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Abstract

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STUDY OF SELECTIVITY AND STEREOSPECIFICITY IN THE HYDROGENATION REACTIONS OF *n*-HEXYNES ON A SKELETAL NICKEL CATALYST

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Catalytic hydrogenation of acetylenic hydrocarbons has been studied by many investigators. A summary of these works is given in reviews ([1]-[5]). In most of the earlier studies these reactions were considered almost exclusively for preparative purposes. In liquid-phase hydrogenation in the presence of a Pt catalyst, hexyne-1 ([6],[7]), hexyne-2 ([8],[9]), and hexyne-3 ([10],[11]) are hydrogenated nonselectively. In the presence of Ni and Pd the selectivity of the process depends on the position of the triple bond in the molecule: in contrast to hexyne-2 and hexyne-3, hexyne-1 is hydrogenated nonselectively ([7]). It has been found that, in catalytic hydrogenation of disubstituted acetylenic hydrocarbons to olefins, only the corresponding cis-isomers are obtained, although in many cases an admixture of the trans-isomer is detected ([2],[5],[11]-[13]).

Fig. 1. Change in the rate of hydrogenation of *n*-hexynes as a function of the amount of hydrogen absorbed: *I* —hexyne-3; *II* —hexyne-2; *III* —hexyne-1

The aim of the present work is to study selectivity and stereospecificity in the hydrogenation reactions of acetylenic hydrocarbons in the liquid phase. As objects, *n*-hexynes were chosen, which makes it possible to trace the influence of the position of the triple bond on the kinetics and mechanism of hydrogenation under identical conditions. The individual hexynes were prepared by the action of bromoalkyls on sodium acetylides in liquid ammonia ([14],[15]). The hexynes obtained were chromatographically pure preparations. The sensitivity of the method made it possible to determine the presence of an impurity in an amount of 0.1%. The properties of the hexynes corresponded to literature data ([16]).

	b.p., °C	d_4^{20}	n_D^{20}
n-Hexyne-1	67.5-70	0.7190	1.3400
n-Hexyne-2	83-85	0.7366	1.4149
n-Hexyne-3	78-80	0.7250	1.4120

Hydrogenation was carried out in a glass duck at 20° with vigorous shaking (about 800 oscillations per min.). The temperature was maintained with an accuracy of up to 0.1°. A skeletal catalyst was used, prepared by leaching a Ni –Al alloy (1 : 1) with a 20% aqueous solution of sodium hydroxide at 100°, and stored for 5 months under water. Absolute methyl alcohol served as the solvent. Before the experiment the catalyst was repeatedly washed with methanol and saturated with hydrogen. In each experiment, 0.01 mole of hexyne in 20 ml of solvent and 0.1 g of catalyst were taken. During hydrogenation, samples were withdrawn from the duck for analysis. The reaction products were analyzed by gas-liquid partition chromatography. As liquid phases, β,β'-oxydipropionitrile, tricresyl phosphate, and a solution of silver nitrate in were used.

ethylene glycol. The results obtained are presented in Tables 1-3 and in Figs. 2-4, which show the dependence of the catalyst composition on the volume of hydrogen absorbed.

Fig. 1 presents the kinetic curves for hydrogenation of all three *n*-hexynes. It is evident from Fig. 1 that absorption of the first mole of hydrogen in all

Table 1

Hydrogenation of hexyne-1

H_2 consumption, mol	0.11	0.32	0.59	0.80	1.07	1.27	1.54	1.73
Catalyst composition, mol. %								
Hexyne-1	89.2	70.0	55.3	37.8	12.2	0.5	0.0	0.0
Hexene-1	7.5	24.0	34.0	47.0	67.1	64.0	29.5	12.0
Hexane	3.3	6.2	10.7	15.2	20.7	35.5	70.5	88.0

cases proceeds at an almost constant rate; moreover, hexyne-2 and hexyne-3 are hydrogenated at the same rate, whereas hexyne-1 is considerably slower. In the hydrogenation of hexyne-1, after absorption of the first mole of hydrogen the reaction rate increases, while in the case of hexyne-2 and hexyne-3, on the contrary, it decreases sharply. From Table 1 and Fig. 2 it follows that, under the chosen conditions,

Table 2

Hydrogenation of hexyne-2

H_2 consumption, mol	0.11	0.31	0.58	0.89	1.14	1.26	1.49	1.72	1.95
Catalyst composition, mol. %									
Hexyne-2	88.2	69.0	43.2	11.0	0.0	0.0	0.0	0.0	0.0
Cis-hexene-2	10.7	28.7	54.4	85.0	67.6	48.0	20.7	4.2	0.0
Trans-hexene-2	0.5	1.0	1.0	2.0	12.3	18.6	22.3	19.0	4.6
Trans-hexene-3	traces	traces	traces	traces	2.2	3.0	4.4	2.8	0.3
Cis-hexene-3*	–	–	–	–	–	–	–	–	–
Hexane	1.0	1.3	1.4	2.0	17.9	30.4	52.6	74.0	95.1

* It is possible that the sensitivity of the method with respect to cis-hexene-3 is insufficient for detecting the latter in small amounts.

Table 3

Hydrogenation of hexyne-3

H_2 consumption, mol	0.11	0.33	0.72	0.96	1.09	1.19	1.39	1.60	1.76	1.87
Catalyst composition, mol. %										
Hexyne-3	88.6	68.0	25.3	3.8	0.0	0.0	0.0	0.0	0.0	0.0
Cis-hexene-3	8.0	27.6	68.7	89.0	78.8	47.0	16.0	8.0	0.0	0.0
Trans-hexene-3	2–3	2–3	2.0	3.0	5.2	15.2	21.0	16.6	8.7	3.0
Cis-hexene-2	traces	traces	2.0	2.0	2.4	2.7	6.7	3.2	3.3	0.0
Trans-hexene-2	traces	traces	traces	traces	4.6	12.4	16.0	14.8	12.2	10.2
Hexane	1.3	1.4	2.0	2.2	9.0	22.7	40.3	58.0	75.8	88.8

hexyne-1 is hydrogenated nonselectively: from the very beginning of the reaction, along with hexene-1, *n*-hexane is detected in the catalyst. The ratio of the amounts of hexene-1 and *n*-hexane formed remains constant, ~3 : 1, until hexyne-1 completely disappears from the catalyst. It should be noted that even after hexyne-1 disappears from the catalyst, only one olefin, hexene-1, is detected in the reaction products. At the end of the process the rate decreases sharply. The total consumption of hydrogen is lower than the theoretically required amount and is approximately 1.9 mol.

It follows from Figs. 3 and 4 and Tables 2 and 3 that hex-2-yne and hex-3-yne, in contrast to hex-1-yne, are hydrogenated with a high degree of selectivity. By the time 1 mole of hydrogen has been absorbed, no more than 1–2% of *n*-hexane is detected in the catalyst. In both cases the hydrogenation process proceeds stereospecifically: the principal reaction products are cis-hex-2-ene and cis-hex-3-ene, respectively. Along with the principal product, from the very beginning of the reaction small amounts of trans isomers and traces of *n*-hexenes with a different position of the double bond are detected in the catalyst. The second

Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

stage of the process proceeds in a more complex manner. From Figs. 3 and 4 and Tables 2 and 3 it is evident that hydrogenation of the cis-olefins formed in the first stage is accompanied by cis–trans conversion and migration of the double bond.

Fig. 2. Change in the composition of the catalyst during hydrogenation of hex-1-yne: *I* —hex-1-yne; *II* —hex-1-ene; *III* —*n*-hexane

As was established above, the hexenes formed are saturated in the second stage of the process. Comparison of these facts with the nature of the kinetic curves shows that hex-1-ene is hydrogenated at a considerably higher rate than hex-2-ene and hex-3-ene. Hydrogenation reactions of acetylenic hydrocarbons may be accompanied by isomerization of monoolefins: migration of the double bond and cis–trans conversion. Migration of the triple bond is also possible. Judging from the composition of the catalysts during liquid-phase hydrogenation of *n*-hexynes in the presence of a skeletal nickel catalyst, all these reactions occur, with the exception of migration of the triple bond. However, their relative rates differ at different stages of the process and depend on the position of the triple bond.

Fig. 3. Change in the composition of the catalyst during hydrogenation of hex-2-yne: *I* —hex-2-yne; *II* —cis-hex-2-ene; *III* —*n*-hexane; *IV* —trans-hex-2-ene; *V* —trans-hex-3-ene

Fig. 4. Change in the composition of the catalyst during hydrogenation of hex-3-yne: *I* —hex-3-yne; *II* —cis-hex-3-ene; *III* —cis-hex-2-ene; *IV* —trans-hex-2-ene; *V* —trans-hex-3-ene; *VI* —*n*-hexane

Disubstituted acetylenic hydrocarbons—hex-2-yne and hex-3-yne (in accordance with the literature data)—are hydrogenated in the first stage of the process with a high degree of selectivity and stereospecifically. In both cases the first mole of hydrogen adds only to the triple bond, with formation of the corresponding cis-olefin (~95%). The hydrogenation and isomerization reactions of the cis-olefins formed proceed at an appreciable rate only after the acetylenic hydrocarbon has been completely hydrogenated.

Figure 4

Figure 3: Figure 4

In the first stage of the process, the cis-olefin, which is probably the only primary product of the reaction [17,12], is displaced from the catalyst surface and practically undergoes no further transformations. After exhaustive hydrogenation of the acetylenic hydrocarbon to the ethylenic one, hydrogenation of the cis-olefins begins, accompanied by cis–trans conversion and migration of the double bond. The decisive importance of adsorption displacement for the selective and stereospecific course of heterogeneous-catalytic processes is well known. In particular, the role of this factor was recently noted in the hydrogenation of dimethylacetylene [12].

It is possible that displacement by the acetylenic hydrocarbon not only of the olefin but also of hydrogen [18] is of substantial importance. An insufficient concentration of active hydrogen on the catalyst surface may also inhibit the conversion of olefins in the presence of the acetylenic hydrocarbon.

The formation of small amounts of *n*-hexane and isomeric *n*-hexenes in the first stage of hydrogenation of hexyne-2 and hexyne-3 may be explained by diffusional complication of the process in the narrow pores of the catalyst or by insufficiently complete adsorption displacement of the cis-olefin. In this connection it is interesting to note that, in the hydrogenation on a Pd catalyst of an acetylenic diol to an ethylenic one in the presence of a displacing component—quinoline—the yield of the trans isomer decreased [19].

As already indicated, from the very beginning of the hydrogenation of hexyne-1, *n*-hexane is formed at a high rate. The saturated hydrocarbon in the first stage of this process may be formed in two ways: as a result of the simultaneous addition of two molecules of hydrogen to the triple bond, or through the intermediate formation of an olefin. In the second case the adsorbability of the olefin is comparable with the adsorbability of the acetylenic hydrocarbon, and mutual displacement occurs. In addition, reactions may proceed in parallel in which the saturated hydrocarbon and olefin are formed from hexyne-1, the latter undergoing adsorption displacement and not being hydrogenated.

It should be noted that in the second stage of the process, after hexyne-1 has disappeared from the solution, the catalyst behaves differently with respect to the hydrogenation and isomerization reactions of hexene-1. The hexene-1 formed does not isomerize, although the catalyst retains high activity with respect to its hydrogenation. Thus, in the hydrogenation of hexyne-1 the catalyst is poisoned with respect to the double-bond migration reaction and is incapable of catalyzing this process even when hexyne is no longer present in the reacting mixture. An analogous case was observed previously in the hydrogenation of phenylbutynediol on an old sample of skeletal nickel catalyst [20].

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