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Abstract

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HYDROGENATION OF 2-METHYLBUTENE-1 IN THE PRESENCE OF PLATINUM BLACK IN DEUTERATED ALCOHOL

Numerous investigators of the hydrogenation reaction on a platinum catalyst have noted the substantial influence of the nature of the solvent on the rate, and sometimes also on the direction, of this reaction ([1–7]). It has been shown that in protolytic solvents, in comparison with neutral ones, there is a considerable acceleration of the hydrogenation reaction of certain compounds; moreover, in most cases their accelerating action is proportional to the mobility of the hydrogen atom in the solvent molecule. For a number of other compounds no such dependence was observed ([5–7]). On this basis some investigators believe that the solvent takes a direct part in the catalytic hydrogenation reaction, participating in the formation of complex intermediate compounds between the catalyst, the hydrogenated substance, and hydrogen ([4,8–10]).

Table 1

Results of experiments on isotope exchange between deuterated alcohol and substances participating in the hydrogenation reaction of 2-methylbutene-1 on a platinum catalyst

Experiment no.	Catalyst charge, g	Pressure, mm Hg	Duration of experiment, h	Content of monodeutero derivative, %
4	0.2081	742	3.00	2
5	0.2036	736	2.30	–
6	0.2036	737	2.50	2.2
11	1.1952	746	9.10	2.3
13	0.1957	without hydrogen	3.00	0.67
14	0.1966	735	1.20	2.4
15	0.2035	without hydrogen	3.15	0.0
16	0.2084	736	–	3.4

Note. In experiment no. 5 the solvent was C_2H_5OH. In experiment no. 6 the

catalyst was used after experiment no. 5. In experiment no. 15 the exchange of 2-methylbutene-1 with C_2H_5OD was studied; 3 ml of isopentane was used. In experiment no. 16 the exchange of H_2 with C_2H_5OD was studied; hydrogen was passed at a rate of 6 ml/min.

In the present work an attempt was made to determine whether the hydrogen of the hydroxyl group of the alcohol takes direct part in the catalytic hydrogenation reaction. For this purpose the reaction of hydrogenation of 2-methylbutene-1 on platinum black in rectified ethyl alcohol containing 3.3% deuterium in the hydroxyl group was studied. The hydrocarbon formed was analyzed on a mass spectrometer in order to determine its deuterium content.

The results of the study, given in Table 1, show that hydrogenation gives isopentane containing about 2.3% monodeuteroisopentane. No dideuteroisopentanes were detected. In the control experiment (no. 15), when isopentane was shaken with deuterated alcohol and platinum black in a nitrogen atmosphere at 20° for 3 h 15 min, no isotope exchange was observed. This is also confirmed by the results of experiment no. 11, where after hydrogenation was carried out with shaking for 8 h in a hydrogen atmosphere, the deuterium content of isopentane did not increase, although the deuterium content of hydrogen under these conditions reaches approximately 3.3%. 2-Methylbutene-1 in the absence of hydrogen (in experiment no. 13) gives 0.67% monodeuteroolefin. When passed through a trap with deuterated

alcohol and platinum black at a rate of 6 ml/min, which corresponds to the rate of its uptake in the hydrogenation of 2-methylbutene-1; 3.4% HD was found in the hydrogen.

Thus, from the results obtained it is seen that, under these conditions, the exchange of hydrogen with deuterated alcohol occurring on platinum reaches equilibrium within the accuracy of the measurement. The magnitude of the isotopic exchange of 2-methylbutene-1 with deuterated alcohol, found in the control experiment to be 0.67%, is undoubtedly greater than the fraction contributed by this exchange reaction to the total deuterium content of the product of the hydrogenation reaction. The magnitude of the isotopic exchange of the olefin with the alcohol decreases during the olefin hydrogenation reaction because the olefin concentration continuously decreases. The surface concentration of olefin sorbed on the catalyst during hydrogenation is also lower than in the control experiment, owing to sorption of hydrogen on part of the active centers of the catalyst.

The formation of monodeuteroparaffin can be explained by the fact that an HD molecule is first formed through isotopic exchange of hydrogen with the alcohol, and then this molecule adds to the olefin; thus, hydrogenation and exchange proceed simultaneously and independently of one another. The absence of noticeable amounts of di- and trideuteroparaffins also confirms this point of view, since the probability of formation of a D_2 molecule under these conditions is very small. In addition, this shows that during the hydrogenation reaction

practically no exchange of the olefin with the alcohol occurs.

It is interesting to note the fact that exchange of hydrogen with deuterated alcohol gives hydrogen containing 3.4% HD, whereas the isopentane obtained upon hydrogenation contains only 2.3% monodeuteroisopentane, although it would seem that all the HD should add to the olefin. This circumstance can be explained by the difference in the rates of the reactions of exchange of C_2H_5OD with H_2 and of olefin hydrogenation on the catalyst surface. It is also evident from this that the hydrogen of the hydroxyl group of the alcohol solvent does not participate directly in the hydrogenation reaction.

The hydrogen of the hydroxyl group of the alcohol exchanges with hydrogen sorbed on the catalyst surface. If, however, olefin is also present in the system, then, being sorbed on platinum, it reacts with sorbed H_2 and HD. In addition, the olefin lowers the surface concentration of hydrogen and, consequently, also the rate of hydrogen exchange with the alcohol.

Thus, the two possible reactions of isotopic exchange of the olefin with the alcohol and of hydrogen with the alcohol, as well as the olefin hydrogenation reaction, have a common limiting stage—the sorption of hydrogen on platinum. When all these processes proceed simultaneously, the rate of the exchange reactions decreases; thus, the exchange of hydrogen with the alcohol falls from 3.4 to 2.3%, while the exchange of olefin with the alcohol is completely suppressed, as is seen from the absence of dideutero derivatives of isopentane.

Experimental Part

2-Methylbutene-1 was obtained by dehydration of isoamyl alcohol over alumina at 400° with subsequent distillation of the dehydration products. B.p. 30.6° (746 mm); d_4^{20} 0.6507, n_D^{20} 1.3774. Literature data ([11,12]): b.p. 31.163° (760 mm); d_4^{20} 0.6504, n_D^{20} 1.3778. Platinum black was prepared according to Willstätter ([13]). Deuterated alcohol was obtained by isotopic exchange between alcohol and heavy water.

Hydrogenation was carried out in a duck-shaped vessel equipped with a jacket for thermostating. To maintain a constant hydrogen pressure in the system and to record its consumption, a gasometer of the Patrikeev system with a burette capacity of 1 l was used. To increase the reliability of operation of this instrument, the circuit of the photoelectronic amplifier was replaced, since the factory circuit ···

needed no adjustment during the experiment. The circuit used [15] with a cathode follower ensured stable operation of the instrument.

Hydrogenation experiments were carried out as follows: 10 ml of alcohol was poured into the flask and a weighed portion of catalyst was introduced under a stream of nitrogen. The entire system was flushed with hydrogen, and, under a stream of hydrogen, 3 ml of isoamylene dissolved in 10 ml of alcohol was poured into the flask. The flask was closed, and the gas burette was connected at an

excess hydrogen pressure of 30 mm water column. The rocker was switched on, and recording on the gas burette was begun simultaneously. All experiments were carried out at 20°. After completion of the experiment the flask was cooled to 10°, and its contents were poured into a cooled 50-ml flask. The catalyst remained in the flask.

Table 2

Mass spectrum of isopentane according to [17] and mass spectra obtained in the present work
(relative intensities)

m/e	iso-C_5H_{12}[17], $U = 70$ V	iso-C_5H_{12}, exp. No. 5, $U = 34$ V	iso-C_5H_{12} + iso-$C_5H_{11}D$, exp. No. 14, $U = 36$ V	iso-C_5H_{10}, $U = 44$ V	iso-C_5H_{10} + iso-C_5H_9D, exp. No. 13, $U = 40$ V
26	4.11	1.48	1.9	2.63	2.25
27	42.2	11.7	13.3	16.0	12.0
28	6.17				
29	45.7	27.8	29.8	22.2	21.4
30				7.2	
39	21.5	4.17	5.2	26.5	22.8
40	3.38	1.7	2.0	4.5	4.1
41	67.3	59	62.0	24.4	25.8
42	86.0	92.0	92.0	31.4	33.0
43	100	100	100	3.5	2.6
51				2.0	1.5
52				1.15	1.0
53				8.9	8.4
54				3.2	3.2
55	4.71	4.2	4.2	100	100
56	16.8	18.9	19.3	5.0	5.0
57	54.0	57.0	57.5		
58		0.08	1.3		
69				3.14	3.2
70				38.6	35.8
71	1.82	1.95	2.0		0.24
72	6.19	7.71	7.71		
73			0.19		

Note. U is the ionizing voltage.

The azeotrope of hydrocarbon with alcohol was distilled off in a water bath up to 50° into a receiving test tube kept at a temperature of −70°, and was treated

twice with equal volumes of a concentrated calcium chloride solution. The hydrocarbon obtained was dried over calcined calcium chloride and distilled up to a temperature of 40°. From the receiving test tube a hydrocarbon sample (0.3 ml) was taken with a 1-ml Record-type medical syringe with a needle. For analysis on the mass spectrometer, the sample taken was introduced into a previously weighed ampoule, the lower end of which was cooled in a mixture of acetone with solid carbon dioxide. Then the upper end of the ampoule was sealed, and the ampoule was weighed again.

Mass-spectrometric analysis of isopentane and isoamylene was carried out on an MS-4 instrument. A glass inlet system was used to introduce the sample into the gaseous ion source of the mass spectrometer. The needle dosing valve employed made it possible to regulate smoothly the gas flow of the sample into the ion source. The small difference in mass of the molecules analyzed made it possible not to maintain a molecular effusion regime and to use a high pressure (50 mm Hg) before the valve [16].

The inlet system with the inserted ampoule was evacuated with a fore-vacuum pump to a pressure of $5 \cdot 10^{-2}$ mm Hg, and the stopcock was set in such a position that all openings were closed. The ampoule was broken, and the evaporated sample was admitted into the buffer volume. The flow of the sample into the ion source was regulated with a metering valve according to the most intense peak of the spectrum, approximately up to 20 V. The mass spectrum of the sample under investigation was taken from the output voltmeter of the electrometric amplifier and recorded by an automatic EPP-09 potentiometer.

Samples of the spectra obtained, with corrections for the natural content of D and C^{13}, are presented in Table 2. The table does not include the small peak with $m/e = 28$, the measurement of which was hindered by the background of the instrument. The spectrum of isopentane has been published in ([17]) and is given for comparison, but it was obtained on a 180° instrument with scanning by accelerating voltage and therefore differs very strongly from that obtained by us. The calculation of the content of deuterium-substituted molecules was carried out from the molecular peaks.

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