DEUTERIUM-HYDROGEN EXCHANGE IN THE COURSE OF THE HYDROGENATION REACTION OF SOLID OLEFINS BY ATOMIC HYDROGEN AT —196°

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DEUTERIUM-HYDROGEN EXCHANGE IN THE COURSE OF THE HYDROGENATION REACTION OF SOLID OLEFINS BY ATOMIC HYDROGEN AT −196°

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Hydrogenation of olefins by H atoms at a temperature of −196° was carried out in studies ([1,2]). It was shown that, in many cases, very rapid reactions occur involving the addition of hydrogen atoms, obtained on a heated tungsten filament, to certain solid olefins (propylene, butene-1, isobutylene, etc.).

The subject of the present investigation was the study, in the course of similar reactions, of the kinetics of deuterium-hydrogen exchange between the gas and solid phases, with the aim of obtaining data on the mechanism of hydrogenation. The reactor in our experiments was a spherical glass vessel connected to an MX-1302 mass spectrometer ([3,4]). In the center of the vessel there was a tungsten incandescent filament, which served for the production of atomic hydrogen. On the inner surface of the reactor, cooled with liquid nitrogen, a layer of olefin was frozen. Deuterium was admitted into the vessel to a pressure of about $4 \cdot 10^{-2}$ mm Hg; then heating of the tungsten filament was switched on, and the change in the total pressure and in the partial pressures of D_2, HD, and H_2 was measured simultaneously from the change in intensity of the corresponding mass-spectral line during the reaction.

Control experiments established that, under the experimental conditions, diffusion in the section reactor—diaphragm of the mass spectrometer is sufficiently rapid and does not distort the kinetic curves.

Experiments were carried out with propylene and isobutylene. At the same temperature of the tungsten filament and the same initial hydrogen pressure, the rate of hydrogenation of isobutylene is several times lower than the rate of hydrogenation of propylene. In the experiments described below, the temperature of the tungsten filament in the reaction vessel in the case of propylene was maintained so much lower than in the case of isobutylene that the rates of hydrogen absorption were approximately the same for both reactions. It turned out that, along with hydrogenation, very rapid isotopic exchange occurs, and HD and H_2 molecules appear in the gas phase.

In Fig. 1 are presented plots of the change in the partial pressures of D_2,

Fig. 1. Change in the pressure of hydrogen (1) and partial pressures of D2 (2), HD (3), and H2 (4) during hydrogenation: a—propylene, b—isobutylene

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Fig. 2. Hydrogenation and isotope-exchange curves in semilogarithmic coordinates. a—propylene, b—isobutylene; 1—relative change in the total pressure; 2—relative change in the deuterium content of hydrogen in the gas phase

Figure 2: Fig. 2. Hydrogenation and isotope-exchange curves in semilogarithmic coordinates. a—propylene, b—isobutylene; 1—relative change in the total pressure; 2—relative change in the deuterium content of hydrogen in the gas phase

HD, and H_2, and of the total hydrogen pressure, during the hydrogenation of propylene (a) and isobutylene (b).

In Fig. 2 are given the curves obtained from these plots for the relative change in total pressure $p_{\text{tot}}/p^0_{\text{tot}}$ and for the deuterium content in the gas mixture

$$\left(p_{D_2} + \frac{1}{2}p_{\text{HD}}\right)/p_{\text{tot}}$$

for propylene (a) and isobutylene (b). It can be seen that, in the case of isobutylene, the exchange rate is close to the rate of hydrogen absorption. In the case of propylene, the exchange rate is considerably lower than the absorption rate. (The small increase in the partial pressure p_{D_2} during 1-2 sec after switching on the tungsten filament is explained by the general slight heating (by 4-5°) of the gas in the reactor.)

Although the data obtained do not yet make it possible to establish unambiguously the nature of the elementary acts leading to exchange, nevertheless, in accordance with the view accepted in the literature ([5]), exchange between H atoms and free alkyl radicals formed as an intermediate product in the hydrogenation of an olefin by hydrogen atoms is the most probable. Of particular interest in the present case would be the elementary process $\dot{R} + H \rightarrow$ olefin $+H_2$ ($Q \sim 60$ kcal), which leads to exchange and at the same time

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is a process retarding the hydrogenation as a whole. The opposite character of the hydrogenation rate and the exchange rate, revealed when these quantities are compared for propylene and isobutylene, could serve as an argument in favor of such a process. If the indicated elementary process does indeed proceed at a high rate, its significance may also be very great in the preparation of frozen alkyl radicals by the radiation method.

Indeed, since in the latter case hydrogen atoms are formed along with alkyl radicals, the indicated process may be one of the causes leading to the early "limiting" of the concentration of frozen radicals, observed in our laboratory for paraffin and also in work ([6]) for polyethylene.

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