Academician of the Academy of Sciences of the Kazakh SSR D. V. SOKOLSKY and L. P. DUNINA

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Academician of the Academy of Sciences of the Kazakh SSR D. V. SOKOLSKY and L. P. DUNINA

COMPARATIVE HYDROGENATION OF SODIUM PROPIOLATE ON Pt, Pd, AND Ni CATALYSTS

This article presents experimental data obtained in studying the catalytic properties of nickel, platinum, and palladium in the hydrogenation reaction of the sodium salt of propiolic acid. Hydrogenation proceeds according to the scheme:

$$\underset{\text{sodium propiolate}}{CH \equiv C - COONa} + H_2 \rightarrow \underset{\text{sodium acrylate}}{CH_2 = CH - COONa} + H_2 \rightarrow \underset{\text{sodium propionate}}{CH_3 - CH_2 - COONa}$$

Raney nickel was prepared by leaching a Ni—Al alloy (30% Ni). Platinum was obtained from the oxide (⁀1), and palladium from palladium hydroxide on barium sulfate (⁀2), by reduction with hydrogen directly in the "duck." A 0.1 N aqueous solution of NaOH was used as the solvent. Before hydrogenation, the catalyst in the solvent was saturated with hydrogen to the reversible hydrogen potential. During hydrogenation the catalyst potential was measured by the compensation method against a 0.1 N calomel electrode. Propiolic acid was introduced into the "duck" in amounts of 0.1, 0.2, and 0.3 g and converted into the salt by neutralization with sodium alkali. The experiments were carried out at 60, 40, 20, and 5°. On a single portion of platinum and palladium, four experiments were conducted successively at different temperatures.

Figure 1 presents the kinetic and potential curves for the hydrogenation of 0.262 g of sodium propiolate on Pd, Ni, and Pt at 40° in an aqueous-alkaline medium (0.1 N NaOH).

It appears possible to divide the kinetic curves into two sections: from the beginning of hydrogenation to the absorption of 64 ml of hydrogen, and from this point to the end. Polarographic analysis showed that, in the stage corresponding to the first section of the curve, the triple bond of sodium propiolate is hydrogenated by 93-94%; in the second stage, the double bond of sodium acrylate and the remaining triple bond of sodium propiolate are hydrogenated.

As can be seen from Fig. 1, on Raney nickel the triple bond is hydrogenated at a monotonically decreasing rate. The transition from hydrogenation of the

Figure 1

Figure 1: Figure 1

triple bond to that of the double bond is expressed on the kinetic curve by a sharp break, followed by an increase in the reaction rate characteristic of hydrogenation of the double bond.

Thus, the rate of hydrogenation of the double bond of sodium propiolate is lower than the rate of hydrogenation of the double bond of sodium acrylate. The displacement of the catalyst potential in the anodic direction upon introduction of the salt into the solution is 60 mV; its change during hydrogenation of the triple bond is very slight. On palladium the transition from hydrogenation of the triple bond to that of the double bond is less clearly expressed. The triple bond is hydrogenated at a considerably lower rate than the double bond, but with a gradually increasing rate. The catalyst potential shifts into the anodic region by 90 mV and remains constant until the main mass of the triple bond has been hydrogenated.

In contrast to palladium and skeletal nickel, on platinum sodium propiolate is hydrogenated almost according to zero order, but with fairly good selectivity (up to 94%). The shift of the catalyst potential in the anodic direction is 50 mV, and the triple bond is hydrogenated at a potential of 1020 mV.

The transition from hydrogenation of the triple bond to the double bond is also clearly marked on the potential curves by a sharp change in the catalyst potential. As noted above, during hydrogenation of the triple bond of sodium propiolate the catalyst potential remains almost constant. But toward the end of hydrogenation of the triple bond on Pt and Pd the catalyst potential shifts sharply into the cathodic region, increasing in absolute value by 25 mV on Pt and by 85 mV on Pd. On skeletal nickel, however, the end of hydrogenation of the triple bond is marked by a shift of the catalyst potential in the anodic direction by 20–30 mV.

Thus, if on Pd and Pt the double bond is hydrogenated at more negative potentials than the triple bond, then on skeletal nickel the potential of hydrogenation of the double bond is more positive than the potential of hydrogenation of the triple bond.

Fig. 1. Kinetic (a) and potential (b) curves for the hydrogenation of 0.262 g of sodium propiolate. Solvent: 0.1 N NaOH in water, $t = 40°$. 1 —on Pd, 2 —on Ni, 3 —on Pt

The former is quite explicable if one takes into account that molecules with a triple bond are adsorbed more strongly than molecules with a double bond. The somewhat unusual behavior of the catalyst potential during hydrogenation of the double bond on skeletal Ni is evidently associated with intradiffusion factors, with the unequal ability of different molecules to penetrate into the

Figure 2

Figure 2: Figure 2

catalyst pores (3).

In this work we also studied the effect of the concentration of sodium propiolate on the kinetics of its hydrogenation. This dependence is shown in Fig. 2. From Fig. 2 it is seen that the rate of hydrogenation of the triple bond decreases with increasing concentration of sodium propiolate, while the rate of hydrogenation of the double bond increases. Analogous results were obtained for platinum and palladium.

Fig. 2. Effect of the concentration of sodium propiolate on the rate of its hydrogenation on a skeletal nickel catalyst. Solvent: 0.1 N NaOH in water. a —rate of hydrogenation of the triple bond, b —rate of hydrogenation of the double bond

On the basis of the views expressed earlier (4,5), we believe that hydrogenation of the triple bond of sodium propiolate is limited by the activation of hydrogen. This is evidently connected with the fact that sodium propiolate is strongly adsorbed by the triple bond on the catalyst surface, displacing hydrogen. Naturally, an increase in the concentration of sodium propiolate in solution leads to a deficiency of active hydrogen on the catalyst surface, which adversely affects the rate of hydrogenation of the triple bond; moreover, on skeletal nickel this is manifested to a greater extent than on palladium. The deficiency of hydrogen on palladium may

can be compensated for by the emergence onto the catalyst surface of dissolved or bulk hydrogen, used mainly for the hydrogenation of the triple bond.

The double bond of sodium acrylate does not have the same ability to displace hydrogen from the catalyst surface that is characteristic of the triple bond. Therefore, in the second half of the reaction hydrogen is able to become activated on the catalyst surface, and this leads to a considerable increase in the rate of hydrogenation on skeletal nickel and palladium.

The activation of the unsaturated compound becomes the stage limiting the process. This is also indicated by the decrease in activation energies on skeletal nickel from 8.0 to 6.0 kcal/mol, and on palladium from 10.0 to 7.0 kcal/mol.

Kazakh State University
named after S. M. Kirov

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