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Abstract

Full Text

CHEMISTRY

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HYDROGENATION OF UNSATURATED COMPOUNDS AT CONSTANT CONCENTRATION IN SOLUTION

Usually catalytic hydrogenation is carried out at a constant hydrogen pressure in the gas phase and at a continuously changing concentration of the unsaturated compound in solution. If the latter are well adsorbed on the surface of the catalyst, then for a certain period of time the reaction rate remains constant. In the present work, the concentration of the unsaturated compound was maintained low, but, on average, constant, which entailed constancy of the hydrogenation rate throughout the entire experiment.

Experimental Part

In the work, sodium maleate and sodium *o*-nitrophenolate were used; these are ordinarily hydrogenated when the catalyst potential is shifted to the anodic side by, respectively, 120–130 mv and 250–270 mv (^{1}). The first series of experiments with these substances was carried out in 0.1 N, 1.0 N, and 5.0 N NaOH at 20, 40, and 60°. Hydrogenation was conducted in an apparatus described earlier (^{2}). The unsaturated compound was fed uniformly into the duck-shaped vessel from a specially designed burette previously used by N. M. Popova (^{3}). The burette (Fig. 1) is a graduated vessel (1), with an elbow (2) fused into it, connected through a two-way stopcock and a thin hose to a capillary (3), through which the hydrogenated substance is supplied to the duck-shaped vessel. Metallic mercury serves as the confining liquid. The bulb is connected by a thread to a drum mounted on the shaft of a Uorren motor. When the motor is switched on, the thread winds onto the drum and uniformly raises the leveling vessel. The mercury displaces the solution through the capillary into the duck-shaped vessel. The rate of dripping of the solution in all our experiments was 0.25 ml/min. The concentration of the unsaturated compound in solution was varied.

Figure 2

Figure 2: Figure 2

Fig. 1. Burette for uniform supply of the hydrogenated substance into the catalytic duck-shaped vessel

The skeletal nickel catalyst was prepared by leaching 1 g of 30% Ni–Al alloy with 80 ml of 20% NaOH for 2 hours on a boiling water bath. The catalyst potential was measured with a semiautomatic potentiometer of type P 2/1 relative to a saturated calomel electrode. The duration of dripping of the unsaturated substance into the cata-

the catalytic cell in all experiments was 30 min. After cessation of the dropwise addition, the catalyst was shaken until it returned to the saturation potential.

Figure 2 gives the dependence of the rate of the potential shift reaction on time in 0.1 N NaOH at 20°. The rate of feed of sodium maleate in these experiments varied from 0.002 to 0.09 g per minute (i.e., from 0.3 to 1.25 ml H_2 per min.). It is seen from Fig. 2 that hydrogenation of sodium maleate proceeds at a constant rate, which increases from 1 to 7.4 ml H_2 per min. as the content of the substance in the solution is increased. The maximum rate of hydrogen absorption in the hydrogenation of sodium maleate in 0.1 N NaOH at 20° is reached when 0.053 g of the salt per min. is fed into the cell. This is the optimum concentration of the substance in solution under the given conditions. With a further increase in the content of the unsaturated compound, the rate of hydrogen absorption does not increase. Unreacted substance begins to accumulate in the catalytic cell. The potential of the catalyst, after equilibrium is established in the system, remains constant throughout the experiment. The shift from the initial saturation potential is the greater, the greater the concentration of the unsaturated compound, and the shift increases from 13 to 120 mV.

Fig. 2. Hydrogenation of sodium maleate and sodium *o*-nitrophenolate in 0.1 N NaOH at 20° on skeletal nickel. Dashed lines—sodium maleate; solid lines—sodium *o*-nitrophenolate. **1′**—0.0075 g sodium maleate/min. (1.0 ml H_2 per min.); **2′**—0.05 g sodium maleate/min. (7.0 ml H_2 per min.); **3′**—0.06 g sodium maleate/min. (8.4 ml H_2 per min.); **4′**—0.07 g sodium maleate/min. (9.8 ml H_2 per min.); **1**—0.0012 g sodium *o*-nitrophenolate/min. (0.5 ml H_2 per min.); **2**—0.020 g sodium *o*-nitrophenolate/min. (8.3 ml H_2 per min.); **3**—0.025 g sodium *o*-nitrophenolate/min. (10.4 ml H_2 per min.); **4**—0.03 g sodium *o*-nitrophenolate/min. (12.6 ml H_2 per min.).

Figure 3 gives the dependence between the rate of hydrogen absorption and the potential shift. It is seen from Fig. 3 that, with a change in temperature from 20 to 60°, the maximum rate of hydrogenation increases from 7.4 to 12 ml H_2 per min. and depends on the degree of filling of the surface by the substance being hydrogenated. With increasing ΔE the rate increases, but only up to a certain limit. The maximum rate is attained at $\Delta E = 100$ mV at all temperatures.

Fig. 3

Figure 3: Fig. 3

On going from 0.1 N to 5.0 N NaOH, a decrease in the rate of hydrogenation is observed. At the same time, the higher the alkali concentration, the deeper the potential shift. The maximum potential shift in all media is constant (120–130 mV) and does not depend on the amount of unreacted substance in the reaction vessel.

Analogous regularities are observed in the hydrogenation of sodium *o*-nitrophenolate. The rate of dropwise addition of sodium *o*-nitrophenolate was varied from 0.0007 to 0.035 g per min. (i.e., from 0.3 to 14.6 ml H_2 per min.). Figure 2 presents the hydrogenation of sodium *o*-nitrophenolate in 0.1 N NaOH at 20°. Hydrogen absorption during the experiment proceeds at a constant rate and increases from 0.4 to 10.5 ml H_2 per min. The maximum rate of hydrogenation of the salt in 0.1 N NaOH at 20° is attained when 0.025 g/min is fed into the cell. The potential during the experiment remains constant. The shift from the saturation potential increases from 70 to 250 mV. Thus, from the potential curves one can immediately judge the state of the surface of the cataly-

catalyst during the experiment (curve 4). The rate is constant, but the potential displacement increases, which indicates a change in the activity of the catalyst (with an increase in the duration of the experiment one can observe a decrease in the reaction rate).

From Fig. 3 it is seen that, as the temperature of the experiment is changed from 20 to 60°, the maximum rate of hydrogenation increases to 15 ml H_2 in 1 min and reaches a maximum at a definite surface coverage (at $\Delta E = 110$ mV) at all temperatures. A further displacement of the potential indicates adsorption of the unsaturated substance that does not participate in the reaction.

Fig. 3. Dependence between the reaction rate and the potential displacement at different temperatures in 0.1 *N* NaOH. Dotted lines—sodium maleate; solid lines—sodium *o*-nitrophenolate.

Thus, the slow and uniform feeding of the unsaturated substance into the catalytic vessel makes it possible to distinguish E_{react} and E_{adsorb}, and makes it possible to determine the optimum concentrations of unsaturated substances in solution at which the rate of hydrogen removal will be equal to the rate of its renewal on the surface of the catalyst. The new hydrogenation method will make it possible to determine the rates of hydrogen activation in different media and at different temperatures.

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CITED LITERATURE

1. K. K. Dzhardamalieva, D. V. Sokol' skii, *Tr. Inst. khim. nauk*, **2**, 94 (1958).

2. D. V. Sokol' skii, V. A. Druz' , *DAN*, **73**, 949 (1950).

3. N. M. Popova, *Tr. Inst. khim. nauk*, **2**, 77 (1958).

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