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Abstract

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THE BEHAVIOR OF STYRENE AND PHENYLACETYLENE ON A PLATINUM CATALYST

The aim of the present study is to investigate the mechanism of the reaction of catalytic hydrogenation of styrene and phenylacetylene on platinum in the liquid phase.

A number of authors have previously dealt with the hydrogenation of styrene and phenylacetylene ([1–3]). It was shown that phenylacetylene on platinum is hydrogenated at a considerably lower rate than styrene, that platinum is a selective catalyst for the hydrogenation of phenylacetylene, and that in catalytic hydrogenation there exists a constant coefficient of distribution of hydrogen between acetylene and ethylene molecules. Potentiometric studies of hydrogenation reactions have shown that, in the case of hydrogenation of a triple bond, the reaction is most often limited by the activation of hydrogen, whereas in the case of a double bond it is limited by activation of the unsaturated compound ([6]). On platinum the energy of bonding of hydrogen to the surface is large, and a change in the pH of the medium has little effect on the change in the amount of hydrogen adsorbed on the surface. Styrene belongs to the compounds whose hydrogenation kinetics are affected by changing the pH of the solution upon transition to alkaline solutions; a change in the pH of the solution does not affect the kinetics of hydrogenation of phenylacetylene ([4,5]).

We investigated the behavior of styrene and phenylacetylene on platinum in aqueous 0.1 N H_2SO_4. As the reaction vessel, a catalytic "duck" was used, with an additional electrode for polarizing the main one. The main electrode-catalyst was platinized platinum gauze with a visible surface of ~ 50 cm^2; the reference electrode was mercurous sulfate. All potential values given are referred to the value of the reversible hydrogen potential in the same solution. For the study, we used the electrochemical method of charging curves proposed earlier by A. N. Frumkin, and for kinetic studies the potentiometric method, which is widely used for studying the mechanism of the reaction of catalytic hydrogenation ([6]).

Phenylacetylene on the degassed surface of platinum showed a greater adsorption capacity than styrene (Fig. 1). Both styrene and phenylacetylene shift the potential of the degassed platinum surface to the cathodic side from 0.6 to 0.255 V and 0.155 V, respectively. The results of analysis of the gas phase showed

Fig. 1

Figure 1: Fig. 1

that, when styrene and phenylacetylene come into contact with the degassed platinum surface, hydrogen is evolved in a considerable amount. The amount of hydrogen evolved for styrene is greater than for phenylacetylene and in both cases exceeds severalfold the adsorption capacity of the catalyst for hydrogen. Consequently, the process of hydrogen evolution was an act of repeated contact of the substances with the catalyst surface. The results of hydrogenation in a monolayer showed that the curves of potential change during adsorption of phenylacetylene and the curves for hydrogenation in a monolayer coincide. This means that, in the presence of phenylacetylene, the bond of hydrogen with the platinum surface is strongly weakened ([8]). Hence, hydrogen with reduced bond energy will be catalytically active. The resul-

the data on electroreduction of phenylacetylene also confirm this point of view. The electroreduction of phenylacetylene begins at a potential of 0.16 V, and at a potential of 0.08 V vigorous evolution of hydrogen is observed.

Electroreduction proceeds with a certain inhibition (an increased value of the coefficient b in the Tafel equation). In the case of hydrogenation of styrene in a hydrogen monolayer, the catalyst potential shifts by a smaller amount in the anodic direction than for phenylacetylene. The electroreduction of styrene begins at a potential of 0.245 V; the process proceeds without visible inhibition (the coefficient b of the Tafel equation is ~ 0.12).

Fig. 1. Change of potential with time upon contact of styrene with the surface of Pt saturated with a monolayer of hydrogen (1), and with the degassed surface of Pt (3); phenylacetylene with the surface of Pt saturated with a monolayer of hydrogen (2), and with the degassed surface of Pt (4).

The kinetic curves and the catalyst potential during the hydrogenation of styrene and phenylacetylene are presented in Figs. 2 and 3. The kinetics of styrene hydrogenation obeys a zero-order equation. The kinetic curve of phenylacetylene hydrogenation shows that the triple bond is hydrogenated at a lower rate than the double bond. The potential curves for the hydrogenation of styrene and phenylacetylene practically coincide and throughout the entire course of the reaction remain approximately constant; upon completion of the reaction the potential rapidly returns to the value for reversible hydrogen, without reaching it. The kinetic curves for the hydrogenation of styrene and phenylacetylene, preliminarily adsorbed on the degassed platinum surface, show that the hydrogenation rate decreases for styrene by more than a factor of 4, and for phenylacetylene by a factor of 2 (for the triple and double bonds). The potential curve for preliminarily adsorbed styrene lies in a more anodic region, while for phenylacetylene it lies in a more cathodic region, in comparison with the potential curves for the hydrogenation of styrene and phenylacetylene on a platinum surface prelim-

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

inarily saturated with hydrogen. Such an arrangement of the potential curves may be explained by a larger amount of hydrogen on the surface in the case of phenylacetylene hydrogenation than in the case of styrene; however, it is also necessary to take into account the greater donor ability of phenylacetylene as compared with styrene.

Of great interest is the question of clarifying the nature of the potential established upon contact of the substances with the degassed platinum surface. Recently, in addition to explanations of the change in potential by direct electron exchange of the adsorbed molecule with the catalyst surface or by the influence of the dipole moments of adsorbed molecules, works have appeared indicating the possibility of dehydrogenation of adsorbed molecules on the catalyst surface (8, 9). The results of gas-phase analysis showed in our case the presence of hydrogen after experiments on adsorption on the degassed platinum surface. The potential-determining species in the interaction of the substances with the degassed surface will be hydrogen. Two stages may characterize the adsorption process: the first is the evolution of hydrogen (possibly due to dehydrogenation of organic molecules on the platinum surface), the second is the addition of the evolved hydrogen to the adsorbed mole-

cule or its fragments, i.e., self-hydrogenation. Phenylacetylene shifts the potential of the catalyst to the cathodic side by a larger amount than styrene. In this case, the amount of hydrogen evolved should be greater in the case of phenylacetylene than for styrene. The result of the experiment shows the opposite. Evidently, here the second stage played a large role—the self-hydrogenation of styrene proceeds at a lower rate than the self-hydrogenation of phenylacetylene. This is confirmed by comparison of the rates of hydrogenation of styrene and phenylacetylene adsorbed on the surface (Figs. 2 and 3). The tendency of styrene toward polymerization also plays a rather important role.

Fig. 2. Kinetic (1, 2) and potential ($1'$, $2'$) curves of hydrogenation of styrene adsorbed on a degassed Pt surface (2, $2'$), and on a surface previously saturated with hydrogen (1, $1'$)

Fig. 3. Kinetic (1, 2) and potential ($1'$, $2'$) curves of hydrogenation of phenylacetylene on a hydrogen-saturated Pt surface (1, $1'$) and of phenylacetylene adsorbed on a degassed Pt surface (2, $2'$)

The principal results of the work may be the fact of hydrogen evolution upon contact of phenylacetylene and styrene with the surface of platinum, and the conclusion that both phenylacetylene and styrene are hydrogenated on platinum in 0.1 N H_2SO_4 by a hydrogen mechanism; that for phenylacetylene, hydrogen with a reduced bond energy is reactive, whereas for styrene, hydrogen with low and medium bond energy is reactive; and that in the presence of phenylacetylene the bond of hydrogen with the platinum surface is weakened.

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