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SEQUENCE OF HYDROGENATION OF THE DOUBLE BONDS OF CYCLOPENTADIENE ON Pd AND Pt BLACKS

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Selective hydrogenation of conjugated double bonds in cyclic hydrocarbons has been little studied. Recently we investigated in detail the sequence of hydrogenation of the double bonds in cyclopentadiene on a skeletal nickel catalyst. It was shown that hydrogen begins to add to cyclopentene only after all the cyclopentadiene has been hydrogenated. It was found that the strict selectivity of the hydrogenation of conjugated double bonds in cyclopentadiene is due to adsorption displacement of the cyclopentene formed by cyclopentadiene.

In the present work the sequence of hydrogenation of the double bonds of cyclopentadiene on Pd and Pt blacks was studied. The reaction was carried out in the liquid phase at 25° and atmospheric pressure. Cyclohexane and 96% ethyl alcohol served as solvents. Electrolytic hydrogen was used. Special experiments established that the rocking rate, the stroke length of the shaker, and the dimensions of the duck-shaped vessel ensure that the reaction proceeds in the kinetic region.

The blacks were obtained by reducing aqueous solutions of Pd and Pt chlorides with formalin in an alkaline medium. Before hydrogenation the catalyst was saturated with hydrogen for 20 min at the same shaking rate as during hydrogenation.

Since the hydrogenation reaction proceeds at a high rate, hydrogen consumption was recorded every 30 sec. The experimental conditions are given in Table 1. The results obtained are represented by kinetic curves characterizing the dependence of the rate of hydrogen absorption $\left(\frac{\Delta v}{\Delta t}\right)$ on the total volume of hydrogen consumed $\left(\frac{\Sigma v}{2}\right)$.

Hydrogenation with Pd black. From Table 1 (experiment 1) and Fig. 1 it is seen that the rate of hydrogenation of cyclopentadiene ($\sim$ 0.002 g-mole) remains constant (11.4 ml per 0.5 min) up to absorption of 45% of the required hydrogen, i.e., the reaction proceeds according to zero order. The break in the kinetic curve for the hydrogenation of cyclopentadiene corresponds to the moment of addition of one mole of hydrogen (46.9 ml; 49.9 ml required). A qualitative reaction with hydroxylamine ([1]) in parallel experiment 2 confirmed that at this moment cyclopentadiene is absent from the solution. The data obtained indicate the sequence of hydrogenation of the double bonds of cyclopentadiene. Obviously, the portion of the kinetic curve after the break represents the rate of hydrogenation of the cyclopentene formed. The reaction rate in this portion is considerably lower. Experiments with cyclopentene confirmed this. In the hydrogenation of cyclopentene (experiment 3, Fig. 1), the first 45% of the required hydrogen is absorbed at a constant rate equal to 5.2 ml/0.5 min.

Table 1

Hydrogenation of cyclopentadiene and cyclopentene on Pd and Pt blacks. Experimental conditions. Temperature 25°, solvent volume 10 ml, 900 oscillations per 1 min, oscillation stroke length 12.7 cm; duck flask dimensions—length 180 mm, diameter 30 mm

Experiment No.	Hydrogenated substance	Weight, g: substance	Weight, g: catalyst	Solvent	Hydrogen consumption, ml: theoretical	Hydrogen consumption, ml: actual	Degree of hydrogenation of cyclopentadiene, %	Reaction to cyclopentadiene	Duration of experiment, min	Average rate of hydrogen uptake, ml per 0.5 min
	Catalyst — Pd black									
1	Cyclopentadiene	0.1275	0.1022	C_6H_{12}	99.8	98.7	—	—	15	11.4
2	Cyclopentadiene	0.1275	0.1020	C_6H_{12}	99.7	44.9	90.7	Positive; Negative	—	—
2	Cyclopentadiene	0.1275	0.1020	C_6H_{12}	99.7	49.8*	100.0	Positive; Negative	—	—
3	Cyclopentene	0.1277	0.1010	C_6H_{12}	49.3	49.8	—	—	10	5.2
4	Cyclopentene	0.2555	0.1010	C_6H_{12}	98.7	98.7	—	—	12	6.3

Experiment No.	Hydrogenated substance	Weight, g: substance	Weight, g: catalyst	Solvent	Hydrogen consumption, ml: theoretical	Hydrogen consumption, ml: actual	Degree of hydrogenation of cyclopentadiene, %	Reaction to cyclopentadiene	Duration of experiment, min	Average rate of hydrogen uptake, ml per 0.5 min
	Catalyst — Pt black									
5	Cyclopentadiene	0.1255	0.0998	C_6H_{12}	97.4	97.8	—	—	—	14.0
6	Cyclopentadiene	0.1255	0.0437	C_6H_{12}	97.4	96.7	—	—	—	7.3
7	Cyclopentadiene	0.1262	0.0244	C_6H_{12}	98.6	98.7	—	—	—	3.1
8	Cyclopentadiene	0.1250	0.0970	C_2H_5OH	97.1	93.8	—	—	6	—
9	Cyclopentadiene	0.0625	0.0970	C_2H_5OH	48.5	43.5	—	—	4	—
10	Cyclopentadiene	0.1267	0.0244	C_6H_{12}	98.6	68.0	138.0	Positive; Negative	—	—
10	Cyclopentadiene	0.1267	0.0244	C_6H_{12}	98.6	82.3*	167.0	Positive; Negative	—	—
11	Cyclopentene	0.2554	0.0437	C_2H_5OH	97.4	97.5	—	—	21	4.1
	Catalyst — Pt/$BaSO_4$									
12	Cyclopentadiene	1.1547	0.0442	C_6H_{12}	122.1	63.0	103.2	Positive	—	—

* In a parallel experiment.

Hydrogenation with Pt black. The conditions and results of the experiments are presented in Table 1 and in Fig. 2. From Table 1 it is evident that the rate of the hydrogenation reaction is directly related to the amount of catalyst (experiments 5–7) and to the amount of cyclopentadiene introduced into the reaction (experiments 8 and 9).

Fig. 1. Hydrogenation of cyclopentadiene *(1)* and cyclopentene *(2)* in cyclohex-

Fig. 1. Hydrogenation of cyclopentadiene (1) and cyclopentene (2) in cyclohexane on Pd black

Figure 1: Fig. 1. Hydrogenation of cyclopentadiene (1) and cyclopentene (2) in cyclohexane on Pd black

Fig. 2. Hydrogenation of cyclopentadiene (1—3) and cyclopentene (4) on Pt black, a—in cyclohexane, b—in 96% ethyl alcohol

Figure 2: Fig. 2. Hydrogenation of cyclopentadiene (1—3) and cyclopentene (4) on Pt black, a—in cyclohexane, b—in 96% ethyl alcohol

ane on Pd black

With 0.1 g of catalyst the reaction in cyclohexane (curve 1) and in an alcoholic medium (curve 2) proceeds with slight acceleration. With a smaller amount of catalyst (0.044 g) in cyclohexane the reaction proceeds to the very end at a constant rate (curve 3). On these kinetic curves, unlike those obtained with Pd black, there is no break. The character of these curves does not make it possible to judge the sequence of saturation with hydrogen of the double bonds of cyclopentadiene. However, by reaction with hydroquinone it was established that cyclopentadiene is still present in the solution after absorption of 138% hydrogen, but is absent when the hydrogen consumption reaches

167% of that required for the hydrogenation of cyclopentadiene to cyclopentene (experiment 10).

On Pt black, cyclopentene is also hydrogenated at a constant rate—lower than that of cyclopentadiene (experiments 6 and 11, curves 3 and 4), although in an alcoholic medium the reaction proceeds at a higher rate.

When Pt (5%) deposited on barium sulfate is used as the catalyst, the hydrogenation of cyclopentadiene also proceeds nonselectively (experiment 12).

Fig. 2. Hydrogenation of cyclopentadiene (1—3) and cyclopentene (4) on Pt black, *a*—in cyclohexane, *b*—in 96% ethyl alcohol

Thus, on Pd black, as on a skeletal nickel catalyst, the conjugated double bonds of cyclopentadiene are hydrogenated consecutively:

$$\text{cyclopentadiene} \xrightarrow{+H_2} \text{cyclopentene} \xrightarrow{+H_2} \text{cyclopentane}$$

whereas on Pt black—simultaneously.

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