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MECHANISM OF THE CATALYTIC REDISTRIBUTION OF HYDROGEN IN UNSATURATED CYCLIC HYDROCARBONS

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1. INTRODUCTION

The catalytic redistribution of hydrogen in hydrocarbons has been studied for more than half a century. The interest taken in these reactions is due to the important part they play in many processes, both in the chemical and petroleum-processing industries and in Nature, for example, in any enzymic oxidation.

The amount of work done on simultaneous hydrogenation and dehydrogenation on metal catalysts has been especially large. The redistribution of hydrogen among molecules of the same substance, going practically to completion without the evolution of gaseous hydrogen, was discovered by Zelinskii and Glinka[1]. Such changes undergone by various hydrocarbons on palladium catalysts were subsequently investigated by Wieland[2] and by Zelinskii and his school[3-10]. On nickel catalysts the conversion was less complete[11] than on palladium catalysts, and it was usually accompanied by hydrogen evolution. With platinum catalysts higher temperatures are required for the redistribution of hydrogen than with palladium catalysts. In many cases this process is accompanied by isomerisation. For example, copper and iron catalysts[12] behave similarly to oxide catalysts[13] towards cyclohexene. Conversion into benzene and cyclohexane has been observed only when a mixture of cyclohexene and hydrogen is used[12]. On metallic rhenium[14] the conversion of cyclohexene at certain temperatures is not accompanied by the evolution of hydrogen, the ratio of benzene to cyclohexane in the products corresponding to that found on palladium catalysts. However, the proportion of cyclohexene which has undergone such reaction on rhenium does not exceed 32% at 300°, whereas on palladium catalysts this process goes to completion at far lower temperatures.

Comparison of these results shows that hydrogen redistribution in unsaturated hydrocarbons takes place differently on different metal catalysts. Insufficient attention has been paid in the literature to the reasons for this, and a possible explanation is suggested below for the decrease in activity, with respect to the redistribution of hydrogen, for the series: palladium, nickel, platinum.

The mechanism of hydrogen redistribution in cyclohexadiene, cyclohexene, and decalin hydrocarbons having an unsaturated bond in the side-chain has been elucidated by Levina[15,16], but the changes undergone by hydrocarbons having an unsaturated bond in the ring are interpreted in two different ways.

Balandin[17] suggested models in which transformations of cyclohexene or cyclohexadiene are effected by direct intermolecular transfer of hydrogen atoms. This scheme is examined in detail in Section 3, as also the closely similar views of Linstead and his collaborators[18,19].

A different view of the mechanism of catalytic hydrogen redistribution was held by Zelinskii[1,3] and Wieland[2], who

regarded this process as the net effect of two simultaneous and opposite reactions, those of dehydrogenation and hydrogenation of the starting material. The redistribution of hydrogen was subsequently interpreted in a similar manner by other workers (see, for example, Shcheglova and Kagan[20]). However, no experimental evidence was given in these papers for the independent occurrence of dehydrogenation and hydrogenation during the redistribution of hydrogen.

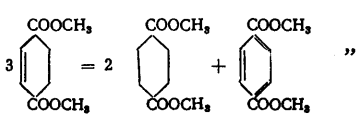
Fresh results[21-38] on the changes undergone by cyclohexene and cyclohexadiene on platinum and palladium films, obtained by spectroscopic, kinetic, adsorption, and conductimetric methods (see Section 4), allow the redistribution of hydrogen to be regarded as a combination of dehydrogenation and hydrogenation reactions. The extent to which these reactions balance one another is governed by thermodynamic factors, the nature of the catalyst (especially its ability to retain hydrogen in a form which is active in hydrogenation), and competitive adsorption of the starting material and its conversion products. Such a view, as will be shown below, provides explanations of several experimental results which had not previously been interpreted.

In spite of the marked differences in hydrogen redistribution on metallic, oxide, and aluminosilicate catalysts, main stages can be found which are common to all these systems, as will be shown in Sections 6 and 7.

Since reviews have been published on reactions involving the redistribution of hydrogen in hydrocarbons[39-43], the present paper will contain mainly new results and information which is essential for determining the mechanism of the process.

2. REDISTRIBUTION OF HYDROGEN AS A COMBINATION OF DEHYDROGENATION AND HYDROGENATION

In 1911 Zelinskii and Glinka discovered[1] that the hydrogenation of dimethyl tetrahydroterephthalate in the presence of palladium black at room temperature is accompanied by its dehydrogenation. They concluded that the second process is linked with the first, since with this catalyst it does not take place in the absence of hydrogen: "The reaction is initiated by palladium hydride, after which the role of palladium as catalyst is in effect to redistribute hydrogen among three molecules of the tetrahydroterephthalic ester[1]:



The reaction is far slower with platinum black than with palladium black.

The important part played in redistribution by hydrogen dissolved in the palladium was noted also by Wieland[2]. He pointed out that, when a large quantity of palladium black is used at room temperature, dihydronaphthalene is almost exclusively dehydrogenated, or this reaction at least predominates. With a small amount of palladium black, however, dehydrogenation is followed by hydrogenation. Unfortunately, no experimental evidence was given to prove that dehydrogenation and hydrogenation take place independently in the redistribution of hydrogen. Wieland[2] regarded the two reactions as two equilibria involving an unstable addition product:

$$\begin{matrix}-R-R-\\ H\ PdH\end{matrix},$$

the conventional formula HPdH (or PdH_2) being used to denote a solid solution of hydrogen in palladium. It was supposed that the unstable complex is formed in the first stage of dehydrogenation, and that the hydrogen absorbed by the palladium then adds on at the double bond in the molecule which is capable of hydrogenation

$$\begin{matrix}-R-R-\\ H\ H\end{matrix} + Pd \rightleftarrows \begin{matrix}-R-R-\\ H\ PdH\end{matrix} \rightleftarrows -R=R- + PdH_2.$$

It is readily seen that, according to this mechanism, the redistribution of hydrogen between molecules of an unsaturated hydrocarbon consists of separate dehydrogenation and hydrogenation stages.

On palladised asbestos at temperatures below 130° in a current of carbon dioxide, the following changes involving cyclohexadiene:

$$2C_6H_8 = C_6H_{10} + C_6H_6, \quad (1)$$

and cyclohexene:

$$3C_6H_{10} = 2C_6H_{12} + C_6H_6, \quad (2)$$

go almost to completion[3,4] and without the evolution of hydrogen. Zelinskii and Pavlov[3] considered that these processes consist in the simultaneous occurrence of two reactions, dehydrogenation and hydrogenation, the catalyst distributing the mobile hydrogen among the molecules of the starting material in such a way that a more stable system is formed. However, these workers left open the question as to whether redistribution is accomplished by combining individual dehydrogenation and hydrogenation stages or by the direct intermolecular transfer of hydrogen atoms.

Shcheglova and Kagan[20] put forward the hypothesis that cyclohexene molecules oriented with the double bond towards the catalyst surface are hydrogenated by hydrogen atoms split off from cyclohexene molecules adsorbed at the saturated carbon atoms. While assuming that dehydrogenation and hydrogenation occur simultaneously, they also noted that hydrogen could appear in the adsorbed layer. The evolution of hydrogen into the gas phase was regarded as impossible under the conditions of hydrogen redistribution. This mechanism is represented schematically as follows:

$$\begin{gathered}C_6H_{10}\,(gas) \longrightarrow C_6H_{10}\,(ads),\\ C_6H_{10}\,(ads) \longrightarrow C_6H_8\,(ads) + 2H,\\ C_6H_{10}\,(ads) + 2H\,(ads) \rightarrow C_6H_{12}\,(ads) \longrightarrow C_6H_{12}\,(gas),\\ C_6H_8\,(ads) \longrightarrow C_6H_8\,(ads) + 2H\,(ads),\\ C_6H_{10}\,(ads) + 2H\,(ads) \longrightarrow C_6H_{12}\,(ads) \longrightarrow C_6H_{12}\,(gas).\end{gathered}$$

There was no experimental confirmation of this scheme. These workers[20] cited the previously discovered[4] stepwise character of the transformation of cyclohexadiene in support of the assumption that hydrogen redistribution consists of two successive stages. However, the models[17] to be described below enable this result to be explained on the basis of the direct intermolecular transfer of hydrogen atoms.

3. DIRECT INTERMOLECULAR TRANSFER OF HYDROGEN ATOMS

In 1929 Balandin[17] attempted to explain peculiarities in the redistribution of hydrogen in cyclohexadiene and in cyclohexene on the assumption that the former reaction takes place on a triplet, *i.e.* on three atoms of the metal catalyst, and the second reaction on two triplets (see Fig. 1). According to these models, two hydrogen atoms pass directly from one cyclohexadiene molecule to another, as do four hydrogen atoms from a cyclohexene molecule to two others. The models were consistent with the experimental results available at that time. The absence of hydrogen evolution in the "irreversible catalysis" of cyclohexene and cyclohexadiene[3,4] could be interpreted as indicating that the hydrogen atoms passing from one molecule to another did not interact with the catalyst atoms. As can be seen from Fig. 1, the direction of movement of the hydrogen atoms, indicated by arrows, is governed mainly by the fact that the C=C bond is stretched owing to two-point adsorption, while the C–C bond in the other molecule is shortened owing to both carbon atoms being attracted to one surface atom of the metal catalyst The planar orientation of the original molecules required by the model is difficult with the *trans*-forms of disubstituted cyclohexenes and cyclohexadienes. In fact, formation of only the hexahydro-*cis*-terephthalic ester was observed in the early work[1]. It is true that still earlier[44] a small amount of hexahydro-*trans*-terephthalic ester had been obtained together with the predominant *cis*-form on heating dimethyl dihydroterephthalate with palladium black, but in these experiments the process took place under quite severe conditions and was accompanied by the evolution of hydrogen.

The rate of conversion of cyclohexadiene into cyclohexene and benzene exceeds that of the "irreversible catalysis" of cyclohexene[4]. This was explained by the above models, since the presence of two triplets side by side and in a definite orientation is less probable than the presence of one triplet.

A scheme of direct intermolecular hydrogen transfer was used[18,19] to explain the low concentration of cyclohexa-1,3-diene found during the redistribution of hydrogen in cyclohexene. This reaction was regarded as termolecular, taking place in a single step with the simultaneous transfer of four hydrogen atoms from one cyclohexene molecule to two others. The kinetic data were regarded as inconsistent with the view that redistribution of hydrogen takes place in two independent stages involving dehydrogenation and hydrogenation. As a proof of direct intermolecular transfer of hydrogen, the fact is cited that the stoichiometric equation of "irreversible catalysis" is satisfied even with a low metal/cyclohexene ratio and boiling tetrahydrofuran as medium, when it could be expected that chemisorbed hydrogen would be removed. However, it has since been shown[34] that, even at 20°, the redistribution of hydrogen in cyclohexene and cyclohexadiene may be accompanied by hydrogen evolution (see next Section). Furthermore, a mechanism involving direct intermolecular transfer of hydrogen atoms does not provide an explanation of why the redistribution of hydrogen in cyclohexene is accelerated by hydrogen chemisorbed on the catalyst. While giving a scheme of "termolecular disproportionation", which is very close to the model of Balandin[17] (*cf.* Figs. 2 and 1*b*), Braude *et al.*[19] also suggest the scheme of termolecular disproportionation in the presence of chemisorbed hydrogen illustrated in Fig. 3. It is readily seen that the resemblance between the mechanisms in Figs. 2 and 3 is quite superficial. Whereas in Fig. 2 the elimination of the particular hydrogen atoms indicated by the letters H can still be explained by hydrogenation of the unsaturated bonds in other cyclohexene molecules, it is not clear in Fig. 3 why only one cyclohexene molecule loses four hydrogen atoms and just two other molecules add on four hydrogen atoms. The statement[19] that chemisorbed hydrogen diminishes the degree of approach of cyclohexene molecules necessary for reaction contradicts the mutual independence of the processes of dehydrogenation and hydrogenation of cyclohexene molecules which clearly follows

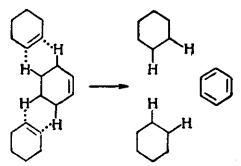


Fig. 2. Termolecular redistribution of hydrogen in cyclohexene[19].

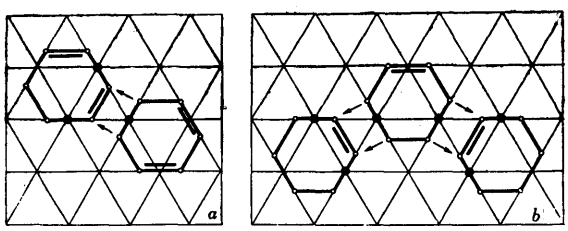


Fig. 1. Arrangement of molecules of (*a*) cyclohexadiene and (*b*) cyclohexene on a metal surface during hydrogen redistribution[17]. The black circles denote metal atoms constituting active centres (triplets), and the arrows indicate movements of hydrogen atoms.

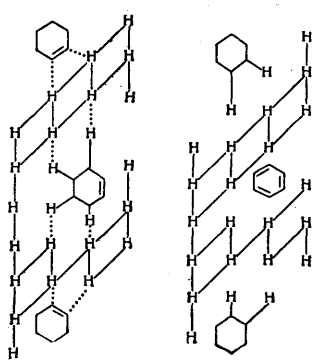
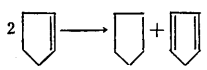


Fig. 3. Termolecular redistribution of hydrogen in cyclohexene involving chemisorbed hydrogen[19].

from Fig. 3. The complete balancing of these processes shown in Fig. 3 requires the additional artificial assumption that the amount of hydrogen retained by the catalyst remains unchanged during the redistribution. Measurements of the electrical conductivity of platinum films during the transformation of cyclohexene and cyclohexadiene on them[33] have shown the limited character of such a treatment (see Section 4). Kinetic studies of the redistribution of hydrogen in cyclohexene on palladium and platinum films[28,37] are also inconsistent with a mechanism of direct intermolecular transfer of hydrogen atoms.

The activity of iron catalysts observed[12] towards reaction (2) could not be expected on the basis of the models[17], since the crystal lattice of iron does not permit formation of two triplets oriented as indicated in Fig. 1*b*. On the other hand, palladium and platinum, which have the same type of lattice, similar atomic radii, and similar metal–carbon and metal–hydrogen bonding energies, differ substantially in their activity with respect to hydrogen redistribution, as had been noted in several papers, and has recently been shown on platinum and palladium films[36]. The models[17] also provide no explanation of the redistribution of hydrogen between five-membered rings, which have no elements of symmetry in common with any crystal lattices. Yet it has been shown[46,47] that cyclopentene is converted into cyclopentane and cyclopentadiene on palladium at 200°



It has recently been discovered[48] that a similar process takes place with dihydromethylfuran on a palladium catalyst.

Thus a mechanism involving direct intermolecular migration of hydrogen atoms in hydrogen redistribution reactions has proved suitable for interpreting some experimental results, but is inconsistent with many others.

4. NEW DATA ON CHANGES UNDERGONE BY SIX-MEMBERED CYCLIC HYDROCARBONS ON PALLADIUM AND PLATINUM FILMS

Since the mechanism of hydrogen redistribution had not been sufficiently elucidated, an investigation was undertaken of the reactions of cyclohexene and cyclohexa-1,3-diene, as well as of the adsorption of these compounds and of the products formed from them[21-38]. The adsorbents and catalysts used were palladium and platinum films prepared by evaporating the metal in a high vacuum, since on them the interaction of the hydrocarbon molecules with the metal surface could be studied by various physicochemical methods, including spectroscopic[22-26,28] and conductivity[29-33] techniques. The investigation of adsorption on metal films is difficult because of their small specific surface, but improvements[35] in the method of feeding the vapour through a capillary have enabled these difficulties to be overcome. The kinetics of the catalytic changes undergone by cyclohexene and cyclohexadiene have been studied both on films of palladium and platinum invisible to the naked eye and on specular layers of the metals. Experiments were made at temperatures between 0° and 600° and vapour pressures of the hydrocarbons differing by a factor of almost a million (between 30 mm and 5×10^{-5} mm).

Since no data had been published on hydrogen redistribution on vacuum-sublimed palladium or platinum films, it was necessary to ascertain whether the composition of the reaction products, for example, from cyclohexa-1,3-diene, was the same on the metal films as on the metal catalysts used previously. Analysis based on the infrared absorption spectra showed[21] that, with palladium films of low catalytic activity or small geometrical surface area, the molecular ratio of benzene to cyclohexene in the products of catalysis was close to unity. This is consistent with the equation[4] for reaction (1) occurring rapidly on palladium black. On palladium films of larger surface at the same temperature (50°), reaction (2) was observed as well as reaction (1). Hence palladium films do not differ substantially from other palladium catalysts.

Calculation of the limiting quantity of hydrogen which the palladium films could contain before entry of cyclohexadiene vapour showed[21] it to be less than the quantity of hydrocarbon used in the experiment by a factor of 10^8. This result also agreed with Zelinskii's data[8] on the catalytic activity of palladised asbestos freed from hydrogen by being heated to 300° in a current of carbon dioxide.

It was found[23] from the infrared spectra that the catalytic activities of transparent palladium films towards hydrogen redistribution in cyclohexadiene vary inversely with the stable adsorption of the starting material observable spectroscopically. Films with an effective thickness of ~100 Å, deposited on quartz or fluorite, show appreciable catalytic activity, while stable adsorption of cyclohexadiene on these films is not revealed by spectroscopic methods. A less dense film of palladium on fluorite possessed a far smaller activity, and the cyclohexadiene which was not removed from the film by evacuating to 10^{-3} mm gave an absorption band. A still less dense palladium film deposited on rocksalt proved catalytically inactive, while the spectrum of cyclohexadiene firmly adsorbed on it remained at a residual pressure of 10^{-4} mm, after the reaction vessel had been evacuated for many hours and had been swept out with benzene vapour.

Fig. 4 shows that the spectrum of cyclohexadiene firmly adsorbed on palladium[24,25] has several absorption bands in common with its spectrum in the vapour state. In particular, the bands in the 1000–1450 cm^{-1} range, corresponding to vibrations of $\rangle C-H$ bonds, remain, but the bands at 750 and 925 cm^{-1}, representing vibrations of $\rangle C-H$ bonds, are not found in the spectrum of the adsorbed cyclohexadiene. This cannot be attributed to rupture of π bonds, since absorption is observed in the range 1600–1700 cm^{-1}, which is characteristic of C=C stretching vibrations. If the spectral differences between firmly adsorbed cyclohexadiene and its vapour are due to molecular changes resulting from interaction with the palladium film, it must be supposed that hydrogen atoms are split off mainly from $\rangle C-H$ groups in the cyclohexadiene.

All these results indicate that the stable absorption of cyclohexadiene detectable from the infrared spectrum does not form an intermediate stage in the catalytic transformation. Elimination of hydrogen is detected also in the stable adsorption of benzene vapour on platinum films, manometrically and from the change in their electrical conductivity[30,49]. A characteristic feature of such stable adsorption is that the elimination of hydrogen atoms from

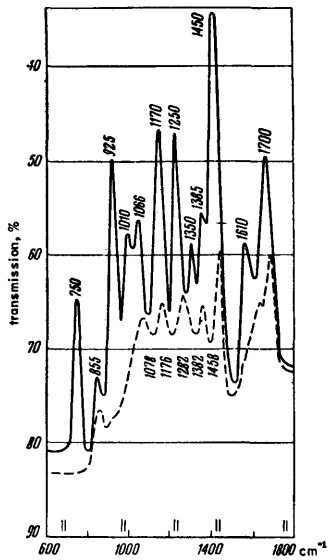


Fig. 4. Infrared absorption spectrum of cyclohexadiene firmly adsorbed on transparent palladium film[23] (broken curve), and absorption spectrum of cyclohexadiene vapour.

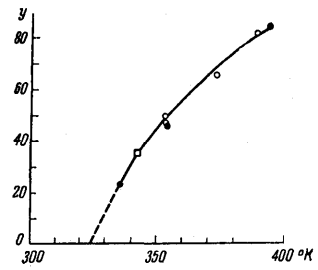


Fig. 5. Temperature variation of proportion of cyclohexene converted when reaction ceases to be of zero order. The full and open circles denote results of experiments on two platinum films[28], and the square indicates a result from Schwab and Lorenzen[50].

>C–H or >C–H groups does not yield simple dehydrogenation products, but may constitute the initial stage of processes of dehydrocondensation and polycondensation (see Section 8), resulting in deactivation of the catalysts owing to their surface becoming covered with resinous or tarry substances.

The kinetics of hydrogen redistribution in cyclohexadiene and cyclohexene on palladium and platinum films has been studied[26,28] under static conditions by a spectroscopic method, in which the changes in absorption in a definite spectral range, due to the decrease in concentration of the starting material or the accumulation of one of the products, are automatically recorded during the reactions. By means of calibration graphs these curves were used to find the variation with time of the partial pressure of the corresponding reactant. A manometric method could not be employed, since with initial vapour pressures of cyclohexene or cyclohexadiene exceeding 1 mm Hg the total pressure remained unchanged during the reaction.

The kinetic results for hydrogen redistribution in cyclohexadiene on palladium films show that a scheme of direct intermolecular transfer of hydrogen atoms does not enable all the experimental data to be explained. Still more marked discrepancies between this scheme and experiment were observed with the kinetics of hydrogen redistribution in cyclohexene. On palladium films this reaction is of zero order until a certain degree of conversion has been reached, this proportion diminishing as the temperature is lowered (Fig. 5). Study of the adsorption of all the reactants on palladium films showed that the change in reaction order was due to competitive adsorption of cyclohexene and benzene. An equation was obtained for the temperature variation of the percentage conversion of cyclohexene up to which the reaction is of zero order at a given total pressure, based on the fact that the adsorption coefficients of these hydrocarbons depend in different ways on temperature owing to differences in their heats of adsorption on the catalytically active surface. The curve calculated by means of this equation satisfactorily reproduces our experimental results and the data given by Schwab and Lorenzen[50] (see Fig. 5). Extrapolation of this relationship shows that the reaction is not zero order at temperatures below 50°. Actually, an analysis[17] of Zelinskii and Pavlov's kinetic experiment[4] at 35° showed that a reaction order of 1.5 gave the most constant values for the rate constant. At higher temperatures (105°–124°) zero order was observed in the redistribution of hydrogen in cyclohexene[20], which also agrees with the curve in Fig. 5. Thus all these results can be explained on the same basis.

An important fact in evaluating the mechanism of hydrogen redistribution is that the reaction order of 1.5, which has been regarded in the literature as an argument in support of the hypothesis that three molecules of cyclohexene undergo transformation on two active centres (triplets), applies only at low temperatures.

Comparison of data on the changes undergone by cyclohexene and cyclohexadiene on palladium and platinum films prepared in the same way has revealed[36] substantial differences in the catalytic action of these films. On palladium films, redistribution of hydrogen was already taking place at 20°, and at pressures exceeding 1 mm was not accompanied by hydrogen evolution. On freshly prepared platinum films no reactions of cyclohexadiene or cyclohexene were observed at temperatures up to 200°, and at higher temperatures it was mainly dehydrogenation of these hydrocarbons which occurred. In subsequent experiments with the same platinum films, hydrogenation was observed as well as dehydrogenation, since the pressure of the hydrogen fell. It is interesting that, after a few experiments in which cyclohexene was dehydrogenated, redistribution of hydrogen in cyclohexadiene on the same platinum film was no longer accompanied by evolution of hydrogen into the gas phase.

Thus dehydrogenation and hydrogenation of cyclohexene and cyclohexadiene are observed on platinum films above 200°. In order to ascertain whether these reactions can occur at lower temperatures, and to study the nature of the interaction of six-membered cyclic hydrocarbons with the platinum surface, measurements were made of the effect

of adsorption of the vapours of benzene, cyclohexadiene, cyclohexene, and cyclohexane and of hydrogen at 20° on the electrical conductivity of the platinum films.

Adsorption was measured by a method involving flow through a capillary with automatic recording of the results. Since the vapours of these hydrocarbons are adsorbed on the glass walls of the apparatus, a technique has been developed[35] for determining their rate of accumulation, which is appropriate under these conditions and does not involve the assumption of molecular flow.

As a result of the varying influence of adsorption of the vapours of these hydrocarbons and of the sorption of hydrogen on the conductivity of platinum films, the conductivity method combined with adsorption measurements proved very useful in elucidating the nature of the interaction between the hydrocarbon molecules and the metal surface. It has been found[29-33] that the first admission of the vapour of any six-membered cyclic hydrocarbon to a freshly prepared platinum film at 20° is accompanied by stable adsorption, together with the evolution of hydrogen. At the same time an unstable adsorption takes place, which can be removed by evacuation at room temperature. The adsorbed molecules gradually redistribute themselves over the surface of the metal film in conformity with the adsorption potential. In the course of unstable adsorption, when the hydrocarbon may be removed by evacuation at room temperature, benzene and cyclohexane remain unchanged, but with cyclohexene and cyclohexadiene hydrogen is split off however many times admission of hydrocarbon vapour and evacuation are repeated.

Curves *I* and *IV* in Fig. 6 represent the variation in the resistance of the platinum films during the first and second admissions of cyclohexene vapour[33]. On the first contact between the vapour and the film prepared by sublimation in a high vacuum, the resistance of the film increases sharply, whereas during the second inflow the resistance increases slightly, passes through a maximum, and then falls below its initial value. Curves *II* and *III* are copies of the traces, on the chart of the potentiometric recorder, of the pressure in the vessel containing the platinum film, made at the same time as the variations in its resistance. *H* denotes the instants at which entry of cyclohexene vapour begins in the first and second experiments, *T* the cessation of entry of vapour, and *B* freezing of the hydrocarbon vapours at the temperature of liquid nitrogen. After entry of vapour had stopped, the pressure remained unchanged with time (section *TB* of curve *II*), and freezing lowered the pressure slightly. This last fact means that the gas phase comprised mainly hydrogen split off from the cyclohexene molecules. After evacuation of the vessel containing the film to a residual pressure of 10^{-7} mm, introduction of cyclohexene vapour had little effect on the resistance of the platinum film because most of the sites on the surface, adsorption on which would involve stronger electronic interaction with the metal, were occupied by reaction products of the cyclohexene, predominantly benzene, as is shown by other experiments. Consequently, the second and subsequent admissions of cyclohexene vapour are no longer accompanied by stable adsorption on the platinum film, but by temporary adsorption with evolution of hydrogen into the gas phase: after freezing (*B* on curve *III*) the pressure does not drop to the very low value observed in the absence of hydrogen.

Further repetitions of evacuation and admission of cyclohexene or cyclohexadiene vapour have practically the same influence on the resistance of the platinum film, as can be seen from Fig. 7, which gives curves similar to those in Fig. 6 but obtained during the fourth and tenth influxes of cyclohexadiene vapour[33].

If the supply of cyclohexene or cyclohexadiene vapour is periodically interrupted, and the hydrocarbon vapour frozen out of the gas phase, the quantity of hydrogen formed passes through a maximum. In particular, curve *1* in Fig. 8 was obtained with cyclohexene, while curve *2* shows the dependence of the ratio between the numbers of hydrogen and cyclohexene molecules $N_{H_2}/N_{C_6H_{10}}$ on the number of cyclohexene molecules admitted. Analogous results were obtained with cyclohexadiene, but only about half the hydrogen is evolved compared with adsorption of

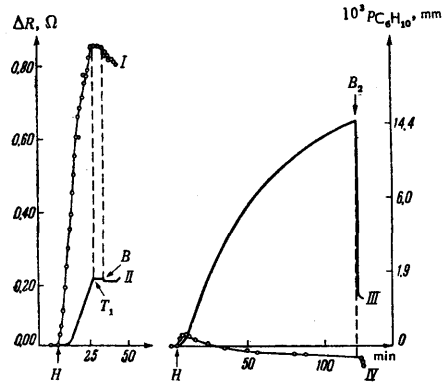


Fig. 6. Variation in resistance of platinum film (curves I and IV) and pressure over it (curves II and III) during first (left-hand half of diagram) and second admissions of cyclohexene vapour[33]. *H* = start of entry of vapour; *T* = termination of entry of vapour; *B* = freezing of hydrocarbon vapours.

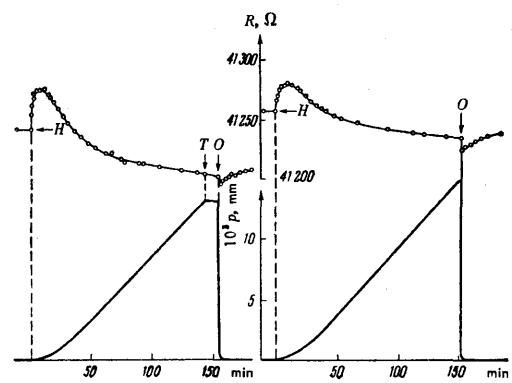


Fig. 7. Dependence of resistance of platinum film (upper curves) and of vapour pressure over it on time of inflow of cyclohexadiene vapour in fourth (left-hand half of diagram) and tenth experiments[33]. *H* = start of inflow; *T* = termination of inflow; *O* = evacuation.

the corresponding amount of cyclohexene. Experiments in which the same quantity of cyclohexene was admitted at a constant rate into a vessel containing a platinum film and different quantities of hydrogen showed that, with a certain amount of the latter, it is neither adsorbed nor evolved during entry of the unsaturated hydrocarbon. Dehydrogenation takes place with a smaller amount of hydrogen, and hydrogenation with a larger amount. Cyclohexadiene, too, can be both dehydrogenated and hydrogenated at 20°.

These results show that hydrogenation and dehydrogenation, both of cyclohexene and of cyclohexadiene, take place simultaneously on platinum films at 20°. If the rates of these processes were made equal, the quantity of hydrogen in the vessel would reach a certain value and then remain unchanged with further entry of hydrocarbon. But actually the quantity of hydrogen passes through a maximum (see curve *1* in Fig. 8). Hence dehydrogenation had predominated at first, and then hydrogenation had become dominant. Such a change in relative velocities may be caused by selective blocking by reaction products of those portions of the platinum surface on which dehydrogenation takes place. It was established in separate experiments that cyclohexane has practically no influence on the transformation of cyclohexene, whereas benzene, which is not hydrogenated under these conditions, actually suppresses the dehydrogenation of cyclohexene. On the other hand, continuous removal of reaction products from cyclohexene markedly increases the yield of hydrogen.

Thus dehydrogenation and hydrogenation of cyclohexene and cyclohexadiene are observed under conditions of hydrogen redistribution in these hydrocarbons. At the start, dehydrogenation predominates. The accumulation of hydrogen and of benzene, the latter preferentially blocking the active centres for dehydrogenation, causes a diminution in the velocity of this process, while the rate of hydrogenation increases. Therefore with increasing amount of unsaturated hydrocarbon the hydrogen content of the gas phase decreases, and the composition of the reaction products is more and more closely represented by Eqns. (1) and (2), although the latter do not reflect dehydrogenation and hydrogenation stages. In spite of the greater capacity of palladium compared with platinum for sorbing hydrogen, evolution of hydrogen is observed also in the conversion of cyclohexene on palladium films, and its amount passes through a maximum. Hence even on the metal most

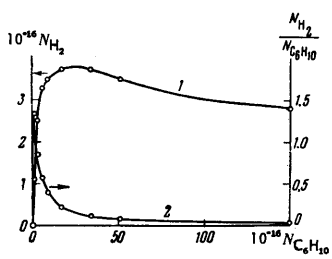


Fig. 8. Dependence of amount of hydrogen formed N_{H_2} (curve 1) and of ratio $N_{H_2}/N_{C_6H_{10}}$ on number of cyclohexene molecules $N_{C_6H_{10}}$ admitted to vessel containing platinum film.

favourable to "irreversible catalysis", the redistribution of hydrogen in cyclohexene and in cyclohexadiene passes through dehydrogenation and hydrogenation stages, and is not effected by direct intermolecular transfer of hydrogen atoms.

A thermodynamic calculation[38] of the maximum partial pressure of hydrogen in the equilibrium mixture formed from cyclohexene at various temperatures has shown that at 20° it is 10^{-3} mm, which is the value found at the end of the experiment represented by curve *1* in Fig. 8. At 120° this pressure is close to 3 mm, which is less than 0.005 atm, and it becomes clear why at this temperature and atmospheric pressure hydrogen evolution was not observed[3] during the conversion of cyclohexene. A rise in temperature at atmospheric pressure favours the dehydrogenation of cyclohexene, whereas an increase in total pressure suppresses it. This latter fact may explain the marked difference[45] in the extent of hydrogen redistribution in cyclohexene at 1 and at 10 atm. Thus it is possible to indicate the conditions under which detectable quantities of hydrogen will be evolved into the gas phase during hydrogen redistribution, and on the other hand when the composition of the reaction products approaches that corresponding to the stoichiometric equations (1) and (2).

Hence the absence of hydrogen evolution accompanying reactions involving the redistribution of hydrogen merely constitutes a particular case, observable when the stages of dehydrogenation and of hydrogenation just balance one another.

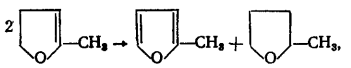
5. DEPENDENCE OF CATALYTIC ACTIVITY TOWARDS HYDROGEN REDISTRIBUTION ON ABILITY OF METAL TO ABSORB HYDROGEN

On the basis of the results reported in Section 4 on the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, it could be expected that the mutual balancing of these reactions would be facilitated on those metals which are capable of absorbing the hydrogen split off from the dehydrogenated molecules, retaining it in an active form for hydrogenation, and transferring it to the molecules of the original hydrocarbon to be hydrogenated. It has been noted several times in the literature[1,3] that palladium catalysts, which dissolve hydrogen readily, are more active than platinum catalysts for the redistribution of hydrogen. Interesting results have been obtained in a study[51,52] of the changes undergone by cyclohexa-1,3-diene dissolved in heptane and in alcohol on platinum, nickel, and palladium catalysts at 25°. Hydrogen redistribution in cyclohexadiene ("irreversible catalysis") and its hydrogenation to cyclohexene occur simultaneously on all three metals, but the velocity ratio for these reactions is close to 0.4 : 1 on platinum black, 1.5 : 1 on Raney nickel, and 3 : 1 on palladium black. From our point of view this means that on platinum black the hydrogenation of cyclohexadiene is far more rapid than its dehydrogenation, while the opposite is the case on palladium black. Raney nickel occupies an intermediate position between these two catalysts.

For the reasons mentioned in Section 3, direct transfer of hydrogen atoms between cyclohexadiene molecules does not explain the differences in the relative rates of hydrogen redistribution and hydrogenation on palladium, nickel, and platinum. If, however, the redistribution is regarded as taking place in two stages, the above results[51,52] indicate

that with cyclohexadiene the balancing of the dehydrogenation and hydrogenation stages, which is required for Eqns. (1) and (2) to be satisfied, is associated with the ability of the metal to dissolve the hydrogen eliminated by dehydrogenation of the hydrocarbon. Catalytic activity is not a simple function of the hydrogen content of a metal (see for example Refs. 53–57), and the hydrogen content is markedly dependent on the conditions of preparation of a metal catalyst and of its saturation with hydrogen. This is probably governed by the kinetics of the sorption and diffusion of hydrogen in a metal, which is sensitive to the surface state and degree of dispersion of the specimen. Therefore for a qualitative comparison let us utilise data on the equilibrium solubility of hydrogen in the massive metals. Below 600° the solubility of hydrogen is[58] a maximum in palladium, lower in nickel, and still lower in platinum. This can explain why the dehydrogenation and hydrogenation of unsaturated hydrocarbons are especially readily balanced on palladium, even with a supply of gaseous hydrogen, whereas this is more difficult on nickel, and still more difficult on platinum.

The above enables us to understand why platinum catalysts are usually inferior to palladium for hydrogen distribution reactions, and are employed at higher temperatures. It has recently been found[48] that, on a palladium catalyst at 200°, dihydromethylfuran is smoothly converted into 2-methylfuran (sylvan) and tetrahydrosylvan



which is completely analogous to the "irreversible catalysis" of cyclohexene. In experiments with a platinum catalyst under the same conditions, the initial portions of the products contain smaller amounts of sylvan than of a ketone formed by isomerisation of tetrahydrosylvan. This difference in the reactions undergone by dihydromethylfuran in the presence of palladium and platinum catalysts is explained[48] by a difference in properties of the hydrogen adsorbed on palladium and on platinum. In particular, it is assumed that hydrogen adsorbed on palladium is incapable of hydrogenating dihydromethylfuran. However, the same paper refers to the high activity of palladium for the hydrogenation of the double bonds in the furan ring. From our point of view these results are due to the greater difficulty of balancing hydrogenation and dehydrogenation on a platinum than on a palladium catalyst, owing to the smaller capacity of platinum for sorbing hydrogen.

In this connection it is interesting that[59] the promoter action of palladium on a Raney nickel catalyst increases the activity of the latter for the hydrogenation of 2-methylbut-3-en-2-ol, whereas platinum decreases it. The reaction velocity was increased with the potential of the catalyst remaining constant, which indicates that hydrogenation is effected by dissolved hydrogen. The diminution in the rate of hydrogenation after 40% coverage of the nickel surface with platinum was not linked[59] with the lower solubility of hydrogen in platinum than in nickel, although such an explanation is quite probable in view of what has been said above.

Since palladium and platinum catalysts are not usually prepared by completely identical procedures, and since specimens can contain different amounts of hydrogen depending on the mode of preparation, it was of interest to compare the catalytic activity of films of these metals prepared under identical conditions of vacuum sublimation and practically free from hydrogen before contact with the vapour of the test substance. Experiments with cyclohexene and with cyclohexadiene showed[36] that on the palladium film, products corresponding to Eqn. (1) and (2) are already obtained at 20°, and appreciable amounts of hydrogen are not evolved. On platinum films below 200° no reaction could be detected spectroscopically, and at higher temperatures the main reaction was dehydrogenation of the cyclohexene and cyclohexadiene. Redistribution of hydrogen in cyclohexadiene on the platinum film was observed only after dehydrogenation of cyclohexene had taken place repeatedly on it. These results indicate that the velocity ratio of the simultaneous dehydrogenation and hydrogenation of the initial hydrocarbon is different on platinum from that on palladium. As several workers have shown[53–55], an important part in the hydrogenation of unsaturated hydrocarbons is played by hydrogen dissolved in the metal. Platinum sorbs hydrogen far more feebly than does palladium, and therefore on the former metal hydrogenation can take place more slowly than dehydrogenation. If after a series of experiments, however, the benzene formed by dehydrogenation of cyclohexene covers part of the surface on which dehydrogenation takes place, the rates of dehydrogenation and hydrogenation will approach one another, and the content of hydrogen in the reaction products will fall. In the limiting case of dehydrogenation and hydrogenation being in balance, the composition of the reaction product will correspond to Eqns. (1) and (2).

6. PECULIARITIES OF HYDROGEN REDISTRIBUTION ON OXIDE CATALYSTS

The redistribution of hydrogen in unsaturated hydrocarbons is different on oxide catalysts from that on metals, and requires higher temperatures. Petrov[60] studied the condensation of cyclohexene in the presence of aluminium oxide under pressure at 400°–440°, and obtained a gas (31% hydrogen and 60% alkanes) together with a tarry liquid containing benzene and cyclohexane. The formation of benzene was attributed to pyrogenic dehydrogenation of the cyclohexene as a side-reaction accompanying the formation of cyclohexane and other polymethylene hydrocarbons. Later Plate[46] showed that neither benzene nor cyclohexane is obtained from cyclohexene on aluminium oxide at the atmospheric pressure and 450°. An investigation by Topchieva[61] of the kinetics of the transformation of cyclohexene on aluminium oxide showed that at 350° only skeletal isomerisation takes place, while neither hydrogen redistribution nor polymerisation occurs.

Goldwasser and Taylor[13] studied the conversion of cyclohexene and cyclohexadiene on chromic oxide. They found that at 305° cyclohexene is 60% converted, without hydrogen evolution, into a mixture of benzene and cyclohexane in the molecular proportions 1 : 2, which corresponds to Eqn. (2). When the temperature is lowered to 163°, the extent of conversion of the cyclohexene drops to 3%, but the ratio of benzene to cyclohexane in the products is maintained. Cyclohexadiene is already 50% converted at 95° into a mixture of benzene and cyclohexane in molecular proportions 2 : 1, and at 137° the extent of conversion reaches 65%. Thus on chromic oxide the redistribution of hydrogen in cyclohexene and cyclohexadiene occurs similarly to that on palladium and platinum, but with lower yields and at somewhat higher temperatures than on these metals. Zelinskii and Arbuzov[62] observed, with cyclohexene on chromic oxide at 400° and 450°, the formation of benzene

and a small amount of cyclohexane accompanied by hydrogen evolution. They noted that at 450° chromic oxide effects the dehydrogenation of methylcyclohexene accompanied by hydrogenation of a small proportion of its molecules by the hydrogen evolved. On aluminium oxide containing silica as impurity at 450°, as also on beryllium oxide and silica gel, cyclohexene merely isomerises to methylcyclopentene[63]. Titanium dioxide at 350°–450° produces, together with this reaction, dehydrogenation of cyclohexene to benzene. On thorium dioxide, zirconium dioxide, vanadium trioxide, and manganous oxide, only partial dehydrogenation of cyclohexene to benzene was observed[62]. It was later shown[64] that, on beryllium oxide at 400°, cyclohexene yields mainly 1-methylcyclopentene together with 3-methylcyclopentene and methylcyclopentane.

A study of the reactions of cyclohexene in the presence of vanadium oxide on aluminium oxide at 450°–500° established[46] that the main products are methylcyclopentene, methylcyclopentane, cyclohexane, and benzene. Under the same conditions cyclopentene is converted into cyclopentane and cyclopentadiene, and also gives some naphthalene. It was suggested that benzene and cyclohexane are formed probably as a result of hydrogen redistribution, although at the temperatures used dehydrogenation of cyclohexene to benzene is also possible. Furthermore, the hypothesis was put forward that cyclopentadiene and cyclopentane are obtained as a result of a new type of irreversible catalysis of cyclopentene, the cyclopentadiene formed being regarded as the probable source of charring on the catalyst.

Alkenylcyclohexanes and alkylcyclohexenes undergo hydrogen redistribution under conditions of contact isomerisation on an alumina–chromic oxide catalyst at 250°.[65] In particular, allylcyclohexane yields propylbenzene and propylcyclohexane in the proportions 1 : 2.

Erbium oxide and erbium oxide on alumina at 515° dehydrogenate cyclohexene and methylcyclohexene to the corresponding aromatic hydrocarbons, and move double bonds within the cyclohexane ring, but do not cause redistribution of hydrogen[66].

The main reactions of 1-methylcyclohexene on a catalyst containing 90% of alumina and 10% of ferric oxide at temperatures between 250° and 450° are isomerisation with migration of the double bond in the six-membered ring, and dehydrogenation of the starting material and of the resulting 4-methylcyclohexene to toluene. Redistribution of hydrogen with the formation of methylcyclohexane and toluene is also regarded[67] as possible. Isomerisation to five-membered hydrocarbons is not observed.

On crystalline α-chromic oxide redistribution of hydrogen in cyclohexene has been observed[68] at temperatures between 210° and 350°, but accompanied at 210°–250° by hydrogenation of the cyclohexene to cyclohexane, and at 280° and above by dehydrogenation of the cyclohexene to benzene. Among the reaction products was detected methylcyclopentane, the amount of which increased with rise in temperature. The products of catalysis between 209° and 235° contained methylcyclopentene. As already mentioned, formation of methylcyclopentene and of methylcyclopentane from cyclohexene has been observed[46] on an alumina–vanadium oxide catalyst.

Valuable results have been obtained from an investigation[69] of the dehydrogenation of cyclohexane containing radiocarbon-labelled cyclohexene on chromic oxide[70] and on rhenium on carbon[71]. It was concluded that irreversible catalysis is not the main reaction of cyclohexene on chromic oxide at 450°, and it does not take place at all on rhenium at 336°. On chromic oxide the rate of formation of benzene from cyclohexene greatly exceeds that of cyclohexane, but on rhenium the opposite is true.

The possibility of dehydrogenation and hydrogenation taking place independently during the redistribution of hydrogen at lower temperatures has been shown previously[34] on platinum films.

Thus the concept of the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, developed in this paper, is applicable not only to metallic but also to oxide catalysts.

Since oxides are far less capable than metals of retaining atomic hydrogen and transferring it from hydrocarbon molecules undergoing dehydrogenation to those undergoing hydrogenation, the lower activity of oxide catalysts towards reactions involving redistribution of hydrogen becomes explicable. Impairment of the link between dehydrogenation and hydrogenation makes balancing of these processes difficult, and hydrogen redistribution on oxide catalysts is accompanied by hydrogenation below 250°,[68] and by dehydrogenation at higher temperatures[62–64,66–68]. The predominance of the latter process over hydrogenation above 450° and at atmospheric pressure is due to thermodynamic causes.

The conclusion that irreversible catalysis does not occur on rhenium[69] constitutes evidence against a mechanism of direct transfer of hydrogen atoms between cyclohexene molecules, but does not fundamentally affect results[14] showing that, at temperatures between 215° and 300° on two rhenium catalysts prepared in different ways, cyclohexene is transformed, without evolution of gas, in conformity with the equation:

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}.$$

At higher temperatures hydrogen containing 6–8% of methane is evolved. In those experiments in which appreciable hydrogen evolution was observed, the reaction velocity was approximately two-thirds of the rate obtained by extrapolating the Arrhenius plot representing results obtained at low temperatures. The lower rate was explained by the greater degree of conversion (60–75%) under these conditions, and a possible deviation from zero order.

It is noteworthy that on the catalyst Re-2, which was more active in the conversion of cyclohexene, the rate of evolution of gas at 316° was 1.4 ml min^{-1}, and the corresponding point of the Arrhenius equation lay on the straight line representing experiments in which no gas was evolved. With the catalyst Re-1, on the other hand, the point corresponding to an experiment with a rather lower rate of gas evolution (1.3 ml min^{-1}) lay on the straight line representing all experiments in which gas was evolved. This shows that gas evolution is not the distinguishing factor between the two regions obtained on the assumption that zero reaction order is maintained throughout the range of temperatures and degrees of conversion studied.

On the view of the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, the evolution of hydrogen must be regarded as a breakdown, in favour of dehydrogenation, of the balance between these two processes. At not too high temperatures, when hydrogenation predominates owing to the conditions of thermodynamic equilibrium, the achievement of preferential dehydrogenation requires that special measures should be taken to

prevent blocking of the sites for dehydrogenation, as discussed above. The results[14] suggest a higher surface concentration of dehydrogenation centres on the catalyst Re-2 than on Re-1. This is consistent with data[72-74] indicating that Re-2 is more active also towards the dehydrogenation of cyclohexane, and with the absence from the reaction products of cyclohexene, which is detected in the products of the dehydrogenation of cyclohexane on Re-1. This last fact was explained by edge dehydrogenation, which occurs to a slight extent together with sextet dehydrogenation.

An interesting confirmation that hydrogen redistribution represents a combination of dehydrogenation and hydrogenation, in which the former reaction governs the rate of the overall process, is the agreement between experimental values for the energies of dehydrogenation of cyclohexane and of the disproportionation of cyclohexene for the two rhenium catalysts[14,73].

The results obtained on rhenium catalysts have been discussed in this Section because of the great similarity in the changes undergone by cyclohexene on them and on chromic oxide. It is interesting that substantially different indications of the nature of hydrogen redistribution in cyclohexene are obtained with different specimens of chromic oxide: Balandin and Rozhdestvenskaya[68] did not observe the applicability of the equation

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}$$

which had been found previously[13]. A chromic oxide gel catalyst[13] had a higher activity than crystalline chromic oxide[68], especially at 210° and below. The peculiarity of chromic oxide[13] is indicated also by the absence, among the conversion products of cyclohexene, of five-membered cyclic hydrocarbons, which were found in experiments with crystalline chromic oxide[68] and with other oxide catalysts[61-63]. Isomerisation of six-membered into five-membered cycloalkenes is observed also in hydrogen redistribution on aluminosilicate catalysts.

7. REDISTRIBUTION OF HYDROGEN ON ALUMINOSILICATE CATALYSTS

Hydrogen redistribution in unsaturated hydrocarbons on natural aluminosilicates was investigated by Lebedev and Koblyanskii[75] and by other workers. Synthetic aluminosilicate catalysts were also employed in many researches.

Frost[76] showed that migration of hydrogen atoms occurs in alkenes on a synthetic aluminosilicate at 250°, the accumulation of unsaturated polymers being accompanied by the appearance of saturated compounds. The hypothesis that the latter are formed from the alkenes by depletion of the hydrogen of the polymers was verified experimentally on activated clays[77,78]. Investigation of the transformation of cyclohexene[79] over an activated clay showed that the action of aluminosilicate catalysts is different from that of metals. The absence of benzene from the light fractions led to the conclusion that on aluminosilicates the hydrogen required to convert cyclohexene into cyclohexane and methylcyclopentane is derived from condensation products. The kinetics of redistribution in unsaturated petroleum derivatives on aluminosilicates has been studied in a series of papers[80-85].

Alkenes having a double bond linking a tertiary carbon atom undergo stronger saturation by hydrogen redistribution on an aluminosilicate catalyst than do other alkenes[86]. On a synthetic aluminosilicate catalyst under conditions excluding cracking, cyclohexene is converted into methylcyclopentane, and 4-methylcyclohexene mainly into methylcyclohexane[87]. Aromatic hydrocarbons were not detected in the monomer fractions, which agrees with other results[79]. Petrov and Frost[88] ascertained, from an investigation of hydrogen redistribution in a series of alkenes and cycloalkenes on an aluminosilicate catalyst, that with no single substance did the monomer fraction of the catalysate contain products containing less hydrogen than the original hydrocarbon. Aromatic hydrocarbons were detected only in the high-boiling polymeric fraction. However, the polymeric fraction contained as many saturated products as did the monomeric fraction, and was able to yield the 9–16% of hydrogen necessary for the observed saturation of the monomeric fraction. On the other hand, formation of condensation products on the catalyst grew in proportion to the quantity of saturated hydrocarbons formed. It was concluded from these results that the chief source of hydrogen for the saturation of olefinic hydrocarbons by hydrogen redistribution is the formation of condensation products (char) on the catalyst[88]. On the assumption that part of the condensation products containing relatively less hydrogen, probably polymers, can split off from the catalyst in the form of aromatic hydrocarbons, the appearance of the latter in the high-boiling fractions was attributed to processes secondary to hydrogen redistribution. In particular, further confirmation was obtained of the earlier conclusion[79] that the action of aluminosilicates on cyclohexene is different from that of metals leading to "irreversible catalysis".

An examination of the kinetics of the changes undergone by cyclohexene on aluminosilicate catalysts of different compositions showed[61] that at 350° hydrogen redistribution and polymerisation take place only on the active centres of the aluminosilicate, while isomerisation to methylcyclopentene occurs also on the active centres of aluminium oxide, reaching its greatest extent with the pure oxide. Hydrogen redistribution resulted in hydrogenation of cyclohexene and methylcyclopentene to the corresponding naphthenic hydrocarbons.

It was suggested[89] that, on aluminosilicate catalysts, dehydrogenation of a six-membered ring to an aromatic ring can occur only together with the formation of polymers, and polymerisation is necessarily linked with isomerisation of one of the rings. This hypothesis was based on experimental results indicating that, on an aluminosilicate catalyst at a temperature excluding cracking, cyclohexene is converted into a mixture of saturated and unsaturated hydrocarbons, the monomeric fraction containing cyclohexane, cyclohexene, methylcyclopentane, and methylcyclopentene, and the polymeric fraction comprising mainly the dimer, cyclohexylmethylcyclopentane, and phenylmethylcyclopentane. It is significant that benzene is absent from the monomeric fraction, and bicyclic hydrocarbons containing two six-membered rings from the polymeric fraction.

However, there are indications that the transformation of cyclohexa-1,3-diene and cyclohexene hydrocarbons having a double bond in the side-chain results, on aluminosilicate catalysts, in the formation of light aromatic hydrocarbons, as also on palladium, but complicated by polymerisation and skeletal isomerisation.

Heating *p*-mentha-1,8-diene with an activated clay at 160°–180° causes polymerisation of this hydrocarbon and its isomerisation products. The unpolymerised residue

contains 1-isopropyl-4-methylcyclohexa-1,3-diene, formed by migration of the double bond from the side-chain into the ring, the hydrogenation product 1-isopropyl-4-methylcyclohexene, and also *p*-isopropyltoluene[90]. It is interesting that a similar transformation of this terpene has been observed also on Raney nickel[91]. On activated gumbrin at 270°–275°, 3-methyl-5-propenylcyclohexene yields[92] a mixture of *m*-propyltoluene and 1-methyl-3-propylcyclohexane in the proportions 2 : 1. This process is characterised as "irreversible catalysis" occurring after migration of the double bond from the side-chain into the ring.

In the presence of gumbrin at 300°–310°, cyclohexa-1,3-diene is partly converted into a mixture of benzene and cyclohexane in proportions close to 2 : 1, and is partly isomerised into methylcyclopentene and methylcyclopentane; it is assumed[93] *via* the formation of cyclohexene by stepwise hydrogenation. These changes are accompanied by the evolution of gaseous products, considerable "charring" on the catalyst, and polymerisation of the cyclohexadiene. Cyclohexane hydrocarbons having unsaturated side-chains yield on gumbrin[87], together with polymerisation products, mixtures of aromatic and cycloalkane hydrocarbons in the proportions 2 : 1. With several of the hydrocarbons investigated, hydrogen redistribution by "irreversible catalysis" is accompanied by hydrogenation by hydrogen evolved in the simultaneous dehydropolymerisation. Thus with gumbrin the type of hydrogen redistribution in cyclohexadiene which is usual for palladium catalysts is combined with that observed for cyclohexene and several other alkenes on aluminosilicate catalysts.

It can be concluded from what has been said that the redistribution of hydrogen, which on aluminosilicate catalysts and on oxides yields a larger number of products than in the case of palladium, nevertheless retains the same basic features. The distinction, even contradistinction, met in some papers between processes of hydrogen redistribution on metallic catalysts on the one hand, and on oxide or aluminosilicate catalysts on the other, was caused by the limited character of the experimental data. As shown above, metals differ markedly from one another in their catalytic behaviour towards hydrogen redistribution reactions, mainly because of their varying ability to absorb hydrogen and transfer it from molecules of the initial hydrocarbon undergoing dehydrogenation to those undergoing hydrogenation. The more feebly developed is this ability, the less active is the metal towards hydrogen redistribution and the higher its isomerising activity. For example, only hydrogen redistribution takes place on palladium, whereas platinum is far less active towards this process, and produces isomerisation, as do aluminosilicates and several oxides. Metallic rhenium is far closer to oxides than to palladium or nickel as regards the character of the hydrogen redistribution processes occurring on it. On the other hand, on some oxides and aluminosilicates processes involving hydrogen redistribution can occur in a similar manner as on metal catalysts, but accompanied by side-reactions.

It can be concluded from what has been reported above that the redistribution of hydrogen in unsaturated hydrocarbons on metal, oxide, and aluminosilicate catalysts represents a combination of dehydrogenation and hydrogenation reactions. Stable adsorption of unsaturated six-membered hydrocarbons on the catalyst surface is probably accompanied by the elimination of hydrogen atoms mainly from $\diagdown\!\!\diagup C-H$ groups. The work of Eischens and Pliskin[94] also indicates dissociative adsorption in the absence of hydrogen and retention of double bonds in chemisorbed molecules of ethylenic hydrocarbons. Study of the effect of the adsorption of hydrocarbon vapours on the electrical conductivity of platinum films has shown[29] that adsorption first takes place on portions of the metal surface having different adsorption potentials. A hydrocarbon molecule adsorbed on the surface of a metal catalyst moves along it until adsorption accompanied by the elimination of hydrogen atoms becomes possible at a site of sufficiently high adsorption potential. Cyclohexane splits off hydrogen only at sites having the highest adsorption potential, *i.e.* with stable adsorption. On the other hand, cyclohexene and cyclohexadiene undergo this change at sites of moderate adsorption potential, from which the dehydrogenation products escape more rapidly than from those centres on which hydrogen is split off from cyclohexane or benzene. The more strongly the metal catalyst absorbs hydrogen, the more strongly is the supply of atomic hydrogen facilitated through the metal layer to centres of low adsorption potential, on which the unsaturated hydrocarbon is adsorbed without elimination of hydrogen but is sufficiently activated for hydrogenation to occur. Hence formation of H_2 molecules occurs only when dehydrogenation and hydrogenation are out of balance; and it is especially important for the redistribution of hydrogen, in contrast to ordinary dehydrogenation, that the catalyst should retain hydrogen in a suitably active form for hydrogenation of the initial hydrocarbon.

On oxide and aluminosilicate catalysts, which display activity towards hydrogen redistribution at higher temperatures than do metals, dehydrogenation of the initial hydrocarbon is often accompanied by its isomerisation and polymerisation. Without attempting to discuss these complicated cases in detail, especially as various opinions have been expressed[95-97] on the nature of the active centres in aluminosilicate catalysts, we give the mechanism of hydrogen redistribution in alkenes on such catalysts suggested by Petrov and Frost[88]. A molecule of the initial alkene, by combining with an active centre on the catalyst (HA), reacts with another molecule to form a dimer

$$CH_2{=}CH{-}R + HA \longrightarrow CH_2{-}CHA{-}R,$$

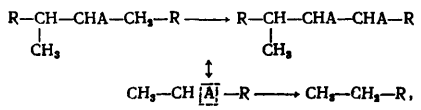
$$CH_2{-}CHA{-}R + CH_2{=}CH{-}R \longrightarrow R{-}\underset{\displaystyle CH_3}{CH}{-}CH{=}CH{-}R + HA,$$

$$R{-}\underset{\displaystyle CH_3}{CH}{-}CH{=}CH{-}R + HA \longrightarrow R{-}\underset{\displaystyle CH_3}{CH}{-}CHA{-}CH_2{-}R.$$

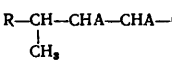
The molecule of the resulting dimer can again react with the catalyst.

By interaction of the dimer molecule linked to the catalyst and a molecule of the original substance, also combined with the catalyst, formation of a dimer molecule becomes possible which is linked no longer with one, but with two, active centres on the catalyst. The two hydrogen atoms which were originally linked to these active centres add on to the alkene. If on desorption of the dimer linked with two active centres, one hydrogen atom remains on each centre, which according to this mechanism[88] is necessary for the maintenance of catalytic activity, the molecule passing into the gas phase contains two hydrogen atoms less than did two molecules of the original alkene. If the

process of depletion of the dimer or other polymer molecules with respect to hydrogen is continued, resinous products (char) are obtained:



and further with formation of a new hydrocarbon molecule and a polymer–catalyst complex which contains still less hydrogen:



Resinification occurs also on metal catalysts, but to a less extent than on aluminosilicates or on oxides, probably owing to the higher activity of metals towards reactions involving hydrogenation. In fact, when benzene is pyrolysed on fire-clay, dehydrocondensation reactions take place, biphenyl being formed at first, and then terphenyls, triphenylene, and resinous and tarry products. On copper at the same temperatures carbon formation is insignificant, and far less hydrogen is evolved than in the experiments with fire-clay[98]. The initial stage in carbon and resin formation may also be the splitting off of hydrogen atoms from $\gg$C–H and $\gg$C–H groups in the hydrocarbons[23-25,30,38]. The mechanism of carbon formation has been investigated[99,100] in the decomposition on silica gel of homologues of benzene, and also of alkanes and cycloalkanes containing six and seven carbon atoms. In all the cases studied, carbonisation represents a multistage dehydrocondensation either of the original hydrocarbons or of products formed by their preliminary transformation. In addition to cracking reactions, destructive hydrogenation of the cycloalkanes and alkanes is effected by the hydrogen evolved.

If on a given catalyst elimination of hydrogen from the original alkene takes place more readily than its polymerisation, resinification can be expected to diminish, and the composition of the hydrogen redistribution products will approach that corresponding to the stoichiometric equations of "irreversible catalysis". If, however, dehydrogenation is preceded by polymerisation, "irreversible catalysis" is impossible, but the dehydrogenation and hydrogenation stages are retained as in the case of metal catalysts.

Thus the hypothesis that the redistribution of hydrogen in unsaturated hydrocarbons takes place in stages enables the results obtained on metallic, oxide, and aluminosilicate catalysts to be considered from a single point of view. The nature of the reaction products depends on the extent of balancing of dehydrogenation and hydrogenation, which is facilitated by the retention, on the surface or in the adjacent layer of the catalyst, of hydrogen in a suitably active form for hydrogenation. The subsidiary processes of isomerisation and polymerisation of the original hydrocarbon indicate that under these conditions precatalytic adsorption results not only in the elimination of hydrogen atoms but also in the rupture of carbon–carbon bonds.

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