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Abstract

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HYDROGENOLYSIS AND MUTUAL INTERCONVERSIONS OF CIS- AND TRANS-1,2-DIMETHYLCYCLOPENTANES IN THE PRESENCE OF RHODIUM, OSMIUM, IRIDIUM, AND PALLADIUM CATALYSTS

Recently, we established (1) that, in the presence of platinized carbon, the stereoisomeric 1,2-dimethylcyclopentanes are converted into one another over a wide temperature range, forming an equilibrium mixture of isomers:

$$\text{cis-1,2-dimethylcyclopentane} \rightleftharpoons \text{trans-1,2-dimethylcyclopentane}$$

At the same time it was shown that, in both directions, these transformations proceed at a high rate, substantially exceeding the rate of hydrogenolysis of the cyclopentane ring.

Having established this fact for a platinum catalyst, we naturally turned to other metals of Group VIII of the periodic system. It seemed important to determine whether the above-mentioned configurational isomerization could occur on the surface of rhodium, osmium, iridium, and palladium catalysts. It was also of interest to compare—if isomerization takes place in the above cases—how rapidly this reaction proceeds on different metals and at what temperatures the mixtures obtained are at equilibrium. From the work of Kemball and co-workers (2), devoted to the mechanism of deuterium exchange of cyclopentane homologs and published in 1962, it followed that palladium and rhodium, like platinum, promote the isomerization of stereoisomeric cyclopentanes. With regard to osmium and iridium, the question remained open. The second group of questions that interested us concerned the hydrogenolysis reaction of the five-membered ring in the presence of the catalysts listed above. It is known (3) that, on the surface of platinized carbon, hydrogenolysis of cyclopentane and its homologs proceeds readily with the formation of paraffinic hydrocarbons; conversely, on palladized carbon this reaction does not occur at all (4). There is no information in the literature on the possibility of hydrogenolysis on the surface of rhodium, iridium, and osmium.

On the basis of the foregoing, in the present work we investigated, under comparable conditions, the possibility and extent of configurational isomerization for stereoisomeric 1,2-dimethylcyclopentanes in the presence of Rh, Ir, Os, and Pd deposited on activated carbon, as well as the hydrogenolysis of cyclopentane hydrocarbons in the presence of the same catalysts.

The results of these investigations, summarized in Table 1, show that cis- and trans-1,2-dimethylcyclopentanes are mutually converted into one another in the presence of all four catalysts over a broad temperature range (150–280°). It should be noted, however, that their isomerizing activity differs (Fig. 1). Thus, Rh/C is almost as active in this reaction as the previously studied Pt/C (^{1}). Conversely, among the five catalysts discussed, Ir/C is the least active catalyst.

isomerization. In this same series, Os/C and Pd/C occupy an intermediate position. It should be especially noted that, on the catalysts studied in this work, the state of equilibrium is reached from the trans form of 1,2-dimethylcyclopentane substantially faster than from the cis form (see, for example, experiments Nos. 32 and 35 on Pd/C, Nos. 42 and 45 on Ir/C, Nos. 50 and 55 on Os/C, and Nos. 64 and 68 on Rh/C).

Table 1

Dependence of the composition of trans- and cis-1,2-dimethylcyclopentane catalyzates on the nature of the catalyst and the temperature of the experiments

Experiment No.	Catalyst	Temperature, °C	n_D^{20} of catalyzate	trans-isomer, %	cis-isomer, %	Hydrogenolysis products C_7, %	Hydrogenolysis products C_6, %	Ratio (cis):(trans) in catalyzate	Calculated equilibrium constant K_p
trans-1,2-dimethylcyclopentane									
33	Pd/C	150	1.4125	97.5	2.5	no	no	0.03	0.121
32	Pd/C	200	1.4135	89.0	11.0	»	»	0.13	0.150
34	Pd/C	255	1.4140	81.1	18.9	»	»	0.23	0.180
38	Pd/C	255	1.4137	83.6	16.4	»	»	0.20	0.180
43	Ir/C	150	1.4129	96.1	3.9	»	»	0.04	0.121
42	Ir/C	200	1.4130	89.7	8.2	2.1	»	0.09	0.150
44	Ir/C	255	1.4116	80.7	12.7	6.6	»	0.16	0.180
48	Ir/C	255	1.4117	78.9	12.9	8.2	»	0.16	0.180
49	Ir/C	280	1.4106	74.4	13.9	10.5	1.2	0.19	0.195
51	Os/C	150	1.4115	93.4	3.5	3.1	no	0.04	0.121
50	Os/C	200	1.4113	82.6	10.1	6.1	1.1	0.12	0.150
53	Os/C	255	1.4108	75.5	14.3	8.2	2.0	0.19	0.180
58	Os/C	255	1.4097	76.8	11.6	9.3	2.3	0.15	0.180
59	Os/C	290	1.4107	79.4	12.9	6.3	1.4	0.16	0.201
61	Rh/C	150	1.4120	100	no	no	no	–	0.121
68	Rh/C	150	1.4129	91.2	8.8	traces	»	0.10	0.121
60	Rh/C	200	1.4059	61.6	10.8	27.5	»	0.18	0.150

Experiment No.	Catalyst	Temperature, °C	n_D^{20} of catalyzate	trans-isomer, %	cis-isomer, %	Hydrogenolysis products C_7, %	Hydrogenolysis products C_6, %	Ratio (cis):(trans) in catalyzate	Calculated equilibrium constant K_p
62	Rh/C	255	1.4013	43.6	8.8	41.4	6.2	0.20	0.180
66	Rh/C	255	1.4008	40.2	8.5	43.3	8.0	0.21	0.180
67	Rh/C	280	1.4012	43.0	8.5	36.3	12.1	0.20	0.195
cis-1,2-dimethylcyclopentane									
36	Pd/C	150	1.4206	16.9	83.1	no	no	4.92	0.121
35	Pd/C	200	1.4161	63.1	36.9	»	»	0.59	0.150
37	Pd/C	255	1.4138	80.5	19.5	»	»	0.24	0.180
46	Ir/C	150	1.4211	14.6	85.4	»	»	5.85	0.121
45	Ir/C	200	1.4180	36.6	61.6	1.8	»	1.68	0.150
47	Ir/C	255	1.4160	53.9	37.9	6.1	»	0.70	0.180
49	Ir/C	290	1.4117	63.2	24.9	10.3	1.0	0.39	0.201
55	Os/C	150	1.4178	21.9	72.8	4.9	0.4	3.32	0.121
54	Os/C	200	1.4130	46.5	40.9	10.7	1.9	0.88	0.150
56	Os/C	255	1.4121	58.9	31.5	7.2	2.4	0.53	0.180
57	Os/C	280	1.4133	58.9	34.0	5.2	1.9	0.58	0.195
64	Rh/C	150	1.4142	74.9	25.1	no	no	0.34	0.121
63	Rh/C	200	1.4102	71.6	14.6	13.8	»	0.20	0.150
65	Rh/C	255	1.4018	42.2	9.4	40.0	7.4	0.22	0.180
69	Rh/C	280	1.4021	43.2	10.4	36.7	9.7	0.24	0.195

This is probably determined by the fact that the thermodynamic equilibrium of these two stereoisomeric forms in the temperature range studied is strongly shifted toward trans-1,2-dimethylcyclopentane.

The isomerization of the stereoisomers on each of the catalysts was carried out in a flow system in a stream of hydrogen. Simultaneously with isomerization, hydrogenolysis of 1,2-dimethylcyclopentane also occurred on the iridium, osmium, and rhodium catalysts, with formation of the corresponding paraffinic hydrocarbons of composition C_7 and comparatively small amounts of paraffins of lower molecular weight. On Pd/C, in agreement with the data of Kazanskii and Areshidze$^{(4)}$, hydrogenolysis of 1,2-dimethylcyclopentane does not occur. The rates of hydrogenolysis of this hydrocarbon on Ir/C, Os/C, Rh/C, and the previously studied Pt/C differ markedly. In the range 150–280°, the most active hydrogenolysis catalyst proved to be Rh/C. The Ir/C and Os/C catalysts are substantially less active in this reaction. Thus, at 255°, trans-1,2-dimethylcyclopentane underwent hydrogenolysis on Rh/C, Os/C, and Ir/C by 51, 11, and 8%, respectively (experiments Nos. 66, 58, and 48). It should be noted that in this reaction also each of the catalysts studied possesses a certain specificity. For example, on Rh/C the reaction proceeds with a high temperature coefficient (Fig. 2); moreover, on this catalyst (as also on Os/C) the secondary conversion of the formed isoheptanes into hydrocarbons of composition C_6 and even C_5 proceeds to an appreciable extent. The appearance of isohexanes in the catalyzate may be explained by the following scheme:

(Figure: reaction scheme: conversion of dimethylcyclopentane through heptane isomers to methylcyclopentane and lower hydrocarbons, with formation of n-C_7H_{16} and i-C_6H_{14})

All the hydrocarbons shown in this scheme were identified in the catalyzates by gas-liquid chromatography. Among the hydrocarbons of composition C_6, 2,3-dimethylbutane has the highest content. It is interesting to note that on Os/C the yield of hydrogenolysis products passes through a maximum with increasing temperature* (see Fig. 2). The reason for this phenomenon is not yet clear, but in any case it is not connected with poisoning of the catalyst, which was checked by special experiments. On Ir/C the hydrogenolysis of 1,2-dimethylcyclopentane in the temperature range studied proceeds to approximately the same extent as on Os/C. However, cracking of the isoheptanes formed on Ir/C proceeds to a quite insignificant extent (experiments Nos. 48 and 49), which makes this catalyst, in its selective action, closer to Pt/C, on which we did not observe any appreciable cracking.

(Figure: Figure 1)

Fig. 1. Change in the ratio of the cis and trans isomers of 1,2-dimethylcyclopentane as a function of temperature on various Group VIII metals

It is interesting that in the catalyzates of 1,2-dimethylcyclopentane on all catalysts, including Pt/C, along with the hydrogenolysis products, methylcyclopentane was detected, the amount of which increased with the temperature of the experiments. Apparently, this fact indicates the possibility of some additional strain along the C_{ring}—$\mathrm{C}_{\text{alkyl}}$ bond arising upon adsorption of the initial molecule on the catalyst surface, as a result of which this bond undergoes hydrogenolysis. This seems all the more probable since the formation of cyclopentane during the hydrogenolysis of methylcyclopentane on Pt/C is practically not observed (3).

(Figure: Figure 2)

Fig. 2. Dependence of the yield of products of hydrogenolysis of trans-1,2-dimethylcyclopentane on temperature on various Group VIII metals

The results obtained, summarized in Table 1 and presented in Fig. 2, demonstrate a substantial difference in the behavior of the catalysts studied with respect to the hydrogenolysis reaction of the pentamethylene ring. Nevertheless, the ratio of the rates of the isomerization and hydrogenolysis reactions, previously found for Pt/C, is preserved here as well: the rate of isomerization in all the cases studied substantially exceeds the rate of hydrogenolysis.

The presence in the catalyzates obtained from 1,2-dimethylcyclopentanes on Rh/C and Os/C of relatively large amounts of isohexanes, as well as methylcyclopentane, shows that on these catalysts hydrogenolysis of any C–C bonds is readily accomplished, and not only in the five-membered ring, as on Pt/C. Consequently, the mechanism of the reaction under discussion on the first two catalysts must differ from the mechanism of hydrogenolysis of cyclopentanes on platinum, which is possible only according to the sextet-doublet scheme (^{5}).

* A similar picture is observed on the surface of the same catalyst also in the hydrogenolysis of cyclopentane.

Obviously, hydrogenolysis of cyclopentanes on Os/C and Rh/C can also proceed according to the usual doublet scheme.

As for the mechanism of configurational isomerization, we still do not have sufficient data for any definite conclusions. However, it seems to us that this reaction can most probably proceed either by a dissociative mechanism through a "semi-dehydrogenated" state, or through a transition complex on the catalyst surface by an associative mechanism formally similar to the Walden S_N2 inversion. In accordance with the latter mechanism, the molecule of the dialkylcyclopentane undergoes edgewise adsorption and reacts with atomic hydrogen, also adsorbed on the surface, for example:

(Figure: reaction scheme: three cyclopentane structures on a catalyst surface with arrows between them)

The considerations presented above concerning the mechanisms of the reactions studied in this work deserve further discussion.

Experimental Part

Starting hydrocarbons. The synthesis and constants of the stereoisomeric 1,2-dimethylcyclopentanes used in the work were described by us earlier (^{1}).

Catalysts. The Ir/C, Os/C, Rh/C, and Pd/C catalysts were prepared by the method of N. D. Zelinskii and M. B. Turova-Polyak (^{6}), by reduction of the corresponding salts with formalin; they contained 20% metal by weight.

Experimental procedure. The experiments were carried out in a flow system over 5-ml portions of catalyst. The hydrocarbon was passed over the catalyst in a stream of hydrogen (hydrogen flow rate at the outlet of the system ~ 1 liter/hour) at an approximately constant volumetric rate (0.2 hr^{-1}). The duration of each experiment was 1.5 hours; the catalyzate collected during the first hour was discarded in order to eliminate the influence of hydrogen adsorbed on the catalyst and of catalyzate residues from the preceding experiment; the catalyzate collected during the last 30 min was analyzed. The catalyzates were analyzed by gas–liquid chromatography on the SKB chromatograph of the Institute of Organic Chemistry, Academy of Sciences of the USSR, in a stream of helium at 80° on a four-meter column packed with diatomaceous brick coated with 20% PFMS-4 silicone oil. Detailed separation of the paraffin portion of the catalyzate was carried out on a capillary chromatograph with a flame-ionization detector, using a copper capillary 50 m long; dioctyl sebacate was used as the liquid phase. The results of all experiments are summarized in Table 1.

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