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THE MECHANISM OF THE HETEROGENEOUS DEUTERIUM–HYDROGEN EXCHANGE REACTIONS OF CYCLOALKANES

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CONTENTS

I. Introduction 756

II. Deuterium exchange in cyclohexane, cyclopentane, and their derivatives 756

1. Reactions on metallic catalysts 756

2. Reactions on oxide catalysts 759

III. Deuterium exchange in cyclopropane and cyclobutane 759

I. INTRODUCTION

The study of the deuterium–hydrogen exchange in hydrocarbons began soon after deuterium had become available for use in chemical research[1]. The reason for the interest in these reactions is that they can be used to elucidate the mechanisms of various processes, in the first place of hydrogenation–dehydrogenation reactions, and also the nature of the interaction between hydrocarbon molecules and the surface of a solid catalyst. The existence of a relation between the mechanisms of hydrogenation and isotope-exchange reactions has been pointed out frequently[2-4]. Fairly complete reviews of the catalytic isotope-exchange reactions of hydrocarbons have been given by Anderson[5] and Kemball[6]. In the present review we have attempted to examine the special problem of the deuterium–hydrogen exchange in cycloalkanes, which is extremely important both theoretically and practically.

Studies in this field began with the work of Horrex and Polanyi[7], who, in addition to investigating the exchange between cyclohexane and heavy water in the presence of a platinum catalyst, also observed the interaction of gaseous deuterium with cyclohexane. These workers together with Greenhalgh[8] made a more detailed study of the kinetics of the exchange between cyclohexane and deuterium oxide and gaseous deuterium over platinum deposited on glass fibre, determined the activation energy, and put forward certain hypotheses concerning the reaction mechanism. Farkas and Farkas[9,10] also investigated the exchange between a number of hydrocarbons, including cyclohexane, and deuterium over platinised platinum. Balandin and coworkers observed deuterium exchange with cyclohexane on platinum and on chromium oxide catalysts[11].

However, a distinctive feature of all the above investigations is that only the total amount of deuterium which had undergone exchange was determined. However, the main problem in the elucidation of the reaction mechanism is the determination of the amounts of products with different degrees of substitution, i.e. the distribution, which became possible only after the application of mass-spectrometric methods of analysis[12-14]. A large part of the investigations in this field have been made using evaporated metallic films as catalysts. This is because they have a number of advantages, such as high purity, high activity, and the convenience of working in a high vacuum, which was pointed out by Beeck and coworkers[15,16], who studied in detail the catalytic and adsorption properties of such films. At the same time the preparation of deposited films with reproducible properties involves considerable difficulties[17-23]. The problem of the relation between the catalytic properties of films and massive catalysts is of considerable importance. Burwell et al.[24] found that the deuterium exchange in a number of saturated cyclic hydrocarbons on evaporated palladium films and on the Pd/Al_2O_3 catalyst takes place by the same mechanism. Anderson et al.[17] demonstrated by electron diffraction that in the cases which they investigated the films have the same crystal structure as the massive metal. However, a number of workers adhere to a different view, namely that the properties of film and reduced catalysts are different[25-27]. In particular, differences have been noted between the lattice constants, electronic work functions, and the electrical conductivities of these catalysts[28-30]. These results are consistent with the data of Hightower and Kemball[31], who found that the behaviour of platinum films and deposited platinum catalysts in the reaction between *p*-xylene and deuterium is fundamentally different.

II. DEUTERIUM EXCHANGE IN CYCLOHEXANE, CYCLOPENTANE, AND THEIR DERIVATIVES

1. Reactions on Metallic Catalysts

One of the theories of hydrogen atom exchange with saturated hydrocarbons was developed by Anderson and Kemball[13,14]. Later their ideas were used to explain the reactions in cycloalkenes[32]. According to Anderson and Kemball, the first stage of the exchange is adsorption of the hydrocarbon with formation of a radical adsorbed on one metal atom and a hydrogen atom adsorbed on a second metal atom. On desorption the radical combines with a deuterium atom which had been adsorbed on a neighbouring metal atom and therefore one hydrogen atom in the hydrocarbon is replaced by a deuterium atom (the so-called simple exchange). This involves the preferential formation of monosubstituted products, polysubstituted products being formed when simple exchange is repeated. This type of exchange has a characteristic form of the probability curve for the distribution of the deuterated products, the concentration of those with a high number of deuterium atoms in the molecule falling sharply. This exchange is typical, in the first place, for reactions of methane and hydrocarbons containing isolated methyl groups linked to quaternary carbon atoms, and for reactions of cycloalkanes on oxide catalysts.

In the reactions on metals the so-called multiple exchange is more characteristic of cycloalkanes. In this type of exchange the molecule is initially adsorbed via two carbon atoms. Then one of the C–M bonds (where M is a metal atom) of the "diadsorbed" cycloalkane breaks and the deuterium adsorbed on a neighbouring metal atom adds on. There is a definite probability that the "monoadsorbed" cycloalkane thus formed again undergoes two-point adsorption in a manner such that the C–M bond is formed at the next carbon atom. When this process is continued, the cyclic molecule as it were "rolls" over the surface. The nature of the distribution of the deuterium-exchange products[13] led Anderson and Kemball to the conclusion that

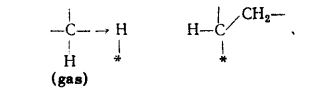
hydrogen atoms can be divided into two groups, those in the first group undergoing exchange more readily than those in the second. In the case of cyclopentane it is quite evident that such groups can only be hydrogen atoms lying on different sides of the plane of the ring. In cyclohexane such classification of hydrogen atoms is not unique but here too examination of the molecular model shows that each group consists of three axial and three equatorial atoms located on one side of the ring (cyclohexane in the "chair" conformation). According to Anderson and Kemball, the exchange of the six hydrogen atoms in the second group is possible only after the molecule turns over on the surface and its opposite side becomes adjacent to the latter. After this, the exchange takes place by the "rolling" method already described. If the possibility of complete desorption of the molecule and its subsequent readsorption via the other side of the ring is disregarded, the turning over of the cyclopentane molecule can only occur via the formation of a second C–M bond, after the rupture of one of these bonds, by a carbon atom already involved in one such bond (adsorption of the $\alpha\alpha$ type[24]). The molecule is then equally likely to lie on the surface on either side. In cyclohexane there is also another possibility — two-point adsorption of the type $\alpha\beta$ in which C–M bonds are formed by two neighbouring equatorial atoms belonging to different groups.

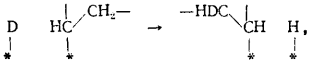
The complex distribution of the products of the deuterium exchange led Anderson and Kemball to the conclusion that two processes can take place simultaneously, one of which is responsible mainly for products with a high deuterium content and the other is responsible for the remaining products. Anderson and Kemball associate these processes with the presence of surfaces having different catalytic activities. On oriented films, where all the crystals are arranged preferentially with the same face directed outward, the distribution is simpler[13].

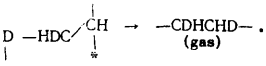
The model proposed by Anderson and Kemball permits a mathematical calculation of the contents of various deuterium exchange products. However, Hayakawa and Sugiura[33] believe that the hypothesis of the simultaneous occurrence of two processes by no means always leads to agreement between the theoretical and experimental results. Anderson and Kemball suggest that the geometrical disposition of the atoms on the surface is not significant, provided that the distances between the metal atoms lie within a fairly wide range, from 2.4 to 3.1 Å, since any inconsistency between the interatomic distances in the molecule and on the surface is compensated by a change in the C–M distance or slight twisting about the C–C bond. Thus in their view the specificity of metals is not associated with their geometry but with the different contributions of the various adsorption–desorption processes which occur on them. This view does not explain the high specificity of metals in exchange of a particular type. Furthermore, it has been shown that the distribution of the products of the deuterium exchange with cyclohexane on platinum, palladium, and nickel, which have a crystal lattice of the A1 type, is quite different from the distribution in the exchange on tungsten, molybdenum, and iron, which have a lattice of the A2 type[34,35]. The deuterium exchange in cyclohexane on germanium and silicon films is more likely to be of the simple type[36].

Hayakawa and Sugiura[33,37], who studied the deuterium exchange in cyclohexane on evaporated molybdenum and tungsten films, raised a number of objections to the explanation proposed by Anderson and Kemball. They believe that there is no hindrance to the turning over of the molecule and therefore the distribution curve should not exhibit any discontinuities. This was confirmed by their experiments. However, they agree that the exchange involves the rolling of the molecule over the surface. In their view the uniformity of the distribution (i.e. the ease of the transition of the exchange interaction from one side of the ring to the other) ensures firstly two-point adsorption of two equatorial atoms belonging to different groups and secondly the readsorption of the desorbed deuterated products. The second factor can play a significant role only at high extents of reaction, since at low extents of reaction the fraction of molecules which have participated in the exchange twice is $y^2/2$, where y is the total fraction of the molecules which have undergone exchange[6]. However, the high isotope dilution by light hydrogen in their experiments unfortunately limits somewhat the validity of their conclusions. Furthermore, the two catalysts which they investigated are very similar in properties and have a crystal lattice of the same type (A2).

The mechanism proposed by Anderson and Kemball was adopted and developed by Burwell and coworkers[24,38-41], who considered the stereochemical aspect of the reactions. They believe that the exchange takes place via the following stages[38] (the asterisk denotes the catalyst):

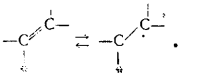

(1)


(2)


(3)

Frequent repetition of stage (2) leads to the formation of highly deuterated products. It is readily seen that this stage is analogous to "rolling" in the mechanism of Anderson and Kemball.

It is known that cyclopentane and hence also the intermediate compound adsorbed at two points may be present in a unique conformation. In this molecule all the hydrogen atoms on one side of the ring lie in pairs in one plane, i.e. they are eclipsed. Thus during the exchange cyclopentane must necessarily form compounds in the eclipsed conformation adsorbed at two points. It has been concluded[24] that, since the mode of distribution and the course of the exchange in cyclohexane and cyclopentane are similar, the intermediates must also be similar and that means that in the case of cyclohexane they are in the eclipsed conformation too. Hence it follows that the "boat" form must be assumed for the adsorbed cyclohexane molecule, since only this conformation gives rise to neighbouring eclipsed hydrogen atoms in cyclohexane. This in fact accounts for the discontinuity in the distribution curve after half the atoms have undergone exchange. Burwell believes[40] that, for the reaction to extend to the other side of the ring, an intermediate compound of the following type must form:



It is readily seen that here a second C–M bond can form on either side of the ring.

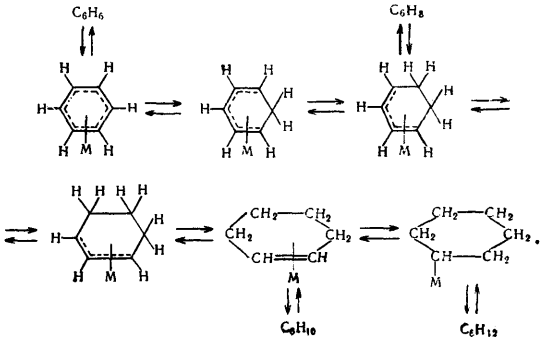
The situation is different in higher cyclic hydrocarbons. Starting with cycloheptane, not only *cis*- but also *trans*--hydrogen atoms may be in the eclipsed conformation, although with some strain in the latter case. In cyclo-octane the formation of the eclipsed conformation in the *trans*--position does not involve any strain. Evidently in such molecules exchange can extend without any hindrance to the other side of the molecule and the distribution curve should not show discontinuities. This view is confirmed by the experimental data of Burwell and coworkers[24]. Whereas the distribution curves for cyclopentane and cyclohexane show distinct peaks corresponding to penta- and hexa-substituted products respectively, in cycloheptane the peak is very small and in cyclo-octane it is virtually absent.

The conclusions of Anderson and Kemball are consistent with the temperature variation of the distribution of the deuterium-exchange products of cyclopentane over palladium found by Burwell et al.[24] They observed a gradual decrease of the maximum corresponding to $C_5H_5D_5$ as the temperature increased from 50° to 170°. Some of their results were obtained for cyclohexane over nickel[38].

The available experimental data demonstrate convincingly the possibility of interpreting the deuterium-exchange mechanism in saturated cyclic hydrocarbons from the standpoint of the multiplet theory of catalysis. Indeed the higher content of hexa-substituted deuteriocyclohexanes in the exchange on metallic catalysts of the platinum group can be explained by models in which the ring lies flat on the surface, in conformity with the sextet mechanism[34,35,42]. The authors of the present review observed[43] that the behaviour of cyclopentane in exchange on metals is quite analogous to that of cyclohexane. The doublet–sextet mechanism, developed by Kazanskii, Liberman, and Plate[44,45], which also requires a planar disposition of the molecule on the surface of the catalyst, was adopted to account for this phenomenon. Thus the higher content of the deuterium--exchange products having the composition $C_nH_nD_n$ can be attributed to the simultaneous exchange of all the hydrogen atoms on the side of the ring turned towards the surface. Evidently, with a planar disposition of the molecule on the surface, cycloalkane molecules with a number of deuterium atoms other than n can also form. This occurs, for example, when the desorption of the cycloalkanes from the surface is rapid, so that the adsorbed molecule has sufficient time to exchange only part of the hydrogen atoms before returning to the space above the adsorbent. Secondary adsorption of partially deuterated molecules can result in the formation of products in which more than half of the hydrogen atoms have been replaced by deuterium. However, the relatively slight excess of molecules having the composition $C_nH_nD_n$ over other exchange products[34,43] suggests that reactions involving two mechanisms, doublet and sextet (or doublet–sextet) take place simultaneously, their superposition yielding the observed distribution[35]. Evidently the sextet mechanism can obtain only on metals which allow a structural correspondence between their crystal lattice and the six-membered ring of the hydrocarbon molecule[42]. Similar hypotheses concerning the superposition of simultaneous processes have been made earlier[13,46]. Anderson and Kemball[13] do not reject the possibility of a doublet mechanism. It is noteworthy that their mechanism and the doublet model of the multiplet theory are not mutually contradictory.

So far we did not concern ourselves with the nature of the bond between the hydrocarbon molecule and the surface of the catalyst. Rooney, Gault, and Kemball[47,48] put forward the hypothesis [and supported it by evidence from experiments on deuterium exchange in various (polymethyl)cycloalkanes on deposited metallic films] that π-complexes are formed as intermediate surface compounds. Essentially the hypothesis is as follows. The usual type of bond between a chemisorbed hydrocarbon molecule and the metal surface is a σ-bond which involves an sp^3-hybridised carbon atom. However, when the molecule contains three or more adjacent non-quaternary carbon atoms there is a possibility of sp^2-hybridisation and delocalisation of p-electrons resulting in the formation of molecular orbitals which arise by the combination of the p-orbitals of the carbon with the unfilled surface d-orbitals of the metal[49]. The energy consumed in the change of hybridisation is compensated by the stability of the bond formed and the delocalisation of π-electrons. Thus the intermediate compound forms a π-bond with the metal similar to that which obtains in ferrocene. As a result of sp^2-hybridisation, the molecule becomes planar and one or other of its two sides turns towards the surface. The metals investigated[48] can be arranged in the following sequence as regards their capacity to form intermediate compounds with π-bonds: Pd > Pt > Ni > Rh.

Developing these ideas, Rooney suggested[50] that during deuterium exchange in cycloalkanes there is a possibility of the formation of three intermediate compounds: initially a σ-bonded alkyl is formed, which is then converted into a π-bonded olefin after the removal of a hydrogen atom (in this process there is $\alpha\beta$-exchange on one side of the plane of the ring), this being followed by the conversion of the olefin into a π-allyl intermediate compound (or a compound with a still more delocalised π-bond). Accordingly, aromatic hydrocarbons and 1,3-dienes are chemisorbed directly as π-bonded complexes. Rooney[50] explained many of the reactions of cyclic hydrocarbons in terms of the mechanism shown below: hydrogenation, dehydrogenation, disproportionation, isotope exchange, and *cis–trans* isomerisation.



Subsequently Rooney emphasised the role of the olefinic π-bond, counterbalanced by the σ-bonds of the intermediate compounds[51]. The problem of intermediate π-complexes in heterogeneous catalysis has been examined in the review of Bond and Wells[52], mainly in connection with unsaturated compounds. The hypothesis of the formation of a planar sp^2-hybridised intermediate compound linked to the surface via a π-bond bears an interesting analogy to the multiplet theory of catalysis, where it is assumed that in the adsorption of cyclohexane on metal catalysts a sextet multiplet complex lying flat on the surface is formed during the dehydrogenation of cyclohexane[42]. Although the molecule forms a π-bond with only one surface atom, this does not

exclude the specificity of the various metals and in particular the effect of geometric factors. The specificity of metals may be due to the relative ease of formation of σ- and π-intermediates. Furthermore, the mode of crystal packing can control the nature of the orbitals in individual metal atoms involved in the formation of the π-bond. In this connection, it may be supposed that the above sextet mechanism of the exchange is associated with the formation of an intermediate π-complex, while the doublet mechanism corresponds to the formation of two σ-bonds with the surface.

This is the general outline of the explanations of the deuterium exchange in cycloalkanes on metals available at the present time. The kinetics of these reactions have been considered to some extent in many of the publications quoted [13,37,38,48]. The kinetic equations obtained are not always the same but they have a certain common feature. Usually the rate of exchange is represented by

$$\omega \propto p_{C_nH_{2n}}^{n} \cdot p_{D_2}^{-m},$$

with $n \simeq 1$ and $m = 0.6-1$. Thus deuterium inhibits the exchange [5]. Ravoire [53] made a special examination of the kinetics of deuterium exchange in cyclohexane under static conditions over platinum deposited on activated charcoal, and found that the reaction order and the apparent activation energy can vary on heating above 100°.

2. Reactions on Oxide Catalysts

In the first study of deuterium exchange in cyclic hydrocarbons over chromium oxide [11] it was shown that the reactions on oxide catalysts differ significantly from those on metals. It follows from what has been said above that multiple exchange reactions play a decisive role in deuterium exchange on evaporated metal films. In contrast, on oxide catalysts simple exchange predominates. In this type of exchange each adsorption step involves the exchange of only one hydrogen atom, the molecule being subsequently desorbed, so that species with a low deuterium content are the main products. The activation energy for deuterium exchange on oxide catalysts is as a rule much higher than on metals.

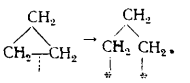
Deuterium exchange in cycloalkanes, mainly cyclohexane, has been investigated on chromium oxide [46,54,55], chromium oxide deposited on alumina [56], and on rare-earth oxides [57-59]. It was shown that the rate of isotope exchange is much higher than the rate of dehydrogenation under comparable conditions [56]. Burwell and coworkers [46] found that, in addition to simple exchange, multiple exchange takes place to a slight extent on chromium oxide (1–2% of the total exchange) and probably also a special type of exchange responsible for the increased content of products with two and three deuterium atoms per molecule. It is suggested that simple exchange involves the interaction between the cycloalkane adsorbed at only one point and a deuterium atom adsorbed at an adjacent site. The hydrocarbon radical may be linked to a chromium atom and the hydrogen to an oxygen atom, the corresponding intermediate product resembling somewhat a carbanion. Burwell attributes the multiple exchange which takes place to a slight extent on chromium oxide to the formation on the surface of an olefin or a π-allyl complex which also incorporates a chromium atom. In view of certain unusual features of the exchange, Burwell and Littlewood [55] suggested that two types of active site are present on the surface of chromium oxide.

Gadzhi-Kasumov, Isagulyants, and ourselves [60,61] arrived at a similar conclusion in a study of the relative extents of deuterium exchange with and dehydrogenation of cyclohexane when the two reactions take place simultaneously on chromium oxide. In these experiments it was found that the degree of dehydrogenation increases steadily with temperature, while the extent of exchange passes through a maximum. It is interesting that, although deuterium exchange in cyclic hydrocarbons is mainly of theoretical interest, it can also acquire some practical value, since this process has been proposed for the enrichment of hydrogen with deuterium [62-64].

III. DEUTERIUM EXCHANGE IN CYCLOPROPANE AND CYCLOBUTANE

Data on the first two, simplest representatives of the cycloalkane series, cyclopropane and cyclobutane, should prove of value for the elucidation of the mechanism of deuterium exchange in these hydrocarbons. Cyclopropane and cyclobutane are somewhat untypical in the series of cyclic hydrocarbons, because of the high Bayer strain in their rings, which reaches 10 kcal per C–C bond in cyclopropane. This excess energy in the molecule can give rise to hydrogenolysis at the same time as deuterium exchange. However, the probability of hydrogenolysis depends to a very great extent on the reaction conditions and primarily on the choice of catalyst. Thus in the reaction of cyclopropane with deuterium in the presence of platinum [65-67], palladium [66,68], rhodium [66,69], and iridium [69] deposited on pumice at temperatures between 0° and 200° cyclopropane is almost completely converted into n-propane. At the same time on an evaporated rhodium film at -100° the exchange and deuterium addition take place at comparable rates [13]; on the other hand, on the chromium oxide catalyst hydrogenolysis becomes appreciable only above 75° and particularly above 100°, while at lower temperatures it does not occur at all [46,54]. The distribution of the exchange products on the chromium oxide catalysts is consistent with the laws of probability — multiple exchange does not take place [54]. In view of the inadequacy of the data for reactions on an evaporated film [13], it is unfortunately impossible to arrive at definite conclusions concerning the mode of distribution. As shown above, under the conditions used for this reaction by Bond and Turkevich [65] and Bond and Addy [66-69], cyclopropane is almost completely decyclised and the main products are n-propanes with 7 and 8 deuterium atoms per molecule.

Since in this case the course of the exchange for cyclopropane and n-propane is almost the same, the reaction mechanisms are probably also identical. Ring opening evidently takes place in the first stage of the adsorption of cyclopropane (this is the rate-limiting stage):



It is noteworthy that under comparable conditions cyclopropane undergoes exchange faster than other cyclic hydrocarbons.

It is apparently more convenient to study deuterium exchange in cyclobutane in view of its greater stability to hydrogenolysis [70]. For example, experiments on the catalytic hydrogenation of ethylcyclobutane showed [71] that the

hydrogenolysis of this compound does not begin until 150°. Despite this, the study of deuterium exchange in cyclobutane itself was undertaken only recently [72]. Until then only derivatives had been investigated — ethylcyclobutane [39,46,54] and 1,1-dimethylcyclobutane [50]. The isotope exchange in ethylcyclobutane on a chromium oxide catalyst at 200–235° yielded a complete set of products containing between 1 and 12 deuterium atoms and also a small amount of products with masses 1–4 units greater than the molecular weight of the fully deuterated ethylcyclobutane [54]. This evidently indicates partial ring opening. The distribution of the deuterium exchange products is consistent with the predominance of simple exchange. Multiple exchange occurs to a comparatively slight extent. In the exchange on an evaporated nickel film partial hydrogenolysis is also observed, but the exchange itself is of the multiple type [39].

It is interesting that in the reaction of 1,1-dimethylcyclobutane on a palladium film only four hydrogen atoms undergo exchange. Rooney [50] attributes this to the fact that for cyclobutane deformation of intermediate $\alpha\beta$-compounds of the olefin type adsorbed on two sites should be hindered, since cyclobutene is less stable than cycloalkanes with larger rings. The formation of an intermediate π-bonded compound of the allyl type is also hindered due to the strain which it must entail in the cyclobutane ring. In the investigation mentioned above, the deuterium exchange with 1,1-dimethylcyclobutane was performed at 68°. An increase of temperature to 150° caused selective cracking to 2,2-dimethylbutane.

Savin and coworkers [72] showed that the reaction of cyclobutane itself with deuterium on evaporated platinum, palladium, nickel, tungsten, and molybdenum films at temperatures between 0° and 171° involves vigorous multiple exchange on all the metals except palladium. It was found that, regardless of the type of the crystal lattice of the metal on which the exchange takes place, the distribution curve for the deuterated products does not show a discontinuity between $C_4H_4D_4$ and $C_4H_3D_5$. This is consistent with the structural postulates of the multiplet theory, according to which there is no structural correspondence between the above metals and the cyclobutane molecule and hence there is no possibility of a process in which initially hydrogen atoms on one side of the ring plane are exchanged and then those on the other side. At the same time, these data contradict the stereochemical hypotheses of Burwell, described above, since according to the latter the distribution curve should have a certain intermediate maximum corresponding to cyclobutane which has undergone exchange to an extent of 50%. It has been pointed out [72] that the exchange in cyclobutane is accompanied by partial hydrogenolysis, which is most intense on nickel. However, this process was slower than the exchange and for short contact times it had relatively little effect on the distribution. Hydrogenolysis was not observed over platinum.

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The study of deuterium–hydrogen exchange constitutes an effective method for determining the mechanism of the interaction between cycloalkanes and the surface of the catalyst. Direct comparison of hydrogenation and deuterium exchange is of particular interest, since it permits a more profound understanding of the mechanisms of these processes. The growing number of studies on these and related problems is clear evidence of the interest which they have for workers in the field of catalysis.

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THE ELECTRONIC FACTOR IN THE KINETICS OF CHEMISORPTION ON SEMICONDUCTORS

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CONTENTS

I. Review of published experimental work 761
1. Kinetic laws 761
2. Reversibility and irreversibility of adsorption 762
3. Change in electrical conductivity and work function of the adsorbent during adsorption 763
II. Review of theoretical work 764
1. Difference in approach between the boundary layer theory and the electronic theory of chemisorption 764
2. The boundary layer theory 765
3. Kinetic model of chemisorption 767
III. The electronic theory of chemisorption 768
1. Role of the electronic factor in the kinetics of chemisorption on a homogeneous surface 768
2. Partial irreversibility of chemisorption on semiconductors 770
3. Electronic aspects of the inhomogeneity of the adsorbent surface 771

I. REVIEW OF PUBLISHED EXPERIMENTAL WORK

1. Kinetic Laws

The physical and chemical properties of semiconductor surfaces, so important in semiconductor technology and in catalysis, are controlled essentially by chemisorption processes taking place on the surface. For this reason, the study of chemisorption on semiconductors has attracted a great deal of interest.

In order to clarify the fundamental mechanism of chemisorption, it is important to investigate the kinetics of the process. The basic characteristic is the variation of the amount adsorbed q with time t at constant temperature: