H–D EXCHANGE OF HETEROCYCLIC COMPOUNDS ON CATALYSTS OF VARIOUS TYPES

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UDC 541.128:546.11.02'212.02:547.728.1'735'841:543.51

The H–D exchange of a number of oxygen-containing heterocyclic compounds with various deuterating agents, viz., D_2O, C_6D_6, and C_2D_5OD, was investigated. Group VIII metals and their salts and oxides, as well as carbon, aluminum oxide, aluminum silicate, and a metal zeolite, were used as catalysts. The mechanism of H–D exchange and the effect of the nature of the catalyst on its activity in the reaction are discussed.

It has been previously shown [1] that in the catalytic transformations of complex organic molecules different structural fragments make different contributions to the interaction of the molecule with the surface of the metal catalysts. It seemed of interest to ascertain the effect of such factors as the nature of the deuterating agent, the method of preparation and activation of the catalysts, and the surface of the metals in the case of isotope-exchange reactions.

In the present research we investigated the H–D exchange of a number of heterocyclic compounds with various deuterating agents (D_2O, CD_3CD_2OD, and C_6D_6) on platinum, activated birch charcoal, metal zeolites, aluminum silicate, and aluminum oxide. In addition, we studied the effect of the compositions of the starting salts and the method of activation on the properties of platinum blacks. The results are presented in Table 1, from which it is apparent that in the case of the platinum catalyst the most active deuterating agent is D_2O. This can be explained by different competitive adsorptions of the organic compounds. In [1] it was shown that the molecules of heterocycles such as benzofuran "displace" benzene from the metal surface, thereby hindering its exchange, whereas they themselves undergo active deuteration by heavy water in this case. Similarly, in our case also benzofuran displaces C_6D_6 from the catalyst surface, and H–D exchange does not take place. At the same time, deuterating agents that contain OD groups (D_2O and C_2D_5OD) are more competitive agents as compared with benzene and participate in H–D exchange with benzofuran to the extent of 67% and 24%, respectively (Table 1). Under the same conditions benzodioxane undergoes only slight exchange only with D_2O. This behavior of 1,4-benzodioxane can be explained by the strong interaction of the electrons of both heteroatoms with the metal surface, which leads to the formation of rather stable surface complexes and hinders active participation of the 1,4-benzodioxane molecules in the adsorption–desorption process. The reasoning presented is confirmed by the data in Table 1 on the H–D exchange of tetralin, which undergoes 96% exchange under the same conditions.

Only the platinum catalysts displayed catalytic activity in H–D exchange, while activated birch charcoal, the metal zeolites, Al_2O_3, and aluminum silicate were not active (Table 2), despite the fact that their specific areas exceeded the area of Pt by many times. At the same time, the platinum obtained from various complexes displayed different degrees of activity in H–D exchange (Table 2). To obtain the platinum blacks we used complexes of various types, viz., potassium tetrachloroplatinite (complex 1), dichloroethylenediaminetetraacetatoplatinum(II) (complex 2), dichloroethylenediamine(N,N')diacetatoplatinum(II) (complex 3), and dichloroethylenediamineplatinum (complex 4). The platinum obtained from complex 1 displayed the highest activity. To ascertain the reasons for this behavior of the catalysts in H–D exchange we investigated their surfaces by the method described in [2]. We determined the number of active centers and the fraction of the active surface by EPR spectroscopy from

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M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 912-916, July, 1983. Original article submitted December 15, 1982.

0009-3122/83/1907-0731$07.50

TABLE 1. Isotope Exchange of Heterocyclic Compounds with Various Deuterating Agents on Pt

No.	Substance	Deuterating agent	Deuterium distribution, %										ΣD_i, %
			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	
1	Tetralin	D_2O	4	5	5	6	9	15	20	18	12	6	96
2	Benzofuran	D_2O	33	48	17	2							67
3	1,4-Benzodioxane	D_2O	82	4	4	3	3						14
4	1,4-Benzodioxane	C_6D_6	100										0
5	Benzofuran	C_6D_6	100										0
6	1,4-Benzodioxane	C_2D_5OD	100										0
7	Benzofuran	C_2D_5OD	76	22	2								24

TABLE 2. Properties of the Catalysts Used in This Research

Catalyst	Specific area, m^2/g	Fraction of the active surface, %	Σ, %, deuteration of benzofuran per m²	Σ, % (deuteration/act. center)·10^{13}
Pt black obtained from complex 1	21	39	48	9,5
from 2	43	13	15	8,8
from 3	69	17	8	4,7
from 4	30	12	1	0,4
Activated birch charcoal	506	0	0	0
NdNaX (0,98)	295	—	—	—
Aluminum oxide	307	—	—	—
Aluminum silicate	405	—	—	—

the number of diphenylpicrylhydrazyl radicals formed in the reaction of diphenylpicrylhydrazine with the oxygen chemisorbed on the surface of the catalyst, which poisons the active centers responsible for exchange [2]. It is apparent from Tables 2 and 3 that the active centers were present only on the platinum catalysts; the platinum catalysts obtained from various complexes differ not only with respect to their "overall" specific areas but also with respect to the number of active centers and their efficiency.

It has been previously shown that the oxides and salts of platinum metals do not display catalytic activity in H-D exchange [2], and prior reduction of these compounds to the metals is therefore required. However, catalytically active forms of the metal may be obtained as a result of reduction of the starting oxides or salts by the substrate during the reaction (the so-called "self-activation"). An interesting peculiarity of this method of activation is the fact that sulfur heterocycles, which poison previously reduced metals, can be thoroughly deuterated [1]. The results of H–D exchange of heterocycles in the presence of compounds of platinum metals of various types, which are reduced to the metals during the reaction, are presented in Table 4. It is apparent from Table 4 that the natures and compositions of the starting compounds have an appreciable effect on the isotope-exchange process. Upon the whole, the salts are more active than the oxides. This is associated with the fact that, first, in the case of soluble salts during "self-activation" the entire mass of the metal is reduced rather rapidly and begins to carry out exchange, while in the case of insoluble salts and oxides reduction occurs only on the surface, which affects the rate of exchange; second, HCl is formed in the reduction of metals from the chlorides, in connection with which, in addition to isotope exchange of the heterocycles on the metal surface, electrophilic replacement of hydrogen by deuterium may also occur. It is precisely owing to the second effect that such intensive deuteration of 3-methylbenzothiophene occurs in the presence of complex 1 (Table 4). It should be noted that the resistance of the starting complexes to reduction affects the H–D exchange. This is confirmed in the case of H-D exchange in the presence of compounds 1-4 (Table 4), which are arranged in the order 1 > 2 ~ 3 > 4 with respect to solubilities and in the order 2 > 3 > 4 > 1 with respect to their resistances to reduction.

One should note the fact of the exchange of 3-methylbenzothiophene with D_2O on platinum(II) dioxide (Table 4). As we have already noted, sulfur compounds, particularly benzothiophenes [1], poison the surface of platinum and do not participate in H–D exchange. It is evident that in the case of "self-activation" the reduced platinum is poisoned by 3-methylbenzothiophene. In this case one may propose a scheme that reflects the simultaneous occurrence of two processes, viz., isotope exchange and oxidation–reduction:

TABLE 3. Isotope Exchange of Benzofuran with D_2O on Platinum Blacks Obtained from Various Complexes (T_{exptl} 120°C)*

No.	Pt obtained from complex	Time of experiment, h	Deuterium distribution, %			ΣD_i, %
1	1	4	89	8	3	11
2	1	8	82	16	2	18
3	2	15	68	28	4	32
4	3	15	71	25	4	29
5	4	15	99	1		1
6	1	20	50	43	7	50

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*D_∞ 100%.

TABLE 4. H–D Exchange of Organic Compounds on "Self-Activated" Catalysts*

No.	Catalyst	Substance	Deuterium distribution, %				ΣD_i, %
			D_0	D_1	D_2	D_3	
1	Complex 1	Benzofuran	42	46	12	1	58
2	,, 2	,,	98	2			2
3	,, 4	,,	100				0
4	,, 3	,,	86	12	2		14
5	$PdCl_2$	,,	92	8			8
6	$PhCl_3 \cdot 4H_2O$	,,	81	19			19
7	$PtO_2 \cdot 2H_2O$	,,	95	5			5
8	PdO	,,	99	1			1
9	$Ph_2O_3 \cdot 5H_2O$	,,	97	3			3
10	$PtO_2 \cdot 2H_2O$	3-Methylbenzothiophene	89	11			11
11	K_2PtCl_4	,,	26	62	12		74

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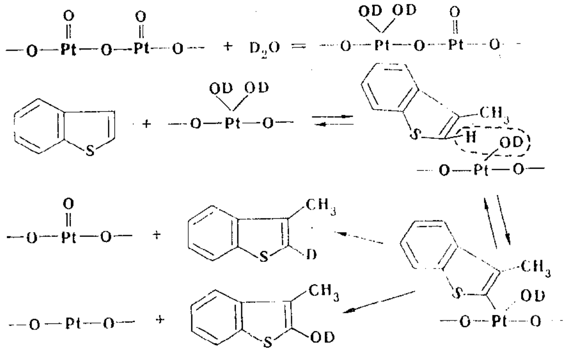
*Experimental conditions: for Nos. 1-4: 120°C, 12 h, on the basis of 0.03 g of the metal; for Nos. 5-8: 130°C, 10 h, on the basis of 0.03 g of the metal; for No. 9: 130°C, 6 h, on the basis of 0.03 g of the metal; for No. 10: 130°C, 20 h, on the basis of 0.038 g of the catalyst; for No. 11: 130°C, 20 h, on the basis of 0.11 g of the catalyst (D_∞ 100%).



EXPERIMENTAL

The chromatographic mass spectra were recorded with a Varian MAT-44S spectrometer at an ionizing-electron energy of 70 eV and an ionization-chamber temperature of 180°C. A 25-m long glass capillary column with an inner diameter of 0.25 mm packed with FFAP as the stationary phase was used for chromatographic separation. The chromatographic column made it possible to isolate the investigated substance and to record its mass spectrum three to five times at the chromatographic peak. The percentage of deuterium was calculated with a correction for the monoisotope effect, which was calculated from the mass spectrum of the unlabeled compound.

The catalyst surfaces were investigated by an exchange method and by EPR spectroscopy [2, 3].

The 1,4-benzodioxane, benzofuran, and 3-methylbenzothiophene were synthesized by the methods in [4-6]. Complexes 1-4 were prepared by the methods in [7-10]. The platinum black was obtained by the method in [11]. The charcoal was prepared by the method in [12].

In our research we used an aluminum silicate catalyst (Ufimsk Plant) with the following composition: 11.0% Al_2O_3, 88.0% SiO_2, 0.1% Fe_2O_3, 0.3% Na_2O, 0.6% CaO, and traces of MgO. According to the results of emission spectroscopy, the industrial-grade aluminum oxide had the following impurities (in percent): 0.001-0.002 Fe, 0.003-0.005 Si, 0.01 Ga, 0.001 Mn, 0.002-0.003 Cu, 0.1-0.5 Ca, and 0.05 Mg, and 0.1 Na. Analysis for fluorine and chlorine showed that these elements were absent in the catalysts. The NdNaX (0.98)* was synthesized by ion exchange.

Catalytic H-D Exchange. The reagents were placed in ampuls, and the ampuls were degassed by three freezing-thawing cycles at 77°K at a pressure of $5 \cdot 10^{-2}$ mm (mercury column), after which they were sealed. A typical experiment under heterogeneous conditions consisted in heating the catalyst with the organic compound (8.3 mmole) and D_2O (50 mmole, isotopic purity 99.8%) in the evacuated ampuls with shaking in a thermostat at 140°C for 30 h. The percentages and positions of the deuterium in the exchange products were determined by chromatographic mass spectrometry.

LITERATURE CITED

1. É. A. Karakhanov and A. G. Dedov, Khim. Geterotsikl. Soedin., No. 8, 1011 (1982).
2. É. A. Karakhanov, A. G. Dedov, and E. V. Lunina, Dokl. Akad. Nauk SSSR, 254, 400 (1980).
3. V. V. Berentsveig and I. I. Kulakova, Methodical Developments for a Practical Course in Organic Catalysis [in Russian], Izd. MGU, Moscow (1977), p. 34.
4. R. Putter, in: Methode der Organischen Chemie, Vol. 10/3, Houben-Weyl (1965), p. 7.
5. A. A. Mndzhoyan and A. A. Aroyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 14, 591 (1961).
6. E. G. G. Werner, Rec. Trav. Chim., 68, 509 (1949).
7. Handbook of Syntheses of Complexes of Metals of the Platinum Group [Russian translation], Mir, Moscow (1964).
8. N. A. Ezerskaya, I. N. Kiseleva, and B. V. Zhadanov, Zh. Neorg. Khim., 15, 1046 (1970).
9. D. H. Busch and J. C. Bailar, J. Am. Chem. Soc., 78, 716 (1956).
10. I. I. Chernyaev and A. I. Fedorova, Izv. Sektora Platiny Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 8, 74 (1931).
11. É. A. Karakhanov, A. G. Dedov, and E. A. Viktorova, Vestn. Mosk. Gos. Univ., Khimiya, No. 2, 215 (1977).
12. L. Yu. Brezhnev, Master's Dissertation, Moscow State University, Moscow (1982).

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*The NdNaX (0.98) was kindly furnished by Ya. I. Isakov.