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Abstract

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DEUTERIUM EXCHANGE OF CYCLOPENTANE OVER EVAPORATED METALLIC CATALYSTS

In our previous works, considering the reactions of isotopic exchange of cyclohexane (^{1}, ^{2}) and cyclobutane (^{3}) with deuterium, we found that the nature of the distribution of the products of deuterium exchange of cycloalkanes depends substantially on the presence or absence of structural correspondence between these compounds and the catalyst. This was expressed in the fact that an intermediate maximum on the distribution curve, corresponding to exchange of half of the hydrogen atoms in the molecule, was observed only in the deuterium exchange of cyclohexane over metals crystallizing in a face-centered cubic lattice with interatomic distances from 2.7746 Å (Pt) to 2.4916 Å (Ni). In the other cases studied, such an intermediate maximum was absent.

In the present work we turned to consideration of the deuterium exchange of cyclopentane. This reaction had previously been studied by Anderson and Kemball (^{4}) and by Berel' and co-workers (^{5}). However, in their work only Pd and Rh were used as catalysts; these have the same crystal lattice and, according to the structural concepts of the multiplet theory, should behave similarly in the deuterium exchange of cycloalkanes. It seemed of interest to compare the behavior of various metallic catalysts in this reaction, in particular in connection with the fact discovered by B. A. Kazanskii and co-workers (^{6}) of the substantially different behavior of Pt, Pd, and Ni in the catalytic hydrogenolysis of cyclopentane.

The metallic catalysts used by us were films evaporated in vacuum. The purity of the initial cyclopentane was checked by gas chromatography. Deuterium (98% D) was purified by passage through a diffusion nickel lamp. The ratio of the reactants in the initial mixture was $D_2 : C_5H_{10}$ 60 : 1. The analysis of the deuterium-exchange products was carried out mass-spectrometrically on an MI-1305 instrument with an SI-01 ion counter. The ionizing voltage was 20 V.

Table 1 presents the main results, showing the distribution of the different products of deuterium exchange over Pt, Pd, Ni, W, Mo, and Fe at temperatures from 0 to 177°. All data correspond to degrees of conversion up to 30%.

From the data of Table 1 it is seen that an intermediate maximum, corresponding to exchange of half of the hydrogen atoms in the cyclopentane molecule, is observed only when using metals crystallizing in a face-centered cubic lattice (type A1). For the other metals, crystallizing in a body-centered lattice (type A2), either there are no intermediate maxima at all, or a small maximum corresponding to mass number 76 is observed, the origin of which will be considered below. We believe that the presence of an intermediate maximum corresponding to exchange of half of the hydrogen atoms in a cycloalkane molecule may indicate the presence of structural correspondence between this cycloalkane and the catalyst and a planar orientation of the molecule upon adsorption on the surface (7). Earlier (1) we had already expressed the supposition that the presence of structural correspondence between five-membered ring and metals with a lattice of the A1 type, on whose surface there are regular hexagons, can be explained by the doublet–sextet mechanism of the cyclopentane reaction, which was developed by B. A. Kazanskii, A. L. Liberman, and A. F. Plate (8). According to this mechanism, cyclopentane can adsorb flat on the surface of metals with a lattice of the A1 type through deformation of one of the C–C bonds. It may be assumed that, at a sufficiently high temperature, such adsorption leads to hydrogenolysis of cyclopentane, while under the conditions of our experiments, where the temperature is relatively low, it leads to exchange of hydrogen atoms

Table 1

Distribution of the products of deuterium exchange of cyclopentane

Catalyst	Temp., °C	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$	$C_5H_5D_5$	$C_5H_4D_6$	$C_5H_3D_7$	$C_5H_2D_8$	C_5HD_9	C_5D_{10}	Exp. no.
Pt	0	10.84	15.93	8.26	7.99	38.53	6.62	3.23	1.92	2.03	4.61	1
Pt	61	5.78	4.18	3.84	4.52	29.90	8.30	5.56	5.90	9.39	22.62	2
Pt	128	4.61	1.23	1.57	3.32	8.87	4.51	4.65	9.82	22.30	36.46	3
Pd	149	2.82	0.48	0.32	1.21	8.13	1.61	1.29	6.63	14.90	62.64	4
Pd	164	6.90	1.18	0.39	1.58	4.93	1.97	0.99	4.73	11.44	65.88	5
Ni	0	35.78	40.58	10.54	4.90	5.11	1.17	0.85	0.64	0.21	0.21	6
Ni	58	11.63	7.67	3.65	6.02	10.65	7.93	9.20	10.25	14.84	18.10	7
Ni	174	5.90	4.46	3.65	3.72	4.17	3.10	3.43	7.77	20.36	43.44	8
W	0	2.03	1.19	0.94	0.96	0.96	1.70	1.39	4.13	20.48	66.22	9
W	146	2.05	1.61	1.31	1.22	1.09	1.43	1.83	8.28	27.68	53.50	10
Fe	71	19.25	12.37	6.88	6.24	5.70	2.58	1.83	3.23	6.24	35.70	11
Fe	110	24.43	8.40	4.20	3.82	3.82	3.44	2.67	3.44	4.96	40.84	12
Fe	177	7.34	7.34	5.05	4.59	4.59	4.59	3.67	4.59	11.01	47.25	13
Mo	0	2.13	1.15	0.74	0.67	0.74	1.72	0.88	4.78	20.37	66.82	14
Mo	41	2.19	1.20	0.83	0.85	0.88	1.60	0.98	6.92	22.58	61.97	15
Mo	100	2.63	1.36	1.05	1.05	1.03	1.20	1.32	6.15	25.53	58.64	16
Mo	155	3.23	1.84	1.66	1.82	2.02	2.95	3.57	10.38	25.89	46.65	17

with deuterium, which requires a considerably lower activation energy. On the surface of W, Mo, and Fe the exchange proceeds, as in the case of cyclohexane, probably by a doublet mechanism. Indirect confirmation of this assumption is provided by the fact that, when the reaction is carried out over W and Mo at low temperatures, a small intermediate maximum forms on the distribution curve, corresponding to mass number 76 (D_6 in experiments nos. 9, 14, and 15, Table 1). We associate the presence of this maximum with the formation of cyclopentene and its complete deuterium exchange to C_5D_8 (it is known that unsaturated hydrocarbons undergo exchange considerably faster than the corresponding saturated ones ([9], [10])). Dehydrogenation of cyclopentane to cyclopentene has previously been observed on oxide catalysts ([11]): it is a doublet reaction. At the same time, doublet reactions of five-membered rings are known when metals are used as catalysts ([12]).

Hydrogenolysis of cyclopentane under the conditions of our experiments was very slight. The most intensive hydrogenolysis was observed when the reaction was carried out over Ni at 174° and over Mo at 155°. In these experiments, the total content of products with mass numbers from 81 to 84, which correspond to *n*-pentane with 11–12 D atoms in the molecule, reached 1.27 and 2.44%, respectively, in 30 min. In the remaining cases, the amounts of highly deuterated *n*-pentanes lay within the limits of analytical accuracy.

Noteworthy is the fact that the relative heights of the intermediate maxima in the deuterium exchange of cyclopentane (Table 2) are considerably greater than the corresponding values for cyclohexane*. It may

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may be connected with the fact that the structure of the cyclopentane molecule is considerably closer to planar than the cyclohexane molecule, which has a rather complex configuration. In accordance with this, "straightening" the cyclopentane molecule on the catalyst surface apparently requires less energy than straightening cyclohexane, and the probability of a planar orientation for cyclopentane is considerably higher than for cyclohexane. As stated above, in our opinion only the planar orientation of a cycloalkane on the surface leads to the formation of an intermediate maximum in the middle of the distribution curve, since only in such an arrangement is simultaneous exchange of all hydrogen atoms on one side of the plane of the ring possible.

Table 2

Relative heights of the intermediate maximum

$$h = \frac{D_5}{{}^1/_2(D_4 + D_6)}$$

Catalyst	Temp., °C	h	Catalyst	Temp., °C	h
Pt	0	5.27	Pd	149	5.77
Pt	61	4.66	Pd	164	2.77
Pt	128	2.52	Ni	0	1.63
			Ni	58	1.52
			Ni	174	1.22

Let us now consider the regularities in the change of the character of deuteroexchange in the series Pt, Pd, Ni in connection with the fact discovered by B. A. Kazanskii and co-workers, namely that platinum selectively carries out hydrogenolysis of cyclopentane, causing cleavage of only one C—C bond, palladium does not catalyze this reaction, and nickel leads to complete cracking of cyclopentane. Earlier we proposed (1) that in deuteroexchange of cyclohexane over Pt, Pd, and Ni two mechanisms coexist—doublet and sextet. A similar phenomenon apparently also occurs for cyclopentane. From the data of Table 2 it is seen that the doublet-sextet mechanism is represented on Pt and Pd to a considerably greater extent than on Ni. On Ni, correspondingly, the doublet mechanism, requiring edgewise orientation (7), plays the greater role. It is possible that the selective hydrogenolysis of one C—C bond of cyclopentane is associated with the doublet-sextet reaction, whereas the doublet reaction leads to random cleavage of bonds in the cyclopentane ring. Thus, the different character of cyclopentane adsorption, which is manifested in the change in the form of the distribution curve during deuteroexchange, evidently also leads to a different course of the reaction. At the same time, for Pt and Pd the character of cycloalkane adsorption, insofar as can be judged from the form of the distribution curve, as well as the structural features of the crystal lattice and the bond energy with cyclopentane (13), are very similar; the sharply different catalytic activity of these two metals in the reactions of hydrogenolysis of cyclopentane may be connected with some other properties of theirs, for example with the different solubility of hydrogen in them.

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