REACTIONS INVOLVING ISOTOPIC EXCHANGE OF HETEROCYCLIC COMPOUNDS WITH D_2O IN THE PRESENCE OF TRANSITION METALS (REVIEW)

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The results of isotopic exchange with D_2O of various O-, N-, and S-containing heterocycles and some hydrocarbons on transition metals are discussed from the positions of the theory of π-complex adsorption. The effect of various fragments of the molecules (the aromatic or alicyclic ring, electron-donor or electron-acceptor substituents, double bonds, and the number and nature of the heteroatoms) on the character of the substrate—catalyst interaction and on the reaction as a whole is examined on the basis of kinetic data from ^1H and ^{13}C NMR spectroscopy and chromatographic mass spectrometry. Isotopic exchange mechanisms are discussed.

The nature of the action of catalysts and the mechanisms of catalytic reactions can be understood only after a thorough investigation of the intermediates that are formed during adsorption and in the course of the catalytic process itself. In this sense valuable information can be obtained by investigation of isotopic exchange reactions, which can be regarded as a model in the elucidation of the mechanisms of more complex catalytic reactions such as hydrogenation, isomerization, etc. [1-8]. The investigation of H—D exchange reactions as model reactions is very convenient, since the chemical changes in this system are minimal, and this makes it possible to form a judgment regarding the formation and cleavage of bonds on the surface, the orientation of the substrate on the catalyst, etc.

The literature data on the isotopic exchange of heterocyclic compounds catalyzed by transition metals are correlated in the review.

Every heterogeneous-catalytic reaction commences with interaction of the substrate with the catalyst surface, and it is natural that the resulting surface compounds and their transformations will determine the subsequent course of the catalytic reaction. A great deal of attention has therefore been directed to the study of the substrate—catalyst interaction and the formation of intermediate surface compounds. The principal advances have been made in research on the adsorption and catalytic transformations of hydrocarbons. Since, the literature on this problem is voluminous [7-16], we will dwell only briefly on the principal results necessary in the discussion of the H—D exchange of heterocyclic compounds.

H—D Exchange of Hydrocarbons

The adsorption of hydrocarbons has been investigated on many metals and alloys [7-9, 14, 17], and conclusions regarding the nature of the complex formed during adsorption have very often been drawn on the basis of an analysis of the decomposition, hydrogenation, and deuteration products.

Various physicochemical methods have been widely used in the study of the adsorption of unsaturated compounds [7-9, 14, 18-21]. However, the data from these investigations make it possible to only conjecture as to which surface formations exist during the reaction (in this case one must deal with a "pure" surface that is reactive to a significant degree and is deactivated very rapidly as the degree of coverage increases: Centers that are widely accessible for adsorption such as D_2O may be absent on almost the entire coated surface).

Two types of adsorbed molecules of unsaturated compounds, viz., σ- and π-adsorbed compounds, are primarily discussed in the literature. Thus σ-diadsorbed (I) and π-adsorbed (II) structures have been proposed for ethylene [8, 9, 14, 22-26]:

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1011-1021, August, 1982. Original article submitted July 20, 1981.

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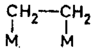
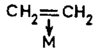
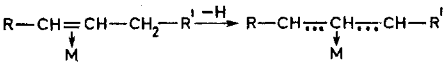


I



II

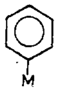
It is assumed [8] that σ-diadsorbed ethylene is formed by rehybridization of the carbon atoms to the sp^3 state with the subsequent formation of two σ bonds between the carbon and metal atoms. π-Adsorbed ethylene may be formed due to interaction of the π electrons with the metal atoms on the surface; according to [8], the resulting formations are related to the isolated π complexes of olefins with Pt, Pd, and Ag. Two types of adsorbed molecules have also been proposed for homologs of ethylene [8, 14]. However, in this case most authors [8, 26-29] give preference to the formation of intermediate π complexes, and π-allyl complexes III may also be formed by detachment of an α-hydrogen atom [14].



III

It should be noted that since both σ- and π-adsorbed ethylene have been established by physical methods, in [14] it is proposed that the initial product is a π complex, which is subsequently converted to a σ complex. The fact that it was observed during an investigation of the adsorption of ethylene on platinum single crystals by means of the diffraction of slow electrons [14, 30, 31] that ethylene initially does not give a distinct diffraction pattern and that a structure corresponding to a σ complex is formed only after a certain amount of time has passed constitutes evidence in favor of this.

A significant number of papers [7, 13, 15, 16, 26, 29] have been devoted to the study of the chemisorption of aromatic hydrocarbons. The results of studies of reactions involving hydrogenation and exchange (with D_2, C_2O, and C_6D_6) on transition metals have primarily been discussed. As in the case of ethylene, two types of chemisorbed benzene, viz., dissociatively chemisorbed benzene (IV or V) and chemisorbed with the formation of a surface π complex (VI), are proposed [7, 14].



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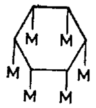

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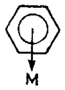
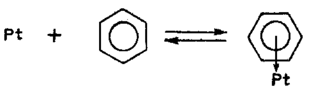


VI

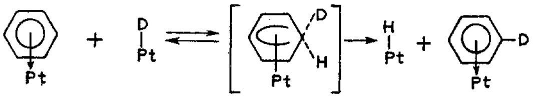
On the basis of voluminous experimental data [7, 12, 13, 15, 16, 26] it has been shown that the initial step in the reactions of unsaturated compounds on transition metals is the formation of surface π complexes of the substrate with the catalyst, and the concept of π-complex adsorption has been introduced [7]. Two possible mechanisms of H—D exchange in organic molecules, viz., associative and dissociative π-complex mechanisms, have been proposed on the basis of concepts regarding π-complex adsorption [7]. The formation of a surface π complex and D radicals, which can then react via two mechanisms, occurs in the first step in both cases [1, 2]:

$$D_2O + 2Pt \rightleftharpoons D{-}Pt + D{-}O{-}Pt \qquad (1)$$



(2)

1. Associative π-complex mechanism:



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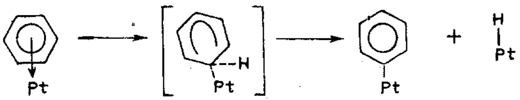
2. Dissociative π-complex mechanism:



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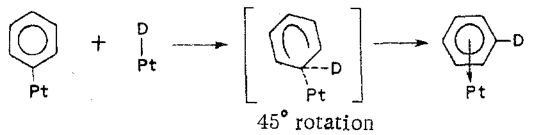


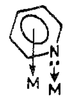
(5)

A unified opinion as to which type (associative or dissociative) of H–D exchange occurs has not been achieved, but there are a number of facts [32-34] that make it possible to assume predominance of the dissociative mechanism. Thus the existence of an ortho-deactivation effect, i.e., a decrease in the rate of exchange of hydrogen in the ortho positions with respect to the substituent, is extremely convincing evidence in favor of dissociative H–D exchange. In the opinion of Garnett and Sollich-Baumgartner [7], exchange via a dissociative mechanism in the ortho positions relative to the substituents should be weakened due to significant steric hindrance. Whereas positions that have one ortho substituent are still capable of undergoing exchange (partial ortho deactivation), exchange does not take place at all (complete ortho deactivation) in the ortho position with respect to two substituents. It is difficult to explain the effects of ortho deactivation starting from the associative mechanism, since molecules that have a π bond with the surface are readily accessible to the attacking atom.

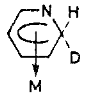
Thus on the basis of the available literature data from investigations of adsorption and catalytic transformations of unsaturated and aromatic hydrocarbons on metals one can, with sufficiently high probability, assume that the first step in the reactions of the cited hydrocarbons on metals is the formation of a surface π complex.

H–D Exchange of Heterocyclic Compounds

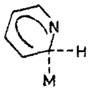
The investigation of H–D exchange of more complex substrates on metals makes it possible to obtain information regarding the character of the interaction of different fragments of the molecule — the aromatic and alicyclic rings, the double bonds, and the heteroatom — with the catalyst surface. As a result of the presence of a heteroatom in molecules of heterocyclic compounds, its electrons can participate in interaction with the catalyst surface and affect the character of the resulting surface compounds. Thus Kishi and Ikeda [35] in a study of the adsorption of pyridine on nickel forms by UV spectroscopy were able to show that the chemisorption of pyridine takes place due to the formation of a coordinate bond between the nitrogen atoms and the metal atom (or active center). However, the results of H–D exchange of pyridine on metals [36-40] show that not only the free electron pair of nitrogen but also the π-electron system of the ring participate in interaction with the catalyst surface, which leads to an oblique orientation of the molecules on the catalyst surface (VII). The H–D exchange of pyridine, thiophene, furan, and some of their derivatives with D_2O on group VIII metals was studied in [36, 38-46]. Upon the whole, the H–D exchange of pyridine proceeds more actively than the H–D exchange of furan and thiophene. It is assumed that the exchange of pyridine [42] proceeds via a π-complex mechanism with intermediate states VIII for the associative mechanism and IX for the dissociative mechanism.



VII



VIII



IX

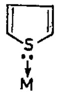
The kinetics of H–D exchange on Pt have been studied in the case of pyridine [38]. All of the hydrogen atoms of the molecule underwent exchange, but equilibrium could be achieved only for H–D exchange in the α positions. The H–D exchange of mono- and dimethylpyridines has been investigated in a number of papers [39, 45, 47, 48]. It has been shown [47] that 16% of the α-hydrogen atoms, 31% of the β-hydrogen atoms, and 54% of the hydrogen atoms of the methyl group do not undergo exchange in the case of H–D exchange of 4-picoline on Pt/C.

In [39] it was established that in the case of H–D exchange of pyridine derivatives on Pt black the position of the substituent does not have a substantial effect on the overall amount of deuterium in the reaction product, but the percentage of deuterium in the ortho positions is decreased appreciably because of the existence of ortho deactivation. The contribution of the heteroatom electrons to adsorption leads to a decrease in the effects of ortho deactivation in the corresponding positions as compared with alkylbenzenes [39, 45, 47, 48].

At the same time, the introduction of alkyl substituents in the α position in pyridine weakens the interaction of nitrogen with the metal and thus increases the contribution of the entire ring to π-complex adsorption of the π electrons, as a result of which the reactivity of the molecule as a whole increases [39, 45, 47, 48].

It should be noted that a "complete" ortho deactivation effect is observed in lutidines; the methyl groups also participate in H–D exchange, and the following order of reactivities of the substituents as a function of their position is observed: 2 > 4 > 3 [39].

Thus the material presented above shows that not only the π-electron system of the ring but also the p electrons of nitrogen (VII) participate in the interaction with the surface in the adsorption of pyridine on metals; this leads to an oblique orientation of pyridine during π-complex adsorption. As compared with pyridine, the H–D exchange of furan and thiophene proceeds to a considerably lesser extent, and they can be arranged in the order pyridine > thiophene > furan with respect to reactivity. This difference can be explained by the fact that, in contrast to pyridine, furan and thiophene are oriented vertically on the surface due to strong interaction of the p electrons of the heteroatoms with the metal surface.



X

The "introduction" of yet another benzene ring in the heterocycles changes the picture substantially. Benzofuran, indole, benzothiophene, and their hydrocarbon analog naphthalene can be arranged in the order indole > benzofuran ≫ naphthalene > benzothiophene with respect to the degree of deuteration. This difference in the behavior of one- and two-ring compounds can be explained within the framework of the concepts of the theory of π-complex adsorption [7]. Two factors, viz., the strength of bonding of the substrate with the surface and the orientation of the molecule on the surface, should affect the course of the reaction on metals. The strength of bonding of the molecule with the surface should be optimal – sufficient for occurrence of the catalytic act but, at the same time, not too strong, so that the substrate may actively participate in the adsorption–desorption process and not displace other reagents from the catalyst surface.

In the case of two-ring systems the presence of two aromatic rings will increase the strength of π-complex adsorption as a result of a decrease in the ionization potential [7, 49], which should give rise to a decrease in deuteration. Thus, for these reasons, quinoline and isoquinoline proved to be less active in isotopic exchange than pyridine [42, 50].

Of the heterocycles that contain more than one heteroatom, pyridazine, pyrimidine, pyrazine, and s-triazine have been studied in H–D exchange reactions with D_2O [38, 51]. The presence of additional, as compared with pyridine, heteroatoms also leads to an increase in the strength of adsorption; this is confirmed by data from a determination of the retarding effect of benzene on H–D exchange.

Data on the H–D exchange of a number of organic compounds with D_2O are presented in Table 1. It is apparent that naphthalene, in contrast to benzene, undergoes only 3% exchange, during which it is assumed [7] that the naphthalene molecule is oriented horizontally on the surface [7], whereas benzofuran undergoes much more intense exchange than furan.

The results of competitive H–D exchange with D_2O of a mixture of the investigated substance with benzene (benzene was used as the standard) are presented in Table 2. Competitive adsorption leads to displacement of benzene (or water) from the catalyst surface and, consequently, to a decrease in deuteration of the latter. The data in Table 2 show that the structure of the substrate has a pronounced effect on the interaction of two-ring compounds with the catalyst surface. Thus, whereas naphthalene and benzothiophene, bonding firmly with the surface, themselves virtually do not participate in the adsorption–desorption process and, consequently, in H–D exchange and hinder the H–D exchange of benzene, benzofuran and indole participate actively in H–D exchange. From a comparison of the data on the competitive exchange of benzofuran, 2,3-dihydrobenzofuran, indene, and naphthalene it may be concluded that the electrons of the heteroatom and the π electrons of the C_2–C_3 bond, which, as shown in [52], has increased multiplicity, make the principal contribution to the interaction with the metal in the case of benzofuran. This should lead to an oblique orientation

TABLE 1. Composition of the Reaction Mixture after H–D Exchange with D_2O of a Number of Organic Compounds on Pt according to Data from Mass-Spectrometric Analysis [46, 53-56]

Compound	Distribution of D, %						ΣD_i, %	D_∞, %*
	D_0	D_1	D_2	D_3	D_4	D_5		
Benzofuran	21	57	20	2			79	100
2,3-Dihydrobenzofuran	56	32	12				44	100
Indole	8	24	35	22	9	2	92	100
Benzothiophene	100	0					0	100
Naphthalene	97	3					3	75
Chroman	83	8	3	3	2	1	17	60
Chromene	44	32	14	8	2		56	75
Coumarin	6	20	30	24	15	5	94	100
Dihydrocoumarin	55	43	2				45	75
2-Methylbenzofuran	96	4					4	100
3-Methylbenzofuran	59	31	7	3			41	100
2-Acetylbenzofuran	20	28	25	16	8	3	80	75
Furan	96	4					4	100

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*The D value shows which part of the substrate molecules can be completely deuterated by half the amount of D_2O used in the reaction.

TABLE 2. Competitive H–D Exchange with D_2O of a Number of Organic Compounds on Pt according to Data from Mass-Spectrometric Analysis [56]

Composition of the reaction mixture	Distribution of D, %						ΣD_i, %
	D_0	D_1	D_2	D_3	D_4	D_5	
Benzofuran	26	59	15				74
Benzene	100						0
Indole	21	43	25	9	2		79
Benzene	93	7					7
Benzothiophene	100						0
Benzene	100						0
Naphthalene	93	7					7
Benzene	93	7					7
2,3-Dihydrobenzofuran	53	29	10	6	2		47
Benzene	63	21	18	4	3	3	37
Indene	36	49	15				64
Benzene	99	1					1

TABLE 3. Composition of the Reaction Mixture after H–D Exchange of Benzofurans with D_2O on Pt according to ^1H and ^{13}C NMR Data [54]

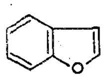
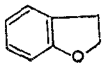
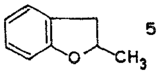
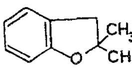
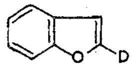
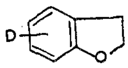
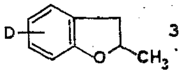
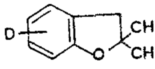
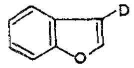
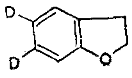
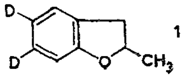
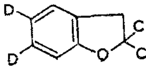
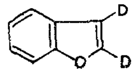
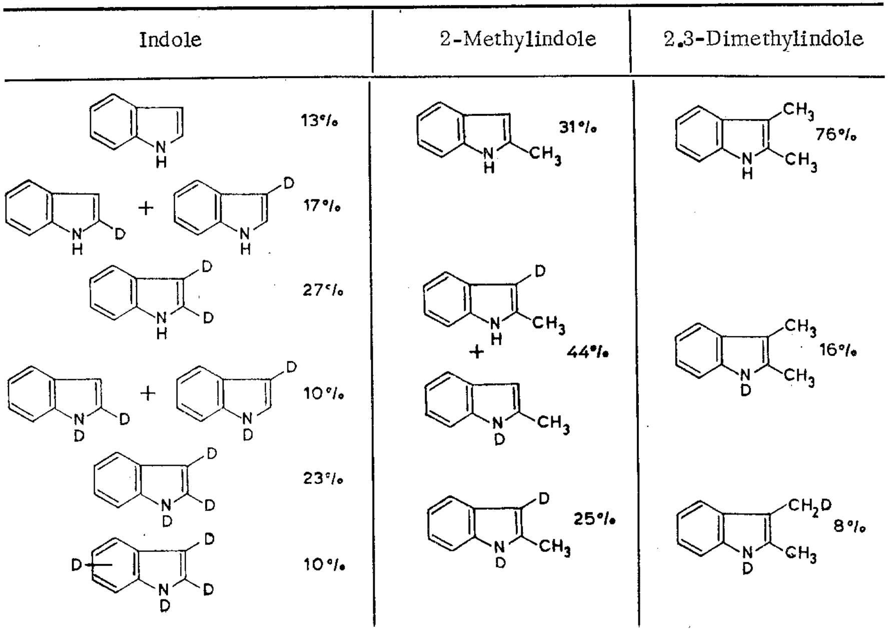
Benzofuran	2,3-Dihydrobenzofuran	2-Methyl-2,3-dihydrobenzofuran	2,2-Dimethyl-2,3-dihydrobenzofuran
 31%	 65%	 55%	 46%
 50%	 25%	 30%	 40%
 5%	 10%	 15%	 14%
 14%			

TABLE 4. Composition of the Reaction Mixture after H—D Exchange of Indoles with D_2O on Pt according to ^1H and ^{13}C NMR Data [55]



of the molecule on the catalyst surface. This orientation entails (Table 2) a decrease in the strength of bonding with the metal (as compared with naphthalene and benzothiophene), as a result of which the substrate molecules can actively participate in the adsorption—desorption process. Thus, as in the case of the one-ring systems, the oblique orientation of two-ring heteroaromatic compounds should promote H—D exchange. The assumption of an oblique orientation was confirmed in an investigation of H—D exchange with D_2O of benzofurans, indoles, and benzothiophenes [46, 49, 53-56].

Data from an analysis of the ^1H and ^{13}C NMR spectra of the products of H—D exchange of benzofuran and 2,3-dihydrobenzofurans that show that in benzofuran only the hydrogen atoms of the oxygen-containing ring (primarily in the 2 position) are presented in Table 3. This makes it possible to assert that the electrons of the oxygen atom and the π electrons of the C_2—C_3 bond participate in the formation of an intermediate complex of benzofuran with the catalyst. The latter is responsible for that orientation of benzofuran in which the plane of the molecule forms a certain angle with the catalyst surface. As a consequence of this, the O, C_2, and, to a lesser extent, C_3 atoms prove to be pressed down against the surface, in contrast to the carbon atoms of the benzene ring. The presence of deuterium only in the benzene ring of 2,3-dihydrobenzofurans (Table 2) shows that it is located closer to the catalyst surface. This is a consequence of the fact that the π electrons of the aromatic ring make the principal contribution to the formation of the π complex.

A pattern similar to that established for benzofurans was observed for indoles (Table 4) [55]. However, a more planar orientation is realized for indole than for benzofuran. This is associated with the fact that in the benzofuran molecule the oxygen molecule has, in addition to the p electrons included in the aromatic system, a pair of p electrons, which also may interact with the metal surface. The nitrogen atom in the indole molecule does not have p electrons, and an oblique orientation on the surface and, consequently, primary H—D exchange in the heteroring can occur only due to interaction with the metal of the π-electron system of the heteroring, in which the p electrons of the nitrogen atom also participate.

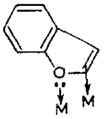
A vertical orientation is proposed for two-ring sulfur compounds [49, 55]. This character of the interaction of O-, S-, and N-containing two-ring heteroaromatic compounds with the catalyst is reflected in the results of H—D exchange: In the case of benzothiophene the p electrons of sulfur bond strongly with the metal, thereby hindering the adsorption—desorption process (Tables 1 and 2), so that benzothiophene does not undergo isotopic exchange under these conditions; in the case of benzofuran the p electrons of the oxygen atom and the π electrons of the heteroring interact with the metal surface, which leads to an oblique orientation and primary H—D exchange at C_2 (Table 3), while in the case of H—D exchange of indole only the π-electron system of the heteroring interacts with the surface, and the hydrogen atoms attached to C_2 and C_3 rather than the hydrogen atom attached to the nitrogen atom primarily undergo exchange (Table 4). The oblique orientation of benzofuran and indole is explained by the stepwise character of the exchange of these compounds with D_2O [55].

The presence and nature of the substituents in two-ring compounds have a substantial effect on both the character of H—D exchange and on the degree of deuteration [46, 53-55]. Alkyl substituents hinder the H—D exchange of heteroaromatic compounds leading to effects of the ortho-deactivation type [54, 55]. With respect to the degree of deuteration they can be arranged in the orders benzofuran > 3-methylbenzofuran > 2-methylbenzofuran and indone > 2-methylindole > 2,3-dimethylindole.

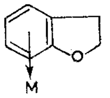
It should be noted that alkyl substituents in the 2 position have a considerably stronger effect on H—D exchange than substituents in the 3 position. The orientation established for benzofuran and indole explains this effect of alkyl substituents on isotopic exchange. Alkyl substituents, on the one hand, facilitate the formation of a surface π complex by decreasing the ionization potential of the molecules and, on the other hand, create steric hindrance during π-complex adsorption, which plays a prevailing role here. In the case of 2,3-dihydrobenzofurans [54], on the other hand, alkyl substituents in the heteroring facilitate H—D exchange (Table 3), and, with respect to the degree of deuteration, can be arranged in the order 2,2-dimethyl-2,3-dihydrobenzofuran > 2-methyl-2,3-dihydrobenzofuran > 2,3-dihydrobenzofuran. Alkyl substituents in the 2 position facilitate the orientation described for 2,3-dihydrobenzofurans and thus facilitate exchange of hydrogen atoms in the benzene ring. Steric factors do not have a decisive effect in this case.

The effect of the nature of the substituent on the H—D exchange of heteroaromatic compounds was investigated in [46]. It follows from the data in Table 1 that, in contrast to alkyl-substituted benzofurans, 2-acetylbenzofuran, which contains an electron-acceptor substituent, undergoes 80% deuteration; the hydrogen atoms of the benzene ring participated in H—D exchange [46]. This difference in the effect of the substituents is associated with the fact that in the case of 2-acetylbenzofuran the presence of an electron-acceptor acetyl group in the 2 position, in addition to creating steric hindrance, decreases the ability of the π electrons of the C_2—C_3 bond to participate in a donor—acceptor interaction with the metal and results in primary interaction of the π electrons of the benzene ring and the electrons of the heteroatom with the catalyst surface, i.e., the 2-acetylbenzofuran molecule, as a result of electronic and steric effects, interacts with the metal in the same way as 2,3-dihydrobenzofuran. This facilitates H—D exchange in the benzene ring. The character of the H—D exchange in the chromene, coumarin, and dihydrocoumarin series can be similarly explained (Table 1). With respect to the degree of deuteration, these compounds can be arranged in the order coumarin > chromene > dihydrocoumarin. It is apparent from Table 1 that, in contrast to chromene, in the products of H—D exchange of which mono- and dideutero derivatives predominate, in the case of coumarin tri-, tetra-, and pentadeuterated analogs are also present in the reaction mixture after H—D exchange, i.e., in the case of coumarin, as in the case of 2-acetylbenzofuran, the hydrogen atoms of the benzene ring also participate in exchange. However, in the case of dihydrocoumarin, in which the carbonyl group does not affect the benzene ring, H—D exchange occurs considerably less intensively, and virtually only monodeuterated derivatives are present in the reaction products.

Thus the material presented above shows that the first step in the catalytic transformations of heterocyclic compounds on metals is the formation of surface π complexes of the VII, XI, or XII type, in the formation of which the electrons of the heteroatoms also participate; this has a substantial effect on the character of the interaction of the substrate with the catalyst and on the reaction as a whole.

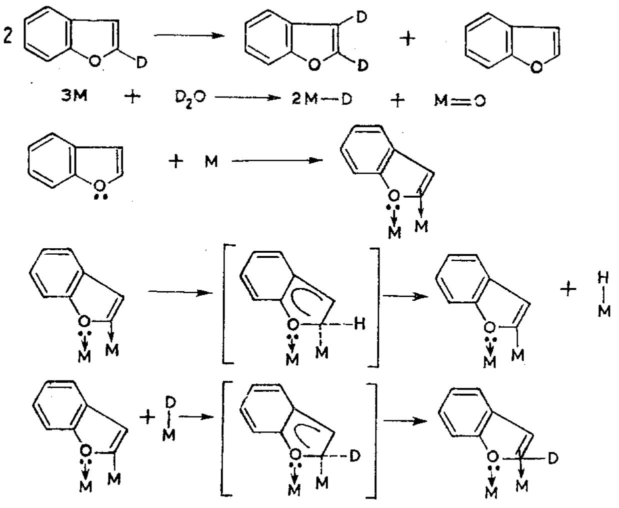


XI

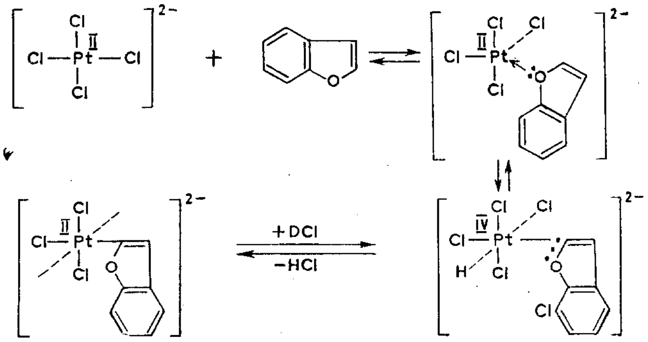


XII

A π-complex mechanism for H—D exchange of heteroaromatic compounds with D_2O on platinum metals was proposed in [54]. The deactivating effect of alkyl groups in H—D exchange and the fact of deuterium redistribution in 2-deuterobenzofuran on Pt [54] make it possible to give preference to the dissociative variant of the π-complex mechanism:



The isotopic exchange of benzofurans in a homogeneous phase in the presence of potassium tetrachloroplatinite was investigated in [57]. It may be noted that in the case of homogeneous H—D exchange also [57] the presence of a heteroatom in the molecules affected the reactions and the distribution of the deuteration products. Thus, according to NMR data, only the hydrogen atoms of the oxygen-containing ring participate in H—D exchange. However, in contrast to H—D exchange on heterogeneous catalysts, the presence of methyl groups in the heteroring facilitates exchange substantially: Whereas benzofuran undergoes 60% exchange, close to 100% exchange is observed when a methyl group is present in the heteroring. The preponderance of monodeuterated analogs in the H—D exchange products in the case of benzofuran and of polydeuterated analogs in the case of 2-methylbenzofuran makes it possible to propose that the unshared pair of electrons of the heteroatom participate in the formation of π complexes of benzofurans with the catalyst. The deuterium distribution of 2- and 3-methylbenzofurans confirms this assumption, since it is evident that in the case of 2-methylbenzofuran the methyl group also participates in exchange. A π-complex mechanism has been proposed for homogeneous H—D exchange of benzofurans [57]:



For 2-methylbenzofuran it may be proposed that the mechanism of the reaction includes the intermediate formation of π-allyl complexes [57].

Thus the electrons of the heteroatom play a substantial role in the substrate—catalyst interaction in both homogeneous- and heterogeneous-catalytic isotopic exchange reactions of heterocyclic compounds in D_2O.

As we have already noted above, the utilization of H—D exchange reactions as model reactions is very convenient, since the data obtained during their study make it possible to explain and even predict the principles of related but more complex catalytic reactions such as hydrogenation. This can be illustrated by the following examples. The hydrogenation of a number of oxygen-containing heterocyclic compounds in the presence of platinum, palladium, and rhodium was investigated in [58, 59]. In contrast to H—D exchange, in which the most active catalyst was Pt [60], Pd displayed the greatest activity in hydrogenation [59]. With respect to their reactivity in hydrogenation on Pt, the investigated benzofurans can be arranged in the order benzofuran > 2-methylbenzofuran > 2-ethylbenzofuran > 2-propylbenzofuran, i.e., as in the case of H—D exchange, alkyl substituents hinder hydrogenation, and they do so to a greater degree when they are in the 2 position than when they are in the 3 position [58].

If it is assumed that in hydrogenation, as in the case of H—D exchange, the first step is the formation of surface π complexes, the results obtained in a study of isotopic exchange make it possible to readily explain the principles observed in the hydrogenation of benzofurans and a number of other compounds [58, 59]. Alkyl substituents in the 2 position create steric hindrance to interaction of the π electrons of the C_2—C_3 bond and the electrons of the heteroatom with the catalyst and thus hinder hydrogenation [58, 59], displaying effects similar to ortho deactivation in H—D exchange. It is interesting that only the dihydro derivative is formed in the hydrogenation of α-methylfuran on Pd [59]; this can be similarly explained.

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