Physical Chemistry

Academician of the Academy of Sciences of the Kazakh SSR D. V. Sokol' skii and A. B. Fasman

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Dependence of the Rate of Hydrogenation on the Amount of Skeletal Nickel Catalyst

The rate of hydrogenation in the liquid phase, as has been shown by a number of investigators (1–4), is proportional to the amount of catalyst in the presence of small charges of it and tends toward a limiting value in the presence of large ones. The more complex regularities found by some authors (5,6) are, in their opinion, associated with a very low intensity of stirring of the reaction mixture.

The purpose of the present investigation was to study the question under model conditions using a potentiometric method, which makes it possible to judge the processes occurring on the surface of the catalyst. Hexyne-1 and trans-piperylene were chosen as the objects of investigation. The experimental procedure is described in work (7).

Hexyne-1 was hydrogenated in absolute ethanol and in *n*-heptane, the nonpolar properties of the latter ensuring that the process proceeded under ideal conditions.

As can be seen from Fig. 1, in an alcohol medium the length of the linear portion of the curve expressing the dependence of the hydrogenation rate on the amount of Ni increases with increasing stirring intensity. The order of the kinetic curves in this series of experiments is close to zero. The drop in the catalyst potential from the reversible hydrogen potential varies from 50 mV (3.384 g Ni) to 360 mV (0.034 g Ni).

Fig. 1. Dependence of the hydrogenation rate of hexyne-1 and the minimum value of the catalyst potential during the reaction on the amount of skeletal nickel catalyst. Amount of hexyne-1, 0.5728 g; temperature 20°; solvent—absolute alcohol. *a*—250, —450, —650, —850 rev/min.

Somewhat different regularities were observed in *n*-heptane. In the region of small amounts of catalyst, the hydrogenation rate is proportional to the amount of Ni to a power greater than one. The specific activity of the catalyst passes through a maximum, which shifts, with increasing stirring intensity, toward larger Ni charges. It should be noted that the rate of hydrogenation in *n*-heptane at small amounts of Ni is lower than in alcohol, while at large amounts it is considerably higher.

During the hydrogenation of trans-piperylene in an alcohol medium, only 70% of the theoretically required amount of hydrogen is absorbed, which is most probably associated with the simultaneous occurrence of side processes. The order of the kinetic curves is close to first; the catalyst potential changes—

varies in the same range as in the case of hexyne-1; the specific activity of the catalyst passes through a maximum.

In the following series of experiments, the hydrogenation of hexyne-1 in alcohol was studied at a constant ratio between the amounts of the unsaturated compound and the catalyst (0.38 g of hexyne-1 per 1 g of Ni). The experiments were carried out at 250, 450, 650, and 850 strokes of the shaker per minute and at temperatures of 2, 20, and 40°. The amount of catalyst was varied from 0.084 to 3.384 g.

The specific catalytic activity with weak stirring decreases as the amount of catalyst is increased, whereas with vigorous stirring it passes through a maximum. It should be emphasized that the maximum of specific activity is observed (see Table 1) at quite definite values of the catalyst potential, i.e., at a definite degree of filling of the active surface by reacting molecules.

Table 1

Stirring intensity, strokes/min	Temperature, °C	Charge of Ni at which the specific activity is maximal, g	Mean absolute potential of the catalyst, mV	Specific activity, ml/min · g
450	2	0.338	610	71
650	2	0.338	620	93
850	2	0.676	690	113
850	20	0.676	675	137
850	40	0.338	685	252

With increasing stirring intensity, the concentration of the unsaturated compound on the catalyst surface falls. When the temperature is varied, the filling of the surface by the unsaturated compound does not change, but the maximum of specific activity shifts toward smaller Ni charges.

The apparent activation energy is a function of the absolute value of the ratio between the charge of substance and the amount of catalyst, varying from 1.5 kcal/mol (3.384 g Ni) to 8 kcal/mol (0.084 g Ni).

In order to elucidate the intermediate stages of hydrogenation of hexyne-1, a series of experiments was interrupted after absorption of a definite volume of hydrogen, and the contents of the shaker were analyzed for the triple bond by the Barnes and Molinini method (8) and for the total content of unsaturated bonds by dehydrogenating part of the catalyst on Adams platinum. One of the graphs obtained in this way is shown in Fig. 2.

Hexyne-1 practically instantaneously extracts from the catalyst part of the sorbed hydrogen (54 ml from 1 g of Ni). Subsequently, a consecutive-parallel process takes place: simultaneous hydrogenation of the alkyne and alkene and saturation of the catalyst with hydrogen from the gas phase. At small amounts of catalyst, selective hydrogenation of hexyne-1 to hexene-1 occurs at first. Formation of the saturated product begins when the olefin concentration reaches its maximum under the experimental conditions and is accompanied by a sharp break in the kinetic and potential curves. The concentration of *n*-hexane in all cases increases according to a first-order equation.

As is known from the works of Elovich, Zhabrova, and Gol' danskii (9–11), the influence of the amount of catalyst on the reaction rate is determined by the rate-limiting stage of the process. With increasing amount of catalyst, the intensity of consumption of the reaction components increases, and a transition is observed from the kinetic region to the diffusion region or even to the region of "dissolution."

It should be taken into account, however, that the kinetics of hydrogenation on a skeletal nickel catalyst is determined by three interrelated processes: hydrogenation of the substance by hydrogen from the gas phase, dehydrogenation of the catalyst, and its subsequent saturation (12, 13). The nature of the influence of each of these processes on the overall reaction rate depends on the magnitude of the catalyst charge. As shown in work (14), removal of 70% of the hydrogen from the skeletal nickel catalyst decreases its surface by only 10–12%, whereas further dehydrogenation leads to a sharp reduction in the active surface of the catalyst. The indicated features of hydrogenation on skeletal nickel are the reason for the dependence noted above between the magnitude of the activation energy and the amount

···by the amount of catalyst. The activation energy in this case relates to the sum of the processes of hydrogenation, dehydrogenation, and saturation; moreover, at small Ni charges it approaches the value characteristic of compounds with a triple bond ([12]).

Substances with triple and conjugated bonds are strongly adsorbed on metallic contacts and, during hydrogenation, are activated at the same centers as hydrogen. Therefore, at small amounts of catalyst the reaction rate is limited by the activation of hydrogen, and at larger amounts by the transport of the reacting molecules, primarily hydrogen molecules, to the catalyst surface. The transition from one limiting mechanism to another occurs when the ratio between the amounts of catalyst and of the compound being hydrogenated changes, and

Fig. 2

Figure 2: Fig. 2

also when the stirring intensity, temperature, volume and shape of the reaction vessel, etc., change.

Fig. 2. Hydrogenation of hexene-1 on skeletal nickel catalyst. Amount of catalyst 1.128 g; hexene-1 0.5728 g; temperature 20°; stirring intensity 250 strokes/min; solvent—absolute alcohol.
a—kinetic curve, —potential curve, —amount of hexene-1 in the catalyst, —amount of hexene-1 in the catalyst, —amount of *n*-hexane in the catalyst, —amount of hydrogen extracted from the catalyst.

Thus, measurement of the catalyst potential, making it possible to establish the influence of various factors on the mechanism of the hydrogenation reaction, can be successfully used in finding the optimum ratios between the amounts of catalyst and reacting substance.

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CITED LITERATURE

1. H. S. Davis, G. Thompson, G. S. Grandall, *J. Am. Chem. Soc.*, **54**, 2340 (1932).
2. S. Yu. Elovich, G. M. Zhabrova, *Theoretical Principles of Hydrogenation and Hydrogenolysis*, M.-L., 1948, p. 153.
3. G. W. Watt, M. T. Walling, *J. Phys. Chem.*, **50**, 7 (1955).
4. D. V. Sokolsky, A. B. Fasman, *Vestn. AN KazSSR*, No. 9, 70 (1955).
5. Z. Czurös, *Res.*, **4**, 52 (1951).
6. T. Erdey-Grus, J. Szabo, *Acta Chim. Acad. Sci. Hung.*, **1**, 46 (1951).
7. D. V. Sokolsky, V. A. Druz' , *ZhFKh*, **26**, 364 (1952).
8. L. Barnes, L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1950).
9. S. Yu. Elovich, G. M. Zhabrova, *ZhFKh*, **19**, 239 (1945).
10. V. I. Gol' dansky, S. Yu. Elovich, *ZhFKh*, **20**, 1085 (1946).
11. V. I. Gol' dansky, *Proceedings of the All-Union Conference on Catalysis*,

Publishing House of the Academy of Sciences of the USSR, 1950.

12. D. V. Sokolsky, *Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 588.

13. L. Kh. Freidlin, K. G. Rudneva, *Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 557.

14. H. A. Smith, A. J. Chadwell, S. S. Kirslis, *J. Phys. Chem.*, **59**, 820 (1955).

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