THE MECHANISM OF CATALYTIC HYDROGENATION AND RELATED REACTIONS

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Introduction

VERY many of the processes of chemical industry require at some stage the use of solid catalysts, and as a result the science of heterogeneous catalysis has become of major interest. The petroleum industry in particular relies to a large extent on certain types of catalyst to effect the cracking of natural oil, and the re-formation of the products to yield high-octane gasoline. The production of synthetic fuels by the Fischer–Tropsch process is becoming of increasingly greater importance. Fundamental knowledge concerning these reactions is in most cases far from adequate, a contributing factor being the complexity of the systems and the large number of variables involved.

The object of this article is to review one particular section of the problem of heterogeneous catalysis, namely, the hydrogenation of unsaturated molecules over transition-group metal catalysts, and the reactions undergone by the resulting saturated molecules. These are reactions in which carbon–carbon and/or carbon–hydrogen bonds are either broken or formed at the catalyst surface. Such reactions are of considerable industrial importance, especially in the hardening of oils, and on a smaller scale have application in preparative organic chemistry. Their importance has resulted in a large amount of experimental work, the more recent part of which is considered in this Review. The situation is somewhat confusing, and an attempt will be made to construct a coherent picture, but this is made difficult by the variety of approaches made to the subject and the divergence of views expressed by various authors. There are, however, considerable areas of agreement, but the emphasis will at all times be on the problems which still remain to be solved.

The evidence suggests that in the course of hydrogenation and exchange reactions of hydrocarbons radicals are formed which are adsorbed on the catalyst surface ; they are not in general " free radicals " in the sense of having an unpaired electron, and they are usually attached to the surface by one covalent bond. They are in fact the " half-hydrogenated states " first suggested [1] in 1934. It is proposed that an interpretation of the experimental work is to be best sought in terms of the properties of these radicals.

Chemisorption.—The distinction between physical or van der Waals adsorption and chemisorption has long been recognised ; [2] for a surface

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[1] Horiuti and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.

[2] Lennard-Jones, *ibid.*, 1932, **28**, 333.

reaction to occur, at least one of the reactants, whether they be chemically different or not, must be chemisorbed. The necessity for the adjacent adsorption of both reactants has not been shown, although it has been suggested that reaction between two such adsorbed entities is more likely than if only one of them is adsorbed and the other collides with it from the gas phase.

It is now generally assumed that the chemisorption of olefins on the surface of transition-group metal catalysts occurs by the " associative " mechanism, in which the double bond is broken and two carbon–metal bonds are formed. This is represented in the following way : $C_2H_{4_{(g)}} \rightarrow \overset{*}{C}H_2{-}\overset{*}{C}H_2$, the asterisk indicating the bond to the catalyst. The alternative " dissociative " mechanism, which in the case of ethylene would initially produce an adsorbed vinyl radical and an adsorbed hydrogen atom, is still occasionally advocated, and may indeed occur under certain conditions. However it will be supposed that it is not operative under hydrogenation conditions. Adsorbed acetylene similarly has an ethylene-like structure :

$$C_2H_{2_{(g)}} \rightarrow \overset{*}{C}H{=}\overset{*}{C}H$$

The geometry of adsorbed ethylene and acetylene has been worked out in detail.[3, 4] Plausible interatomic distances and bond angles being assumed, it has been shown that the optimum distance between, say, two nickel atoms is 2·87 Å for ethylene and 3·33 Å for acetylene. On this picture, adsorbed ethylene could be accommodated on the (110) and (111) faces of nickel, and acetylene on the (110) and (100) faces, each packing sufficiently tightly to cover all possible sites without mutual interference. Maxted [5] has suggested that adsorbed ethylene may have a resonating structure : it is also possible that partial bonds may be formed between the carbon atom and several catalyst atoms.

The process of chemisorption is accompanied by the liberation of energy, and the resulting heats of adsorption have been measured in a number of cases.[6] Unfortunately, owing to certain ambiguities, such determinations are not of great value in assisting the understanding of the mechanism of surface reactions. First, heats of adsorption vary very widely with the method of preparation and state of the catalyst ; much higher values have been found over evaporated films of high purity than over less pure supported metals. Partly as a result of this, films are less active and more readily poisoned than supported catalysts.[7] Secondly, there is doubt concerning the measurement of high surface coverages ; thus, recent work on the hydrogen–tungsten system has shown that heats of adsorption fall to much lower values than was previously thought, and this has resulted in a changed view concerning the mode of hydrogen exchange on this metal.[8] Furthermore, disproportionation reactions occur over metal films at high coverages.[6] The third and most serious difficulty is the inability to measure

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[3] Sheridan, *J.*, 1944, 373.

[4] Herington, *Trans. Faraday Soc.*, 1941, **37**, 361.

[5] Maxted, *J.*, 1949, 1990.

[6] Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118.

[7] H. S. Taylor, *ibid.*, p. 9.

[8] Rideal and Trapnell, *ibid.*, p. 114.

the heats of adsorption of two reactants under experimental conditions ; thus the mutual interfering effects in a case such as hydrogen and ethylene are unknown quantities. Regardless of these difficulties, an attempt has been made to use data on heats of adsorption for estimating the heats of reaction of individual steps in surface reactions.[9]

Determination of Kinetics and Product Analysis.—In hydrogenation reactions, manometric measurements of the decrease in pressure as a function of time are necessary for determining the kinetics of the addition reaction. Orders of reaction may be found by measuring the initial rate of the fall in pressure as a function of the partial pressures of the reactants over a catalyst of steady activity. It is necessary to distinguish carefully between the results so obtained, which constitute an " initial rate law ", and the " course rate law " found by analysing the pressure–time curves. This last procedure is not always easy, although in many isotopic exchange reactions approaching equilibrium the course rate law is accurately of the first order. However, initial rate laws frequently involve fractional powers of concentrations, which imply that the fundamental rate expression is of more complex form. In reactions not involving change in chemical composition, it is not necessary to use the initial rate law results to interpret the course rate law, but in cases involving change in chemical composition and pressure, where application of the initial rate law results should reproduce the pressure–time curves, this is often found not to be the case. The reason for this is not well understood.[10] Problems of considerable difficulty therefore arise merely from manometric data.

Almost all the recent advances of greatest interest in the field of catalytic hydrogenation have come from the use of deuterium as a tracer element, and the analysis of complex mixtures of deuterated olefins and paraffins has therefore become important. Infra-red analysis has limited applicability,[11] but the weapon of greatest value is the mass-spectrometer ; it is therefore in order briefly to consider how it may be employed for this purpose.

It is necessary in some way to separate the olefin and paraffin constituents ; this may be done chemically by treating the mixture with bromine or sulphuric acid. The spectrum after such treatment is that of the paraffins, while the difference between the spectra before and after treatment supplies the spectrum of the olefins. Separation of the olefins may also be achieved by using electrons of such low energy that the paraffin molecules are not ionised. Direct translation of the observed positive-ion currents into partial pressures of the species is possible if contributions due to fragments arising from the breakdown of the parent ions may be ignored. When this is not so, the conversion involves calculations depending on assumptions which seem to be not greatly in error.[12]

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[9] Wilson, Otvos, Stevenson, and Wagner, *Ind. Eng. Chem.*, 1953, **45**, 1480.

[10] Thon and H. A. Taylor, *J. Amer. Chem. Soc.*, 1953, **75**, 2747.

[11] Douglas and Rabinovitch, *ibid.*, 1952, **74**, 2486.

[12] Bond and Turkevich, *Trans. Faraday Soc.*, 1953, **49**, 281.

The Reaction of Hydrogen and Deuterium with Olefins

A General Survey.—The analytical developments outlined in the last section are very recent, and the remarkable complexity of the reactions under this heading thus revealed is only just being realised. It is becoming increasingly evident that it is no longer permissible to talk of one sole mechanism of hydrogen addition to olefins ; it seems likely that, although the principal elementary steps may be similar under most conditions, the relative importance they assume is largely dictated by the reaction climate, *i.e.*, temperature, partial pressures, catalyst, olefin, etc.

It will be useful first to catalogue the various types of reaction which occur when olefins react with deuterium. They are (1) *addition*, producing a saturated molecule in the gas phase. Addition may be of two types ; it may be "straight", when the product will be entirely the dideutero-compound, or it may occur with redistribution, in which case the products will be molecules having various numbers of deuterium atoms. (2) *Classical exchange* produces both hydrogen and deuterated olefins in the gas phase in corresponding amounts, *i.e.*, one HD or $\frac{1}{2}$ H_2 molecule per deuterium atom in the olefin. However, under certain conditions hydrogen deuteride may be detected without any deuterated olefins, and also deuterated olefins are found without any hydrogen deuteride ; these reactions will be referred to as (3) *hydrogen exchange* and (4) *olefin exchange reactions*, respectively. (5) *Double-bond migration* can occur in molecules containing three or more carbon atoms, although it has so far only been studied in the butene series. (6) cis-trans-*Isomerisation* again has only been studied in the butene series, although it could be studied in the C_2 and C_3 series with suitably labelled molecules. Reactions (3) to (6) inclusive usually occur in combination.

Of these reactions the addition and exchange reactions are the more important, since the others are only results of these. A reaction is therefore primarily characterised by the rates of appearance of deuterated olefins, hydrogen deuteride, and hydrogen relative to the rate of addition, and by the composition of the deuterated paraffins. The factors likely to affect these rates have already been noted. The relevant experimental work will now be presented.

Hydrogenation and Exchange Reactions of Ethylene.—*Nickel as catalyst.* Little progress in elucidating the mechanism of hydrogenation was possible until the discovery and application of deuterium. In 1934 [13] it was found that hydrogen deuteride was a product of the reaction of ethylene with deuterium, and this was attributed to a reaction written as

$$C_2H_4 + D_2 \longrightarrow C_2H_3D + HD$$

At that time no evidence existed for the formation of C_2H_3D in the gas phase, but this has recently been provided by the work of Turkevich *et al.*,[14a, b] who investigated the products of the ethylene–deuterium reaction

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[13] Farkas, Farkas, and Rideal, *Proc. Roy. Soc.*, 1934, *A*, **146**, 630.

[14] (*a*) Turkevich, Schissler, and Irsa, *J. Phys. Chem.*, 1951, **55**, 1078 ; (*b*) D. O. Schissler, Thesis, Princeton University, 1951.

over a nickel filament at 90° using a mass-spectrometer. They found that ethylenes containing up to four deuterium atoms were formed and that the partial pressures of each passed through successive maxima as shown in Fig. 1. The return of hydrogen deuteride and hydrogen to the gas was also followed. It was established that ethanes containing from 0 to 6 deuterium atoms were produced : the relative proportions of these changed through the course of the reaction, in the sense that the first-formed ethanes contained less than the stoicheiometric amount of deuterium and their deuterium content increased as the reaction proceeded, as is demonstrated by Fig. 2. From this it must be inferred that the number

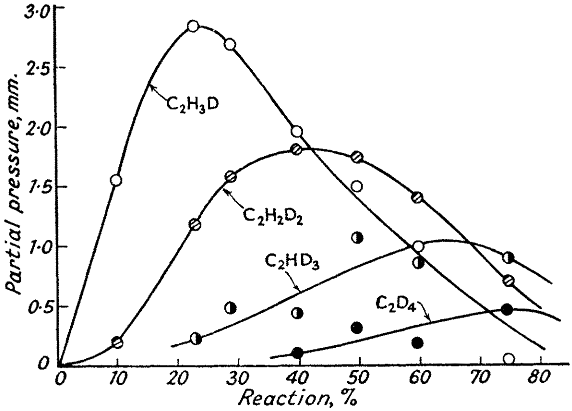

FIG. 1

The course of the reaction of 10 *mm. of ethylene and* 40 *mm. of deuterium at* 90° *: ethylene analyses.*

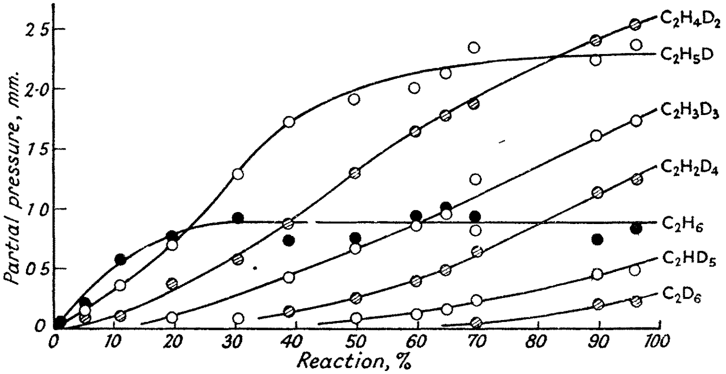

FIG. 2

The course of reaction of 10 *mm. of ethylene and* 20 *mm. of deuterium at* 90° *: ethane analyses.*

of deuterium atoms appearing in the ethylenes is not balanced by a corresponding number of hydrogen atoms in the deuterium, and that the classical exchange reaction as written above is not perfectly accurate. The extensive production of deuterated ethylenes is a point of some importance ; this must mean that the attainment of equilibrium between adsorbed and gaseous ethylene is rapid, in spite of the supposedly fairly high heat of adsorption of ethylene. It is possible that the energy which a molecule requires for desorption is partly provided by the heat of adsorption of the molecule which is to take its place.

These results show that the act of addition does not occur in one step, as had been formerly proposed, but that the reaction proceeds in two stages, the first of which is the production of a " half-hydrogenated state ", which in this case is an adsorbed ethyl radical. The reactions undergone by this radical result in the formation of gaseous deuterated ethylenes as well as hydrogen deuteride and hydrogen, and eventually lead to ethanes containing different numbers of deuterium atoms.

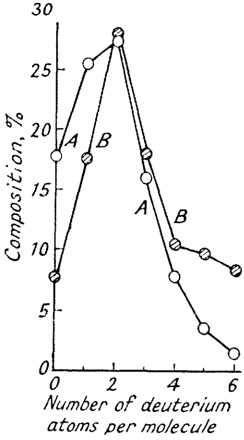

FIG. 3

The distribution of ethanes from the reaction of 1 mmole of ethylene and 10 mmoles of deuterium : A, at − 50° ; B, at + 50°.

Further evidence that the act of addition does not take place in one step has been provided by the experiments by Twigg.[15] These showed that the ethanes formed by reaction of ethylene with equilibrated and non-equilibrated mixtures of hydrogen and deuterium had identical infra-red spectra ; the hydrogen and deuterium molecules must therefore have dissociated before adding to the ethylene. Twigg further stated that these spectra are different from that of a mixture of dideuteroethane and ethane ; he prepared his dideuteroethane by the low-temperature (− 78°) addition of deuterium to ethylene, and under these conditions classical exchange is negligible. However, in the light of recent work, it appears that this constitutes no proof that the product is entirely dideuteroethane. It has been found [16] that over a nickel–kieselguhr catalyst at − 78° a redistribution reaction occurs which yields ethanes containing other than two deuterium atoms, but having an empirical composition of $C_2H_4D_2$, without accompanying classical exchange ; such a reaction must have been occurring in Twigg's experiments. Caution is therefore necessary in the interpretation of such infra-red spectra, but it must be stressed that this does not affect his main conclusions.

Wilson *et al.*[9] have recently studied the ethylene–deuterium reaction over a commercial nickel catalyst, using a ten-fold excess of deuterium. Both at − 50° and 50° the distribution of the ethanes was approximately

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[15] Twigg, *Discuss. Faraday Soc.*, 1950, **8**, 152.
[16] Turkevich and Thompson, unpublished results.

constant throughout the course of the reaction, and the final distributions are given in Fig. 3. No deuterated ethylenes were detected at either temperature, but at the end of the reaction the deuterium contained 0·45% of hydrogen at − 50° and 5·2% of hydrogen at 50°. These figures being used to perform a mass-balance, the corresponding compositions of the ethanes should be $C_2H_{3\cdot90}D_{2\cdot10}$ and $C_2H_{3\cdot00}D_{3\cdot00}$ respectively, whereas the experimental values are $C_2H_{4\cdot14}D_{1\cdot86}$ and $C_2H_{3\cdot48}D_{2\cdot52}$. Evidently their method of analysis overestimates the lighter ethanes ; the authors concede that their analysis of these species is subject to error.

As already mentioned, the relative rates of addition and hydrogen exchange are temperature-dependent in the sense that the latter process has the higher temperature coefficient. Thus in the original experiments,[13] the " deuterium " contained 30% of deuterium, but the rate of introduction of hydrogen into the gas phase at 20° was masked by its more rapid removal by the addition process, so that the deuterium content actually rose. However, at 120°, the decreasing deuterium content was very marked. In the range 55—110°, the hydrogen exchange reaction has an activation energy of 17·2 kcal., whereas the activation energy for addition is only 8·2 kcal. in the same range.[17] Above about 110° both activation energies decline with increasing temperature, but their difference remains approximately constant.[18] Twigg has shown that this is consistent with his theoretical treatment.[15] Para-hydrogen conversion is inhibited by the presence of ethylene, and only proceeds through the hydrogen exchange reaction.[13] This is taken to mean that the concentration of adsorbed hydrogen is very small.

No data relating to the kinetics of the olefin exchange process have yet been obtained. It is known that no deuterated ethylenes are formed in the presence of a ten-fold excess of deuterium at 50°, but that they are rapidly formed from equimolar mixtures of reactants at 90°.[9, 14] The difference in the reactant ratios used and also the different catalysts employed may each exert effects.

The overall initial rate kinetics are invariably of the form

$$- \mathrm{d}P/\mathrm{d}t = k[H_2][C_2H_4]^0 ;$$

the kinetics of the hydrogen exchange reaction are the same. The exponent of the ethylene concentration is sometimes reported as being slightly negative ; however, this inhibition is not such as to imply that both reactants are competing for the same surface. The falling-off of the activation energy for addition at temperatures above about 100° has been reported several times ; references to this and to the overall kinetics have been given before.[19]

Sufficient experimental results have now been presented to make a discussion of mechanisms profitable. The first requirement is the formation

[17] Twigg, *Trans. Faraday Soc.*, 1939, **35**, 934.

[18] Rideal and Twigg, *Proc. Roy. Soc.*, 1939, *A*, **171**, 55.

[19] (*a*) Eley, *Quart. Reviews*, 1949, **3**, 209 ; (*b*) Keii, *J. Chem. Phys.*, 1954, **22**, 144.

of an adsorbed ethyl radical, for which there are at least four possible mechanisms, *viz.*,

$$\overset{*}{H} + \underset{\vdots}{C_2H_4} \rightarrow C_2\overset{*}{H}_5 \tag{1}$$

$$\overset{*}{H} + \overset{*}{C}_2\overset{*}{H}_4 \rightarrow C_2\overset{*}{H}_5 \tag{2}$$

$$\overset{*}{C}_2\overset{*}{H}_4 + \underset{\vdots}{H_2} \rightarrow C_2\overset{*}{H}_5 \quad \overset{*}{H} \tag{3}$$

$$2\overset{*}{C}_2\overset{*}{H}_4 + \underset{\vdots}{H_2} \rightarrow 2\overset{*}{C}_2H_5 \tag{4}$$

The first two mechanisms assume the independent adsorption of hydrogen, the evidence against which has already been given ; these two are therefore unlikely. The third mechanism has been widely advocated by Twigg, Rideal, and others : Twigg has however suggested [15] that the adsorbed hydrogen atom formed by this reaction undergoes a rapid reaction corresponding to (2) above. Thus the net result of (3) followed rapidly by (2) is given by (4) ; whether or not it is justifiable to write the addition to two ethylene molecules in one act is at present disputable.

It is now possible to explain the production of hydrogen deuteride, deuterated olefins, and ethanes by mechanisms not involving hydrogen or deuterium atoms. If mechanism (4) above is correct, the reaction of ethylene and deuterium will first produce $C_2\overset{*}{H}_4D$ radicals : these may then react in the following ways :

$$2C_2\overset{*}{H}_4D \rightarrow \overset{*}{C}_2\overset{*}{H}_4 + \overset{*}{C}_2\overset{*}{H}_3D + \underset{\vdots}{HD} \tag{5}$$

$$2C_2\overset{*}{H}_4D \rightarrow \overset{*}{C}_2\overset{*}{H}_3D + C_2H_5D \tag{6a}$$

$$\rightarrow \overset{*}{C}_2\overset{*}{H}_4 + C_2H_4D_2 \tag{6b}$$

$$2C_2\overset{*}{H}_4D + \underset{\vdots}{D_2} \rightarrow 2C_2H_4D_2 \tag{7}$$

$$C_2\overset{*}{H}_4D + \overset{*}{C}_2\overset{*}{H}_4 \rightarrow C_2\overset{*}{H}_5 + \overset{*}{C}_2\overset{*}{H}_3D \tag{8}$$

Reaction (5) is the reverse of (4) and produces hydrogen deuteride. Both reaction (4) and (5) are disproportionation reactions. Deuteroethylene is formed by the evaporation of the products of reactions (5), (6*a*), and (8), although some part may remain on the surface and undergo further type (4) reaction. Reaction (8) is considered to be rapid and involves the ready migration of hydrogen and deuterium atoms through the chemisorbed ethylene layer. The ethyl radicals so formed lead to the preponderant initial formation of ethane. The distribution of deuterium atoms among the ethanes formed at any instant will be a function of the composition of the olefins and the deuterium in the gas phase ; as already stated, the former are probably in equilibrium with those adsorbed on the surface. The deuterium content of the summed reactants therefore rises as the reaction proceeds, and the yield of the more heavily deuterated ethanes therefore increases. This system is qualitatively in accord with the experimental results, but no quantitative treatment has yet been published. This system would predict that the kinetics of the olefin exchange reaction are complex but, as formerly noted, information is lacking on this point. The main feature of the scheme is that the ratio of addition to hydrogen exchange depends on two different modes of disproportionation of ethyl radicals, the two modes having differing activation energies.

Platinum as catalyst. It is incorrect to assume that the pattern of reactions described for the ethylene–deuterium reaction over nickel necessarily applies unchanged to other catalysts. Of the many transition-group metals which catalyse the reduction of olefinic bonds, platinum is the only other one over which any detailed investigations have been carried out. Farkas and Farkas [20] studied the reaction over platinised foil between 0° and 235°, and concluded that in this range the hydrogen exchange reaction had an activation energy of 22 kcal., while that of the addition reaction was 10 kcal. They too assumed the occurrence of a "classical" exchange reaction, but were unable to study the composition of the ethylenes and ethanes produced.

Recent work on this and other types of platinum catalyst has confirmed and amplified their findings, and has revealed marked differences from the behaviour of the reaction over nickel.[21] In the region of room temperature, the overall addition kinetics over platinised foil are of the form $-\mathrm{d}P/\mathrm{d}t = k[\mathrm{H_2}]^{1\ 3}[\mathrm{C_2H_4}]^{-0\ 8}$, in rough agreement with those found by Farkas and Farkas [20] who, however, quoted no explicit exponents. Their assumption that dideuteroethane was the principal product at low temperatures has been shown to be incorrect, since ethanes containing from 0 to 6 deuterium atoms were detected. At 0°, the production of hydrogen deuteride was negligible and of deuterated olefins very slight.

The negative order with respect to ethylene suggests that both hydrogen and ethylene may compete for the available surface sites. If this is so, it will be necessary to include in the reaction scheme steps involving hydrogen atoms ; these are of the type :

$$\overset{*}{\mathrm{C}}_2\overset{*}{\mathrm{H}}_4 + \overset{*}{\mathrm{D}} \longrightarrow \mathrm{C_2}\overset{*}{\mathrm{H}}_4\mathrm{D} \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\mathrm{C_2}\overset{*}{\mathrm{H}}_4\mathrm{D} + \overset{*}{\mathrm{D}} \longrightarrow \mathrm{C_2H_4D_2} \quad . \quad . \quad . \quad . \quad (10)$$

Redistribution could occur via the steps already proposed.

Hydrogenation and Exchange Reactions of Propylene.—*Nickel as catalyst.* The kinetics of the hydrogenation reaction have been studied over nickel powder by Toyama,[22] who found that they are similar to those for ethylene under corresponding conditions, that is, the rate is proportional to hydrogen pressure and almost independent of propylene pressure. Twigg [17] showed that all the hydrogen atoms underwent exchange over a nickel wire at

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[20] Farkas and Farkas, *J. Amer. Chem. Soc.*, 1938, **60**, 22.

[21] Bond and Turkevich, to be published.

[22] Toyama, *Rev. Phys. Chem. Japan*, 1940, **14**, 86.

97°, and there was no discontinuity in the exchange–time curve. All the hydrogens are therefore equivalent, and so both adsorbed normal- and *iso*-propyl radicals must be intermediates. The activation energy for addition was 6·0 kcal., and for hydrogen exchange 13·7 kcal., between 55° and 120°.

The reactions analogous to (4) are :

$$2CH_3—\overset{*}{C}H—\overset{*}{C}H_2 + D_2 \rightarrow 2CH_3—\overset{*}{C}H—CH_2D \quad . \quad . \quad . \quad . \quad . \ (11a)$$

$$\rightarrow 2CH_3—CHD—\overset{*}{C}H_2 \quad . \quad . \quad . \quad . \quad . \ (11b)$$

$$\rightarrow CH_3—CHD—\overset{*}{C}H_2 + CH_3—\overset{*}{C}H—CH_2D \ . \ (11c)$$

and to (9) are

$$CH_3—\overset{*}{C}H—\overset{*}{C}H_2 + \overset{*}{D} \rightarrow CH_3—\overset{*}{C}H—CH_2D \quad . \quad . \quad . \quad . \quad . \ (12a)$$

$$\rightarrow CH_3—CHD—\overset{*}{C}H_2 \quad . \quad . \quad . \quad . \quad . \ (12b)$$

and may be followed by the corresponding analogues of (5) to (8). Owing to its molecular geometry, propylene is unlikely to be able to pack as tightly on the surface as ethylene, and so stray hydrogen atoms may perhaps be present ; reactions such as (12) may therefore be involved.

Platinum as catalyst. The kinetics of the addition reaction over a pumice-supported platinum catalyst are approximately of the form $-\,dP/dt = k[C_3H_6]^{-\frac{1}{2}}[H_2]^{\frac{1}{2}}$, and a rate expression simulating this has been derived.[12] Both reactants were assumed to be competing for the same surface, with the adsorption coefficient of propylene being about ten times that of hydrogen. The effect of varying both the temperature and partial pressures on the distribution of products from the propylene–deuterium reaction was also investigated. The products from an equimolar mixture of reactants at 18° contained all possible isotopic propanes, distributed so that their empirical composition was $C_3H_6D_2$, the maximum yield being that of monodeuteropropane ; a little hydrogen deuteride was also found. Increasing the temperature caused the yields of di- and mono-deuteropropane to decrease, while the yield of propane rose. Similar results were found when a ten-fold excess of deuterium was employed, and in this case the deuterium content of the propanes also rose with increasing temperature. When propylene was initially present in large excess, the formation of hydrogen deuteride was suppressed, but deuterated propylenes appeared ; the propanes contained large amounts of propane and monodeuteropropane and their excess of hydrogen over the stoicheiometric quantity was balanced by the deuterium contained in the propylenes. It is therefore evident that much of the "hydrogen" added comes not directly from the gaseous deuterium, but rather from other propylene molecules. This results from the occurrence of a type (8) reaction. Increasing the deuterium pressure caused the yield of propane to fall to zero, while increasing that of dideuteropropane to a maximum of about 45%.

These results are readily explained by the elementary steps already postulated ; however, the concentrations of the various species on the surface change with the conditions in the gas phase. Thus when propylene is in large excess, the only species present are adsorbed propylene molecules and various propyl radicals, whereas when deuterium is in large excess there are only propyl radicals and adsorbed deuterium atoms : in some intermediate conditions, all three may be present simultaneously. Experiments with mixtures of light and heavy propylene confirmed these views.

Hydrogenation, Exchange, and Other Reactions of Butenes.—The four-carbon molecule increases the number of possible types of catalytic reaction. First, there is the possibility of skeletal isomerisation which occurs in the presence of acid catalysts by way of a carbonium-ion mechanism, and is therefore not the concern of this Review. Secondly, in *n*-butene there may be double-bond migration between the 1 and the 2 position. Thirdly, the Δ^2-molecule can exist as either a *cis*- or a *trans*-isomer, and their interconversion can therefore be studied. It is theoretically possible to study these last two reactions with suitably labelled propylene and *iso*-butene, but such studies have not yet been carried out. All experimental work so far reported has been over nickel catalysts.

The reactions of n-*butenes.* The rate of addition of hydrogen to but-1-ene at 100° over a nickel wire is, under certain conditions, given by $-\mathrm{d}P/\mathrm{d}t = k[C_4H_8]^{\frac{1}{2}}[H_2]^{\frac{1}{2}}$. In the presence of a large excess of hydrogen, the rate becomes proportional to the butene pressure and independent of hydrogen pressure.[23, 24] No explanation has yet been offered for the half order with respect to butene, and it is safe to suppose that the apparent half orders represent an approximation to a more complex rate expression. Activation energies reported are : for addition of hydrogen to but-1-ene, 2·0 kcal. ; to *cis*- and *trans*-but-2-ene, each 3·5 kcal. ;[23] and to an equilibrium mixture of *cis*- and *trans*-isomers, 3·3 kcal.[17]

cis–trans-Isomerisation proceeds at about the same rate, regardless of whether the *cis*- or the *trans*-isomer is taken as the reactant, and of whether hydrogen or deuterium is employed. Activation energies are about 5 kcal. for each system. The isomerisation is about ten times as fast as the olefin-exchange reaction.

Twigg [24] investigated the hydrogen exchange and double-bond migration of but-1-ene, and reported activation energies of 9·0 and 5·9 kcal., respectively. Taylor and Dibeler [23] in a thorough investigation unfortunately marred in part by misinterpretation of the mass-spectral data have studied these reactions in greater detail. Double-bond migration is faster with hydrogen than with deuterium, and the activation energies are respectively 5·0 and 7·8 kcal. This suggests that either the breaking or the formation of a H–X or a D–X bond is the rate-controlling step ; X may be either carbon or nickel. Such is presumably not the case for the *cis–trans*-isomerisation reaction.

The rate of exchange of deuterium with but-1-ene as measured by the appearance of deuterobutene in the gas phase is about the same as the double-bond migration with deuterium ; this does not confirm Twigg's

[23] T. I. Taylor and Dibeler, *J. Phys. Chem.*, 1951, **55**, 1036.
[24] Twigg, *Proc. Roy. Soc.*, 1941, *A*, **178**, 106.

finding that double-bond migration is five to six times as fast as exchange. However, it must be remembered that Twigg measured formation of hydrogen deuteride only, that is, the hydrogen-exchange reaction, and this may be the cause of the discrepancy. The activation energy for exchange was given by Taylor and Dibeler as 7·1 kcal., and is probably, within experimental error, the same as that for double-bond migration in the presence of deuterium. The kinetics of both these reactions are the same as for hydrogen addition.

The reaction of *cis*-but-2-ene with a ten-fold excess of deuterium has been studied over a commercial nickel catalyst by Wilson *et al.*[9] At − 78°, the butane formed contained all possible isotopic species in amounts corresponding to a random distribution of $C_4H_8D_2$. However, the species dideuterobutane itself was present in more than the calculated quantity, and so part of the reaction was supposed to occur by a straight addition mechanism. At this temperature, no deuterobutene was formed, and very little hydrogen deuteride. As the temperature was increased, the formation of hydrogen deuteride became more evident, and the deuterium content of the butanes rose accordingly ; at the same time, monodeuterobutene was detected, but no butenes containing more than one deuterium atom were found.

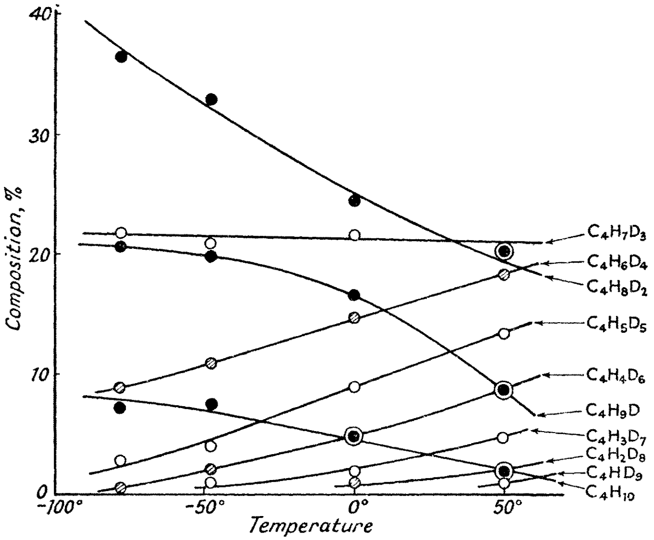

FIG. 4

The dependence of the products formed from 1 *mmole of butene and* 10 *mmoles of deuterium on temperature.*

At temperatures between − 78° and 50° the composition of the butanes did not change in the course of a particular experiment, and the effect of temperature on the distribution of the isotopic species after about 100% reaction is shown in Fig. 4. The principal effect of increasing the temperature is to decrease the yields of butanes containing 0, 1, and 2 deuterium atoms, while the yields of those containing 4 or more deuterium atoms increase. The general trends are thus similar to those found with ethylene and propylene over nickel and platinum catalysts.

Double-bond migration occurs as a natural consequence of the elementary steps previously proposed. Thus the isomerisation of but-1-ene to but-2-ene in the presence of deuterium can be represented :

$$\underset{\text{adsorbed but-1-ene}}{CH_3—CH_2—\overset{*}{C}H—\overset{*}{C}H_2} + \overset{*}{D} \longrightarrow CH_3—CH_2—\overset{*}{C}H—CH_2D \longrightarrow$$

$$\underset{\text{adsorbed but-2-ene}}{CH_3—\overset{*}{C}H—\overset{*}{C}H—CH_2D} + \overset{*}{H}$$

while the intermediate butyl radical, in which free rotation is possible, will be responsible for the *cis–trans*-isomerisation. A satisfactory explanation of the relative rates and kinetics of all the reactions has not yet been offered.

The reactions of iso*butene.* All the hydrogen atoms of the *iso*butene molecule are apparently exchangeable, and over a nickel wire the activation energies for hydrogen exchange and addition are respectively 10·0 and 3·3 kcal., that is, exactly the same as those reported for but-2-ene.[17] Owing to the bulky methyl groups, *iso*butene cannot pack tightly on the catalyst surface, and this is demonstrated by the ease with which the hydrogen–deuterium exchange proceeds in its presence, by reason of the independent adsorption of hydrogen.[25]

At – 78° over a commercial nickel catalyst, the *iso*butane formed from the reaction of *iso*butene with deuterium is 97% dideutero-compound, the deuterium having been added across the double bond.[9] Small amounts of more deuterated *iso*butanes were detected. Direct addition with little redistribution is therefore favoured at low temperatures. A possible interpretation is that the adsorbed butyl radicals formed by the addition of a deuterium atom to an adsorbed *iso*butene molecule is $(CH_3)_2CD—\overset{*}{C}H_2$ rather than $(CH_3)_2\overset{*}{C}—CH_2D$: the reverse reaction in the case of the former could only reproduce the original reactants, whereas in the latter case the three methyl groups are chemically equivalent, and exchange should be possible. No kinetics of these reactions have been reported.

Theoretical Approaches and Summary.—The experimental evidence relating to the reactions undergone by olefins in the presence of hydrogen or deuterium on catalytic surfaces having been presented in some detail, reference must now be made to the numerous efforts to apply the theory of absolute rates of reaction to the problem.[26–28] The object of these

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[25] Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **36**, 533.

[26] Eyring, Colburn, and Zwolinski, *Discuss. Faraday Soc.*, 1940, **8**, 39.

[27] Laidler, *ibid.*, p. 47.

[28] (*a*) Markham, Wall, and Laidler, *J. Chem. Phys.*, 1953, **21**, 949 ; (*b*) Laidler, " Catalysis ", ed. P. H. Emmett, Reinhold Publ. Corp., New York, 1954, Vol. 1, chaps. 4 and 5.

efforts is to decide the mechanisms by which the reactions proceed, by comparing observed rates with those calculated for various models. This is a difficult and somewhat dangerous procedure, first because differentiation between various mechanisms depends on subtle differences between observed kinetics, which may not be established beyond question, and secondly because consideration has not been given to the numerous important variables.

Much of the difficulty arises from an incomplete knowledge of what species are present on the surface, of their concentrations, and of the reactions they undergo, in a particular set of circumstances. There is, for example, uncertainty concerning the existence of hydrogen atoms in the ethylene–hydrogen–nickel system. As already stated, the complete inhibition of the hydrogen–deuterium exchange reaction and of para-hydrogen conversion suggests that there are no (or very few) hydrogen atoms. Isolated hydrogen atoms may not however respond to these tests if the evaporation mechanism is correct, and this is still the subject of debate. Laidler *et al.*[28] assume the independent adsorption of hydrogen, and find that the two possible ethane-forming processes (6*a* and 10) lead to similar rate equations in which the rate passes through a flat maximum as the ethylene pressure is raised. The results of Toyama [29] are quoted in support. Calculated absolute rates for either of these mechanisms or for Twigg's mechanism [15] agree to within a factor of ten with experimental values from several independent investigators. The situation in regard to the exchange reactions is even more unsatisfactory, a contributory factor perhaps being the confusion between the hydrogen and the olefin exchange processes.

Many attempts have been made to correlate the rate of the addition process with various parameters of the metal employed as catalyst. Beeck [30] originally plotted the rate as a function of the interatomic distance in the metal lattice, but later [6] plotted it as a function of " *d*-band character × valency " : the latter procedure resulted in a satisfactory linear relationship. This aspect of the subject will not be pursued, since it will be covered in another Review.[31]

By way of summary, attention may now be drawn to certain general features. (i) The effect of the olefin : increasing the number of methyl groups substituted around the double bond decreases the tightness with which the molecules can be geometrically packed on the surface. As a result, independent adsorption of hydrogen is possible in the case of propylene and the butenes, and reactions involving hydrogen atoms probably occur. However, the radicals are sufficiently near for inter-radical reactions to take place, except perhaps in the case of *iso*butene. No information regarding larger molecules is available. As the number of substituted methyl groups is raised from 0 to 2, the activation energies for addition and hydrogen exchange over nickel decrease ; however, the similarity of the rates of addition for all three olefins in the temperature range studied shows that the frequency factors must be in the ratio $1 : 10^{-2} : 10^{-4}$. The

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[29] Toyama, *Rev. Phys. Chem. Japan*, 1937, **11**, 153.

[30] Beeck, *Rev. Mod. Physics*, 1948, **20**, 127.

[31] Trapnell, to be published.

same is also true of the hydrogen-exchange reaction. As already stated, the kinetics also change in a surprising fashion between propylene and butene. These facts suggest that the rate-controlling step is not the same for each olefin, or perhaps that various addition-producing steps contribute to differing extents. This may be due to the part played by hydrogen-atom reactions of type (10).

(ii) The effect of the metal : only with nickel and platinum has sufficient work been done to enable any comparative conclusions to be drawn. It appears that on nickel the adsorption of olefins is very much stronger than that of hydrogen, whereas on platinum the difference may only be of the order of a factor of ten.

(iii) The effect of temperature : broadly speaking, rise of temperature accelerates relatively those reactions which tend to complicate the addition and redistribution reactions. These are the evaporation of olefin and hydrogen deuteride from the surface, both of which processes have higher activation energies than the addition reaction. This is qualitatively true regardless of olefin or catalyst, and this lends support to the thesis that the same primary steps operate under all conditions, although the parameters associated with them vary from case to case.

The Reaction of Hydrogen and Deuterium with Acetylenes

In contrast to the case of olefins, where the addition of hydrogen invariably results in a saturated product containing the same number of carbon atoms, it frequently happens that the hydrogenation of acetylenes is complicated by an accompanying polymerisation ; this is especially important in the case of acetylene itself, and the reaction occurs at temperatures far lower than those at which the catalytic polymerisation of acetylene alone begins. It has therefore been termed " hydropolymerisation ", and a considerable part of the following paragraphs will be concerned with the kinetics and mechanism of this process.

The Hydrogenation and Exchange Reactions of Acetylene.—*Nickel as catalyst.* Sabatier and Senderens [32] recorded that considerable formation of hydrocarbons of higher molecular weight containing aromatic and hydroaromatic materials accompanied the hydrogenation of acetylene over nickel. Many other workers have subsequently confirmed this and have investigated the process in greater detail. It is convenient to classify the reactions which are taking place in the following manner :

$$\text{Type I:}\quad C_2H_2 \xrightarrow{+H_2} C_2H_4 \xrightarrow{+H_2} C_2H_6$$

$$\text{Type II:}\quad C_2H_2 \xrightarrow{+H_2} \text{higher hydrocarbons}$$

The amount of ethylene and ethane formed divided by the amount of acetylene removed is called the " percentage recovery " or " yield " of C_2 hydrocarbons, and this may be determined by analysis. The relative extents of the two types of reaction can thus be found.

The overall initial rate law [3] over a pumice-supported nickel catalyst at

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[32] Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173.

79° is $-\mathrm{d}P/\mathrm{d}t = k[H_2][C_2H_2]^0$ and product analysis showed that this expression was approximately applicable to both types of reaction. This rate law only accounts for pressure–time curves when acetylene is in excess ; in the presence of an excess of hydrogen, pressure–time curves are accurately of zero order until nearly all of the acetylene has been removed from the system. This behaviour is often encountered in addition to triple bonds and no explanation has yet been offered. It seems probable, however, that some surface chain mechanism is operative, but no details are known. de Pauw and Jungers [33] found kinetics of the form, $-\mathrm{d}P/\mathrm{d}t = k[H_2][C_2H_2]^{-0\cdot5}$, under somewhat different conditions.

The ratio of the rates of production of ethylene and ethane is referred to as the " selectivity " of the reaction. This ratio is about five [3] for an equimolar mixture of reactants over nickel at 80° and decreases as the initial hydrogen : acetylene ratio is raised, and also as the temperature is increased. The formation of ethane in the earliest stages of the reaction is of importance from the mechanistic point of view, especially since added ethylene behaves only as an inert diluent. In the presence of a sufficient excess of hydrogen, the hydrogenation of the ethylene will proceed to completion after the removal of all the acetylene, and at a rate either faster or slower than this depending mainly on the temperature.[3, 33] This is consistent with the differing activation energies of the two reactions. On the basis of pressure–time curves alone some workers have incorrectly assumed the completely selective production of ethylene in the first stage ; care is necessary in drawing deductions from such curves.

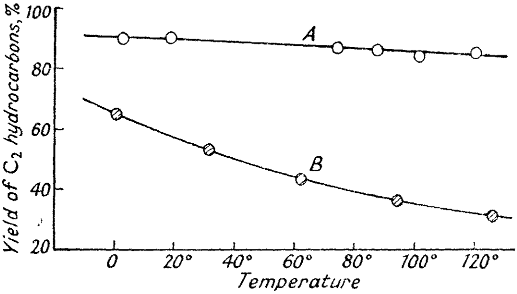

FIG. 5

Percentage yields of C_2 *hydrocarbons as a function of temperature :*
A over platinum,
B over nickel.

The type II reaction has a greater activation energy than type I, as witnessed by the decreasing yields of C_2 hydrocarbons found as the temperature is raised. It has been reported [34] that the C_2 yield is 65% at 0° and 31% at 126° (see Fig. 5), and that E_{I} is 10·9 kcal. and E_{II} 12·7 kcal. at 126°, rising to 14·5 kcal. at 0°. There is no evidence for the inversion

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[33] de Pauw and Jungers, *Bull. Soc. chim. Belg.*, 1948, **57**, 618.
[34] Sheridan, *J.*, 1945, 133.

of the temperature coefficient of the reaction at high temperatures, as is found for ethylene.

Some information is available concerning the composition of the polymeric hydrocarbons.[34] The material obtained from the reaction at 200—250° was completely hydrogenated and distilled, and it was shown that C_4—C_8 hydrocarbons were present, as well as much higher-boiling material. Infra-red analysis showed that the C_6 fraction was mainly *n*-hexane and 3-methylpentane, while the presence of *n*-pentane, 2-methylbutane and 3-methylhexane was also established. The following Table gives the estimated percentage yields for various molecular weight ranges:

TABLE 1. *Yields of higher hydrocarbons from the hydrogenation of acetylene at 200—250°*

Molecular species . .	C_4	C_5	C_6	C_7	C_8	$C_{9\to14}$	$C_{15\to30}$	$C_{31\to}$
Estimated percentage yield	25	2	25	2	5	7	17	17

Particularly noteworthy is the sharp decline in yield between C_6 and C_8, and the almost constant yield for each molecular species from C_{10} to C_{30}. Vassiliev [35] confirmed that the bulk of the products were mainly saturated and unsaturated aliphatic hydrocarbons, but in addition he was able by Raman spectroscopy to demonstrate the presence of *cyclo*hexane, *cyclo*hexene, and some of their methyl derivatives, as well as benzene, toluene, xylene, and trimethyl- and *iso*propyl-benzenes.

The reaction of acetylene with deuterium over nickel–kieselguhr at room temperature produces all the possible isotopic ethylenes, besides ethane and "polymerised material".[11] *cis*- and *trans*-Dideuteroethylene were formed in amounts greater than statistically expected and together accounted for about half of the total ethylenes. Early products contained predominantly light ethylene and monodeuteroethylene; there was no marked production of deuterated acetylenes. The use of equilibrated and non-equilibrated mixtures of hydrogen and deuterium showed clearly that addition was proceeding atomically rather than molecularly.

Acetylene is adsorbed very strongly on nickel wires and films, which are rapidly poisoned by it. Most work has therefore been done with supported catalysts which are not so poisoned, although the reason for this is not apparent. The form of the reaction on evaporated nickel films is controlled by the strongly held acetylene molecules, and the rate shows a maximum as the acetylene pressure falls.[36]

Platinum as catalyst. The kinetics [37] of reaction over a platinum-pumice catalyst at 73° are represented by: $-\mathrm{d}P/\mathrm{d}t = k[H_2]^{1\cdot2}[C_2H_2]^{-0\cdot7}$. This suggests that the adsorption of acetylene on platinum is not as strong as on nickel, and that consequently hydrogen may be able to displace acetylene from the surface when the former is present in sufficient excess. This is

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[35] Vassiliev, *Bull. Soc. chim.*, 1948, 381.

[36] Personal communication from Dr. A. Wheeler. [37] Sheridan, *J.*, 1945, 305.

in harmony with observations in the olefin series. Zero-order kinetics are again observed when acetylene is not in excess.

The kinetics of both types of reaction are similar, as with nickel, but the yield of C_2 products is 70—80% at temperatures around 150°. The polymeric hydrocarbons are of lower molecular weight than those formed over nickel, and contain not more than eight carbon atoms. The effect of temperature on the C_2 yield is not marked (see Fig. 5), and values for the activation energies are E_{I}, 12 kcal., and E_{II}, 13—14 kcal. The selectivity, which is in general less than that shown by nickel, apparently rises with temperature; however, the acceleration in rate due to the hydrogenation of the ethylene is more marked at lower temperatures.

The amount of hydrogen deuteride formed from acetylene and deuterium is very low, and the conversion of para-hydrogen, which is suppressed three-fold by ethylene, is suppressed fifteen-fold by acetylene, probably indicating a very low concentration of adsorbed hydrogen atoms.[38]

Palladium as catalyst. Palladium shows very marked resemblances to platinum, but is more active. The initial rate law over palladium–pumice at 49° is $-\,\mathrm{d}P/\mathrm{d}t = k[H_2][C_2H_2]^{-0\cdot4\rightarrow-0\cdot7}$. Both types of reaction have kinetics of this type, and zero-order kinetics are again found. At 24° the selectivity is about ten, palladium thus being the most selective of the three metals discussed. The yield of C_2 hydrocarbons is 75% at 24°, and the polymers are of low molecular weight.[39] The rate of hydrogenation of ethylene is faster than that of acetylene below about 75°.[40] Both types of reaction have activation energies of about 12 kcal.[39] Supported palladium catalysts were employed by the German chemical industry during the second World War for the production of ethylene from acetylene.[41]

The reaction of deuterium with acetylene over palladium leads to all possible deuteroethylenes.[11]

Other metals as catalysts. Iron behaves very similarly to nickel, but is less active; cobalt is only weakly active and becomes deactivated rapidly. Copper catalyses the conversion of acetylene into cuprene when insufficient hydrogen is present, but when it is in excess ethylene and ethane are produced with a high selectivity; copper catalysts also become deactivated readily.[39]

Rhodium is about as active as nickel, and gives C_2 yields of 70—80%; the overall activation energy is 15·5 kcal. Iridium is active at 175°, and both metals give the usual initial rate kinetics. Ruthenium and osmium are scarcely active.[42]

Various combinations of metals have also been studied.[39]

The mechanism of the reaction. The construction of general mechanisms is greatly facilitated by the finding that the kinetics of both the type I and the type II reaction are similar on all the catalysts studied, although

[38] Farkas and Farkas, *J. Amer. Chem. Soc.*, 1939, **61,** 3396.

[39] Sheridan, *J.*, 1945, 470.

[40] Tamaru, *Bull. Chem. Soc. Japan*, 1950, **23,** 64.

[41] B.I.O.S. Surveys Report No. 30 (H.M.S.O., 1951).

[42] Sheridan and Reid, *J.*, 1952, 2962.

their differing activation energies show that their rate-controlling steps cannot be the same. It is reasonably certain that the same type of mechanism operates on each catalyst. Reaction schemes have been constructed [34] by analogy with those postulated to explain the reactions of olefins.

As previously stated, acetylene is supposed to be associatively adsorbed on the longer lattice spacing of the transition-group metals. Now the form of the initial-rate kinetics for addition to acetylene is very closely parallel to those recorded for addition to ethylene, especially in regard to the negative orders with respect to acetylene found over platinum but not over nickel. Following the earlier arguments, it seems likely that there is no (or very little) independently adsorbed hydrogen over nickel, while over platinum and palladium competition between acetylene and hydrogen may be occurring, and hence reactions involving hydrogen atoms may take place.

Initiating steps may therefore be :

$$H\overset{*}{C}{=}\overset{*}{C}H + H_2 \longrightarrow H\overset{*}{C}{=}CH_2 + \overset{*}{H} \quad . \quad . \quad . \quad (13a)$$

or

$$H\overset{*}{C}{=}\overset{*}{C}H + \overset{*}{H} \longrightarrow H\overset{*}{C}{=}CH_2 \quad . \quad . \quad . \quad . \quad (13b)$$

There now arises the interesting possibility that the half-hydrogenated state, which is here an adsorbed vinyl radical, may isomerise into a free-radical form, thus

$$H\overset{*}{C}{-}CH_2 \rightleftharpoons \cdot H\overset{*}{C}{-}\overset{*}{C}H_2 \quad . \quad . \quad . \quad . \quad (14)$$

It must be noted that the free-radical form cannot be the first product of (13*a*) or of (13*b*), since it presumably has an ethane-like structure, and hence can only be adsorbed on the shorter lattice spacing. Free rotation about the carbon–catalyst bond might permit the radical to find the requisite second site. The normal form of the vinyl radical can react with more hydrogen to give gaseous ethylene, and the free-radical form to give adsorbed ethylene, thus :

$$H\overset{*}{C}{=}CH_2 + \overset{*}{H} \longrightarrow H_2C{=}CH_2 \quad . \quad . \quad . \quad (15a)$$

$$\cdot H\overset{*}{C}{-}\overset{*}{C}H_2 + \overset{*}{H} \longrightarrow H_2\overset{*}{C}{-}\overset{*}{C}H_2 \quad . \quad . \quad . \quad (15b)$$

The ethane formed in the early stages of the reaction may arise from the further hydrogenation of this adsorbed ethylene before it evaporates from the surface. The possibility that it arises from re-adsorption of gaseous ethylene on planes which can also accommodate acetylene is unlikely because the latter is far more strongly adsorbed, as shown by the fact that added ethylene invariably behaves as an inert diluent. Nor can it arise from re-adsorption of ethylene on planes which cannot adsorb acetylene, otherwise no selectivity could be observed where the rate of hydrogenation of ethylene is faster than that of acetylene. The selectivity would thus appear to be controlled by the equilibrium (14) and by the rate of evaporation of ethylene from the surface.

The presence of a free-radical elegantly explains the occurrence of the hydropolymerisation reaction.[34] This is in fact a vinyl-type polymerisation in which the free-radical form of the vinyl radical is the initiator and adsorbed acetylene is the monomer, thus

$$H_2\overset{*}{C}—\overset{*}{C}H\cdot + H\overset{*}{C}{=}\overset{*}{C}H \longrightarrow H_2\overset{*}{C}—\overset{*}{C}H—\overset{*}{C}H—\overset{*}{C}H\cdot \quad . \quad . \quad (16)$$

The geometric requirements of this reaction have been worked out,[34] and are met on transition-group metal catalysts. There is little evidence concerning the mechanism of the termination step, mutual termination and reaction with hydrogen atoms or molecules all being possibilities. The polymer may be removed from the surface by evaporation or by the further addition of hydrogen, or both. The experimental finding that most of the polymers consist of an integral number of C_2 units is thus explained: molecules containing odd numbers of carbon atoms probably arise from the cracking or rearrangement of the primary products. The six-membered ring species reported by Vassiliev [35] may result from the cyclisation of adsorbed C_6 residues.

The factors governing the extent to which the polymerisation reaction proceeds on various metals are not yet well understood. The geometric factor is obviously important, and this may also affect the equilibrium (14); polymerisation is in general more extensive on metals of small atomic radius.[42]

The slight formation of hydrogen deuteride and deuteroacetylene in the acetylene–deuterium reaction suggests that reactions of the type

$$H\overset{*}{C}{=}CHD \longrightarrow H\overset{*}{C}{=}\overset{*}{C}D + \overset{*}{H} \quad . \quad . \quad . \quad (17a)$$

or

$$\cdot H\overset{*}{C}—\overset{*}{C}HD \longrightarrow H\overset{*}{C}{=}\overset{*}{C}D + \overset{*}{H} \quad . \quad . \quad . \quad (17b)$$

cannot be of great importance. However, the occurrence of all deuteroethylenes must involve the formation of adsorbed deuteroacetylenes by reactions of this type; it must be concluded that they do not frequently vacate the surface before suffering addition.

The Hydrogenation of Monosubstituted Acetylenes.—*Methylacetylene.* The hydrogenation of methylacetylene over nickel, platinum, and palladium catalysts has been studied; [43] orders of reaction are similar to those for acetylene, but activation energies are slightly higher, for example, E_I is 13·8 kcal. for methylacetylene over nickel compared with 10·9 kcal. for acetylene. Zero-order kinetics are again observed. Higher selectivities were also found; for example, the selectivity for methylacetylene over nickel is about 14 at 90°, compared with about 5 for acetylene under comparable conditions. The yield of C_3 hydrocarbons was about 87% at 90°, compared with only about 40—45% of C_2 hydrocarbons from acetylene. A similarly higher yield was found over platinum but not over palladium; it was suggested that over palladium a polymerisation reaction occurred involving physically adsorbed hydrocarbon molecules.

The higher C_3 yields found over nickel and platinum demonstrate the effect of the methyl group on the tightness of packing on the surface, and

[43] Bond and Sheridan, *Trans. Faraday Soc.*, 1952, **48**, 651.

the consequent reduction in the ease with which the polymerisation process can occur. Palladium catalysts rapidly lost their ability to hydrogenate propylene, and propylene was produced exclusively by well-used samples of catalyst.

Acetylene and methylacetylene in admixture are hydrogenated simultaneously on nickel and platinum catalysts, and it was deduced that the former occupies rather more of the surface than the latter.[44] This result was independently confirmed.[45]

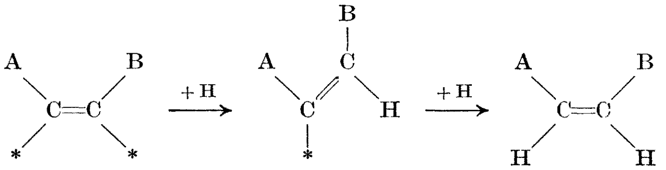
Vinylacetylene. Vinylacetylene is reduced to 1 : 3-butadiene by palladium and Raney iron catalysts, although some butene and polymers are also formed.[46] No but-1-yne or buta-1 : 2-diene has been detected.[47] Neither platinum nor nickel–alumina shows selective action.[48] 3-Methylbutenyne has been reduced to isoprene by Raney iron.[49]

Other monosubstituted acetylenes. Sabatier and Senderens [50] hydrogenated *n*-heptyne to *n*-heptane over nickel at 170°, but over copper, heptene and polymers containing two and three C_7 units were also formed.

The same authors [51] hydrogenated phenylacetylene to ethyl*cyclo*hexane over nickel at 180° but over copper at slightly higher temperatures ethylbenzene, styrene, and diphenylbutane were produced, as well as a crystalline fluorescent solid not identified.

The Hydrogenation of Disubstituted Acetylenes.—*The stereochemical course of the reaction.* The general consensus from a large body of work is that the catalytic reduction of disubstituted acetylenes results in the formation of *cis*-olefins, whereas chemical methods lead to the usually stabler *trans*-compound ; many examples are quoted in a review published in 1942.[52] It may be noted that the stereochemistry of chemical reductions is still under discussion.[53] Although the *cis*-olefin is invariably the major product, it is frequently accompanied by some of the *trans*-compound, and much work [52, 54] has been done to elucidate the factors controlling the *cis* : *trans* ratio.

The adsorption of a disubstituted acetylene as a *cis*-olefin–catalyst complex must lead to a gaseous *cis*-olefin by the following steps :



(18)

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[44] Bond and Sheridan, *Trans. Faraday Soc.*, 1952, **48**, 664. [45] *Idem, ibid.*, p. 715.

[46] Hubukawa, *J. Electrochem. Assoc. Japan*, 1939, **7**, 346.

[47] See ref. 56, Vol. I, p. 55.

[48] Lebedev *et al.*, *Zhur. Obshchey Khim.*, 1935, **5**, 1421.

[49] Thompson and Wyatt, *J. Amer. Chem. Soc.*, 1940, **62**, 2555.

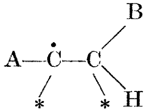
[50] Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 87. [51] *Idem, ibid.*, p. 88.

[52] Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77.

[53] Rabinovitch and Looney, *J. Amer. Chem. Soc.*, 1953, **75**, 2652.

[54] Crombie, *Quart. Reviews*, 1952, **6**, 101.

The isomerisation of the intermediate radical into its free-radical form



would cause it to lose its stereospecificity, and result in the formation of the *trans*- as well as the *cis*-isomer. The fact that this does not generally occur may mean that the free-radical does not usually lead to the gaseous olefin, but only to the saturated product, by reason of its remaining adsorbed.

There are indications that the speed of the reaction may affect the *cis* : *trans* ratio,[55, 56] in the sense that faster reactions lead to higher percentages of the *cis*-compound. It is frequently suggested that the *trans*-products arise by subsequent isomerisation of the first-formed *cis*-compound. This may explain the last finding if the isomerisation proceeds slowly and independently of the addition ; thus in a fast addition there would be no time for isomerisation, but in a slow reaction it might occur appreciably.

It is at present impossible to decide whether *trans*-products (when they are detected) are formed as an integral part of the reaction, or whether they arise by an entirely separate isomerisation process. No detailed kinetic study has been made.

Selectivity. The results of much work on the hydrogenation of disubstituted acetylenes are summarised in references 52 and 56. It is only necessary here to draw attention to certain general features. The order of selectivities previously found for acetylene holds good in almost all circumstances, although the differences exhibited by the metals are more pronounced when larger molecules are used.

Thus platinum never shows high selectivity but colloidal palladium catalysts are always highly selective. Sometimes the reaction ceases at the olefin stage, but even when the olefin is hydrogenated at a rate similar to that of the acetylene, the olefin may be recovered in good yield if the reaction is stopped at the appropriate time. Raney nickel and Raney iron are both highly selective, although the latter is less active than the former. The general problem of selectivity will be discussed in the next section.

Summary and Discussion.—The problems which arise in studying the hydrogenation of acetylenes are somewhat different from those met with in similar studies with the olefins, because the former undergo polymerisation, react in two stages, and when disubstituted give rise to geometrical isomers. Some similarities between the two types of molecule are apparent, particularly in so far as the variation from metal to metal of the initial rate kinetics is concerned.

Activity in the transition-group series for the hydrogenation of acetylenic bonds is chiefly associated with those metals (nickel, palladium, platinum, rhodium, iridium, copper) having a face-centred cubic structure, although

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[55] Ott and Schürmann, *Ber.*, 1928, **61**, 2119.

[56] Johnson, " Acetylenic Compounds ", Vols. I and II, Arnold, 1946.

iron with a body-centred cubic lattice is also active. Metals with a hexagonal close-packed structure (osmium and ruthenium) are least active. The hydropolymerisation reaction, which is most marked with nickel, is of less importance with metals of larger atomic radius.

The problem of selectivity is more difficult, particularly because of the difference between palladium and platinum which have similar atomic radii and electronic properties. The high selectivity shown by palladium is at least in some cases due to its complete inability to reduce the olefin, although in other cases this is not so. Palladium and also iron catalysts show a distressing tendency to change in selectivity as the sample ages. The higher selectivity of palladium might be caused by a higher percentage of the adsorbed vinyl radical being in the normal form, although no reason for this is apparent.

It must be concluded that there is as yet no satisfactory interpretation of the differing selectivities shown by the transition-group metals.

The Exchange Reactions of Saturated Hydrocarbons with Deuterium

In the processes considered so far, it has been supposed that the adsorption of both the reactants proceeds rapidly and with negligible activation energy, and that the rate-controlling step is one of the surface reactions : these ideas are in harmony with all the observations. Neither supposition is true in the exchange reactions of saturated hydrocarbons with deuterium ; in such cases, although the adsorption of deuterium may be effected rapidly, the hydrocarbon can only become chemisorbed following the breaking of a carbon–hydrogen bond, as :

$$C_2H_6 \longrightarrow C_2\overset{*}{H}_5 + \overset{*}{H} \quad . \quad . \quad . \quad . \quad (19)$$

This is a " dissociative " adsorption, and the process requires a considerable activation energy because of the strength of the bond which has to be broken. Thus the adsorption step (or its reverse, which in the steady state must proceed at the same rate) may well be rate-determining ; consequently deuterium atoms may cover most of the surface, while the concentration of adsorbed hydrocarbon radicals remains small.

However, the adsorbed species are identical with those met in olefin hydrogenation, and the exchange reactions of saturated hydrocarbons therefore provide a valuable additional method of obtaining information concerning the behaviour of adsorbed radicals.

The Reaction of Methane with Deuterium.—Methane exchanges with deuterium over nickel–kieselguhr at temperatures greater than 138°, and the activation energy is 28 kcal. between 184 and 302°.[57] Recently the reaction has been thoroughly studied by Kemball over a series of evaporated-metal films ; [58, 59] the course of the reaction was followed by mass-spectrometric analysis of the deuteromethanes. Over nickel and rhodium, the first-exchanged methane was predominantly tetradeuteromethane, whereas

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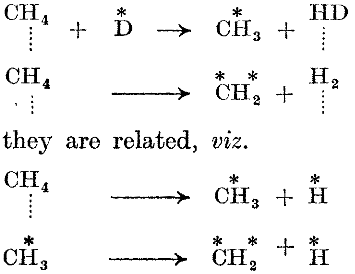
[57] Morikawa, Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1936, **58,** 1445.

[58] Kemball, *Proc. Roy. Soc.*, 1951, *A,* **207,** 539.

[59] *Idem, ibid.*, 1953, *A,* **217,** 376.

over platinum, palladium, and tungsten it was chiefly the monodeutero-compound. It was concluded that there are two separate reaction paths, the first of which leads only to monodeuteromethane, and the second of which produces all the more deuterated methanes. Pressure and temperature dependences of both reactions were determined for each metal, but the precise values depend on the mechanisms assumed.

Two possibilities were considered: the first supposed that the two processes are independent, *viz.*



$$\underset{\vdots}{\mathrm{CH_4}} + \overset{*}{\mathrm{D}} \longrightarrow \overset{*}{\mathrm{CH_3}} + \underset{\vdots}{\mathrm{HD}} \quad . \quad . \quad . \quad . \quad (A)$$

and

$$\underset{\vdots}{\mathrm{CH_4}} \longrightarrow \overset{*\ *}{\mathrm{CH_2}} + \underset{\vdots}{\mathrm{H_2}} \quad . \quad . \quad . \quad . \quad (B)$$

and the second that they are related, *viz.*

$$\underset{\vdots}{\mathrm{CH_4}} \longrightarrow \overset{*}{\mathrm{CH_3}} + \overset{*}{\mathrm{H}} \quad . \quad . \quad . \quad . \quad (C)$$

and

$$\overset{*}{\mathrm{CH_3}} \longrightarrow \overset{*\ *}{\mathrm{CH_2}} + \overset{*}{\mathrm{H}} \quad . \quad . \quad . \quad . \quad (D)$$

The hydrogens of the adsorbed methylene radicals are thought to exchange readily, so resulting chiefly in tetradeuteromethane; however, tri- and di-deuteromethane can also be formed in this manner. Table 2 gives values of activation energies and frequency factors per 100 cm.^{2} of surface, obtained on the assumption that mechanisms A and B are valid.

TABLE 2. *Activation energies and frequency factors for methane–deuterium exchange on evaporated films*

Catalyst	E_A, kcal.	log A_A	E_B, kcal.	log A_B	Temp.
Nickel . . .	23·8	24·2	29·4	27·3	206—255°
Palladium . .	22·0	24·6	34·2	28·6	243—308
Platinum . .	20·8	24·3	24·5	25·9	159—275
Rhodium . .	20·0	24·4	24·4	27·4	138—217
Tungsten . .	8·9	19·3	11·3	20·0	92—174

The orders of reactions A and B over nickel are both first in methane and $-$ 0·5 and 1·0, respectively, in deuterium; strong adsorption of deuterium and weak adsorption of methane are thus indicated. The other metals show smaller positive orders in methane and smaller negative orders in deuterium for both reactions. Tungsten shows much smaller activation energies and frequency factors than the other metals, which is attributed to the ready adsorption of methane on this metal; an activation energy of 11 kcal. was deduced for its adsorption on nickel.

Mechanisms A and B have been supported on the basis of absolute rate calculations.[60] There is no apparent correlation between activation energies and lattice parameters.

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[60] Laidler, Markham, and Wall, *J. Phys. Chem.*, 1953, **57**, 321.

The Reaction of Ethane, Propane, and Butane with Deuterium.—The exchange reaction of ethane with deuterium proceeds on nickel–kieselguhr at temperatures greater than 100°, with an activation energy of 15 kcal.; this is lower than the temperature at which hydrogenolysis to methane becomes appreciable.[61] The reaction also takes place on platinised platinum foil at 72°.[62(a)] Anderson and Kemball [62(b)] have recently carried out a study of the reaction on a series of evaporated metal films. Ethane undergoes exchange at very much lower temperatures than methane, and once again two mechanisms operate. The first results in the predominant initial formation of monodeuteroethane; this takes place on tungsten, molybdenum, and tantalum films, and also on oriented nickel films. Exchange occurs through successive adsorption–desorption steps without the intermediate formation of adsorbed ethylene. However, a second mechanism, operative especially on palladium and rhodium films, causes the major initial product to be perdeuteroethane, and results from a sequence of ethyl radical–ethylene exchanges without intermediate desorption. Over some other metals, both mechanisms occur to comparable extents. Activation energies and pre-exponential factors are given for each metal examined.

Propane exchanges with deuterium over nickel–kieselguhr with an activation energy of about 19 kcal. between 65° and 110°; the order in propane is 0·62 and in deuterium $-$ 0·76.[63(a)] Experiments with evaporated films of tungsten, nickel, and rhodium show that these metals behave as in the ethane reaction with regard to the types of product.[63(b)] Of the monodeuteropropane formed over a nickel film at low temperatures, 90% is $CH_3{\cdot}CHD{\cdot}CH_3$; this confirms earlier work [64] in which a platinised platinum catalyst was used and is in harmony with the well-known fact that secondary carbon–hydrogen bonds are weaker than primary.

Butane behaves very similarly to propane over platinum, and the course of the reaction is accurately of the first-order.[62(a)] *iso*Butane undergoes exchange with deuterium over evaporated films of tungsten, nickel, and rhodium, the principal initial product over nickel films being $(CH_3)_3CD$.[63(b)]

The Reaction of Hexanes, Heptanes, and Octanes with Deuterium.—*n*-Hexane has been shown [65] to exchange with deuterium over platinum with an activation energy of 9 kcal. between 55° and 124°; *cyclo*hexane exchanges at a similar rate and with a similar activation energy. Greenhalgh and Polanyi [66] reported an activation energy of 13·7 kcal. (50—90°) for this latter reaction, and kinetics of the form : rate $= k[C_6H_{12}]^0[H_2]^{-0{\cdot}3}$.

Burwell and Briggs [67] have studied the reaction of *n*-heptane, (+)-3-methylhexane, 3 : 3-dimethylhexane, and 2 : 2 : 3-trimethylbutane with

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[61] Morikawa, Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1936, **58,** 1795.

[62] (*a*) Farkas and Farkas, *Trans. Faraday Soc.*, 1940, **36,** 522; (*b*) Anderson and Kemball, *Proc. Roy. Soc.*, 1954, *A*, **223,** 361.

[63] (*a*) Morikawa, Trenner, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1937, **59,** 1103; (*b*) Kemball, *Proc. Roy. Soc.*, 1954, *A*, **223,** 377.

[64] Kauder and T. I. Taylor, *Science*, 1951, **113,** 238.

[65] Farkas and Farkas, *Trans. Faraday Soc.*, 1939, **35,** 917.

[66] Greenhalgh and Polanyi, *ibid.*, p. 520.

[67] Burwell and Briggs, *J. Amer. Chem. Soc.*, 1952, **74,** 5096.

deuterium. Racemisation of the (+)-3-methylhexane in the presence of hydrogen and deuterium was investigated at the same time, a nickel-kieselguhr catalyst being used. The reactions proceeded between 90° and 130°, and the rates under equivalent conditions decreased in the order in which the molecules are listed above. The exchange process was followed by mass-spectrometric analysis of the hydrocarbons; *n*-heptane and (+)-3-methylhexane gave products containing up to sixteen deuterium atoms; the heavily deuterated molecules were present in much greater than statistical proportions. However, in 3 : 3-dimethylhexane and 2 : 2 : 3-trimethylbutane no more than seven deuterium atoms were detected. It would therefore appear that in 3 : 3-dimethylhexane exchange occurs only in the propyl chain, that is, that the hydrocarbon is adsorbed at some point in the propyl chain, and then exchanges by going through the adsorbed olefin, *viz.*

$$\mathrm{CH_3{-}\overset{*}{C}H{-}CH_2R \xrightarrow{-\,H} CH_3{-}\overset{*}{C}H{-}\overset{*}{C}HR \xrightarrow{+\,D} CH_3{-}CHD{-}\overset{*}{C}HR}\ \text{etc.}$$
$$(\text{where } \mathrm{R} = \mathrm{CMe_2Et}) \quad . \quad (20)$$

As this type of exchange could not propagate past a quaternary carbon atom, subsequent re-adsorption at the methyl or ethyl group must be ruled out. Similarly in the case of 2 : 2 : 3-trimethylbutane, exchange must take place only in the *iso*propyl chain, *viz.*

$$\mathrm{CH_3{-}\overset{*}{C}Me{-}R \xrightarrow{-\,H} \overset{*}{C}H_2{-}\overset{*}{C}Me{-}R \xrightarrow{+\,D} CH_2D{-}\overset{*}{C}Me{-}R}\ \text{etc.}$$
$$(\text{where } \mathrm{R} = \mathrm{CMe_3}) \quad . \quad (21)$$

The rate of racemisation of (+)-3-methylhexane is rather slower than its exchange, and is within experimental error the same with deuterium as with hydrogen, the activation energy being 26 kcal. between 103° and 137°. The kinetics are of the form: rate $= k[\text{3-methylhexane}]^{0\cdot 3}[\mathrm{H_2}]^{x}$, values of x being given as $-\,0{\cdot}47$ and $-\,0{\cdot}65$. The authors believe that the racemisation must involve a symmetric adsorbed radical, and possibilities are suggested, but it cannot be concluded that the mechanism of this reaction is yet settled.

Summary.—In their simplest terms, the exchange reactions of saturated hydrocarbons may be said to involve the dissociative chemisorption of the hydrocarbon followed by the recombination of the resulting radical with a deuterium atom. In the case of methane, this is complicated by a second reaction which is thought to involve an adsorbed methylene radical. When two or more carbon atoms are present in the hydrocarbon molecule, the first-formed radical (ethyl from ethane, *iso*propyl from propane, etc.) may undergo loss of a hydrogen atom to give the adsorbed olefin, a step which has been previously postulated to explain the exchange reactions of olefins.

The kinetics usually involve a positive order in the hydrocarbon and a negative order in deuterium, indicating that the latter is more strongly adsorbed than the former. Each adsorbed radical or olefin molecule is thus surrounded by deuterium atoms, and inter-radical reactions become improbable. These are also unlikely to occur with bulky molecules such as hexanes, etc. The sequence of reactions

$$C_2H_6 \rightarrow \overset{*}{C}_2H_5 \xrightarrow{-\mathrm{H}} \overset{*\,*}{C_2H_4} \xrightarrow{+\mathrm{D}} \overset{*}{C}_2H_4D \text{ etc.} \qquad (22)$$

may therefore continue until complete substitution is effected (*e.g.*, in *n*-heptane and 3-methylhexane), provided the hydrogen atoms released are exchanged rapidly with gaseous deuterium, and that there is no interference from other radicals. The known ease with which the exchange step $C_2H_5 \rightarrow C_2H_4$ occurs in olefin hydrogenation makes this scheme quite plausible. There is thus a close connection between the mechanisms of exchange of saturated hydrocarbons and of addition and exchange of olefins, the main difference lying in the relative concentrations of the adsorbed species.

Exchange Reactions Between Similar Hydrocarbons

Catalytic reactions occurring between isotopically different hydrocarbons in the absence of hydrogen give additional information of relevance to the systems already examined.

The Methane–Tetradeuteromethane Reaction.—This reaction was first studied over nickel–kieselguhr between 138° and 255°, and in this range an activation energy of 19 kcal. was reported.[61] A more detailed study has since been carried out,[68] a nickel–chromia catalyst being used, and in this work a mass-spectrometer was employed for analysis of the methanes. The rates of disappearance of tetradeuteromethane and of appearance of tri- and di-deuteromethane gave first-order plots, and an activation energy of 20·9 kcal. is associated with the former rate. The results are consistent with the view that exchange occurs stepwise, that is,

$$CD_4 \rightarrow \overset{*}{C}D_3 + \overset{*}{D} \quad \text{and} \quad CH_4 \rightarrow \overset{*}{C}H_3 + \overset{*}{H} \qquad (23)$$

followed by

$$\overset{*}{C}D_3 + \overset{*}{H} \rightarrow CHD_3 \quad \text{and} \quad \overset{*}{C}H_3 + \overset{*}{D} \rightarrow CH_3D \text{ etc.} \qquad (24)$$

Only one atom is exchanged each time a methane molecule is adsorbed. Under steady-state conditions, rates of adsorption and desorption are equal, but owing to the high activation energy for methane adsorption, the concentrations of methyl and hydrogen atoms will be low. Reactions as Kemball's type *A* (see p. 302) are therefore improbable; moreover the rate-controlling step cannot be the same here as in the methane–deuterium reaction owing to the lower observed activation energy, which indicates that *A* rather than *C* is the more probable mechanism of methane adsorption in the presence of deuterium, since *C* is the only mode of adsorption possible here.

The Ethylene–Tetradeuteroethylene Reaction.—The negative findings reported by Conn and Twigg [69] for this reaction have frequently been used as powerful evidence for the associative method of olefin adsorption; however, recent work [11] has shown that the reaction proceeds over nickel wire

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[68] Wright and H. S. Taylor, *Canad. J. Res.*, 1949, **278,** 303.

[69] Conn and Twigg, *Proc. Roy. Soc.*, 1939, *A*, **171,** 70.

at 100° and higher, and much more rapidly on nickel–kieselguhr. If *trans*-dideuteroethylene is the reactant, its isomerisation to the *cis*-form is more rapid than its exchange over either catalyst. No detailed kinetic studies have been made and interpretation is therefore difficult, but it seems reasonably certain that ethylene will undergo dissociative adsorption on an active catalyst in the absence of hydrogen, and the adsorbed intermediates may include the vinyl radical. A subsequent polymerisation may set in, which would account for the frequently observed poisoning of catalysts by olefins. The presence of hydrogen apparently suppresses dissociative adsorption, and as already shown the experimental results are adequately explained in terms of the associative mechanism.

The exchange of tetradeuteroethylene with propylene and butenes has also been recorded.[70]

The Acetylene–Dideuteroacetylene and the Methylacetylene–Dideuteroacetylene Reactions.—The reaction between light and heavy acetylene has been studied [45] on nickel–pumice catalysts between 40° and 120°, and the course of the reaction followed by infra-red analysis of reactants and product. Monodeuteroacetylene is formed and the reactants are removed by a first-order reaction; the equilibrium constant is 3·2 ± 0·5, compared with a calculated value of 3·6 ± 0·3. The activation energy is 10·7 kcal., and the rate is proportional to the 0·65th power of the total pressure when the ratio of the concentrations of the reactants is kept at unity. The rate as measured by the time of half-reaction is independent of the reactant ratio provided that the total pressure is kept constant.

Dideuteroacetylene reacts with methylacetylene under similar conditions, but only one of its four hydrogen atoms is exchangeable, presumably that directly linked to the triply-bonded carbon. The reactions occurring in this system are:

$$C_2D_2 + C_3H_4 \rightleftharpoons C_2HD + C_3H_3D \quad . \quad . \quad . \quad (25)$$

$$C_2HD + C_3H_4 \rightleftharpoons C_2H_2 + C_3H_3D \quad . \quad . \quad . \quad (26)$$

$$2C_2HD \rightleftharpoons C_2H_2 + C_2D_2 \quad . \quad . \quad . \quad (27)$$

and the course of reaction results is in harmony with this scheme. Equilibrium measurements gave a mean value of $1/K_{27}$ as 3·0 ± 0·2, in good agreement with the value given above. The order in total pressure was 0·47, and the activation energy was 12·5 kcal. in the range 74—133°. The rate was a function of the initial ratio of reactants whence it was deduced that acetylene was adsorbed about 1·5 times as strongly as methylacetylene.

A mechanism involving the exchange of hydrogen atoms between a chemisorbed and a physically adsorbed molecule was advocated, the motive force being the polarity of the acetylenic C–H bond.

Conclusion

It has been shown that the phenomena of reactions on metal surfaces can be conveniently described in the language of free-radical chemistry. However, owing to numerous ambiguities in the reaction mechanisms, it is

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[70] Koidzumi, *J. Chem. Soc. Japan*, 1942, **63**, 1512, 1715.

seldom if ever possible to assign activation energies or frequency factors to individual steps, although it is frequently possible to say which is most likely to be rate-controlling. Relative values of frequency factors in a series of similar reactions may sometimes be found, although absolute values depend on a precise knowledge of the active surface area.

Rate-controlling steps are in general probably the interaction of two radicals, or of a radical and an atom, such as

$$2\overset{*}{C}_2H_5 \longrightarrow \overset{*}{C}_2\overset{*}{H}_4 + C_2H_6 \quad . \quad . \quad . \quad . \quad (6a)$$

or

$$C_2\overset{*}{H}_5 + \overset{*}{H} \longrightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

both of which have their homogeneous counterparts. The homogeneous reactions proceed with much lower activation energies than do the surface reactions,[71] but third bodies are no longer required since the catalyst can act as an energy sink.

The homogeneous addition of hydrogen to unsaturated hydrocarbons needs a much greater activation energy than the corresponding catalysed reaction, presumably because of the strong H–H bond which has to be broken. This the catalyst does easily, and hence the necessary activation energy is lower. It is also likely that the removal of some if not all of the translational degrees of freedom in the adsorbed state results in a more favourable steric factor.

I am grateful to Dr. D. O. Schissler of the Shell Development Co., Emeryville, California, for permission to quote results presented in his thesis,[14b] some of which have not been previously published.

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[71] Ivin and Steacie, *Proc. Roy. Soc.*, 1951, *A*, **208**, 25.