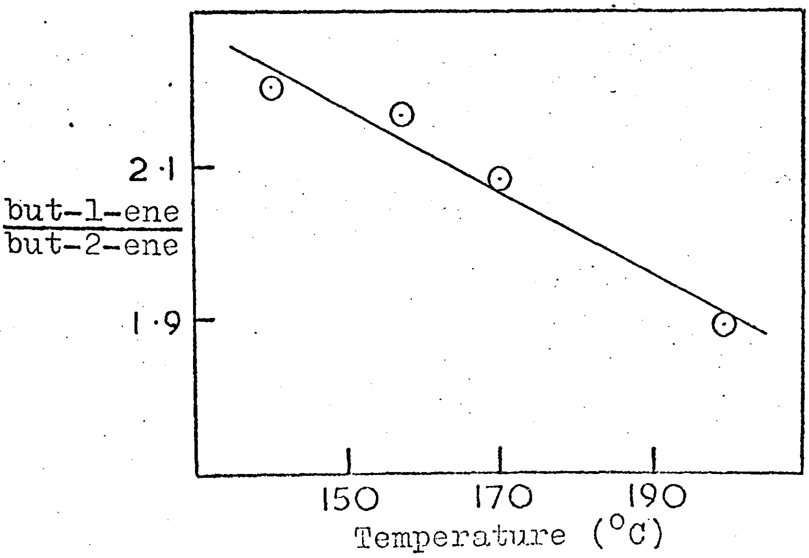


Fig.8.6. The variation of but-1-ene/but-2-ene ratio with temperature over Cu/silica.

TABLE 8.4

Variation of the butene distribution with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 157°C; pressure fall at extraction = 14 ± 1.0 mm.; wt. of catalyst = 0.25 g.

Reaction	P_{D_2} (mm.)	Butene Distribution			T/C
		1-BUT	TRANS	CIS	
M/2	50	69.6	15.3	15.1	1.01
M/1	100	73.2	13.7	13.1	1.04
M/4	150	67.9	16.1	16.0	1.01
M/3	200	74.9	12.1	13.0	0.93

TABLE 8.6

Variation of the butene distribution with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 13.5 ± 2.0 mm.; wt. of catalyst = 0.10 g.

Reaction	Tp.(°C)	Butene Distribution			T/C	1-BUT/2-BUT
		1-BUT	TRANS	CIS		
0/4	140	68.7	16.3	15.0	1.09	2.194
0/1	157	68.3	16.4	15.3	1.07	2.162
0/3	170	67.6	16.0	16.5	0.97	2.080
0/2	198	65.4	18.6	16.0	1.16	1.890

Initial butadiene pressure (mm.)	25	50	75	100
Initial rate (mm./min.)	2.30	2.40	2.35	2.45

8.5 Temperature dependence of the butene distribution and the activation energy.

The initial butene distribution was studied as a function of increasing temperature in a series of reactions between 140 and 198°C. Table 8.6 shows the butene composition after extraction between 23 and 31% conversion. A second series of reactions between 148 and 230°C was used to study the variation of initial rate.

TABLE 8.7

Variation of initial rate with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; Wt. of catalyst = 0.10g.

Tp. (°C)	148	186	206	230
Initial rate (mm./min.)	0.79	2.08	3.43	6.43

From the Arrhenius plot of $\log_{10}$ (initial rate) against $^{1}/T$ (Fig. 8.5), a value of 10.8 ± 1.0 kcal mol^{-1} was obtained for the activation energy. It can also be seen (Fig. 8.6) that with increasing temperature the but-1-ene:but-2-ene ratio decreases linearly; the trans-but-2-ene:cis-but-2-ene is not markedly dependent on temperature. This is in agreement with the butene distributions obtained from the series of reactions at 157 and 200°C (section 8.2).

8.6 Dependence of deuterated product distributions upon conversion.

The conditions and butene distributions for these series are described in section 8.2. The deuterated product distributions and the hydrogen number of the 'deuterium' are shown in Tables 8.8 and 8.9.

TABLE 8.8

Variation of deuterated product distributions with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; initial deuterium pressure = 107 ± 0.5 mm.; Tp. = 200°C; wt. of catalyst = 0.10 g.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
K/4	Conversion = 35.8%				Final H.N. = 0.30					
1-BUT	21.4	36.7	29.4	9.8	2.3	0.5	0.0	0.0	0.0	1.36
TRANS	15.6	38.4	31.7	10.3	3.0	0.9	0.0	0.0	0.0	1.49
CIS	15.3	42.0	31.6	9.2	2.0	0.1	0.0	0.0	0.0	1.40
1-3BUT	65.5	26.9	6.5	1.1	0.0	0.0	0.0	-	-	0.43
K/2	Conversion = 48.6%				Final H.N. = 0.32					
1-BUT	19.2	32.2	29.8	13.8	4.0	1.0	0.2	0.0	0.0	1.55
TRANS	15.0	35.9	30.8	13.2	4.1	1.1	0.1	0.0	0.0	1.59
CIS	14.4	37.8	31.1	12.5	3.5	0.6	0.1	0.0	0.0	1.55
1-3BUT	65.0	26.9	6.9	1.3	0.1	0.0	0.0	-	-	0.44
K/5	Conversion = 81.2%				Final H.N. = 0.36					
1-BUT	14.4	29.2	30.0	17.4	6.9	1.9	0.3	0.0	0.0	1.80
TRANS	11.2	29.7	31.1	18.0	7.4	2.1	0.5	0.0	0.0	1.89
CIS	11.6	34.1	30.3	16.0	6.1	1.7	0.3	0.0	0.0	1.77
1-3BUT	51.9	20.6	16.5	8.2	2.1	0.6	0.1	-	-	0.90
K/3	Conversion = 86.8%				Final H.N. = 0.35					
1-BUT	12.3	26.1	28.0	19.6	9.6	3.7	0.8	0.0	0.0	2.02
TRANS	9.8	26.2	29.7	20.1	9.8	3.7	0.7	0.0	0.0	2.08
CIS	9.0	27.2	30.3	19.9	9.5	3.4	0.6	0.0	0.0	2.06
1-3BUT	83.8	3.8	4.4	3.7	2.6	1.2	0.6	-	-	0.43
K/1	Conversion = 87.1%				Final H.N. = 0.36					
1-BUT	11.5	23.6	28.5	20.5	10.7	4.2	1.2	0.1	0.0	2.13
TRANS	10.3	25.9	29.5	19.7	10.3	3.6	0.8	0.0	0.0	2.08
CIS	9.8	28.1	29.5	18.7	9.4	3.7	0.9	0.0	0.0	2.04
1-3BUT	77.9	3.2	5.1	5.4	4.5	2.5	1.4	-	-	0.69

TABLE 8.9

Variation of deuterated product distributions with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; initial deuterium pressure = 107 ± 0.5 mm.; Tp. = 157°C; wt. of catalyst = 0.25 g.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
L/6	Conversion = 24.5%				Final H.N. = 0.16					
1-BUT	28.8	39.4	24.8	5.9	1.0	0.2	0.0	0.0	0.0	1.12
TRANS	23.7	40.2	27.2	7.0	1.5	0.4	0.0	0.0	0.0	1.23
CIS	22.1	44.9	24.6	6.7	1.4	0.3	0.0	0.0	0.0	1.21
1-3BUT	69.3	25.2	4.6	0.7	0.2	0.0	0.0	-	-	0.37
L/2	Conversion = 42.0%				Final H.N. = 0.20					
1-BUT	29.4	37.6	24.1	7.3	1.4	0.2	0.0	0.0	0.0	1.14
TRANS	24.0	39.6	26.4	7.9	1.8	0.3	0.0	0.0	0.0	1.25
CIS	23.3	41.9	25.4	7.7	1.4	0.3	0.0	0.0	0.0	1.23
1-3BUT	59.3	30.6	8.3	1.6	0.3	0.0	0.0	-	-	0.53
L/4	Conversion = 48.0%				Final H.N. = 0.23					
1-BUT	23.3	37.4	26.9	9.6	2.5	0.3	0.0	0.0	0.0	1.32
TRANS	18.0	38.3	29.3	10.9	3.0	0.4	0.0	0.0	0.0	1.44
CIS	14.5	44.6	29.0	9.5	2.1	0.3	0.0	0.0	0.0	1.41
1-3BUT	50.7	34.2	12.4	2.4	0.3	0.0	0.0	-	-	0.67
L/1	Conversion = 62.4%				Final H.N. = 0.25					
1-BUT	26.1	32 8	26.8	10.0	2.9	0.7	0.4	0.2	0.0	1.36
TRANS	22.2	32.8	26.8	11.5	4.3	1.5	0.6	0.3	0.0	1.51
CIS	20.6	36.6	26.0	10.9	3.9	1.3	0.5	0.2	0.0	1.48
1-3BUT	46.3	31.7	16.3	4.4	1.0	0.3	0.0	-	-	0.83

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
L/5	Conversion = 75.0%				Final H.N. = 0.21					
1-BUT	18.0	32.0	30.5	13.4	4.8	1.2	0.1	0.0	0.0	1.59
TRANS	13.2	30.8	32.2	15.7	6.3	1.6	0.3	0.0	0.0	1.77
CIS	11.5	35.6	31.8	14.6	5.1	1.2	0.1	0.0	0.0	1.70
1-3BUT	36.7	29.9	22.2	8.4	2.2	0.5	0.1	-	-	1.11
L/3	Conversion = 83.1%				Final H.N. = 0.25					
1-BUT	17.4	30.5	28.6	15.9	6.0	1.5	0.2	0.0	0.0	1.68
TRANS	12.8	29.1	31.4	16.7	7.3	2.3	0.3	0.0	0.0	1.85
CIS	12.1	33.3	30.9	15.5	6.3	1.8	0.2	0.0	0.0	1.77
1-3BUT	43.1	21.5	18.3	12.0	3.8	1.0	0.2	-	-	1.16

The dependence of the deuterium number of the trans-but-2-ene and butadiene upon conversion is illustrated graphically in Fig. 8.7 and Fig. 8.8 respectively. In each case the deuterium numbers increase with increasing conversion. The butene samples all exhibit a high proportion of d_0-, d_1- and d_2-species, with the maximum at d_1 except at high conversions in series K when it increases to d_2. In none of the samples did the exchange products extend beyond the d_6-species. The irregular trend of the deuterium number of the butadiene in series K may be a result of the remoteness of the small remaining pressure of diolefin from the catalyst surface in reactions K/1 and K/3 and the consequent inability to undergo exchange. The deuterium numbers of the three butenes were closely similar but a definite trend was established; throughout the reaction cis-but-2-ene contained slightly less deuterium than trans-but-2-ene, but slightly more than but-1-ene. The hydrogen number of the residual deuterium increased very slightly with conversion, but this effect is not marked. With increasing temperature, the deuterium number of the butenes and the hydrogen content of the deuterium showed an increase.

8.7 Dependence of deuterated product distributions upon initial deuterium pressure.

The general procedure and butene distribution is described in section 8.3. The deutero-butene and deutero-butadiene distributions are shown in Table 8.10. The deuterium numbers of the butenes showed a slight increase as the initial deuterium pressure was increased, and the hydrogen content of the residual deuterium was diminished. Little change is apparent in the exchange of butadiene.

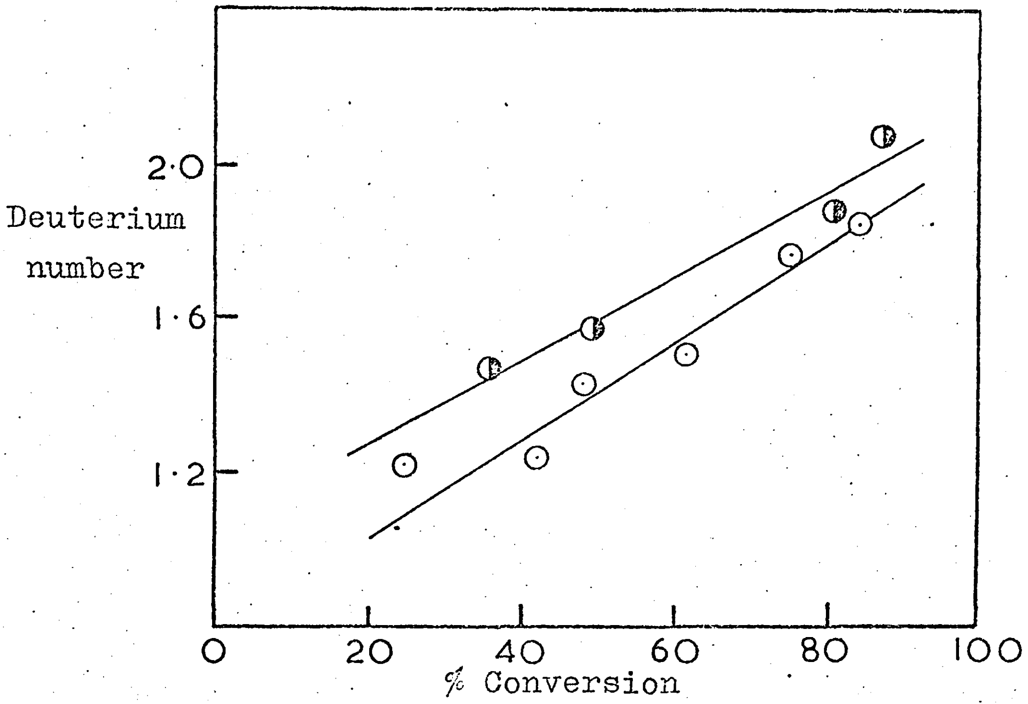


Fig.8.7. The variation witn conversion of the deuterium number of the trans-but-2-ene over Cu/silica at 157°C (-⊙-) and 200°C (-◐-).

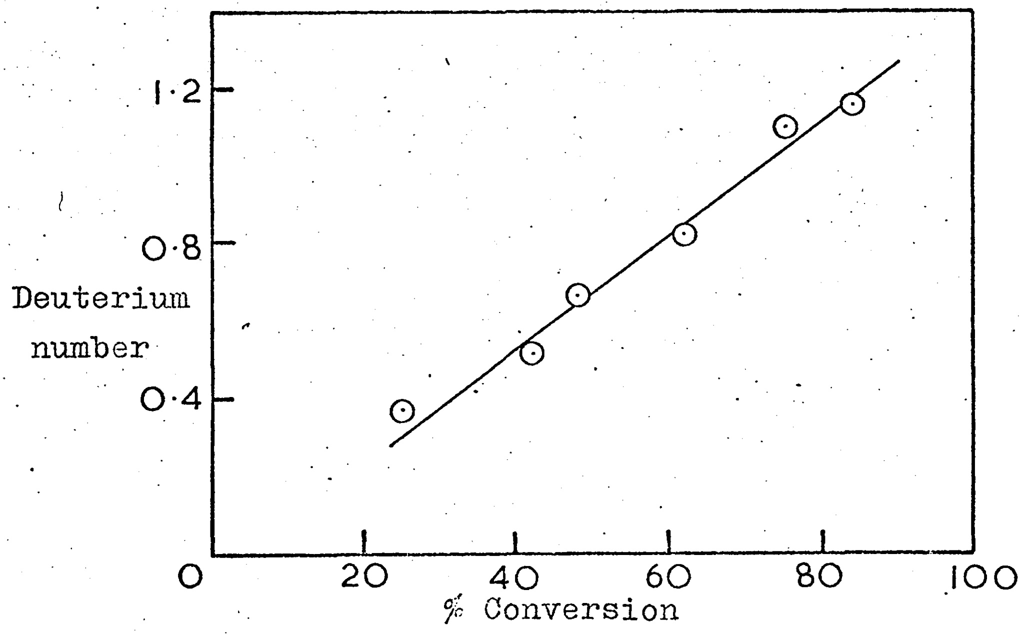


Fig.8.8. The variation with conversion of the deuterium number of butadiene over Cu/silica at 157°C.

TABLE 8.10

Variation of deuterated product distributions with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp.= 157°C; pressure fall at extraction = 14 ± 1.0 mm.; wt. of catalyst = 0.25 g.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
M/2	Initial D_2 pressure = 50 ± 0.5 mm.; Final H.N. = 0.61									
1-BUT	32.7	38.9	22.8	4.8	0.8	0.1	0.0	0.0	0.0	1.02
TRANS	25.9	39.6	27.3	5.8	1.1	0.2	0.1	0.0	0.0	1.18
CIS	23.2	47.2	23.9	4.8	0.7	0.1	0.0	0.0	0.0	1.13
1-3BUT	70.2	25.0	4.1	0.6	0.2	0.0	0.0	-	-	0.36
M/1	Initial D_2 pressure = 100 ± 0.5 mm.; Final H.N. = 0.25									
1-BUT	33.8	36.7	23.0	5.4	1.0	0.1	0.0	0.0	0.0	1.03
TRANS	28.6	38.0	25.8	6.4	1.1	0.2	0.0	0.0	0.0	1.14
CIS	26.4	42.4	24.7	5.5	0.9	0.1	0.0	0.0	0.0	1.12
1-3BUT	68.8	24.9	5.2	0.8	0.3	0.0	0.0	-	-	0.39
M/4	Initial D_2 pressure = 150 ± 1.0 mm.; Final H.N. = 0.19									
1-BUT	23.8	38.9	28.5	7.3	1.5	0.2	0.0	0.0	0.0	1.24
TRANS	19.1	39.0	31.0	8.6	1.8	0.5	0.0	0.0	0.0	1.36
CIS	16.2	44.6	30.7	6.7	1.6	0.3	0.0	0.0	0.0	1.34
1-3BUT	66.8	26.3	5.6	1.0	0.3	0.0	0.0	-	-	0.42
M/3	Initial D_2 pressure = 200 ± 1.0 mm.; Final H.N. = 0.14									
1-BUT	23.9	37.7	29.4	7.5	1.4	0.2	0.0	0.0	0.0	1.26
TRANS	19.7	38.3	31.6	8.3	1.7	0.3	0.0	0.0	0.0	1.35
CIS	17.5	43.0	31.0	7.0	1.3	0.2	0.0	0.0	0.0	1.32
1-3BUT	68.0	25.5	5.5	0.8	0.3	0.0	0.0	-	-	0.40

8.8 Dependence of deuterated product distributions upon temperature.

The analysis figures shown in Table 8.11 correspond to the results in section 8.5. The deuterium content of the butenes show only very small changes; nevertheless the trend is toward increasing deuterium number with increasing temperature. The appearance of hydrogen in the residual deuterium is apparently unaffected. Any variation is the exchange of butadiene can be attributed to the small differences in the degree of conversion.

8.9 The mass balance.

The results of the mass balance calculations are shown in Tables 8.12 - 8.15. The absolute amounts of deuterium and hydrogen are expressed in units of mm. atoms. Good mass balance was unobtainable for all reactions.

TABLE 8.12

Variation of mass balance with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; initial deuterium pressure = 107 ± 0.5 mm.; Tp. = 200 °C.

wt. of catalyst = 0.10 g.

Initial hydrogen = 304.80

Initial deuterium = 195.20

Reaction	% Conversion	Final hydrogen	Final deuterium
K/4	35.8	321.77	178.23
K/2	48.6	323.68	176.33
K/5	81.2	320.57	179.43
K/3	86.8	315.34	184.66
K/1	87.1	311.15	188.86

TABLE 8.11

Variation of the deuterated product distributions with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 13.5 ± 2.0 mm.; wt. of catalyst = 0.10 g.

Reaction	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	D.N.
0/4	Temperature = 140°C					Final H.N. = 0.23				
1-BUT	23.8	37.7	32.5	5.0	0.9	0.1	0.0	0.0	0.0	1.22
TRANS	19.2	40.6	32.9	5.9	1.0	0.3	0.0	0.0	0.0	1.30
CIS	17.8	40.6	32.0	5.4	1.0	0.2	0.0	0.0	0.0	1.28
1-3BUT	77.4	19.1	2.6	0.6	0.3	0.0	0.0	-	-	0.27
0/1	Temperature = 157°C					Final H.N. = 0.22				
1-BUT	28.2	36.9	28.1	5.9	0.9	0.0	0.0	0.0	0.0	1.14
TRANS	23.1	39.0	30.1	6.7	1.1	0.0	0.0	0.0	0.0	1.24
CIS	21.0	39.0	28.8	6.1	0.9	0.0	0.0	0.0	0.0	1.23
1-3BUT	71.5	22.8	4.7	0.8	0.3	0.0	0.0	-	-	0.36
0/3	Temperature = 170°C					Final H.N. = 0.21				
1-BUT	22.1	39.0	32.1	6.2	0.6	0.0	0.0	0.0	0.0	1.24
TRANS	19.6	36.6	33.3	8.8	1.9	0.1	0.0	0.0	0.0	1.36
CIS	16.8	43.0	33.1	5.9	1.3	0.1	0.0	0.0	0.0	1.32
1-3BUT	75.0	20.5	3.7	0.8	0.0	0.0	0.0	-	-	0.30
0/2	Temperature = 198°C					Final H.N. = 0.24				
1-BUT	20.5	38.7	31.0	8.1	1.5	0.2	0.0	0.0	0.0	1.32
TRANS	18.5	35.8	33.4	9.6	2.4	0.3	0.0	0.0	0.0	1.42
CIS	16.6	39.5	33.1	8.8	1.7	0.2	0.0	0.0	0.0	1.40
1-3BUT	68.5	24.4	5.7	1.0	0.4	0.0	0.0	-	-	0.40

TABLE 8.13

Variation of mass balance with conversion.

Initial butadiene pressure = 43 ± 0.5 mm.; inital deuterium pressure = 107 ± 0.5 mm.; Tp. = 157 °C;

wt. of catalyst = 0.25 g.

Initial hydrogen = 304.80

Final hydrogen = 195.20

Reaction	% Conversion	Final hydrogen	Final deuterium
L/6	24.5	310.55	189.65
L/2	42.0	317.89	182.12
L/4	48.0	316.69	184.33
L/1	62.4	298.00	202.00
L/5	75.0	312.96	187.06
L/3	83.1	316.47	183.94

Differences in mass balance are very slight and probably arise from experimental error.

TABLE 8.14

Variation of mass balance with initial deuterium pressure.

Initial butadiene pressure = 50 ± 0.5 mm.; Tp. = 157 °C; pressure fall at extraction = 14 ± 1.0 mm.; wt. of catalyst = 0.25 g.

Initial hydrogen = 305.60

Initial deuterium = 194.40

Reaction	P_{D_2} (mm.)	Final hydrogen	Final deuterium
M/2	50	352.17	147.83
M/1	100	323.45	176.55
M/4	150	312.99	187.01
M/3	200	309.01	190.99

Table 8.14 shows that better mass balance was obtained as the initial pressure of deuterium was increased.

TABLE 8.15

Variation of mass balance with temperature.

Initial butadiene pressure = 50 ± 0.5 mm.; initial deuterium pressure = 100 ± 0.5 mm.; pressure fall at extraction = 13.5 ± 2.0 mm.; wt. of catalyst = 0.10 g.

Initial hydrogen = 305.60

Initial deuterium = 194.40

Reaction	Temperature (°C)	Final hydrogen	Final deuterium
0/4	140	318.75	181.25
0/1	157	317.29	182.71
0/3	170	315.65	184.35
0/2	198	316.37	183.63

Variations of mass balance are very small and fall within the limits of experimental error.

CHAPTER 9

REACTIONS OF BUTA-1,3-DIENE WITH DEUTERIUM OVER SUPPORTED GOLD CATALYSTS.

In the ensuing discussion the results obtained over the Au/γ-alumina and Au/Boehmite catalysts will be correlated in order to postulate possible reaction mechanisms. The different nature of the supports will be discussed in an attempt to explain the contrasting features of the two catalysts and also the inability of the Au/silica and Au/α-alumina to catalyse the hydrogenation reaction. In both discussion sections the term 'butadiene' will be used to refer exclusively to buta-1,3-diene.

The results in chapters 6 and 7 show that in many respects the reactions are fundamentally very similar over Au/γ-alumina and Au/Boehmite. The butene distributions, for example, illustrate similar trends and the respective kinetic orders and activation energies are similar for the two types of catalyst. Similarly both catalysts exhibit complete selectivity for butene formation. However the deutero-butene distributions show a number of interesting differences. Thus, for example, whereas the most abundant deutero-butene obtained over Au/Boehmite is the d_0-species, over Au/γ-alumina the d_1-species is usually the predominant product.

9.1 The kinetics of the reaction.

The initial rate orders of zero in butadiene and one in deuterium, observed over both catalysts indicate the strong chemisorption of butadiene and the relatively weak adsorption of 'hydrogen'.

The following mechanism involving atomic hydrogen is consistent with the kinetics.

$$C_4H_6\ (g) \rightleftharpoons C_4H_6(a) \qquad (a,a')$$

$$H_2\ (g) \rightleftharpoons 2H(a) \qquad (b,b^1)$$

$$C_4H_6(a) + H\ (a) \rightleftharpoons C_4H_7(a) \qquad (1,2)$$

$$C_4H_7(a) + H\ (a) \longrightarrow C_4H_8(a) \qquad (3)$$

If it is assumed that (3) is the rate controlling step, a steady state treatement shows that;

$$\theta_{C_4H_7} = (k_1.\theta_{C_4H_6}.\theta_H)/(k_2+k_3\theta_H)$$

$$\text{and rate} = k_3.\theta_{C_4H_7}.\theta_H$$

$$\therefore \text{rate} = k_1k_3.\theta_{C_4H_6}.\theta_H^2/(k_2+k_3\theta_H)$$

The appropriate Langmuir isotherms may be applied to obtain the surface coverages of diolefin and hydrogen. Thus

$$\theta_D = \frac{b_Dp_D}{1 + b_Dp_D + b_{H_2}^{0.5}p_{H_2}^{0.5}} \quad \text{and } \theta_H = \frac{b_{H_2}^{0.5}p_{H_2}^{0.5}}{1 + b_Dp_D + b_{H_2}^{0.5}p_{H_2}^{0.5}} \quad (\theta_D = \theta_{C_4H_6}$$

Under conditions where the butadiene is strongly adsorbed and the hydrogen relatively weakly adsorbed, these may be simplified to

$$\theta_D \sim 1 \qquad \text{and} \qquad \theta_H \propto p_{H_2}^{0.5}$$

By assuming that θ_H is small and that $k_2 \gg k_3\theta_H$ and substituting for θ_D and θ_H

$$\text{rate} \propto (k_1k_3/k_2).p_{H_2}$$

and therefore the rate of butene formation will be proportional to the hydrogen pressure, in agreement with the experimental observations.

The only assumptions made in the above treatment are that θ_H is small, and that $\theta_{C_4H_7}$ does not approach unity under the steady state conditions. θ_H will be small provided that hydrogen is relatively weakly adsorbed, and $\theta_{C_4H_7}$ will never approach unity provided that either (a) step (3) is only slow compared with step (1) in that (3) is kinetically the rate-determining step or (b) step (2) is at least as fast as step (3)

A second mechanism in which molecular hydrogen is involved can also be written;

$$C_4H_6\,(g) \rightleftharpoons C_4H_6\,(a) \qquad (a,a')$$

$$C_4H_6(a) + H_2\,(g) \xrightarrow{\text{slow}} C_4H_7\,(a) + H(a) \qquad (4)$$

$$C_4H_7(a) + H\,(a) \xrightarrow{\text{fast}} C_4H_8\,(a) \qquad (5)$$

From kinetic observations alone it is not possible to distinguish between the two reaction mechanisms. An interesting consequence, however, of the simple mechanism involving molecular 'hydrogen' is that d_0-butene should not be observed when butadiene reacts with deuterium; the least deuterated product according to such a mechanism would be d_1-butene.

The mechanisms postulated above do not explain the discrepancy between the orders determined by the initial rate method and the course orders determined from the pressure-time curves. However, the hydrogenation of many other hydrocarbons is subject to catalyst poisoning (124) and it seems reasonable to expect that this feature is common to the butadiene hydrogenation. If the extent of the poisoning increases, then the rate at any given time would be less than expected, in agreement with the experimental observations.

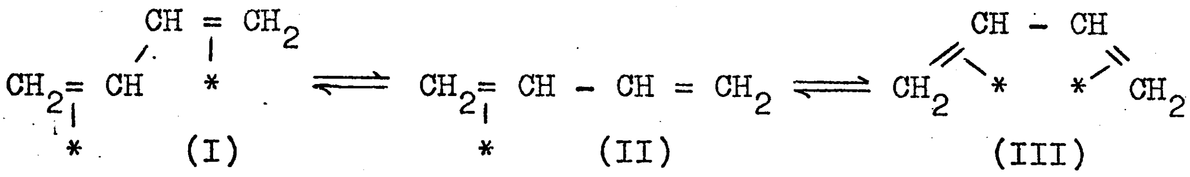
It is likely that the deactivation is caused by the accumulation on the surface of very strongly adsorbed hydrocarbon residues which reduce the number of catalytically active sites available for the adsorption of reactants in successive reactions. Such residues have been reported in radio-active tracer studies (85). At least some of the residue is irreversibly adsorbed for storage of the catalyst for 18 hours in hydrogen did not regenerate catalytic activity.

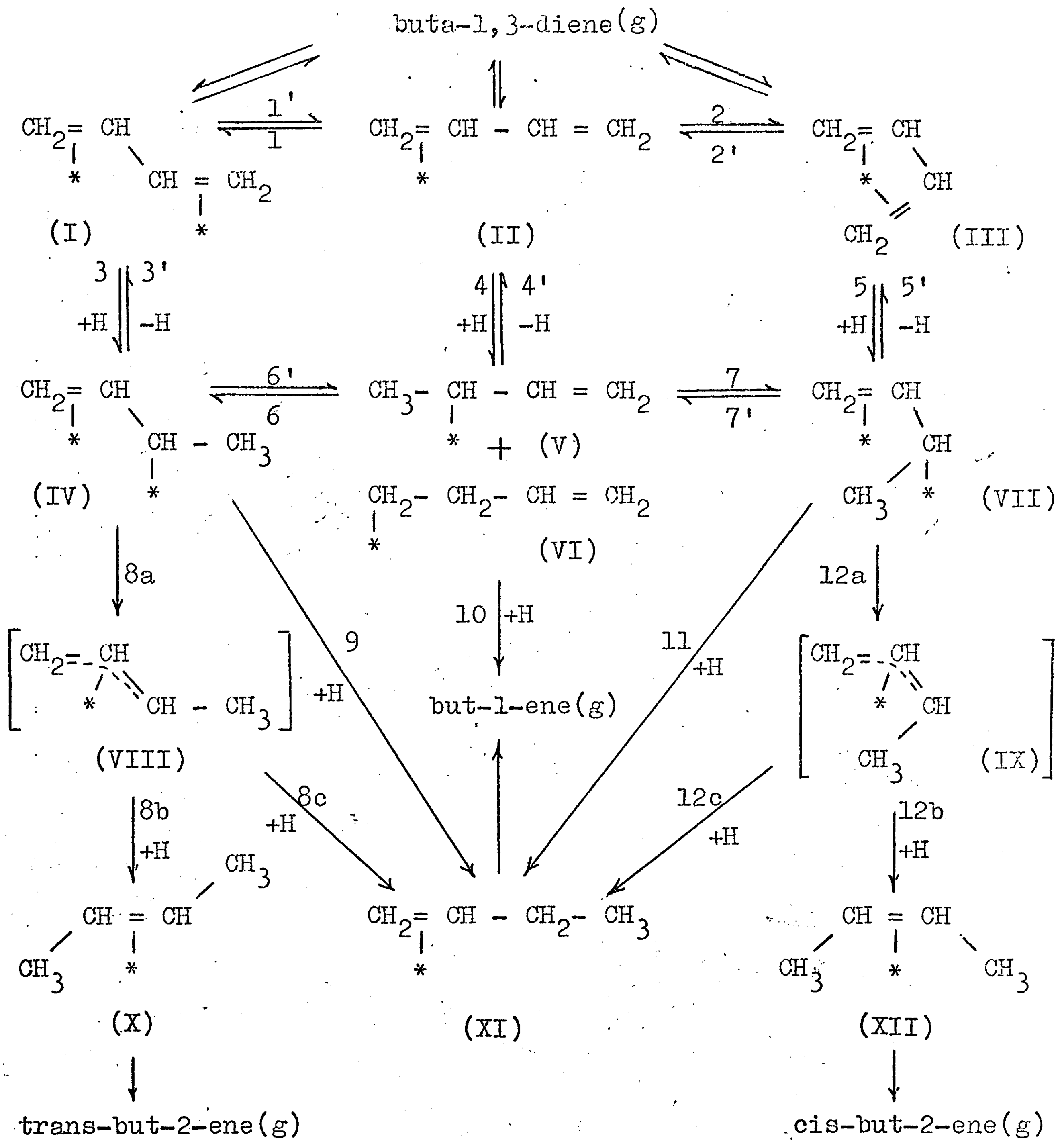
9.2 The distribution of butenes.

The object of this section is to derive a mechanism consistent with the butene distribution.

The experimental results show that the butene distributions are similar over both catalysts, but-1-ene being the major product and the trans-but-2-ene : cis-but-2-ene ratio being ~ 1:2. The distribution is independent of conversion until the later stages of reaction when the yield of but-1-ene decreases and there is a corresponding increase in the trans-and cis-but-2-ene yields.

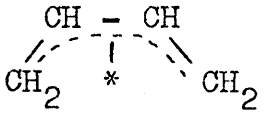
These observations are consistent with mechanism A (scheme 1, section 1.4.4), postulated by Wells et al. (67) whereby butadiene is chemisorbed as a mono-π-bonded species (II) and the two conformations of the di-π- bonded species (I) and (III) are formed from it.





Scheme 1. Reaction mechanism A

This mechanism affords an explanation of the observed trans-but-2-ene : cis-but-2-ene ratio. Smith and Massingill (75) have reported the ratio of gas phase transoid : cisoid butadiene to be approximately 95 : 5 at ambient temperatures. If it is assumed that butadiene adsorbs directly as (a) a di-π-complex with interconversion between the mono-and di-π-complex unimportant or (b) a π-allyl species which prohibits interconversion, provided that the two gas phase conformations have equal sticking probabilities one would expect a trans : cis ratio of around 20, since this ratio is governed by the ratio of syn : anti conformations of diadsorbed butadiene. However, if butadiene is considered to chemisorb as a mono-π-adsorbed species which converts rapidly to the two di-π-bonded species then the ratio of syn to anti diadsorbed butadiene need not be governed by the corresponding ratio in the gas phase, since the mono-adsorbed complex can rotate about the central C - C bond. The observed trans : cis ratio of 1 : 2, for both catalysts, suggests that the anti conformer of di-π- adsorbed butadiene is formed preferentially. This may be due to geometric restrictions which can arise in the formation of the syn complex, since this species involves two metal atoms, whereas the anti-complex may only involve one metal atom. It is also possible that the two complexes have different stabilities since the formation of the anti-complex offers scope for some degree of delocalisation of the π-electrons of the butadiene molecule, i.e.



This species will have a resonance energy of stabilisation which will not be present in the syn-complex, since the latter can only be regarded as involving two distinct independent π-olefin metal bonds. The geometric factor may also result in adsorbed hydrogen being able to react more readily with this species than with the syn-complex.

The reaction scheme also interprets the experimental observation that but-1-ene was initially the major product, since only but-1-ene can be formed by the independent hydrogenation of one double bond. It can also be seen that but-1-ene formed from the mono-π- bonded species may be formed as a gas phase product, whereas the butenes formed from the di-π- adsorbed species are formed as π-butene metal complexes and must undergo desorption before appearing in the gas phase.

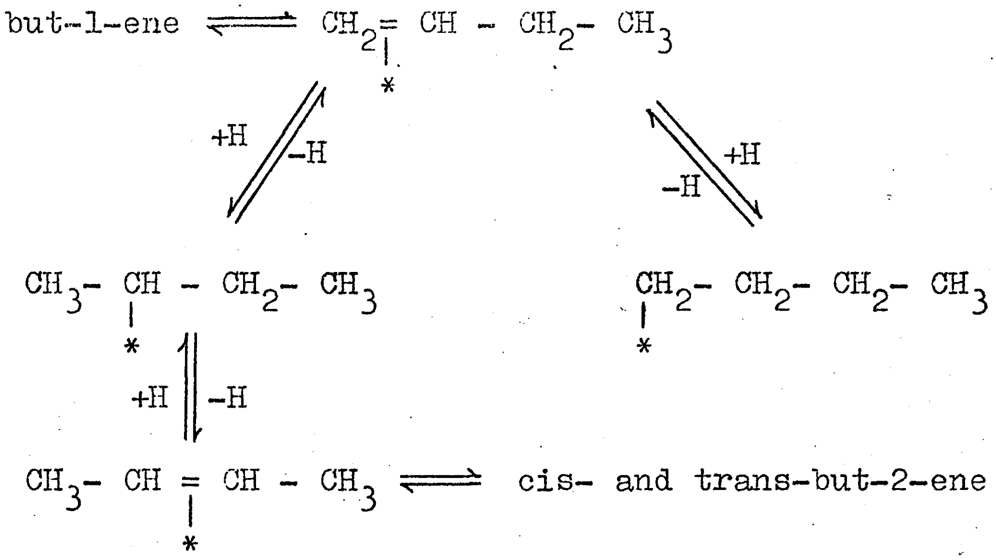
It seems unlikely, however, that the high but-1-ene yield is wholly a result of the hydrogenation of the mono-π-bonded butadiene. Firstly, the surface coverage of the mono-π-bonded species relative to the di-π- bonded species would be expected to be very small; secondly, the supported gold catalysts are unable to hydrogenate butenes, which are adsorbed as mono-π- bonded species.

Considering the mechanism of the reaction, it is readily apparent that 1,2-addition of hydrogen would be expected to be the predominant process. Thus, if the formation of the C_4H_7 species is a random process, one would envisage a but-1-ene : but-2-ene ratio of 3 : 1.

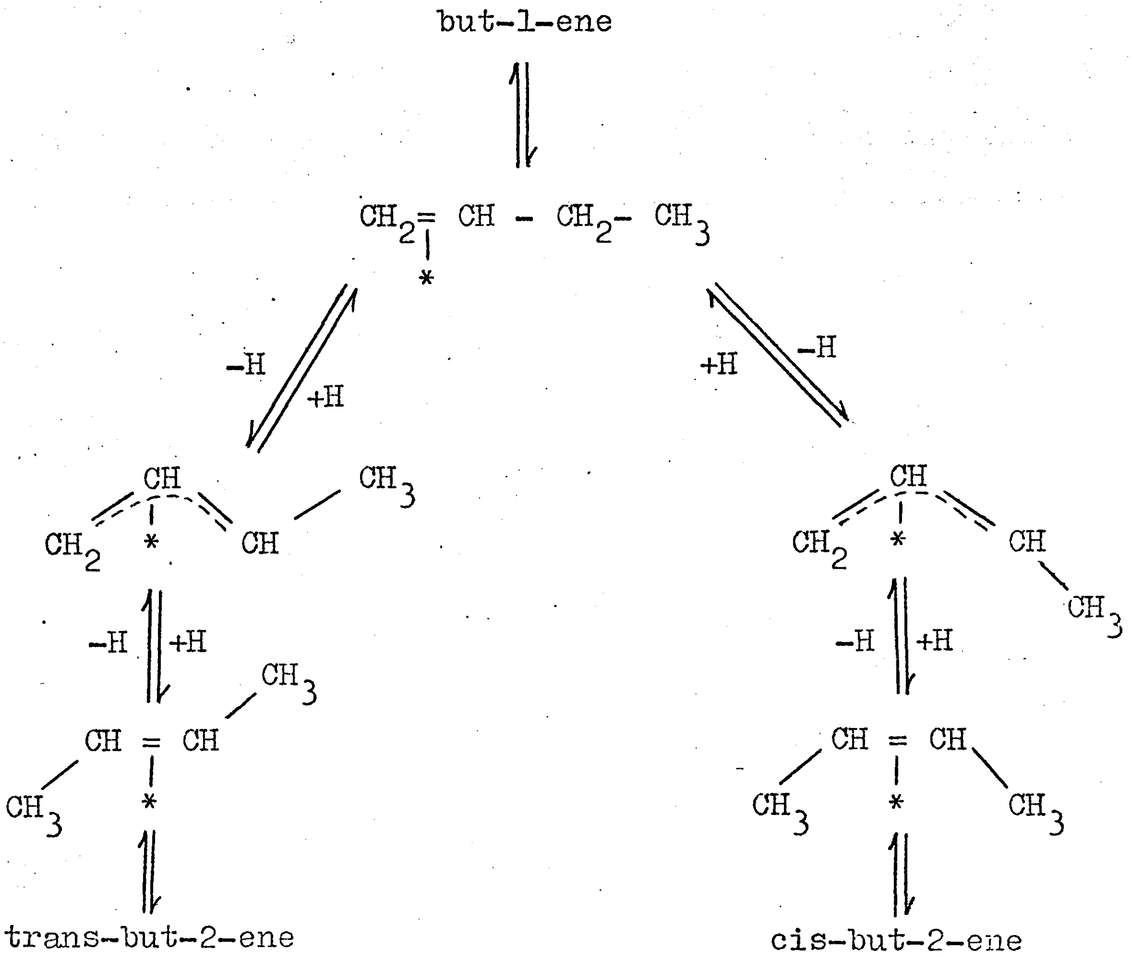
The mechanism postulates the direct formation of but-1-ene and the but-2-ene in the initial stages by separate 1,2- and 1,4- addition processes respectively, thus refuting a previous suggestion by Bond et al. (63) that the but-2-ene may be formed by 1,2-addition and subsequent isomerisation of but-1-ene. Mass spectrometry and nuclear magnetic resonance analysis provide conclusive evidence for the formation of the but-2-ene by the 1,4- addition process over alumina-supported cobalt (67). A sample of trans-but-2-ene formed from the reaction of an equimolar butadiene-deuterium mixture was examined and it was shown that 97% of the deuterium was located on the terminal carbon atoms. This shows unequivocally that this product has been formed by a 1,4- addition process, and that the mechanism involves very little exchange of hydrogen atoms bonded to non-terminal carbon atoms.

Constant surface coverage of butadiene is maintained up to 70% reaction. At this stage but-1-ene competes with the butadiene, subsequently undergoing isomerisation; a 1: 2 butadiene-deuterium mixture left over either catalyst will eventually reach thermodynamic equilibrium proportions. The but-1-ene which undergoes further reaction may be either (a) gas phase but-1-ene which is readsorbed, or (b) but-1-ene which is formed from the di-π-adsorbed butadiene and which does not desorb but remains on the surface as a π-complex. In either case, the extent to which isomerisation occurs will depend on the ability of the but-1-ene to compete with butadiene for the surface.

The isomerisation of but-1-ene on metal catalysts is generally assumed to occur by either of two general isomerisation



scheme I



scheme II

Mechanisms for isomerisation of but-1-ene.

mechanisms, namely scheme I, involving adsorbed alkyl intermediates or scheme II, via adsorbed π-allylic species.

If isomerisation of but-1-ene involved an adsorbed but-2-yl intermediate, it might be expected that, even though the surface concentration of hydrogen is extremely low at least some n-butane would be observed. Since no n-butane is observed, it seems unlikely that the isomerisation of but-1-ene to cis- and trans-but-2-ene occurred according to scheme I.

An alternative mechanism, involving 1-methyl-π- allyl intermediates, has been postulated to occur in the hydroisomerisation of but-1-ene over alumina- and silica-supported rhodium (124) and led Webb et al. (125) to investigate the site of the isomerisation process. The use of mercury as a catalyst poison shows that on supported rhodium catalysts the hydrogenation and hydroisomerisation of but-1-ene occur independently of each other and further, the support may have a significant role in determining the isomerisation activity of supported metal catalysts.

From the butene distribution alone, it is not possible to put forward an unequivocal mechanism for the isomerisation of n-butenes on the gold supported catalysts. However, the above study suggests that the nature of the support may influence the isomerisation process; this will be discussed more fully in the following section dealing with the deuterobutene distributions.

9.3 The butadiene exchange reaction and the deutero-butene distributions.

As the butadiene is strongly adsorbed, the probability of its desorption is relatively low in the temperature range under consideration. However, the formation of deuterated butadiene shows that chemisorption was reversible over both catalysts, and that chemisorbed butadiene equilibrated with some other species, probably chemisorbed C_4X_7 (X = H or D). This provides evidence for the reversibility of (a) some or all of the adsorption steps and (b) steps 3,4 and 5 of mechanism A.

The object of this section is to explain the variation of the deuterium distribution of the reaction products and the hydrogen content of the residual deuterium with (a) run number, (b) conversion, (c) initial deuterium pressure and (d) temperature. Other dominant features which require explanation are as follows

(i) the deuterium content of the trans-but-2-ene is always greater than that of the but-1-ene or cis-but-2-ene.

(ii) The most abundant butene obtained from the reaction over Au/γ-alumina is the d_1-species while that obtained over Au/Boehmite is the d_0-species.

(iii) butenes produced in series B (over the more active Au/γ-Alumina catalyst) have a higher deuterium content than those produced in series A.

Although the deuterium content of the trans-but-2-ene is slightly greater than the but-1-ene or cis-but-2-ene, the very small differences observed imply that each of the n-butenes are formed by the same mechanism. The small differences in deuterium number between butenes produced in the same reaction are considered to arise as a result of very small differences in the behaviour of the adsorbed species that give rise to these products.

The variation of deutero-butene distribution with run number has been shown to have a rather nebulous effect on other investigations involving the deuterium content of the butenes. It is postulated that this feature is linked with the striking observation of the low deuterium incorporation over both catalysts; for example, in the trans-but-2-ene obtained by reaction to 24% conversion at 200°C over Au/γ-alumina, the d_0- and d_1- species were 25 and 47% abundant respectively while in a corresponding reaction over Au/Boehmite, the relative yields were 46 and 40% respectively.

It is extremely unlikely that the reactant butadiene will yield sufficient hydrogen by an exchange process for two reasons

a) good "hydrogen" mass balance is not observed

b) the yield of exchanged butadiene especially over Au/Boehmite is very low.

There is also the possibility of dissociative adsorption of butadiene to give carbon-rich residues and hydrogen. However, the amount of hydrogen produced would not be expected to be sufficiently large to satisfy the observed deutero-distributions.

This implies that there is in the system a ready source of hydrogen which is associated with thecatalyst.

This postulate is upheld by one's inability to obtain good mass balance. Furthermore, although unique N-profiles cannot be obtained under the experimental conditions used, results indicate that in the equilibrated surface 'pool' of HD, the ratio of deuterium to hydrogen is very low.

The question arises as to why unique N-profiles cannot be obtained for the reaction of butadiene over supported gold catalysts. The method for calculating the N-profile described by Burwell(123) assumes that the hydrogenation of the hydrocarbon occurs by the conventional mechanism developed by Horiuti and Polanyi (48,49). According to this theory the active 'pool' on the surface of the catalyst contains adsorbed deuterium and hydrogen atoms which originate from the reactant molecules. The low deuterium content of the butenes obtained over the supported gold catalysts, the inability to obtain good mass balance and the hydrogen to deuterium ratio of the surface 'pool' all point to hydrogen from the support taking part in the reaction. This constitutes a source of hydrogen to the surface 'pool' which is not accounted for in Burwell's method of calculating the N-profile. If however there is more than one hydrogen-deuterium 'pool' on the surface, it may be possible to calculate a series of N-profiles for each 'pool'. Then by selecting a certain combination of particular N-profiles, one ~~from~~ for each surface 'pool', one may be able to find N-profiles which together fit a deuterodistribution.

A later section will consider in detail the manner in which the support hydrogen is incorporated into the reaction scheme. In the present context, however, it is sufficient to consider a 'pool' of hydrogen from the support and deuterium from the gas phase on the catalyst surface. It is apparent that in the presence of the diolefin the hydrogen and deuterium of the 'pool' reach equilibrium rapidly, as is evidenced by the percentage abundancies of the d_0- and d_1- butene found in the early stages of reaction.

The existence of hydroxyl groups on the surface of alumina has been demonstrated by several workers (126-129) Thus the number of hydrogen atoms or molecules available to the surface 'pool' is determined by the number of terminal hydroxyl groups and adsorbed water molecules on the support. The introduction of gas phase deuterium with each succeeding reaction means that the surface concentration of deuterium increases and hence the higher deutero-content of the butenes produced in later reactions is explained.

A consequence of this postulate is that variations in the structure of the support will be reflected in the number of hydrogen atoms or molecules available to the surface 'pool'. The observed activity of the gold catalysts studied is Au/Boehmite > Au/γ-alumina > Au/α-alumina ~ Au/silica $\sim$ O. Although the BET surface area for the γ-alumina (180 ± 5 m^2g^{-1}) is greater than for α-alumina (5 ± 1 m^2g^{-1}), that for silica (175 ± 5 m^2g^{-1}) is very similar. Also Hall et al. (37,126) have demonstrated that the surface density of terminal hydroxyl groups is approximately the same on γ-alumina and silica, whilst Altham and Webb (85) have shown that the reactivities of these -OH groups in hydrogen exchange are similar for γ-alumina and silica. Furthermore these hydroxyl groups readily undergo exchange at 200°C both in the presence and absence of metal (85). It is unlikely therefore that, in the present study, the terminal hydroxyl groups on the support are the source of hydrogen atoms and it is postulated that the differences in activity of the various supported gold catalysts are determined by the amounts of water associated with the catalyst support.

If water associated with the support plays an important part in the hydrogenation of butadiene over the supported gold catalysts, it would be expected that boehmite would be a better donor of hydrogen than alumina since in the hydrated species there is an increased reservoir of hydrogen due to the water in the lattice. This would lead to a greater concentration of hydrogen on the surface of the Au/Boehmite catalyst and thus butenes formed from reaction over that catalyst would have a lower deuterium content than those obtained over Au/γ-alumina. This is in agreement with the experimental observations. Examination of the mass balance figures supports the concept of hydrogen from the water of the boehmite being involved in the reaction. It can be seen that the ~~degree~~ extent of ~~balance~~ imbalance is consistently much less for reactions over Au/Boehmite; this is expected in view of this catalyst being able to supply more hydrogen to the surface 'pool'. The difference in the deutero-content of the butenes obtained in reaction series A and series B is also taken to reflect the different amounts of water associated with the alumina supports.

No obvious relationship between the deuterium number of the butenes and conversion is readily discernible. However, it seems likely that the relationship observed over the other Group VIII metals (67) is maintained, i.e. the deuterium content of the butenes increases with conversion. This is due to butadiene undergoing exchange and subsequent readsorption and hydrogenation of the deutero-butadienes. This implies that the deutero-butene distributions are essentially determined before hydrogenation occurs, and hence that exchange of the adsorbed butene does not play a major role. This is consistent with the earlier supposition that isomerisation of adsorbed but-1-ene is unlikely to be responsible for formation of but-2-ene up to 70% conversion.

Consideration will now be given to the mechanisms for the formation of the but-1-ene and the but-2-ene in the light of their respective deuterium distributions. If isomerisation of adsorbed but-1-ene is an important source of the trans- and cis-but-2-ene, it would be expected that the deuterium content of the but-2-ene isomers would be the same, and also different from that of but-1-ene; this would be true regardless of the mechanism by which the isomerisation occurred. Whether the deuterium number of the but-2-ene would be greater or less than that of but-1-ene would depend on the relative concentrations of hydrogen and deuterium on the catalyst surface. Only in reaction F/7, left for 18 hours over Au/Boehmite was the deuterium content of the trans- and cis-but-2-ene identical ; in this case the deuterium numbers were less than that of but-1-ene. This is consistent with the surface 'pool' being rich in hydrogen.

Reaction F/7 provides the only direct evidence for the formation of the but-2-enes by isomerisation. That there is no variation in the normal trend of the deuterium content in the butenes is due to (a) the high concentration of hydrogen relative to deuterium on the surface, and (b) the limited extent to which isomerisation occurs while but-1-ene is in competition with the more strongly adsorbed butadiene for the surface.

The deutero-butene distributions show that over Au/Boehmite, with increasing deuterium pressure, the amounts of d_2- and d_3- butenes increase relative to the yields of the other isotopic isomers. This is best interpreted by considering that the surface concentration of deuterium increases with increasing deuterium pressure and consequently the ratio $\theta_H : \theta_D$ will decrease, and that the chance of the reaction intermediates acquiring a deuterium atom will increase. This is consistent with the observation that the hydrogen number of the residual deuterium decreases with increasing deuterium pressure.

Over Au/γ-alumina, the increase in yield of multi-exchanged species is not immediately as evident. However, if the variation in deutero-distributions with run number is taken into account, it is apparent that increasing the deuterium pressure produces the same effect. This is explained in the same manner as over Au/Boehmite.

As might be expected, better mass balances were obtained when higher partial pressures of deuterium were used. As before, better balances were obtained over Au/γ-alumina although even in the extreme case of a 4 : 1 ratio of deuterium : diolefin some hydrogen is involved in the reaction.

Experimental observations show that over Au/Boehmite the deuterium content of the butenes decreases with increasing temperature; this trend is also distinguishable over Au/γ-alumina if the run number effect is taken into consideration. This is indicative of an increase in the surface ratio $\theta_H : \theta_D$ with increasing temperature. This is consistent with the observations that (a) the hydrogen content of the residual deuterium increases with temperature and (b) better mass balances are obtained at low temperature.

9.4 The role of the support.

It has already been suggested in section 9.3 that the catalyst support is not simply an inert carrier for the metal, but plays an active part in the reaction by acting as a source of hydrogen. Consideration will now be given to the manner in which the support is involved.

Since hydrogen is not measurably chemisorbed on gold films below 200°C (40,93) it is important to consider the manner whereby the hydrogen in the catalysed hydrogenation reaction enters into the system. There are two possible modes of influence of the support. First, the support may, due to electronic interactions, cause a change in the chemical behaviour of the gold, such that the metal may chemisorb hydrogen. Alternatively the support may in some way act as the source of hydrogen atoms which can freely migrate from the support to the metal and participate in the hydrogenation reaction.

The former of these postulates can be ruled out on the evidence of the results obtained from the interaction of butadiene with deuterium, in particular the failure to obtain satisfactory "hydrogen" mass balances between reactants and products, the failure to obtain satisfactory N-profiles to describe the deutero-butene distributions and the high yield of d_0- and d_1-butene observed with both the gold/γ-alumina and gold/Boehmite catalysts. Furthermore, the E.S.R. and ultraviolet spectroscopic examinations of the catalyst suggest that the electronic properties of the supported catalyst are not appreciably different from those of the unsupported gold.

Considering the alternative postulate, the support may act as a source of hydrogen in either of two ways; (1) gas phase hydrogen may be chemisorbed on the support and then migrate on to the metal where reaction occurs; (2) hydrogen atoms migrate fromthe support to the metal and there activate the chemisorption of the gas phase hydrogen.

The possibility of migration of hydrogen between the support and the metal is now generally accepted (10,84-86). Wells and Wilson (84), when reporting the isomerisation of butenes catalysed by supported metals in the absence of molecular hydrogen, suggested that, over alumina-supported metals, the isomerisation occurs by an addition-abstraction mechanism which was initiated by hydrogen atoms which migrated from the alumina to the metal. Sancier and Wise (108) have studied the reaction between hydrogen and deuterium catalysed by gold foils. They pointed out that the energy barrier for the dissociative chemisorption of hydrogen on gold could be circumvented by exposing the metal foil to atomic hydrogen. It is thus possible that in the present work, hydrogen atoms from the support migrate on to the metal, thereby establishing a hydrogen atom pool on the gold surface which may either react with adsorbed hydrocarbon species or may "catalyse" the dissociative adsorption of gas phase "hydrogen". In this way it is possible to envisage the establishing of separate "hydrogen" and deuterium pools on the metal surface, in the butadiene-deuterium reaction, and hence the difficulty in interpreting the deutero-butene distributions. Furthermore, although it is not possible at this stage to define precisely the source of hydrogen atoms on the alumina, the decreasing activity of the catalyst with successive reactions is explicable by considering that the migration of hydrogen ~~from~~ to metal ~~to~~ from support is effectively prohibited under reaction conditions. This will be the case, if the rate of migration is slow relative to the rate of hydrogen atom uptake by adsorbed hydrocarbon.

Last, in the context of the hydrogenation activity of supported gold catalysts, it is interesting to note the studies of the hydrogenation of but-1-ene and cyclohexene by Wood and Wise (109,110). Hydrogen was supplied to a gold surface by diffusing it through a palladium-silver alloy membrane on which a gold surface was electroplated. This work demonstrates the importance of chemisorbed hydrogen in the catalytic hydrogenation of olefins, a notion not without support in recent literature. For example, McCabe and Halsey (130) correlated an enhanced ethylene hydrogenation activity on copper with the quantity of adsorbed hydrogen.

CHAPTER 10

REACTIONS OF BUTA-1,3-DIENE WITH DEUTERIUM OVER SUPPORTED COPPER CATALYSTS.

The object of this section is to postulate possible mechanisms which will explain the observed kinetics, the distributions of butenes and the deuterated product distributions for the reaction of butadiene with deuterium over Cu/silica. An attempt will also be made to correlate the results with those obtained in a previous study (67) of the hydrogenation of butadiene over Cu/alumina.

Since the experimental observations were similar over both catalysts, the mechanisms will be discussed simultaneously, differences being discussed when the occasion arises.

10.1 The kinetics of the reaction.

The pressure fall against time curve was characterised by a much diminished rate corresponding to near removal of butadiene; no n-butane was formed under any conditions until all butadiene had been removed. The curve also indicated a first order reaction, in agreement with the orders determined by the initial rate method - first order in hydrogen, zero order in deuterium. The activation energy is 10.8 ± 0.1 kcal mol^{-1} over Cu/silica. These features are common to reactions catalysed by the noble Group VIII metals (63,67) and suggest that a similar mechanism is involved.

The initial rate order of unity in hydrogen can be explained by the following mechanism;

$$C_4H_6(g) \rightleftharpoons C_4H_6(a) \qquad (a,a')$$

$$H_2(g) \rightleftharpoons 2H(a) \qquad (b,b')$$

$$C_4H_6(a) + H(a) \rightleftharpoons C_4H_7(a) \qquad (1,2)$$

$$C_4H_7(a) + H(a) \longrightarrow C_4H_8(a) \qquad (3)$$

This mechanism is the same as that postulated for the hydrogenation of butadiene over the supported gold catalysts (section 9.1). Applying the steady state treatment as before, the rate of reaction is given by:

$$\text{Rate} = k_1k_3 . \theta_{C_4H_6} . \theta^2_H / (k_2+k_3\theta_H)$$

and applying the condition that θ_H is small so that $k_2 \gg k_3\theta_H$ and also assuming that $\theta_H \propto P_{H_2}^{0.5}$

$$\text{rate} = (k_1k_3/k_2).\theta_{C_4H_6} . P_{H_2}$$

The other possible mechanism is

$$C_4H_6(g) \rightleftharpoons C_4H_6(a) \qquad (a,a')$$

$$C_4H_6(a) + H_2(g) \xrightarrow{\text{slow}} C_4H_7(a) + H(a) \qquad (4)$$

$$C_4H_7(a) + H(a) \xrightarrow{\text{fast}} C_4H_8(a) \qquad (5)$$

This mechanism would also show an initial rate order of unit in hydrogen.

10.2 The distribution of butenes.

All three butenes were formed initially with but-1-ene the most abundant product and almost equal yield of trans- and cis-but-2-ene. Consideration will be given to the initial composition of the butenes and their variation with (a) conversion, (b) initial 'hydrogen' pressure, and (c) temperature.

The observed distributions can be interpreted by the reaction scheme put forward by Wells (67), shown in section 9.2. The mechanism was constructed on the assumption that butadiene was chemisorbed as a mono-π-bonded species and the syn and anti di-π-adsorbed species were formed rapidly and in equal proportions from it. The reasons for assuming that mechanism A is operating are essentially the same as those described in section 9.2.

The but-1-ene and but-2-ene yields closely resemble that expected from a random addition of hydrogen to the adsorbed butadiene molecule. This factor is therefore concluded to be responsible for the high but-1-ene : but-2-ene ratio although some hydrogenation of the mono-π-bonded species may still occur.

Although the ratio in the gas phase of transoid : cisoid butadiene is ~ 15, chemisorption of butadiene as a mono-π-adsorbed species allows rotation about the central C-C bond and the syn and anti di-π-adsorbed species can be formed in equal proportions. This would lead to equal yields of trans- and cis-but-2-ene. The scheme assumes that 1,2-addition results in the formation of but-1-ene and trans- and cis-but-2-ene are formed exclusively from the 1,4-addition process.

10.2.1 The dependence of butene distribution upon conversion.

The distribution of butenes was independent of conversion during the first stage of diolefin hydrogenation; in the second stage which commenced when all butadiene had been removed the but-1-ene : but-2-ene ratio decreased. This was accompanied by the production of n-butane. The but-1-ene which undergoes further reaction when the hydrogenation of the diolefin is complete could either be (a) gas phase but-1-ene which is readsorbed or (b) but-1-ene, which is formed from the di-π-adsorbed butadiene and which does not desorb but remains on the surface as a π-complex. The increase in but-2-ene yield suggests that isomerisation of but-1-ene occurs, either by the but-2-yl reversal or by the π-olefin/π-allyl mechanisms outlined in section 9.2. The corresponding production of n-butane may indicate that isomerisation of but-1-ene occurs by scheme I, the alkyl reversal mechanism, since the same intermediate is involved in both reactions, i.e. adsorbed but-2-yl.

10.2.2 The dependence of butene distribution upon increasing 'hydrogen' pressure.

The butene composition was independent of the initial hydrogen pressure which may indicate that if, as appears to be the case, the butenes are all formed directly from butadiene, the initial step in the formation of each butene is the same.

10.2.3 The dependence of butene distribution upon temperature.

It was observed that the but-1-ene : but-2-ene ratio decreased with increasing temperature and the trans : cis ratio was virtually independent of temperature.

This was interpreted by Bond et al. (63) to mean that the isomerisation of but-1-ene to cis- and trans- but-2-ene was important. Increasing temperature was found to increase the rate of isomerisation of but-1-ene and thus one would have expected that, if but-1-ene isomerisation occurred in the butadiene reaction, increasing temperature would increase the but-2-ene yield relative to the but-1-ene yield. The constant trans : cis ratio was interpreted to mean that the same intermediates are involved in butadiene hydrogenation and but-1-ene isomerisation. It became apparent in a preceeding section, however, that the mechanism of separate 1,2- and 1,4-addition of hydrogen to butadiene offered the more satisfactory explanation of the butene distribution and thus other factors must determine the temperature-variation of the butene yield.

It is possible that the mono-π-bonded species becomes progressively less important as the temperature is raised. Consideration of the dependence of the trans : cis ratio on temperature yields no information on the rates of conformational interconversion since the ratio is virtually constant over the temperature range studied. The results over metal wires (66), however, show that in these reactions the trans : cis ratio is temperature dependent and suggest that conformational interconversion of the syn and anti π-adsorbed species is more important at high temperatures with the result that the but-1-ene yield is increased with increasing temperature.

It may therefore be concluded that the temperature-dependence of the butene yield is a result of the activation energy for 1,4-addition being higher than 1,2-addition. Previous results (63) suggest that this is, in fact, the case.

10.3 The butadiene exchange reaction and the deuterobutene distributions.

As with supported gold catalysts, the formation of deuterated butadiene shows that chemisorption was reversible and that chemisorbed butadiene equilibrated with some other species, probably chemisorbed C_4X_7(X = H or D). This provides evidence for the reversibility of (a) some or all of the adsorption steps and (b) steps 3,4 and 5 of mechanism A.

Consideration will now be given to the behaviour of the butadiene exchange reaction, the hydrogen-deuterium exchange reaction and the deutero-butene distributions with respect to (a) conversion, (b) initial 'hydrogen' pressure, and (c) temperature.

10.3.1 The effect of conversion.

The deuterium content increases with increasing conversion because exchanged butadiene is eventually readsorbed and hydrogenated. Thus over Cu/silica at 157°C the deuterium number of the butadiene increases from 0.37 at 25% conversion to 1.16 at 83% conversion while the deuterium number of trans - but-2-ene increases from 1.23 to 1.85 for the same pressure falls. Variation of the hydrogen number of the residual deuterium with conversion is very small although a trend of increasing hydrogen content with conversion may just be discernible. This is also a result of the butadiene exchange process.

Although the deuterium numbers of all butenes are closely similar, a small but consistent variation is apparent, i.e. throughout the series cis-but-2-ene contained slightly less deuterium than trans-but-2-ene but slightly more than but-1-ene. It appears likely that the differences in deuterium content reflect small differences in the reactivity of the intermediates leading to the isomers. The relatively non-deuterated character of the but-1-ene can be explained in the following way.

When the syn and anti di-π-bonded species are formed randomly from the mono-π-adsorbed species, areas of surface will remain uncovered, and the geometry is such that further formation of these species is sterically precluded. Scale drawings show that dissociative chemisorption of hydrogen may occur on these areas, and that butadiene, may still be chemisorbed as the mono-π-bonded species. The experimental observations suggest that diolefin exchange by this species followed by desorption occurs rapidly to cause the adsorbed 'hydrogen' in the vicinity of these 'special' sites to become H-rich. Since hydrogenation at these 'special' sites will give only but-1-ene the relatively non-deuterated character of this isomer is interpreted.

Good mass balance over Cu/silica is not obtained. No definite trends are visible but the balance is slightly better at 157°C than at 200°C. It appears therefore that hydrogen from the support must also participate to at least a small extent in this reaction. No mass balance calculations are available for the reactions over Cu/alumina. However, a comparison between the deutero-content of the butenes obtained over the two catalysts indicates that the deuterium number of the butenes are quite similar and differences may be attributed to the effect of temperature.

	% Con.	Tp. (^{o}C)	1-BUT	TRANS	CIS
Cu/Al_2O_3(67)	80	120	1.35	1.48	1.44
Cu/SiO_2	75	157	1.59	1.77	1.70
Cu/SiO_2	87	200	2.02	2.08	2.06 .

The support therefore does not appear to be a dominant feature in the determination of the deuterium content of the products of the reaction of butadiene with hydrogen over copper catalysts.

10.3.2 The effect of initial deuterium pressure.

Increasing the initial deuterium pressure results in an increase in the yields of multi-exchanged species relative to the amount of the other isotopic isomers. This is indicative of a decrease in the ratio $\Theta_H : \Theta_D$, the surface concentrations of atoms, with increasing temperature, and as a result the chance of the reaction intermediates acquiring a deuterium atom will increase. This is consistent with the observation that the hydrogen number of the residual deuterium decreases with increasing deuterium pressure. Alao, as expected, better mass balance is obtained at high deuterium pressure.

10.3.3 The effect of temperature.

It was observed that the deuterium content of the butenes increased with temperature. The trend however was not marked. These observations suggest small variations in the surface concentration of hydrogen atoms, the ratio $\Theta_H : \Theta_D$ increasing with temperature. The similarity of the hydrogen numbers of the residual deuterium and the degree of unbalance from mass balance calculations indicate that variations are in fact slight.

CHAPTER 11

SUMMARY AND CONCLUSIONS.

From the discussion sections it would appear that the butene distributions can be explained by considering a reaction scheme whereby butadiene adsorbs initially as a mono-π-adsorbed species which rapidly undergoes further adsorption to the di-π-adsorbed complexes. The mono-π-bonded species is of importance in determining the trans-but-2-ene : cis-but-2-ene ratio since it affords a way of changing the gas phase equilibrium proportions for the transoid and cisoid conformations of butadiene from around 95 : 5 to the observed ratio. The resonance energy of stabilisation associated with the anti di-π-adsorbed complex, in which the electrons may be delocalised, is believed to be of importance in determining the trans-but-2-ene : cis-but-2-ene ratio of 1: 2 observed over the supported gold catalysts. In the initial stages of the reaction but-1-ene and the but-2-ene have been concluded to arise from separate 1,2- and 1,4-addition processes although in the later stages of reaction over the supported gold catalysts isomerisation occurs, possibly via a 1-methyl-π-allyl intermediate.

Since the deuterium content of the butenes increases with successive reaction over Au/γ-alumina and Au/Boehmite, it is necessary to take into account the order in which reactions were carried out when examining the variation of the deutero-butene distribution with conversion, initial deuterium pressure and temperature. However, if this is done, trends are observed which are closely similar to those observed over Cu/silica and Cu/alumina (67). The deuterium content of the butenes increases with conversion due to butadiene undergoing exchange before being readsorbed and hydrogenated. The effect of variation of temperature and initial deuterium pressure is to alter the surface ratio of hydrogen : deuterium atoms; the ratio decreases with increasing deuterium pressure and increases with temperature and hence butenes of increased deuterium content are obtained at higher initial deuterium pressure and lower temperature. As the surface hydrogen to deuterium ratio increases, the hydrogen number of the residual deuterium is seen to increase.

Over the gold supported catalysts, the low deuterium incorporation and the inability to obtain good "hydrogen" mass balance and unique N-profiles is interpreted as suggesting that hydrogen from the support takes part in the reaction. Migration is postulated to occur between the support and the active sites on the metal where the hydrogenation takes place. Over Au/Boehmite the d_0-species is the predominant product while over Au/γ-alumina the d_1-species is most abundant. This is thought to reflect the different nature of the supports; the boehmite is a better donor of hydrogen due to the water associated with the boehmite lattice. Although good mass balance and unique N-profiles cannot be obtained over the supported copper catalysts, the influence of the support is less important. Hence butenes obtained under similar conditions over Cu/alumina (67) and Cu/silica show very similar deutero-content.

APPENDIX A.

Equations for calculation of parent ion concentrations in mass spectrometric analyses.

The reason for the need to correct the measured intensity of each mass for the fragmentation of higher masses has been described in section 4.5. The full equations are listed below.

X = parent ion concentration ($X = A, B, C, \ldots\ldots\ldots$ etc.)

x = measured positive ion current ($x = a, b, c, \ldots\ldots\ldots$ etc.)

X' = parent ion concentration after correction for C^{13}

($X = A', B', C', \ldots\ldots\ldots$ etc.)

f_1 and f_2 are the fractions of the first and second fragments respectively.

A. n- Butane

m/e

68 $A = a$

67 $B = b$

66 $C = c - f_1(A + .10B)$

65 $D = d - f_1(.90B + .20C)$

64 $E = e - f_1(.80C + .30D) - f_2(A + .200B + .022C)$

63 $G = g - f_1(.70D + .40E) - f_2(.80B + .356C + .067D)$

62 $H = h - f_1(.60E + .50G) - f_2(.623C + .467D + .133E)$

61 $I - i - f_1(.50G + .60H) - f_2(.467D + .534E + .222G)$

60 $J - j - f_1(.40H + .70I) - f_2(.333E + .556G + .333H)$

59 $K = k - f_1(.30I + .80J) - f_2(.222G + .534H + .467I)$

58 $L = l - f_1(.20J + .90K) - f_2(.133H + .467I + .623J)$

57 $M = m - f_1(.10K + L) \quad 1\, f_2(.067I + .356J + .800K)$

56 $N = n - f_2(.022J + .20K + L)$

A. n-Butane /

Correction for C^{13}.
$L' = L$
$K' = K - 0.044L'$
$J' = J - 0.044K'$
etc.

B. n-Butenes

m/e

64 $A = a$
63 $B = b$
62 $C = c - f_1(A + .125B)$
61 $D = d - f_1(.875B + .25C)$
60 $E = e - f_1(.375D + .750C) - f_2(.250B + .036C + A)$
59 $G = g - f_1(.500E + .625D) - f_2(.107D + .429C + .750B)$
58 $H = h - f_1(.625G + .500E) - f_2(.214E + .536D + .536C)$
57 $I = i - f_1(.750H + .375G) - f_2(.357G + .572E + .357D)$
56 $J = j - f_1(.875I + .250H) - f_2(.536H + .536G + .214E)$
55 $(K = k - f_1(J + .125I) - f_2(.750I + .429H + .107G))$
54 $(L = l - f_2(J + .250I + .036H))$

Correction for C^{13}.
$J' = J$
$I' = I - 0.044J'$
$H' = H - 0.044I'$
etc.

C. 1,3-Butadiene

m/e

60 $A = a$
59 $B = b$
58 $C = c - f_1(A + .167B)$
57 $D = d - f_1(.833B + .333C)$
56 $E = e - f_1(.667C + .500D) - f_2(A + .333B + .067C)$
55 $G = g = f_1(.500D + .667E) - f_2(.400C + .600D + .400E)$

C. 1,3-Butadiene/

54 $H = h - f_1(.333E + .833G) - f_2(.400C + .600D + .400E)$

53 $I = i - f_1(.167G + H) - f_2(.200D + .536E + .667G)$

52 $J = j - f_2(.067E + .333G + H)$

Correction for C^{13}.

$H' = H$

$G' = G - 0.044H'$

$E' = E - 0.044G'$

etc.

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