LITERATURE CITED

1. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 9, 1195 (1981).
2. H. Kirner and R. Wizinger, Helv. Chim. Acta, 44, 1768, 1773 (1961).
3. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 903 (1980).
4. G. G. Dyadyusha, A. A. Ishchenko, N. A. Derevyanko, and A. I. Tolmachev, Dokl. Akad. Nauk Ukr. SSR, Ser. B, No. 1, 58 (1981).
5. R. Thummel and D. Kohli, J. Org. Chem., 42, 2742 (1977).
6. C. F. H. Allen and H. R. Sallans, Can. J. Res., 9, 574 (1933); C., 1934 (II), 1926.

HYDROGENATION OF OXYGEN-CONTAINING HETEROCYCLIC COMPOUNDS ON GROUP VIII METALS

É. A. Karakhanov, A. G. Dedov,
and A. S. Loktev

UDC 542.941.7:547.728'722:541.128.1

The hydrogenation of a number of oxygen-containing heterocyclic compounds on Pt, Pd, and Rh blacks in the liquid phase at atmospheric pressure was investigated. The results are compared with data on H–D exchange with D_2O and are interpreted from the point of view of the theory of π-complex adsorption.

We have previously reported the hydrogenation and H–D exchange of benzofuran and its alkyl derivatives on group VIII metals [1-3]. In the present research we investigated the hydrogenation of a number of oxygen-containing heterocycles under mild conditions in the presence of Pt, Pd, and Rh blacks. The results are presented in Tables 1 and 2.

It is apparent from Table 1 that the reaction proceeded selectively in the hydrogenation of benzofuran in the presence of Pd and Rh: the C_2–C_3 bond was hydrogenated to give 2,3-dihydrobenzofuran. In addition to this process, hydrogenolysis of the O–C_2 bond occurred in the presence of Pt. As a result, phenols are present along with 2,3-dihydrobenzofuran in the reaction products. With respect to their activity* in the investigated reaction the metals can be arranged in the order Pd > Rh > Pt. It should be noted that the most active catalyst, viz., Pd, upon storage in air retains approximately the same activity for 10 days after its preparation; its activity decreases only after this period. When Pd upon which hydrogenation has already been accomplished was used again, the activity of the catalyst was also quite high in the hydrogenation of benzofuran (Table 1).

With respect to their reactivities in hydrogenation (see Table 2) the investigated benzofurans can be arranged in the order benzofuran > 2-methylbenzofuran > 2-ethylbenzofuran > 2-propylbenzofuran. Thus alkyl substituents retard the hydrogenation of benzofurans on Pd, evidently due to steric hindrance vis-à-vis π-complex adsorption. It is apparent from Table 2 that the nature of the substituent in the heteroring also affects the rate of hydrogenation.

The results obtained in a study of H–D exchange of the investigated heterocycles [2, 3] make it possible to explain the principles of hydrogenation of these compounds and to examine them from the point of view of the theory of π-complex adsorption [4], according to which the first step in the catalytic reaction of aromatic and unsaturated compounds on transition metals is the formation of a surface π complex. In the case of complex molecules their various fragments may make different contributions to the interaction with the catalyst [2, 3, 5], which affects the orientation of the molecule on the surface and the reaction pathway as a

---

*By activity here we have in mind the amount of hydrogen absorbed per unit time at the start of the reaction relative to the area of the catalyst.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No.10, pp. 1332-1334, October, 1981. Original article submitted March 3, 1981.

0009-3122/81/1710-0993$07.50

TABLE 1. Results of the Hydrogenation of Benzofuran on Group VIII Metals for an Experimental Time of 3 h with 9.3 mmole of the Substrate and 0.05 g of the Catalyst

Catalyst	t, °C	Activity, $\frac{\Delta V_0}{\Delta t_0}/S$, ml/min-m^2	Composition of the reaction mixture, %		
			benzofuran	2,3-dihydrobenzofuran	phenols
Pt	60	2,25	51	40	9
Pt	50	1,75	63	29	8
Pt	40	1,00	78	16	6
Pt	30	1,25	77	19	4
Rh	70	4,45	66	34	0
Rh	65	4,45	67	33	0
Rh	60	4,88	62	38	0
Rh	55	3,56	73	27	0
Rh	50	5,11	54	46	0
Rh	45	2,22	60	40	0
Rh	40	3,11	58	42	0
Rh	35	4,00	61	39	0
Rh	30	2,66	59	41	0
Pd	65	4,70	17	83	0
Pd	60	5,75	9	91	0
Pd	55	5,89	7	93	0
Pd	50	7,86	3	97	0
Pd	45	4,94	8	92	0
Pd	40	5,41	9	91	0
Pd	35	5,65	10	90	0
Pd	30	3,76	25	75	0
Pd*	50		30	70	0

---

*The Pd was taken from previous experiments on the hydrogenation of benzofuran and was washed with ether and dried; the experimental time was 5 h.

TABLE 2. Results of the Hydrogenation of Heterocyclic Compounds on Pd*

No.	Compound	Activity, $\frac{\Delta V_0}{\Delta t_0}/S$, ml/min-m^2	Conversion, %	Reaction product
1	Benzofuran	5.43	100	2,3-Dihydrobenzofuran
2	2-Methylbenzofuran	1.85	22	2-Methyl-2,3-dihydrobenzofuran
3	2-Ethylbenzofuran	0.65	33	2-Ethyl-2,3-dihydrobenzofuran
4	2-Propylbenzofuran	0.11	5	2-Propyl-2,3-dihydrobenzofuran
5	2-Acetylbenzofuran	0.80	5	2-Ethylbenzofuran
6	Silvan (2-methylfuran)	1.00	10	Dihydrosilvan
7	2,3-Dihydrobenzofuran	0.09	1	Octahydrobenzofuran
8	2-Methyl-2,3-dihydrobenzofuran	0.04	3	2-Methyloctahydrobenzofuran
9	Coumarin (1,2-benzopyrone)	2.35	83	Dihydrocoumarin
10	Benzene	0	0	—

---

*A 0.05-g sample of Pd was used, and the reaction temperature was 50°C; the reaction time was 3 h, in experiments Nos. 1-4 and 7-10 and 2 h in experiments Nos. 5 and 6. An 8.3-mmole sample of the substrate was used in experiments Nos. 4-10, 7.4 mmole of the substrate was used in experiment No. 1, 4.15 mmole of the substrate was used in experiment No. 2, and 5.1 mmole of the substrate was used in experiment No. 3.

whole [1-3, 5]. Thus when benzofuran is oriented in such a way that the O, C_2, and C_3 atoms are closer to the surface (with C_2 closer to the surface than C_3), the heteroring is hydrogenated to give the 2,3-dihydro derivative due to interaction of the electrons of the heteroatom and the π electrons of the C_2—C_3 bond with the metal surface [2].

The presence of alkyl substituents in the 2 position of the heteroring interferes with the described interaction, thereby hindering the hydrogenation of 2-alkylbenzofurans (Table 2). It is interesting to note that only a dihydro derivative is formed in the hydrogenation of silvan (2-methylfuran) on Pd (see Table 2); this can be similarly explained.

In contrast to benzofurans, the benzene ring is closer to the surface of the catalyst in the case of 2,3-dihydrobenzofurans during π-complex adsorption [2]. This orientation should promote the hydrogenation of 2,3-dihydrobenzofurans to give their hexahydro derivatives, which was also observed on Pt [1]. However, virtually no hydrogenation of 2,3-dihydrobenzofurans and benzene is observed on Pd (see Table 2).

In the case of 2-acetylbenzofuran the presence in the 2 position of an electron-acceptor aceteyl group, in addition to the creation of 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. As a result of all of these factors, the 2-acetylbenzofuran molecule interacts with the catalyst surface in the same way as 2,3-dihydrobenzofuran. 2-Acetylbenzofuran undergoes only a small degree of hydrogenation, and only 2-ethylbenzofuran is present in the reaction products.

This reasoning is confirmed by the results of hydrogenation of coumarin (Table 2), which undergoes hydrogenation to a lesser extent than benzofuran but to a greater extent than 2-acetylbenzofuran.

EXPERIMENTAL

Hydrogenation was carried out at atmospheric pressure in a thermostatted long-necked hydrogenation flask; the rate of oscillation was 500-600 oscillations/min at 30 to 70°C. The starting composition of the reaction mixture was as follows: 0.05 g of the metal, 8.3-9.3 mmole of the substrate, and 1 ml of absolute ethanol. Prior to introduction of the substrate, the catalyst was activated with hydrogen in a long-necked hydrogenation flask at 30°C for 1 h.

Analysis was carried out by gas-liquid chromatography (GLC) with a column (h = 3000 mm, d = 4 mm) filled with 10% PEG-20000 on Chromosorb W (80-100 mesh) and by chromatographic mass spectrometry with a Varian Mat-111 (Gnom) apparatus at 50°C and an ionization energy of 80 eV.

The catalysts were prepared in the following way. Sodium borohydride was added in small portions to a solution of $RhCl_3 \cdot 3H_2O$, K_2PtCl_4, or Na_2PdCl_4 or a suspension of $PdCl_2$ in distilled water until vigorous hydrogen evolution characterized by pronounced foaming ceased. Another small portion of $NaBH_4$ was then added, and the mixture was allowed to stand for 2-3 h. It was then diluted to twice its original volume with distilled water and heated at 70°C for 30 min to hydrolyze the excess $NaBH_4$. The resulting mixture was washed with distilled water until the washings had pH 7 with respect to a universal indicator, after which it was washed with acetone and ether and air dried.

The specific areas of the metal blacks obtained were determined by a volumetric method at constant pressure [6] and were found to be 16 m^2/g for Pt, 19 m^2/g for Pd, and 9 m^2/h for Rh.

LITERATURE CITED

1. É. A. Karakhanov, A. G. Dedov, I. I. Pakhomova, L. G. Saginova, and E. A. Viktorova, Vestn. Mok. Gos. Univ., Ser. Khim., No. 3, 334 (1977).
2. É. A. Karakhanov, A. G. Dedov, and P. A. Sharbatyan, Proceedings of the 4th Soviet-French Seminar on Catalysis [in Russian], Tbilisi (1978), p. 168.
3. É. A. Karakhanov, A. G. Dedov, A. L. Kurts, and A. S. Loktev, Khim. Geterotsikl. Soedin., No. 4, 451 (1981).
4. D. L. Garnett and V. A. Sollich-Baumgartner, Catalysis [Russian translation], Mir, Moscow (1968), p. 100.
5. É. A. Karakhanov, A. G. Dedov, A. L. Kurts, and Yu. N. Luzikov, Dokl. Akad. Nauk SSSR, 256, 1397 (1981).
6. V. V. Berentsveig and I. I. Kulakova, Methodical Developments for a Practical Course in Organic Catalysis [in Russian], Izd. MGU, Moscow (1977), p. 34.