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HOMOGENEOUS H–D EXCHANGE OF HETEROCYCLES AND SOME HYDROCARBONS WITH D_2O IN THE PRESENCE OF Pt(II) COMPLEXES

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The homogeneous isotope exchange of O-, N-, and S-containing heterocyclic compounds and a number of hydrocarbons with D_2O in the presence of platinum(II) complexes, viz., potassium tetrachloroplatinite, platinum(II) monochlorodiethylenetriaminepentaacetate, chlorodiethylenediamineplatinum(II), dichloroethylenediamineplatinum(II), dichloroethylenediaminetetraacetatoplatinum(II) and, in the case of hydrocarbons, potassium tetrachloroplatinite, was investigated. The M factors were calculated for the H–D exchange of the hydrocarbons. It was shown that the H–D exchange of benzene has multiple character, whereas it has stepwise character in the case of cyclohexane.

The elucidation of the nature of the intermediate particles and the character of the substrate–catalyst interaction is a key problem in the investigation of the mechanisms of catalytic reactions. A study of H–D exchange reactions may be extremely effective for the solution of this problem [1-3]. Of particular interest is the study of the homogeneous H–D exchange of heterocycles that is catalyzed by complexes of group VIII metals, since many compounds that contain a heteroatom are catalyst poisons for heterogeneous metals or lead to reduction to the metal in the case of homogeneous catalysts. For these reasons, despite the fact that homogeneous-catalytic reactions of hydrocarbons, particularly H–D exchange reactions [2, 3], in the presence of complexes of group VIII metals have been studied in depth, there have been very few such studies devoted to heterocycles.

The homogeneous isotope exchange of heterocycles has been previously investigated [4] in the case of benzofurans in the presence of potassium tetrachloroplatinite.

In the present research we studied the homogeneous-catalytic H–D exchange of a number of heterocycles and hydrocarbons with D_2O in the presence of Pt(II) complexes, viz., potassium tetrachloroplatinite (complex I), dichloroethylenediamineplatinum(II) (complex II),

TABLE 1. Homogeneous-Catalytic Isotope Exchange of Hydrocarbons with D_2O at 120°C

No.	Substance	Time, t, h	Deuterium distribution, %							Σd_i, %	Catalyst
			d_0	d_1	d_2	d_3	d_4	d_5	d_6		
1	Benzene	6,9	18	14	16	17	16	12	7	82	I
2	Cyclohexane	8,0	72	26	2					28	I
3	Toluene	6,7	21	20	24	20	8	6	1	79	I
4	Naphthalene	7,0	6	18	31	30	13	2		94	I
5	Benzene	5,0	98	2						2	III
6	Cyclohexane	7,0	98	2						2	III
7	Toluene	7,0	100							0	III
8	Naphthalene	7,0	90	10						10	III
9	Tetralin	7,0	97	3						3	III
10	Benzene	6,9	97	3						3	—
11	Cyclohexane	7,3	97	3						3	—
12	Toluene	7,0	97	3						3	—

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TABLE 2. Homogeneous-Catalytic Competitive H–D Exchange of Hydrocarbons with D_2O in the Presence of Potassium Tetrachloroplatinite

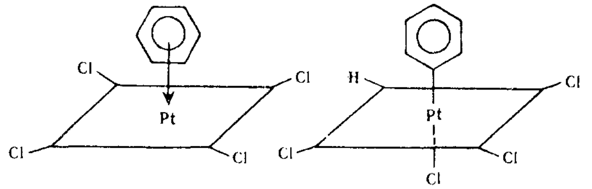
No.	Substance	Time, h	Deuterium distribution							Σd_i, %
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	
1	Toluene	6,7	27	31	22	15	3	2		73
	Cyclohexane		78	22						22
2	Naphthalene	7,0	3	9	21	33	28	5	1	97
	Cyclohexane		88	12						12
3	Naphthalene	7,0	7	18	31	29	13	2		93
	Benzene		30	19	18	17	13	1	2	70

chlorodiethylenediamineplatinum(II) (complex III), dichloroethylenediaminotetraacetatoplatinum(II) (complex IV), and monochlorodiethylenetriaminopentaacetatoplatinum(II) (complex V). The results are presented in Tables 1-5.

Complex III displayed the greatest activity in the H–D exchange of thiophenes (Tables 1 and 3), whereas complex I displayed the greatest activity in the case of hydrocarbons. Complexes II, IV, and V proved to be unstable under the reaction conditions.

It is apparent from Table 1 that the aromatic hydrocarbons participate in H–D exchange much more actively than cyclohexane. This difference in the behavior of the investigated hydrocarbons can be explained by the character of their interaction with the catalyst.

The examined $Pt(2^+)$ complexes have the same number of valence electrons, viz., 16. It is known [5] that processes that take place with the participation of such complexes proceed via an associative path. Thus, the first step in the H–D exchange of benzene is the formation of π complex A [3], which then undergoes transformation via a π-complex substitution mechanism with the formation of σ complex B [3].



A B

In the case of benzene the formation of a π complex in the first step facilitates the subsequent transformations and the occurrence of the reaction as a whole. At the same time, in the case of cyclohexane there is no possibility for the formation of complexes of the A type, and a σ complex of the B type should most likely be formed immediately via a mechanism involving oxidative addition, as described in [2]. The rationalizations presented above are confirmed by the multiple character of H–D exchange in the case of benzene and by the stepwise character of the H–D exchange in the case of cyclohexane, as attested to the different values of the M factor. The M factor was calculated as described in [6, 7]. The following equation was proposed in [6] for the H–D exchange reaction:

$$d\varphi/dt = K_\varphi(1 - \varphi/\varphi_\infty), \tag{1}$$

where $\varphi = \Sigma i d_i$, i is the number of hydrogen atoms capable of H–D exchange, d_i is the percent of deuterated molecules that contain i deuterium atoms, q_∞ is the equilibrium value of φ, and K_φ is the rate constant, which is equal to the number of deuterium atoms that enter into 100 molecules of the hydrocarbon per unit of time. Integration of Eq. (1) gives

$$-\lg(\varphi_\infty - \varphi) = Kt/2.303\varphi_\infty - \lg(\varphi_\infty - \varphi_0), \tag{2}$$

where φ_0 is the φ value at the initial time.

For the rate of decrease in the amount of the undeuterated substrate we obtained the empirical equation

$$-\lg(x_0 - x_\infty) = \frac{Kt}{2{,}303(100 - x_\infty)} - \lg(100 - x_\infty), \tag{3}$$

where x_0 is the percentage of undeuterated substrate up to time t, while x_∞ is the percent-

TABLE 3. Homogeneous-Catalytic H—D Exchange of Sulfur Compounds with D_2O at 120°C

No.	Substance	Time, h	Deuterium distribution					Σd_i, %	Catalyst
			d_0	d_1	d_2	d_3	d_4		
1	Thiophene	7	3	10	28	38	21	97	I
2	Thiophene	7	7	29	52	11	1	93	—
3*	Thiophene	1,5	71	17	6	6		29	I
4	Thiophene	7	89	10	1			11	III
5	Thiophene	7	86	12	2			14	III
6	Thiophene	27	72	20	4	4		28	III
7	Thiophene	7	94	6				6	—
8	2-Isobutylthiophene	7	12	82	4	2		88	III
9	2-Isobutylthiophene	7	13	79	6	2		87	III
10	2-Isobutylthiophene	7	94	5	1			6	—
11	Benzothiophene	7	98	1	1			2	III
12	3-Methylbenzothiophene	7	86	12	2			14	III

*The experimental temperature was 100°C.

age of undeuterated substrate at the start of the reaction and upon reaching equilibrium. From the data in Tables 4 and 5 and Figs. 1 and 2 one can calculate K_φ and K and M factor = k_φ/K. For benzene M = 2.2, which indicates multiple exchange and is in agreement with the character of the deuterium distribution in the reaction products. An M value of 0.88 is found for cyclohexane, i.e., exchange takes place in a stepwise manner. It is clear that the formation of a π complex will promote the occurrence of multiple exchange.

The results of competitive H—D exchange of hydrocarbons are presented in Table 2. It is apparent that, in contrast to H—D exchange for heterogeneous catalysts [1], in the case of homogeneous H—D exchange hydrocarbons do not interfere with one another in their participation of the reaction.

It is apparent from Table 3 that the most active catalyst for the isotope exchange of heterocyclic compounds was complex III and that the sulfur compounds can be arranged in the following order with respect to the degree of deuteration in the presence of this complex: 2-isobutylthiophene > thiophene > 3-methylbenzothiophene > benzothiophene.

It should be noted that complex I displayed the greatest activity in the H—D exchange of hydrocarbons (Table 1), whereas complex III was inactive. On the other hand, 2-isobutylthiophene underwent the most intensive exchange (88%) in the presence of complex III (Table 3) and destabilizes complex I.

These results of H—D exchange can be explained by the symbatic influence of two effects, viz., by a specific effect that the heteroatom introduces into the substrate—catalyst interaction, and by the differences in the π-donor properties of the ligands, which also has a significant effect on the substrate—catalyst interaction.

The strength of the interaction of the substrate with the catalyst should be optimal for the successful occurrence of the catalytic reaction [1]. This is achieved, for example, in the case of H—D exchange of aromatic hydrocarbons (with the formation of particles of the A

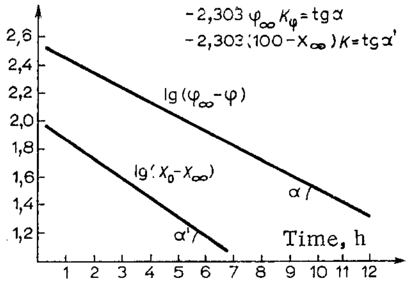


Fig. 1

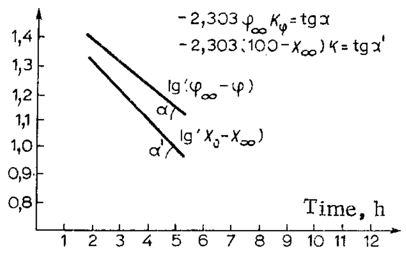


Fig. 2

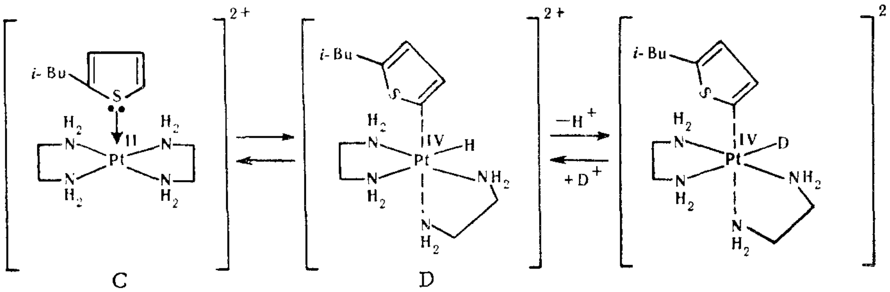
Fig. 1. Graph for the calculation of the M factor of benzene.

Fig. 2. Graph for the calculation of the M factor of cyclohexane.

TABLE 4. Kinetics of H–D Exchange of Benzene

d_i	Time, h											
	0,25	0,5	0,66	0,83	1	1,3	1,66	2	5	7	10	12
$d_0 = x_0$	96	87	90	72	74	74	67	52	26	17	6	7
d_1	4	4	3	11	7	7	10	12	16	14	10	11
d_2		3	3	6	7	7	8	11	16	16	15	17
d_3		2	2	4	5	5	7	10	16	17	20	22
d_4		2	1	3	4	4	4	8	14	16	22	22
d_5		1	1	2	2	2	3	5	9	12	20	15
d_6				1	1	1	1	3	4	7	7	6
$\varphi = \Sigma i d_i$	4	29	24	63	68	84	139	221	263	330	330	310
$\lg(\varphi_\infty - \varphi)$	2,51	2,48	2,48	2,43	2,42	2,42	2,40	2,28	2,04	1,83	–	1,30
$\lg(X_0 - X_\infty)$	1,95	1,91	1,92	1,82	1,83	1,83	1,78	1,6	1,30	1,04	–	0

type in the first step) in the presence of complex I, in which the rather labile ligands make possible the subsequent transformations via the mechanisms described in [3]. If we take a complex with bidentate ligands such as III as the catalyst, then for hydrocarbons there is "not enough strength" for bonding with the metal ion to the extent of weakening of the Pt–N bond for transformation to intermediate complex B, by virtue of which H–D exchange does not take place. In the case of isotope exchange of 2-isobutylthiophene in the presence of complex III the electrons of the sulfur atom interact quite actively with the metal ion to the extent that they actively weaken one of the Pt–N bonds and convert the complex from pentacoordinated state C to hexacoordinated state D, and exchange is realized via the scheme



C

D

In the case of K_2PtCl_4 strong bonding of the sulfur electrons with the metal ion leads to destruction of the complex. With respect to interaction with the metal ion in complexes I and III, thiophene occupies an intermediate position between hydrocarbons and 2-isobutylthiophene: For the H–D exchange of thiophene in the presence of K_2PtCl_4 a lower temperature was necessary as compared with the hydrocarbons, whereas in the presence of complex III, as a consequence of the fact that the sulfur atom in thiophene is less basic than in 2-isobutylthiophene because of the effect of the isobutyl group, less intensive exchange occurs (Table 3). A similar conclusion can also be drawn for the benzothiophene–3-methylbenzothiophene pair.

Another factor that determines the observed principles for the H–D exchange of hydrocarbons and thiophenes is, as noted above, the difference in the π-donor properties of the ligands in the case of complexes I and III. According to the data in [8], in the case of hydrogenation of thiophene on mononuclear palladium complexes the strength of the donor properties of the ligands hinder poisoning of the catalysts via the mechanism

$$L-\mathrm{Pd}-L' + :\mathrm{S}< \rightarrow L-\mathrm{Pd} \leftarrow :\mathrm{S}< \rightarrow L + \mathrm{Pd} \leftarrow :\mathrm{S}<,$$

which leads ultimately to destruction of the complex.

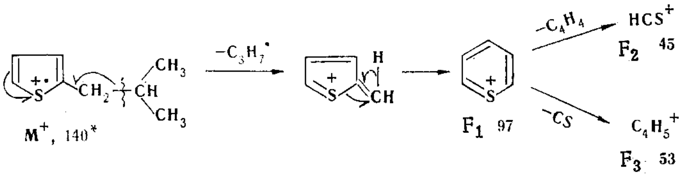
Stronger donors such as ethylenediamine ligands hinder strong bonding of the metal ion with sulfur and its poisoning or destruction of the complex as a result of irreversible complexing with the substrate.

The rationalizations presented above are confirmed by the character of the distribution of the deuterium label in thiophene and 2-isobutylthiophene (Table 3). It is apparent that monodeuterated derivatives predominate in the deuteration products; deuteration occurs in the α position. The position of the deuterium in the thiophenes after H–D exchange was determined on the basis of an analysis of the mass spectra.

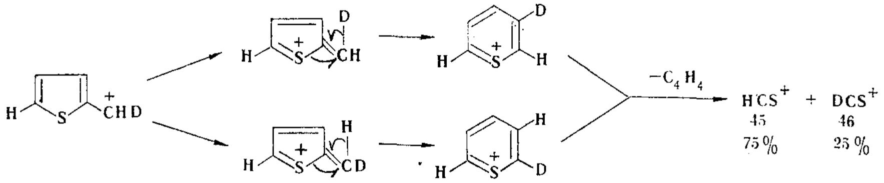
TABLE 5. Kinetics of H—D Exchange of Cyclohexane

d_i	Time, h				
	2	3,5	5,33	7,58	10,33
$d_0=x_0$	92	86	82	72	73
d_1	8	14	18	26	21
d_2				2	6
d_3					
$\varphi=\Sigma i d_i$	8	14	18	30	33
$\lg(\varphi_\infty-\varphi)$	1,39	1,25	1,14	0,36	—
$\lg(X_0-X_\infty)$	1,32	1,13	0,98	—	0,1

The principal pathway for the fragmentation of the M^+ molecular ion of 2-isobutylthiophene is elimination of an isopropyl radical as a result of β cleavage of the C—C bond in the side chain; tropylium ions, which subsequently undergo fragmentation via two pathways, viz., with splitting out of C_4H_4 or CS [9], are formed in this case:



In the case of the deuterium-labeled compound (see No. 8 in Table 3; MH 12%, MD 82%, MD_2 4%, and MD_3 2%) the deuterium label is retained completely in the F_1 fragment ion in the elimination of an isopropyl fragment (MH 9%, MD 82%, MD_2 8%, and MD_3 1%) and is also completely retained in the F_3 ion, which is confirmed by the presence in the mass spectrum of a peak with m/z 54.* In the formation of F_2 ions 50% of the deuterium label is lost, and, consequently, the deuterium in the F_1 ion is found in the α position. Proceeding from the mechanism of the formation and fragmentation of the F_1 ion it may be concluded that the deuterium label in the starting substance is in the α position of the thiophene ring, since in the case of the presence of a deuterium atom in the methylene group it is equally likely that it is distributed in the α and β positions of the tropylium cation, and the subsequent fragmentation should have led to the formation of DCS^+ and HCS^+ ions in ratios of 25 and 75%. However, the ratios of the intensities of the ion peaks with m/z 45 and 46 are 50 and 50%. On the basis of the above information it may be asserted that the hydrogen atoms only in the α position undergo exchange in the H—D exchange of 2-isobutylthiophene.



In the case of H—D exchange of thiophene in the presence of complex III (Table 3) primarily the monodeutero derivative is observed in the reaction products. An analysis of the mass spectrum [8] showed that in this case deuterium is retained only in the α position of the thiophene ring.

In addition to S-containing heterocycles we also investigated the isotope exchange of O- and N-containing heterocyclic compounds (furans, benzofurans, chromans, N-methylpyrrole, and indoles). In the case of O-containing compounds the investigated complexes did not display sufficient stability under the selected conditions, whereas in the case of nitrogen-containing heterocyclic compounds we observed intensive exchange via an acid-base mechanism, and this did not make it possible to investigate the catalytic action of the complexes. In addition, in the case of benzofuran and indole we studied the reaction of these compounds with potassium tetrachloroplatinite in aqueous solution. In the case of indole we were able to isolate a complex and investigate it by means of IR spectroscopy. The spectrum does not

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*Here and subsequently, the m/z values are given for the ion peaks.

contain the most characteristic and intense (for indole) band of N—H stretching vibrations, nor does it contain bands at 500-700 cm^{-1}, whereas the remaining absorption bands that are characteristic for indole [10, 11] are retained; on the basis of this information, one may assume the existence of a Pt—N bond. This confirms the conclusion that the electrons of the heteroatoms make the principal contribution in the interaction of heterocyclic substrates with metal ions.

EXPERIMENTAL

Complexes I-V were synthesized by the methods of [12-14]. The methods used to carry out the catalytic experiments and the analysis of the reaction products were described in [4, 15].

The compositions of the reaction mixtures are described below.

In Table 1: substrate $4.4 \cdot 10^{-3}$ mole, catalyst $3 \cdot 10^{-5}$ mole; for Nos. 2-4 and 6-9 we used 1.8-ml aliquots [CH_3COOD—D_2O (1.6:1)], for Nos. 1 and 5 we used 2.0-ml aliquots [CH_3COOD—D_2O (1:1)], and for Nos. 1-4, 7, and 10 the HCl concentration was $3 \cdot 10^{-3}$ mole.

In Table 2: see Table 1; 1.8-ml aliquots, and substrate concentrations of $2.2 \cdot 10^{-3}$ mole.

In Table 3: for Nos. 1 and 2, substrate $4.4 \cdot 10^{-3}$ mole, catalyst $3 \cdot 10^{-5}$ mole, HCl concentration $3 \cdot 10^{-3}$ mole; for Nos. 3-12 the compositions were the same as for No. 1 but without concentrated HCl; for Nos. 1-4, 6-8, 10, and 11 we used CH_3COOD—D_2O (1:1), whereas for Nos. 5, 9, and 12 we used CH_3COOD—D_2O (1.6:1).

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded at 400-4000 cm^{-1} with a UR-20 spectrometer.

The chromatographic mass spectra were recorded with a Varian MAT-111 spectrometer at an ionization energy of 80 eV; column length l = 1.5 m, and the packing was 10% SE-30 on Chromosorb W.

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