CHEMISTRY

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1964

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

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HYDROGENOLYSIS OF CYCLOHEXANE WITH FORMATION OF *n*-HEXANE AT ATMOSPHERIC PRESSURE

Hydrogenolysis of cyclanes with formation of open-chain hydrocarbons in the presence of Group VIII metals as catalysts has long attracted considerable attention. First of all, such hydrogenolysis was observed for small rings—cyclopropane ([1]) and cyclobutane ([2]). This reaction proceeds on platinum, palladium, and nickel catalysts. In 1933 it was found that, in the presence of platinum and nickel, cyclopentane can undergo hydrogenolysis ([3],[4]); on palladium this reaction does not proceed. Quite recently (1960–1963) it was shown that hydrocarbons with rings from seven- to twelve-membered ([5]) can also undergo hydrogenolysis, likewise on platinum and nickel. Hydrogenolysis of all the above-mentioned rings proceeds at atmospheric pressure and at temperatures from 50 to 320°, depending on the nature of the ring. The only exception is the six-membered ring. It is true that hydrogenolysis of cyclohexane to *n*-hexane has recently been observed on a nickel catalyst ([6]), but under substantially more severe conditions: at elevated hydrogen pressure and an even higher temperature (360°, 20 atm) than those indicated above.

Fig. 1. Chromatogram of the cyclohexane catalyzate passed over Ir/C at 270°; I —*n*-butane, II —*n*-pentane, III —*n*-hexane, IV —cyclohexane, V —benzene

The inability of cyclohexane to undergo ring opening under the action of hydrogen on one catalyst or another could be explained by competition between the reactions of hydrogenolysis and dehydrogenation to benzene. If the hydrogenolysis reaction had a significantly lower rate than dehydrogenation, or were inhibited by benzene, rupture of the six-membered ring might remain unnoticed, despite the ability of the catalyst to bring about such a reaction and despite appropriate conditions. Therefore, in order to decide conclusively whether hydrogenolysis of the six-membered ring is possible on a given catalyst, it is necessary either somehow to reduce the rate of dehydrogenation, or to use a very sensitive analytical method that makes it possible to detect hydrogenolysis products even if it proceeds to a very slight extent. On platinized carbon the first possibility

had already been investigated ([7]). As early as 1947, experiments were carried out on this catalyst with 1,1-dimethylcyclohexane, whose dehydrogenation rate is considerably lower than that of cyclohexane. However, this hydrocarbon also did not undergo hydrogenolysis at all within the limits of the analytical accuracy possible at that time. The creation—

The use of effective capillary chromatographs has now made it possible to follow the second path as well, with incomparably higher accuracy than before. Passing cyclohexane at various temperatures in the range 170–300° over platinized carbon and examining the resulting catalyzates on a chromatograph with a copper capillary of efficiency ~10,000 theoretical plates, we fully confirmed the conclusions drawn earlier. Indeed, no signs of products of cyclohexane hydrogenolysis were detected, although the method used would have made it possible to observe even 0.005% of *n*-hexane. Thus, hydrogenolysis of cyclohexane on platinized carbon does not in fact occur.

Table 1

Composition of catalyzates of cyclohexane passed over Ir/C, Rh/C, and Os/C

No.	Catalyst	Experimental temperature, °C	*n*-hexane	*n*-pentane	*n*-butane	benzene	cyclohexane
1	Ir/C	240	1.7	0.4	—	5.4	91.5
2	Ir/C	260	6.0	2.2	Traces	22.4	69.5
3	Ir/C	270	6.3	2.8	»	37.8	53.3
4	Ir/C	300	3.3	1.0	»	86.0	9.7
5	Rh/C	240	2.6	1.5	Traces	8.9	87.0
6*	Rh/C	260	4.0	3.1	~1.0	25.6	65.5
7*	Rh/C	280	3.1	2.8	~1.0	62.0	30.3
8*	Rh/C	300	1.1	1.0	Traces	84.2	13.1
9	Os/C	150	3.5	0.8	~0.5	—	95.2
10	Os/C	200	6.1	5.3	~1.5	Traces	87.1
11	Os/C	250	4.8	10.3	~5.0	19.1	60.8
12	Os/C	300	1.3	2.2	~1.0	63.3	32.2

* The catalyzate contained about 1% methylcyclopentane and 0.5% products of its hydrogenolysis—isohexanes.

At one time, two reaction mechanisms were proposed for the hydrogenolysis of cyclopentane on platinum. According to one of them (^8), the cyclopentane molecule, in the course of the reaction, is adsorbed on the catalyst by two carbon atoms, between which the bond is then broken (the doublet mechanism). Against this mechanism speaks the inability of cyclohexane and alkanes

to undergo hydrogenolysis on platinum, although they can be adsorbed in an entirely analogous manner. The second mechanism, called the sextet–doublet mechanism (⁀9), is based on the idea that, during the reaction, cyclopentane is adsorbed by all five carbon atoms in the interstices of the (111) face of the platinum lattice. With such adsorption, special strains arise in cyclopentane for steric reasons, strains that are absent in unadsorbed or doublet-adsorbed cyclopentane. It is easy to show that, with similar multiplet adsorption of cyclohexane and alkanes, such strains as in cyclopentane do not arise in them. One may think that this is precisely why they are not subjected to hydrogenolysis on this catalyst. On other catalysts, however, matters might be different. Thus, while studying the behavior of *cis*- and *trans*-1,2-dimethylcyclopentanes in the presence of certain noble metals of Group VIII (⁀10), we noticed that in the presence of osmium and rhodium on carbon (Os/C and Rh/C) not only the immediate hydrogenolysis products—heptanes—are formed, but also their lower homologs. Consequently, hydrogenolysis of alkanes takes place. This gave us grounds to suppose that on these metals hydrogenolysis of cyclopentanes may proceed not only by the sextet–doublet (⁀9), but also by the doublet mechanism (⁀8) of the multiplet theory. But if this is so, then any not-too-strongly shielded C—C bond—including those in cyclohexanes and alkanes—should acquire the ability to undergo hydrogenolysis on such catalysts. This conclusion deserved prompt verification.

In connection with the considerations given above, in the present work we decided to investigate the possibility of hydrogenolysis of cyclohexane in the presence of Os/C and Rh/C, and also, for a more complete picture, on Ir/C. The experimental conditions were the same as for platinized carbon. In the case of Ir/C and Rh/C, the catalyzate contained quite appreciable amounts of *n*-hexane and *n*-pentane (Fig. 1,

Table 1). On Os/C, the hydrogenolysis of cyclohexane proceeded still more completely: in the catalyzate obtained at 250° (Fig. 2), there was 20.1% of *n*-paraffins, namely 5% *n*-butane, 10.3% *n*-pentane, and 4.8% *n*-hexane; i.e., substantial hydrogenolysis of the *n*-hexane formed in the first instance took place. The other catalysts (Table 1), in addition to cyclohexane, *n*-hexane, and benzene, also contained relatively appreciable amounts of hydrocarbons of composition C_5 and C_4 (predominantly *n*-pentane and *n*-butane).

Fig. 2. Chromatogram of the catalyzate of cyclohexane passed over Os/C at 250°. The designations are the same as in Fig. 1.

Fig. 3. Chromatogram of the catalyzate of *n*-hexane passed over Os/C at 250°. The designations are the same as in Fig. 1.

On Rh/C the secondary hydrogenolysis reactions were manifested somewhat more weakly. It should be especially emphasized that on all three catalysts it was *n*-hexane, and not its isomers, that was the only or almost the only product of the reaction of composition C_6. This confirms its formation by direct hydrogenolysis of the six-membered ring. We believe that hydrogenolysis here

proceeds according to a doublet scheme.

Table 2

	n-Hexane	*n*-Hexane	Cyclohexane	Cyclohexane
	our preparation	lit. data ([11])	our preparation	lit. data ([11])
B.p., °C/760 mm	69.0	68.740	80.7	80.738
n_D^{20}	1.3749	1.37486	1.4262	1.42623
d_4^{20}	0.6594	0.65937	0.7785	0.77855

To what has been said above it is necessary to add that the ease of hydrogenolysis of hydrocarbons on Ir/C, Os/C, and Rh/C was demonstrated not only with examples from the alicyclic series (cyclohexane, cyclopentane, and its homologs). A representative of the alkane series was also studied: *n*-hexane, passed in a stream of hydrogen over Os/C at 250°, underwent hydrogenolysis to the extent of 50% (Fig. 3). The catalyzate obtained by passing *n*-hexane over Rh/C at 250° contained ~ 10% *n*-pentane and *n*-butane, and at 300° their content increased to 25%.

Thus, the possibility of hydrogenolysis of the C—C bond by the doublet scheme on Ir/C, Os/C, and Rh/C may be considered quite probable. The question remains open for the present as to whether hydrogenolysis of cyclopentanes on these catalysts proceeds only by such a mechanism, or whether both directions (doublet and sextet–doublet) occur simultaneously as parallel reactions.

Experimental Part

Starting hydrocarbons. The *n*-hexane and cyclohexane used in the work were preliminarily purified by chromatography on silica gel and by rectification on high-efficiency columns. Their properties practically do not differ from the most reliable data reported in the literature (Table 2).

The methods of experiment and catalyst analysis, as well as the preparation of the catalysts, have been described previously [10].

In all experiments, the catalyst collected during the second hour was subjected to gas–liquid chromatographic analysis. The yields of liquid catalyzates obtained as a result of passing the hydrocarbons over Os/C are substantially (approximately by a factor of two) lower than the yields of catalyzates obtained under analogous conditions over Ir/C and Rh/C.

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Received
25 III 1964

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Note: Figure translations are in progress. See original paper for figures.