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The Application of Deuterium in the Study of Heterogeneous Organic Catalysis

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The use of deuterium for the study of the mechanisms of heterogeneous-catalytic organic reactions and of the adsorption of organic molecules on the surface, the structure of the active centres and properties of catalysts, as well as other aspects of catalysis is examined. The possibilities of employing data obtained by measuring the rate of deuterium exchange, by the analysis of the isotope distribution in the products, and by the determination of kinetic isotope effects are demonstrated. The bibliography includes 168 references.

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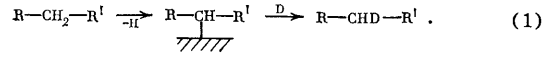
I. INTRODUCTION

Increased attention to the reaction mechanism is a characteristic feature of present day studies in the field of heterogeneous catalysis. Among the numerous methods used to solve problems associated with this factor, the isotope methods, in particular those based on the use of deuterium, occupy a notable place. The employment of deuterium in catalysis began as early as the 1930s–1940s in the well known studies by the brothers Farkas, Grinev, and Polanyi. However, it began to be used widely and comprehensively only after the publication in the 1950s of a cycle of the fundamental studies by Kemball, which have since become classical.[1] Extensive literature data have been surveyed in the existing reviews[2-4], but the methodological procedures which assist in the determination of the mechanism of a particular heterogeneous-catalytic reaction by the introduction of the deuterium label have never been examined systematically. Nevertheless the number of studies on catalysis using deuterium has been growing continuously and the attempt at this kind of systematic account undertaken in this review has been fairly urgently needed. As a consequence of the limited space available in the review, we shall deal only with organic heterogeneous catalysis.

It is possible to differentiate three main methods of using deuterium in the study of organic heterogeneous-catalytic reactions: (1) measurement of the rate of deuterium exchange involving compounds participating in the reaction, frequently combined with its comparison with the rate of the main reaction of the compounds; (2) analysis of the isotope distribution in the initial reactants or the final products of the catalytic reaction; (3) measurement of the kinetic isotope effects when hydrogen is replaced by deuterium in one or several components of the reaction mixture. Depending on the specific features of the catalytic system investigated, each of these methods is used in different versions.

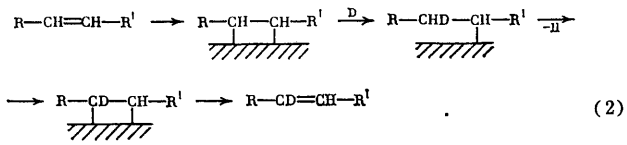
II. RATE OF DEUTERIUM EXCHANGE

A heterogeneous-catalytic reaction is known to have more than one elementary stage. In the study of the reaction mechanism the queston of which stage is the slowest always arises. If hydrogen participates in the reaction, important information about this stage can be obtained by measuring the rate of deuterium exchange involving the initial compounds. A bond with a hydrogen atom must be broken in the deuterium exchange and a new bond must be formed with a deuterium atom. In the case of saturated hydrocarbons, the main pathway leading to the breaking of the C–H bond in deuterium exchange is dissociative adsorption on the catalyst:



(1)

For unsaturated compounds, there is yet another pathway, namely the addition of a deuterium atom to the multiple bond with formation of a semihydrogenated form and subsequent elimination of a hydrogen atom:



(2)

Since dissociative adsorption or the formation of the semihydrogenated form can occur as stages in other reactions of hydrocarbons, for example, in dehydrogenation or hydrogenation, comparison of the rates of deuterium exchange [processes (1) and (2)] with the rate of the given reaction investigated helps to establish the rate-limiting stage.

1. Determination of the Rate of Deuterium Exchange

Thus the problem arises of the correct estimation of the rate of deuterium exchange. If the reaction proceeds in a static system, Kemball's equations are used:[1]

$$k_0 = \frac{100 - d_{0,\infty}}{t} \ln \frac{100 - d_{0,\infty}}{d_0 - d_{0,\infty}}, \quad (3)$$

where k_0 is the initial rate of consumption of the non-deuteriated organic molecules, d_0 the fraction (as a percentage) of the non-deuteriated molecules at time t, $d_{0,\infty}$ their equilibrium fraction (as a percentage), and

$$k_\varphi = \frac{\varphi_\infty}{t} \ln \frac{\varphi_\infty - \varphi_0}{\varphi_\infty - \varphi}, \quad (4)$$

where k_ϕ is the number of deuterium atoms entering 100 molecules of the organic compound per unit time, $\phi = \sum_{i=1}^{m} i d_i$ (d_i is the fraction of the organic molecules C_mH_n containing i deuterium atoms), ϕ_0 is the initial value of ϕ, and ϕ_∞ its

equilbrium value, defined by

$$\varphi_\infty = \frac{100n \cdot 2y}{n+2y}$$

(y is the ratio of the initial molar concentrations of D_2 and C_mH_n).

If the initial deuterium content in the organic molecule is zero ($\phi_0 = 0$), which is usually the case, the gaseous deuterium is present in the system in an excess so that $d_{0,\infty} \cong 0$, then Eqns.(3) and (4) simplify and become respectively

$$k_0 = \frac{100}{t} \ln \frac{100}{d_0}$$

and

$$k_\varphi = \frac{\varphi_\infty}{t} \ln \frac{\varphi_\infty}{\varphi_\infty - \varphi} \quad .$$

Having plotted $\ln d_0$ against t and $\ln(\phi_\infty - \phi)$ against t, it is possible to find k_0 and k_ϕ respectively from the slopes of the straight lines.

It is seen from Eqn.(3) that k_0 has the dimensions of the reciprocal of time, i.e. it is a relative quantity indicating the fraction of the molecules (as a percentage) involved in the exchange per unit time. The rate of disappearance of non-deuteriated molecules can be obtained by multiplying $k_0/100$ by the concentration of the organic compound. The rate of incorporation of deuterium into organic molecules can be obtained in exactly the same way from k_ϕ. The quantities k_0 and k_ϕ may not be identical because several hydrogen atoms of one organic molecule can be substituted by deuterium simultaneously. The ratio

$$M_D = k_\varphi / k_0 \qquad (5)$$

characterises the multiplicity or extent of the exchange, i.e. the number of D atoms entering one organic molecule per reaction step.

Isotope exchange is a first-order reaction with respect to the isotope,[5] i.e. in any specified initial mixture involved in deuterium exchange in the static system the rate of consumption of the hydrogen-containing molecules on all gaseous deuterium is described by the first-order Eqn.(3). At the same time the form of the kinetic equation describing the rate of deuterium exchange as a function of the concentration of the reaction components is determined by the mechanism of a specific process. The rate of exchange usually increases with increasing concentration of hydrocarbon molecules, while an increase in the deuterium concentration entails a retardation of the exchange.[2]

The estimation of the rate of deuterium exchange in a flow-circulation system has certain specific features. In contrast to the usual reactions where a chemical transformation takes place, in deuterium exchange a molecule which has reacted once is not "removed from play" and can undergo new isotope exchange steps. The experimental degree of reaction (exchange) is then too low. In the usual formula for the calculation of the rate of reaction in a flow-circulation system one therefore introduces a correction which takes into account the possibility of such repeated exchange:[6]

$$r_{об} = \frac{u_0 x_{exch} M_{av}}{g M_D} \quad ,$$

where u_0 is the flow rate of the exchanging molecules, $x_{exch} = (100-d_0)/100$ the degree of exchange, g the weight of the catalyst sample, M_{av} the average number of D atoms in the exchanging molecules after the experiment, and M_D the number of D atoms entering one molecule in one exchange step.

The quantity M_{av} can easily be determined from the results of the mass-spectrometric analysis of the products and M_D can be found from Eqn.(5). One must bear in mind in the calculation of k_ϕ and k_0 in Eqn.(5), that the quantities d_0 and ϕ are determined in the given instance at only two points—the initial point and the time t, and the accuracy of the estimate can therefore be low. In order to improve the accuracy, one can set up special experiments, but the rate of exchange and the rate of the main reaction usually differ sufficiently and there is no doubt which of these processes predominates.

The methods for the determination of the rate of exchange when the molecule contains hydrogen atoms which are not equivalent as regards reactivity are described below.

2. The Use of Data for the Rate of Deuterium Exchange

In the first place we shall consider specific examples where information about the mechanism of the catalytic reaction can be obtained by comparing its rate with that of deuterium exchange.

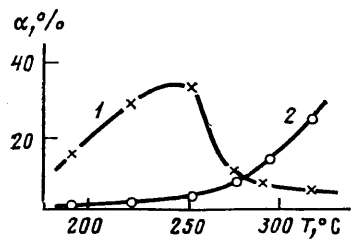


Figure 1. Temperature dependence of the degrees α of exchange involving cyclohexane (curve *1*) and of its dehydrogenation (curve *2*) on the nickel catalyst.[7]

The mechanism of the dehydrogenation of cyclohexane and the related benzene and cyclohexene hydrogenation reactions on a nickel catalyst has been investigated[7] with the aid of deuterium. It was found that the deuterium exchange involving cyclohexane begins at a lower temperature and is much faster than its dehydrogenation. However, with increase of temperature, the rate of dehydrogenation (which in the given case, in a flow-circulation system, is proportional to the degree of reaction) increases and the rate of exchange falls after passing through a maximum (Fig.1), so that dehydrogenation now becomes the faster process. The high rate of deuterium exchange at the beginning of the experimental temperature range evidently demonstrates that the dissociative adsorption stage, which is common to both reactions, cannot limit the rate of dehydrogenation. An increase of temperature promotes a further reaction (dehydrogenation) of the dissociatively adsorbed cyclohexane and the suppression of the competing process involving its desorption with substitution of the eliminated H atoms by D (i.e. the deuterium exchange is retarded). This entails the reversal of the ratio of the rates of the exchange process and the cyclohexane dehydrogenation reaction. A similar phenomenon has been observed also in the deuterium exchange involving a series of paraffinic hydrocarbons on nickel under the conditions of hydrogenolysis and dehydrocyclisation.[8]

The rate of deuterium exchange involving the potential intermediate of this reaction, namely cyclohexene, is extremely low under the same conditions and is much lower than the rate of its hydrogenation.[7] Presumably the adsorption of cyclohexene (probably with dissociation of the double bond) is in this instance virtually irreversible and the intermediate surface compound formed reacts further rapidly.

The deuterium exchange involving benzene, which has been investigated in both flow-circulation[7] and static[9] systems, is faster than the hydrogenation of benzene. However, comparison of the temperature variations of the rates of both reactions (Fig. 2) shows that they proceed independently via different surface intermediate species.

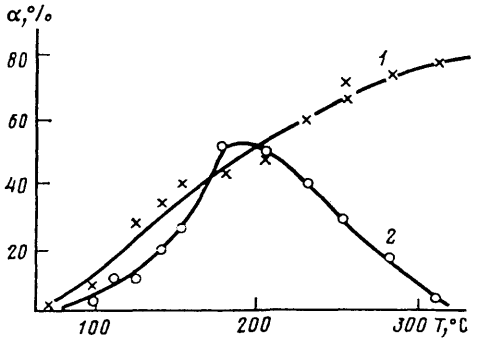


Figure 2. Temperature dependence of the degrees α of exchange involving benzene (curve *1*) and of its hydrogenation (curve *2*) on the nickel catalyst.[7]

Analysis of the relations obtained using kinetic, adsorption, and other data made it possible to develop a fairly convincing general mechanism of the reactions in the benzene–cyclohexane system on a nickel catalyst.[7] Analogous conclusions have been reached by comparing the rates of exchange and deuteriation also for the reaction with participation of toluene.[10]

One may point to a series of other studies in which comparison of the rates of deuterium exchange and a chemical reaction yielded valuable information about the mechanisms of the processes investigated. Such data have been obtained for the hydrogenation of ethylene on Al_2O_3,[11] propene on rhodium,[12] isoprene on palladium,[13] benzene on a series of metals,[14] and mesityl oxide on palladium,[15] for the hydrogenation of a series of alkanes on titanium dioxide,[16] n-decane on alumir.oplatinum[17] and platinum–tin[18] catalysts, and isopentene on the calcium–nickel–phosphate catalyst,[6] for the conversion of cyclohexanol into cyclohexanone on a copper–magnesium catalyst,[19] for the hydrogenolysis of thiophen on an industrial aluminonickel–molybdenum catalyst,[20] for the hydrogenation and isomerisation of hexenes on "sulphided" palladium,[21] for the hydrogenolysis and isomerisation of propane and butane on platinum[22] and n-pentane on nickel, platinum,[23] and platinum–lead and platinum–copper catalysts,[24] for the hydrogenolysis and dehydrogenation of cyclohexanes on platinum and nickel,[25] for the *cis–trans* isomerisation and migration of the double bond in butenes on nickel,[26] and for a number of other processes.

The measurement of the rate of deuterium exchange involving not only the starting materials but also the reaction products can also be of considerable interest. Thus the high rate of exchange involving the methane formed in the hydrogenolysis of hydrocarbons on sputtered iron films[27] and on rhodium–iridium catalysts[28] made it possible to reject the hypothesis that the rate-limiting stage in this reaction is the desorption of its products. However, there exist also contradictory data according to which the rate of hydrogenolysis of hydrocarbons on iridium, rhodium, ruthenium[29,30] and on palladium–silver alloys[31] is determined precisely by the rate of the desorption stage.

The rate of deuterium exchange is not measured solely in order to compare it with the rate of the chemical reaction investigated to establish the process mechanism. Deuterium exchange has proved to be a sensitive instrument for the investigation of the catalysts themselves. By estimating the influence of the composition of the catalyst, of the degree of its dispersion and its genesis, of its treatment by various substances, etc., on the rate of deuterium exchange, it is possible to obtain information about the nature, structure, and properties of the active centres of the catalysts. Thus it has been possible to establish with the aid of deuterium exchange involving ethylene that the active centres of catalysts containing chromium in a magnesium oxide matrix are Cr^{2+} ions.[32] Deuterium exchange has been used also to investigate a series of other oxide catalysts.[33–36] Measurement of the rate of deuterium exchange involving hydrocarbons made it possible to elucidate the way in which the temperature of the preliminary treatment influences the activity of γ-Al_2O_3 [37] and barium oxide[38] and to obtain data on the active centres in these catalysts.

In many studies the active centres have been investigated by treating the catalysts with various substances, mainly sulphur-containing substances, which influence the rate of deuterium exchange and other reactions of organic molecules. The unequal effects of the treatment of molybdenum sulphide with hydrogen sulphide on the hydrogenation of ethylene and on the exchange between the latter and C_2D_4 led to the conclusion that two types of active centres exist on the surface of this catalyst[39] and differ in the degree of coordination unsaturation of the molybdenum atoms.[40] Similar data have been obtained also for nickel sulphide.[41] Different active centres, responsible for the isomerisation of n-butene and for the deuterium exchange involving benzene and n-butene, have been detected also on the surface of alumina: the former incorporate Al_2^{3+} and sometimes also O_2^- and the latter incorporate O_2^- ions differing from those participating in isomerisation.[42] The influence of the poisoning of the Pt/Al_2O_3 catalyst with hydrogen sulphide, sulphur dioxide, and other poisons on the hydrogenation, hydrogenalysis, and deuterium exchange reactions of certain hydrocarbons.[43,44]

Investigation of the dependence of the rate of deuterium exchange involving ethane,[45] cyclopentane,[46] and cyclohexane[47] on the degree of dispersion of platinum led different investigators to different conclusions, so that the question of the structural sensitivity of these reactions remains controversial. The assignment of the reaction to a particular type is believed[48] to depend on the degree of reaction and, after the attainment of complete surface coverage of the catalyst, the structure-sensitive reaction can become "structure-insensitive". Doubt have been cast on the validity of the usual methods for the determination of the structural sensitivity of catalytic reactions on metals[49] in view of the results of the study of the deuterium exchange involving 2,2-dimethylbutane on platinum and palladium.

The rate of deuterium exchange involving benzene proved to be different on different crystallographic faces of a platinum single crystal,[50] in contrast to the rate of its hydrogenation, which constitutes an additional argument in support of the view that the mechanisms of these reactions are different.[7]

The measurement of the rate of deuterium exchange involving hydrocarbons is used particularly widely in comparisons with the rates of other reactions, in the study of bimetallic catalysts. This usually makes it possible to estimate the role of the cluster and ligand effects in such systems.

It has been postulated[51-54] and confirmed by calculation[55] by Dalmon's method[56] that deuterium exchange takes place in clusters smaller than those required for hydrogenolysis. The fact that the rate of hydrogenolysis of hydrocarbons (dissociation of C–C bonds) depends more strongly on the composition of nickel–copper[51-53] and platinum–gold[54] alloys than the rate of deuterium exchange (dissociation of C–H bonds) has been interpreted as evidence for the decisive role of the size of the *ensembles*, i.e. of the geometrical factor, in these and similar systems. However, in subsequent studies using deuterium exchange involving cyclohexane and n-hexane on nickel–copper alloys,[55] ethane and neopentane on ruthenium–copper and ruthenium–silver alloys,[57] and methane and neopentane on palladium–gold alloys[58] it was emphasised that, together with the geometrical factor, account must be taken also of the electronic factor. It is appropriate to mention, if only selectively, also certain other studies in which deuterium exchange involving various hydrocarbons has been used to investigate the catalytic properties of Pt–Re,[56-60] Pt–Ir, Ir–Os,[60] Pt–Pd,[61] Pd–Ni,[62] Ni–Mo,[63,64] Ni–Cu,[65] and Pd–Ag [31] alloys. The isotope exchange between methane and deuterium has been suggested as a method for the determination of the composition of the surfaces of platinum–palladium alloys.[61]

Finally the measurement of the rate of deuterium exchange can be used to estimate the strength of the C–H bonds and the reactivities of the hydrogen atoms in various groups in organic molecules. It was found that the rate of deuterium exchange in a series of cycloalkanes is correlated with the "bond indices" calculated by quantum-chemical methods and characterising the strength of the C–H bonds after adsorption on nickel.[66] The reactivities of all the hydrogen atoms in cycloalkanes are approximately equal, which follows from the linearity of the relation plotted in terms of the variables of Eqn.(4) over a fairly wide range of degrees of exchange. However, there are many compounds in the molecules of which the hydrogen atoms are not equivalent. Such non-equivalence leads to a break in the straight line plotted in terms with the variables of Eqn.(4), as shown for toluene in Fig. 3.

A method is known whereby it is possible to determine separately the rate of exchange in each group.[67] For the initial section of the curve illustrated in Fig. 3, the quantity $k_\phi = k_A + k_B$, which corresponds to the overall rate of exchange in groups A and B, is found by equations of type (4). The second section of the curve, beyond the break, corresponds to the exchange of hydrogen in the less reactive group B (the exchange in group A has already terminated by this time). The constant k_B for the second group of atoms can be found from the second section by means of the equation

$$k_B = \frac{\varphi_{B,\infty}}{t} \ln \frac{\varphi_{B,\infty} - \varphi_0}{\varphi_\infty - \varphi} .$$

However, for this purpose, it is necessary to know the quantity $\phi_{B,\infty}$ which corresponds to ϕ_∞ but refers only to the second group. The quantity $\phi_{B,\infty}$ is calculated from the relations

$$\varphi_\infty = \varphi_{A,\infty} + \varphi_{B,\infty} ,$$

$$\varphi_{A,\infty}/\varphi_{B,\infty} = n_A/n_B ,$$

where n_A and n_B are the numbers of hydrogen atoms in groups A and B respectively. The quantities n_A and n_B are found by analysing the molecular structure and the dynamics of the time variation of the concentrations of the various deuterio-products.[68] Thus it is possible to determine the rate of deuterium exchange in each of the groups A and B.

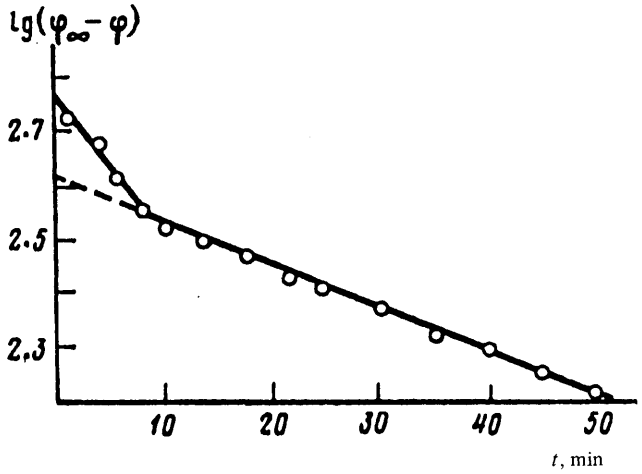


Figure 3. Time variation of the rate of deuterium exchange involving toluene in terms of the variables of Eqn.(4).[68]

The rates of exchange of the hydrogen atoms in the ring and in the side groups in alkylbenzenes have been measured by this procedure.[68,69] It is of interest that, whereas the rate of hydrogenation varied consistently as a function of the positions and numbers of the alkyl substituents, the rate of exchange within each group (in the ring and in the substituents) remained fairly constant for the entire series of compounds investigated. Correlations between the rate of exchange and the quantum-chemical quantities characterising the average population of the C–H bonds after the adsorption of hydrocarbons on nickel were found from these data:[70] the higher the population, the lower the rate of exchange.

The unequal reactivities of the α- and β-hydrogen atoms in the thiophen molecule[71] and of the hydrogen atoms in the methyl, methylene, and methylidyne groups in saturated hydrocarbons[72] were demonstrated in a similar way.

III. ISOTOPE DISTRIBUTION

The determination of the isotope distribution in the reaction products is a widely used procedure, which is at the same time difficult to subject to a formal treatment. It is used in the study of catalytic processes involving deuterium. In each specific case different aspects of the distribution can be of greatest interest: the type of exchange (simple or multiple) in the initial and final products and the possible intermediates, the most probable site where deuterium enters the molecule, the dependence of the distribution

on the molecular structure, reaction temperature, other conditions, etc.

We shall examine initially the possibilities for the theoretical calculation of the isotope distribution in deuterium exchange products.

1. Calculation of the Distribution

Deuterium–hydrogen exchange processes are usually subdivided into simple and multiple. In the former case one hydrogen atom is substituted by deuterium in each reaction step and the quantity M_D calculated by Eqn.(5) is unity. When $M_D > 1$, the occurrence of multiple exchange is indicated, where more than one hydrogen atom is replaced by deuterium in at least some of the molecules. When the molecule contains only equivalent hydrogen atoms, the simple exchange is a statistical process and is readily susceptible to calculation. Up to a certain degree of exchange x, the fraction of each isomer d_i, whose molecule contains i deuterium atoms, can be found from the formula[73]

$$d_i = \frac{n!}{i!\,(n-i)!}\, x^i (1-x)^{n-i} \quad , \qquad (6)$$

where n is the number of hydrogen atoms capable of exchange and x the average fraction of hydrogen atoms in the hydrocarbon molecules substituted by deuterium. However, there exist compounds whose molecules contain groups of hydrogen atoms which are not equivalent as regards reactivity. Although the exchange in each group can be of the simple type, nevertheless one must not calculate the overall distribution of the deuterioisomers by Eqn.(6) in this instance. For such compounds, a method of calculating the distribution,[74] based on the statistical analysis of the independent exchange processes in two different groups A and B, has been developed. Agreement between calculated and experimental distributions is achieved by selecting the appropriate ratio of the rates of deuterium exchange in these groups k_A/k_B. If reliable independent evidence showing that the exchange does in fact proceed via a non-equivalent substitution mechanism is available, then k_A/k_B can be calculated from the distribution data, i.e. the relative reactivities of different hydrogen atoms in a given process can be estimated quantitatively as a function of the process conditions.[74,75]

The situation is much more complex as regards the theoretical calculation of the distribution in multiple deuterium exchange. Attempts at such a calculation have been made,[76–79] but they are all based on an artificial selection of parameters, which are not determined directly from experimental data; their value is therefore fairly limited.

Another approach, namely the kinetic approach, has been used by Nekrasov et al.[80] The study of the kinetics of deuterium exchange makes it possible to find a series of rate constants k_n for the formation of products with the composition d_n. Taking into account the statistical probabilities of the formation of the exchange products of the initial molecule d_0 and from molecules which have already been partly substituted, it is possible to derive an expression for the rate of formation of any deuterium-substituted molecule d_n, which assumes the following form when the molecule contains, for example, 12 equivalent hydrogen atoms:[80]

$$r'_n = k_n d_0 + \sum_{i=1}^{n-1} C_{12-i}^{n-i} \sum_{m=0}^{i} \frac{C_i^m}{C_{12}^{n-i+m}}\, k_{n-i+m} d_i \quad ,$$

where the symbol C denotes the number of combinations. The equation for the rate of consumption of deuterium-substituted molecules can be obtained similarly:

$$r''_n = \left(k_0 - \sum_{i=1}^{n} k_i C_n^i / C_{12}^i \right) d_n \quad .$$

The observed rate of accumulation of each product containing n deuterium atoms is defined by the expression

$$r_n = r'_n - r''_n \quad .$$

Knowing the constant k_n, the concentrations of all the deuterium-substituted products at any instance can be calculated by means of these equations. The experimental distribution of the products of the deuterium exchange involving cyclohexane on nickel[80] and platinum[81] agrees satisfactorily with the calculated distribution.

The distribution, redistribution, and transfer of isotopic atoms both in the "pure" exchange and under the conditions of the occurrence of another accompanying reaction have been subjected to mathematical analysis in a general form in a series of investigations.[82–85] Unfortunately this analysis has not so far found application in research, possibly because of its complexity.

2. The Use of Isotope Distribution Data

As can be seen from the foregoing discussion, analysis of the isotope distribution is of a specific character in each case and it is extremely difficult to achieve a general classification of the procedures used for this purpose. One can only conclude that the character of the distribution in deuterium exchange usually serves as an indication of a particular form of adsorption of the test compound. Simple exchange, which is typical for oxide catalysts, occurs in one-point adsorption, while multiple exchange, which is more characteristic of metals, presupposes multipoint adsorption.[86] Incidentally, both simple and multiple exchange can take place on metals depending on the size of the *ensembles*.[87] A noval concept concerning the mechanism of the deuterium exchange involving alkanes and alkenes on metals, based on the hypothesis of the formation of intermediates of the carbene type, has been recently proposed by Dolgoplosk and co-workers.[88]

It was already stated above that a monotonic isotope distribution curve is as a rule observed in those cases where the hydrogen atoms are approximately equivalent as regards their reactivities.[7,13,19,23,89] On the other hand, if the hydrogen atoms can be subdivided into separate groups differing in their positions in the molecule and reactivities, characteristic deviations from monotonic variation appear on the distribution curve, which has been observed, for example, in the exchange involving methyl-substituted aromatic molecules,[10,67–69] cyclohexane,[80,81] and other compounds.[20,51,72,75,90] Incidentally, one should exercise a certain amount of caution as regards this problem, because the non-uniformity of the distribution can be caused in some cases also by purely kinetic factors (for further details about this, see Vlasveld and Ponec[62] and Nekrasov et al.[81]).

Among the characteristics of deuterium exchange of more or less general importance, one may name also the lower degree of exchange involving unsaturated compounds compared with the related saturated hydrocarbons.[4,6,13,91] It is of interest that the deuteriation of olefins is usually accompanied by the appearance in the initial instant of the reaction of a considerable amount of saturated molecules with the composition d_0 and d_1,[4,91–93] although the simple insertion of deuterium in the double bond should have yielded

only d_2 molecules. This can be explained by the slowness of the dissociative adsorption of deuterium in the presence of unsaturated compounds and also by the addition to the adsorbed molecule of the protium evolved in the dissociative adsorption of other hydrocarbon molecules,[4] i.e. by the redistribution of hydrogen.

We shall now proceed to the consideration of specific examples illustrating the possibility of employing hydrogen isotope distribution data for the elucidation of the mechanisms of catalytic reactions.

The study of the thiophen hydrodesulphurisation reaction yielded fairly unexpected results, which led the authors[94] to the conclusion that the hydrogen sulphide evolved in the presence of deuterium does not have the composition D_2S, as should have been the case when sulphur is abstracted by deuterium, but H_2S. This served as a basis for the hypothesis of an intramolecular mechanism of this reaction, according to which the dissociation of the C–S bonds is followed by the addition to the sulphur atom of the less mobile β-hydrogen atoms of thiophen and the "external" hydrogen (deuterium) is consumed only in the hydrogenation of hydrocarbon residues. This hypothesis was, as it were, supported by data for the isotope composition of the hydrogen sulphide in the deuteriolysis of thiophen containing deuterium in the α-positions and hydrogen in the β-positions.[20] Examination of the mass spectrum also demonstrated in this instance that mainly hydrogen sulphide having the composition H_2S is formed in the reaction. However, subsequent careful investigation under conditions including also low degrees of reaction, in which the very first portions of the hydrogenolysis products evolved were analysed, demonstrated that the conclusion concerning the intramolecular mechanism was incorrect.[95] In fact the main sulphur-containing product of the deuteriogenolysis of thiophen on five different hydrodesulphurisation catalysts proved to be D_2S. This was confirmed also by the analysis of the isotope composition of the products of the hydrogenolysis of perdeuteriothiophen. The intense mass-spectrometric peak corresponding to a mass number of 34 (which formally corresponds to the mass of H_2S) was indeed observed, but it was of secondary origin. Its appearance is probably associated with the hydrogenolysis of the thiophen decomposition products, because an increase in the degree of hydrogenolysis entails also an increase in this peak. The above example demonstrated the necessity to resort to the greatest possible amount of additional evidence in assessing the isotope distribution data.

Another example is associated with the skeletal isomerisation of n-pentane. The results of a kinetic study of this reaction suggested that it involves hydrogen, although the latter does not enter into the stoichiometric equation. As a test, the isomerisation of n-pentane on a platinum catalyst was carried out in the presence of deuterium.[23] It was found that the reaction product (isopentane) contains significantly more deuterium than was present in the initial n-pentane. This effect was shown even more strikingly on platinum–lead and platinum–copper catalysts.[24] These results served as important evidence in support of the hypothesis of the direct involvement of hydrogen in skeletal isomerisation. Similar evidence indicating the participation of hydrogen has also been obtained by the deuterium exchange method for the double bond migration reaction[96] and the *cis–trans* isomerisation of hydrocarbons.[96,97]

There are reactions which cannot be detected at all without an isotope label because of the identity of the chemical properties of the initial reactants and final products. Thus the metathesis of olefins, for example of propene:

$$2CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + CH_2{=}CH_2, \quad (7)$$

must inevitably be accompanied also by a process in which the methylene group is replaced not by an ethylene group but by a methylene group from another molecule. The replacement of some of the molecules of normal propene by the deuteriated analogues makes it possible to detect this "degenerate" or "latent" metathesis:

$$CH_3{-}CH{=}CH_2 + CD_3{-}CD{=}CD_2 \rightarrow CH_3{-}CH{=}CD_2 + CD_3{-}CD{=}CH_2. \quad (8)$$

Furthermore, the metathetical reaction of ethylene, in which products of a different chemical composition cannot be formed in principle, becomes accessible to observation:[98–100]

$$CH_2{=}CH_2 + CD_2{=}CD_2 \rightarrow 2\,CH_2{=}CD_2, \quad (9)$$

The appreciable difference between the rates of the explicit and latent metathesis of propene [reactions (7) and (8)] compared with the rate of reaction (9) served as important evidence[100] in support of the view that the reaction proceeds under the conditions of heterogeneous catalysis via a carbene chain mechanism, which has been proved for homogeneous systems.[101] Deuterium-labelled olefins have been used also in the metathetical reaction for the study of its stereospecificity[102,103] and its relation with the isomerisation reaction[104,105] and also for the determination of the mechanism of the formation of the intermediate carbene complex.[106]

Not only the isotope distribution in the products as such but also the position of the deuterium atoms in the molecule is important for the elucidation of the mechanism of this and other reactions. The isotope distribution, i.e. the relative contents of different deuterium-containing molecules, is usually determined mass-spectrometrically, most frequently by analysing the spectrum of molecular ions. Other methods, including microwave spectroscopy,[12,107–110] NMR,[111–118] and infrared spectroscopy[19] are used to determine the location of deuterium atoms in the molecule.

The study of the detailed distribution of deuterium yielded valuable information about the mechanism of the isomerisation of hydrocarbons,[107,108,110] the hydrogenation of propene,[118] butadienes,[116] cyclopentene,[115] substituted cyclohexenes,[112] various ketones,[117] and ethers,[114] the selective hydrogenation of dimethylethynylmethanol,[111] the dehydrogenation of cyclohexanol,[19] and other reactions.[109,113]

However, in certain cases mass-spectromatic analysis also provides certain definite possibilities for the determination of the position of the deuterium atoms. The point is that the mass spectrum usually represents not only molecular but also fragment ions formed as a result of the abstraction of entirely definite groups, for example, methyl groups from the molecule. Comparison of the isotope compositions of the molecular and fragment ions can yield some information about the part of the molecule in which deuterium atoms are preferentially located. For example, Fig. 4 shows that the isotope distribution of the fragment ions of *cis*-1,2-dimethylcyclohexane, formed by the abstraction of one methyl group, exactly reproduces the distribution of the molecular ions and that characteristic breaks in the monotonic variation of one curve correspond to analogous breaks in the monotonic variation of the other.[119] Since the difference between the mass numbers of these characteristic points is 18, the implication is that the hydrogen in the abstracted methyl groups has been fully replaced by deuterium, i.e. that they have the composition CD_3. The difference between the isotope compositions of the methyl groups in *cis*- and *trans*-1,2-dimethylcyclohexanes observed from the mass spectra[97] served as confirmation of the hypothesis that the molecules are arranged in different ways on the catalyst surface.

Comparative analysis of the mass spectra of the molecular and fragment ions of 5-methylfurfural and the products of its simultaneous decarbonylation and hydrogenation, 2-methylfuran and 2,5-dimethylfuran respectively, made it possible to determine the way in which the molecules are adsorbed on the palladium catalyst and to elucidate important details of the reaction mechanisms.[120] A similar approach has been used also to separate the hydrogen atoms of ethylbenzene into groups differing in their reactivity.[68]

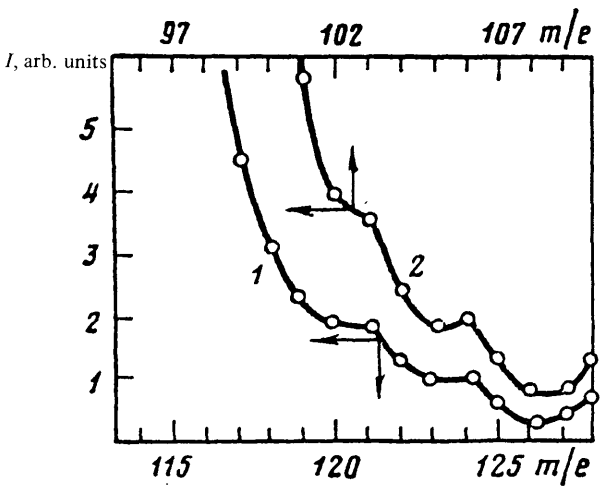


Figure 4. Isotope distribution of the products of the deuterium exchange involving *cis*-1,2-dimethylcyclohexane on platinum:[119] the intensities *I* of the peaks of the molecular (*1*) and fragment (*2*) ions.

Sometimes the intensity of the molecular ion peaks is so low that the isotope composition must be wholly estimated from fragment ions.[19]

One of the widely used procedures in isotope investigations involves the study of the reactions of certain compounds on the surface of a catalyst subjected to a preliminary treatment with deuterium. Information about the active centres on alumina catalysts,[121–125] niobium hydride,[126] molybdenum disulphide,[127] aluminosilicates,[122] and zeolites[128] has been obtained by this procedure. Evidently, this method is particularly useful for the study of catalysts with acid or basic centres but it is also useful in the study of the mechanisms of reactions on metals. Thus it has been shown[129,130] that intense deuterium exchange involving benzene takes place in the absence of deuterium from the gas phase on the surface of a nickel catalyst saturated with deuterium, but deuteriation hardly occurs.

Only after the introducton of deuterium into the gas phase, is the rapid formation of cyclohexane observed. Consequently hydrogen in a molecular form must participate in the benzene hydrogenation reaction, while in deuterium exchange it is involved in an atomic form, which confirms the mechanism proposed previously.[7]

There exist many other examples of the use of isotope distribution data for the investigation of the mechanisms of catalytic processes. We shall mention only some of them. Comparison of the observed calculated isotope distributions of the products on the hypothesis of a particular mechanism has been suggested[131] as a procedure for the determination of the rate-limiting stage of a process consisting of a series of parallel-consecutive reactions. The calculated and observed distributions have also been compared in the study of the hydrogenation of methylacetylene on platinum-group metals:[132] complete agreement between the calculated and experimental data has been noted only for reactions on palladium, platinum, and nickel.

Isotope distribution data have led to conclusions about the associative mechanism of the hydrogenation of methylene on magnesium oxide[133] and the involvement of dissociatively adsorbed intermediates in olefin hydrogenation reactions on the Al_2O_3 catalyst[134] and in their isomerisation on iron.[135] Data have also been obtained for the mechanisms of the selective hydrogenation of conjugated dienes,[91,136] the hydrogenation[137–139] and isomerisation[139,140] of olefins, the hydrogenolysis of paraffins,[141,142] and the dehydrogenation of n-decane[17,18] and isobutane[143] on platinum catalysts. A not altogether usual instance of the slow exchange involving a saturated hydrocarbon (isobutane) on a metal up to a fairly high temperature (400 °C) and conversely a rapid exchange involving an olefin (isobutene) has been observed.[143] These data and also comparison of the isotope distributions in the initial and final products led to the conclusion that the dissociative adsorption cannot be the slow stage of the dehydrogenation reaction in this instance.

Analysis of the isotope distribution in the methane and ethylene formed when carbonaceous deposits on the Co/Al_2O_3 and Co/C catalysts are treated with deuterium showed that they include both the CH_2 fragments and carbide carbon.[144] The adsorption-chemical equilibrium involving methane on nickel has been studied by a similar procedure with the aid of perdeuteriomethane.[145]

IV. KINETIC ISOTOPE EFFECT

Measurement of the kinetic isotope effect (KIE) is the simplest way of using deuterium for the study of catalytic reactions. Here there is no need to determine the isotope composition and hence there is no need to employ the mass-spectrometric or another complex analytical method. One compares the rate of the reaction with participation of the usual reactants with its rate after the replacement of hydrogen by deuterium in one or several components or in specific sites in the initial molecule: the non-identity of these rates indicates the involvement of the corresponding hydrogen atoms in the slow stage of the reaction. However, in practice the measurement of the KIE is associated with certain difficulties.

The theory of kinetic isotope effects in homogeneous systems has been fairly highly developed,[146] which unfortunately cannot be said of heterogeneous-catalytic processes. This is not an appropriate place for the consideration of the theoretical aspects of the problem and it is sufficient to say that, in the measurement of the KIE in heterogeneous catalysis, one may encounter, apart from the trivial experimental errors associated, for example, with the different degrees of purification of the deuteriated and non-deuteriated reactants, also difficulties due to the incorrect estimation of the reaction rates, the deactivation of the catalyst, the influence of side processes, an incorrect interpretation of the reverse effects, their dependence on temperature, etc.

The kinetic isotope effect is characterised by the ratio β of the rates of the processes occurring with participation of the light and heavy isotopes under identical conditions and for the same composition of the reaction mixture (for identical degrees of reaction):

$$\beta = r_H/r_D .$$

If the kinetic equation for the reaction is known and the rate constants involved in it has been determined for the reactions with participation of hydrogen and deuterium, then the constancy of the degree of reaction is not an obligatory condition, because the rate of reaction can be easily calculated for any composition. However, as a rule, such data are not available and the failure to meet this requirement may be a source of errors. In the case of kinetic power equations the ratio of the rates is equal to the ratio of the rate constants.

The reverse values of the KIE, i.e. the increase and not the decrease of the rate of reaction following the replacement of the light isotope by the heavy isotope, at first sight conflict with the elementary theory of isotope effects based on the transition state method.[146] This phenomenon has been explained[147] by the multistage nature of the hetereogeneous-catalytic processes and the swamping of the decrease of the rate in the slow stages by the shift of the equilibrium in the fast stages, including the adsorption and desorption stages, and also by the specific shift of the zero-point energy levels of the activated complexes in the slow stages on isotope substitution. We may note that, in principle, one cannot rule out the complete compensation of the forward effect by the reverse effect, which would outwardly appear as the absence of a KIE. It is therefore useful to carry out measurements under different conditions by altering, for example, the temperature.

The true KIE, i.e. the change in the rate constant for the slow stage after the replacement of one isotope by another, can be masked by the thermodynamic effects of the preceding fast stages. The change in the contribution to the overall process by side reactions whose rates are different in the presence of hydrogen and deuterium can also be reflected in the observed KIE for the reaction investigated.[148]

As a result, for the same reaction under similar conditions, different investigators have frequently obtained markedly different values of the KIE. Thus in a study of the hydrogenation of benzene on the Ni/SiO_2 catalyst at 240 °C, measurements were made of the rates of the following reactions:

$$C_6H_6 + 3H_2 \xrightarrow{r_1} C_6H_{12},$$
$$C_6H_6 + 3D_2 \xrightarrow{r_2} C_6H_6D_6,$$
$$C_6D_6 + 3D_2 \xrightarrow{r_3} C_6D_{12},$$
$$C_6D_6 + 3H_2 \xrightarrow{r_4} C_6H_6D_6.$$

The following values of the KIE were obtained: $r_1/r_2 = 0.60$, $r_1/r_4 = 0.53$, $r_4/r_3 = 0.55$, and $r_1/r_3 = 0.28$. On the other hand, in another study[149] the KIE obtained on a similar catalyst at 85 °C were respectively 0.7, 1.1, 0.8, and 0.9. Evidently the discrepancies are fairly considerable, particularly for the ratio r_1/r_4 and r_1/r_3. This may be partly associated with the difference between the temperatures; for example, according to Kiperman et al.[7], the ratio r_1/r_2 changed from 0.60 to 0.51 when the temperature increased from 240° to 270 °C. If the comparison has been made solely on the basis of only one ratio, for example r_1/r_4, then the results obtained in the two studies[7,149] might have led to opposite conclusions. The authors' interpretations in the two cases are based on fairly extensive experimental data and the role of random conclusions is reduced to a minimum. One can therefore assume that at 240 °C, i.e. in the region where the reaction is reversible, the ratio of the rates of the individual stages is different than at 85 °C, where "pure" hydrogenation takes place.

In the reverse reaction involving the dehydrogenation of cyclohexane, the replacement of hydrogem by deuterium in C_6H_{12} led to the observation of the direct KIE ($\beta = 2.3$ at 293 °C).[7]

On the platinum catalysts, the rates of hydrogenation of benzene were identical whatever the combination of the deuteriated and light molecules, i.e. there were no KIE.[149] However, one should note that the measurements were performed at only one temperature (85 °C). Comparison of the rates of the exchange reactions in the $C_6H_6 + D_2$ and $C_6D_6 + H_2$ systems showed that the KIE is then fairly large and that β ranges from 6.0 to 7.0 on both nickel and platinum.[149]

An example of the discrepancies between the estimates of the KIE can also be provided by the data of an investigation[100] where the disproportionation of propene on rhenium oxide was studied and of one[106] where the same reaction was carried out on a molybdenum catalyst. In the former case no KIE was observed, while in the latter the rate of reaction changed in the presence of deuterium at specific sites in the molecule. The absence of the KIE in the hydrogenolysis of n-pentane on platinum and nickel[23] conflicts with the significant isotope effect in the hydrogenolysis of various paraffins on the oriented crystal faces of platinum.[150]

The reverse KIE are not rare in hydrogenation reactions when H_2 is replaced by D_2.[147] They have been noted in the hydrogenation of acetone,[151] toluene,[10] and 2-methylfuran [152] on nickel and of 5-methylfurfural on palladium,[120] in the reaction between methane and carbon monoxide on the ruthenium,[153] nickel,[154,155] and palladium [156] catalysts, and in the synthesis of methanol on the $ZnO-Cr_2O_3$ and $Cu-ZnO-Al_2O_3$ catalysts.[157] The reverse KIE in the hydrogenation of benzene was already mentioned above. However, the manifestation of the reverse KIE in hydrogenation can be in no way regarded as a general rule. Reverse KIE have been observed, for example, in the hydrogenolysis[150] and skeletal isomerisation[23,150] of paraffins on platinum. On the other hand, the direct effects have been observed in the hydrogenation of isoprene,[13] hexene,[21] cyclopentadiene,[91] mesityl oxide,[15] and dimethylethynylmethanol [111] on various palladium catalysts, of cyclohexanone on the copper–magnesium catalyst,[19] of isoprene on the calcium–nickel phosphate catalyst,[6] and of piperylene on the NaY zeolite.[158] In all the studies quoted the occurrence of the KIE was regarded as evidence for the involvement of hydrogen in the slow stage of the reaction. On the other hand, the absence of the KIE in the hydrogenation of n-decane,[17] the dehydrogenation of cyclohexanol $C_6H_{11}OD$,[19] the hydrogenolysis of thiophen[20] and n-pentane,[23] and the disproportionation of propene[100] is regarded as proof that hydrogen is not involved in the slow stages of these processes.

The measurement of the KIE when hydrogen is replaced by deuterium in specific positions in the molecule constitutes a very effective procedure. This makes it possible not only to infer the very fact of the involvement of a bond with hydrogen in the slow stage of the reaction, but also makes it possible to determine the location of such bonds. For example, a KIE has been observed in the hydrogenation of toluene when fully deuteriated or ring-deuteriated molecules were made to react (the values of β at 216 °C were 0.73 and 0.85 respectively), whereas the KIE was absent when hdyrogen was replaced by deuterium in the methyl group,[10] i.e. as was to be expected, the hydrogen in the methyl groups is not involved in the slow stage.

In the study of the *cis–trans* isomerisation of mixtures of *cis*-but-2-enes having the compositions C_4H_8 and C_4D_8 and also of $CH_3CDCDCH_3$ and C_4D_8 on aluminophosphate catalysts, an appreciable KIE was observed ($\beta \cong 2.5$).[140] On the

other hand, the coisomerisation of a mixture of *cis*-but-2-enes C_4H_8 and $CH_3CDCDCH_3$ took place without an isotope effect. Hence follows the conclusion that the methyl groups of but-2-ene participate in the slow stage.

Similar examples are known also for oxidation reactions. In the extensive oxidation of perdeuteriopropene and propene having the formula CD_3CHCH_2 on the irridium catalyst, a large isotope effect was observed following the oxidation of CH_3CDCH_2 and especially CH_3CHCD_2 molecules. $\beta \cong 1$ was obtained.[159] Consequently the slow stage of this reaction involves the dissociation of a C–H bond in the methyl group. Comparison of the rates of oxidation of the methanols CH_3OH, CH_3OD, and CD_3OD to formaldehyde on molybdate catalysts also showed that here the rate-limiting stage is the abstraction of hydrogen from the methyl group.[160] The dissociation of a C–H bond also limits the rate of oxidation of butanol on platinum,[161] because a KIE was observed only in the presence of deuterium in the hydrocarbon component of the molecule but not in the hydroxy-group.

The extensive oxidation reactions of cyclohexene, acetaldehyde,[161] and formic acids[162] on platinum also occurred with a large isotope effect. On the other hand a KIE was not observed in the oxidation of acetic acid,[162] benzene,[161] and aniline.[163]

As already mentioned, the magnitude of the KIE depends on the reaction temperature: β usually approaches unity as the temperature increases,[15,24,150] but a linear increase of the KIE has also been observed—in the reaction between methane and carbon monoxide on the nickel catalyst.[155] The temperature dependence of the KIE in the hydrogenolysis and isomerisation of saturated hydrocarbons has been studied.[150] The pressure of the reactants can also influence the magnitude of the effect.[148,150] A change in the sign of the effect, from direct to the reverse, has been observed with decrease of the ratio $H_2(D_2)$/hydrocarbon in the dehydrocyclisation of isooctane on platinum.[148,164] This emphasises yet again that it is insufficient to measure the KIE under only one set of arbitrarily selected conditions.

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To what has been said above, we may add that an important feature of many studies carried out in recent years is the use of isotope methods in combination with other procedures for the investigation of the mechanisms of catalytic reactions. This results in a mutual enrichment of their possibilities and promotes a deeper understanding of the characteristics of the reactions of organic molecules on the surfaces of catalysts. In particular, analysis of the isotope composition of the products formed when hydrogen is replaced by deuterium has been applied successfully to the study of catalysis by the thermal desorption and programmed temperature reaction methods[165–167] and also by the mass spectrometry of secondary ions.[168] The use of deuterium in the study of the mechanisms of catalytic reactions by the non-stationary response method has also proved very useful.[148]

The great interest aroused in the mechanism of catalysis will undoubtedly promote a wider adoption of isotope methods involving the use of deuterium, especially in combination with other procedures.

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