Chemistry

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Abstract

Full Text

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On the Behavior of Vinyl Butyl Ether on a Platinum Catalyst

The hydrogenation of simple vinyl ethers has been little studied. Work has been carried out mainly on hydrogenation over palladium and nickel catalysts in alkaline solution and in alcohol ([1,4]). On a platinum catalyst it is known that simple vinyl ethers are hydrogenated on it at a very low rate. We carried out several experiments to study the kinetics of hydrogenation of vinyl butyl ether in an aqueous solution of $0.1\,N\,H_2SO_4$ and in 50% ethyl alcohol on a platinum catalyst, with simultaneous measurement of the catalyst potential during the reaction. As catalyst we used platinized platinum foil with an apparent surface area of 50 cm^2. Platinization was carried out from a 2% aqueous solution of chloroplatinate at a current density of $1.2 \cdot 10^{-2}$ A/cm^2. To study the kinetics of hydrogenation, a catalytic "duck" was used, which, unlike the ordinary one, also had an auxiliary electrode for polarizing the main electrode-catalyst. The reference electrode was a mercurous sulfate half-cell. As an inert gas for the electrochemical measurements, argon containing 0.003% oxygen was used. Assuming that the capacitance of 1 cm^2 of ideal surface is 36 μF, from charging curves recorded in $0.1\,N\,H_2SO_4$ we found the "true" surface of the catalyst-electrode to be $S_{\text{true}} = 95{,}000$ cm^2.

Experiments on hydrogenation in $0.1\,N\,H_2SO_4$ at 20°C showed that hydrogenation of vinyl butyl ether proceeds at a rate not exceeding 0.1 ml/min, which during a 5-hour experiment decreases to 0.02 ml/min; the catalyst potential in this case shifts by 5 to 15 mV in the anodic direction relative to the reversible hydrogen potential. In 50% ethyl alcohol the hydrogenation rate at 20° increases to 0.25 ml/min, remaining approximately constant during a 2-hour experiment; correspondingly, the catalyst potential falls below the reversible hydrogen potential by 17 mV and remains constant throughout the entire experiment. For electrochemical studies of the platinum catalyst, the method developed by A. I. Shlygin was used ([2,3]).

In the present work, data are presented on the study of the change in catalyst potential with time upon contact with vinyl butyl ether on a degassed surface and on a surface covered with a monomolecular layer of hydrogen. In addition, electrohydrogenation of this ether was carried out.

As can be seen from Fig. 1, vinyl butyl ether, upon adsorption, shifts the

Fig. 1. Change in catalyst potential with time upon contact with vinyl butyl ether. I, II, III—on a degassed surface at 20, 40, and 60° in 0.1 N H_2SO_4. 1, 2, 3—on a surface covered with a monomolecular layer of hydrogen at the same temperatures.

Figure 1: Fig. 1. Change in catalyst potential with time upon contact with vinyl butyl ether. I, II, III—on a degassed surface at 20, 40, and 60° in 0.1 N H_2SO_4. 1, 2, 3—on a surface covered with a monomolecular layer of hydrogen at the same temperatures.

catalyst potential from +0.6 V (relative to the reversible hydrogen electrode) in the cathodic direction, the final adsorption potential at 20° being 0.18 V. With an increase in temperature from 20 to 60°, the catalyst potential with time shifts in the anodic direction until a certain constant value is established: 0.248 V for 40° and 0.34 V for 60°. Hydrogenation in a monolayer (Fig. 1, *1, 2, 3*) also proceeds in a not quite usual manner. In the first minutes the catalyst potential shifts in the anodic direction, but then with time changes in the cathodic direction, approaching the reversible hydrogen potential. The higher the temperature, the sharper and higher the maximum. The final

the hydrogenation potential in a monolayer is 107 mV (20°) and 51 mV (40 and 60°). According to the charging curves in 0.1 N H_2SO_4, the hydrogen region ends at a potential of 0.35 V relative to the reversible hydrogen electrode. Consequently, in this case not all the hydrogen is reactive.

When considering these curves it is necessary to take into account the hydrolysis of vinyl butyl ether. In an aqueous medium, especially sulfuric acid, it is readily hydrolyzed with formation of acetaldehyde and butyl alcohol (4). Analytical data (oxime method) show that hydrolysis under these conditions proceeds to 50%. Obviously, with increasing temperature the hydrolysis proceeds more extensively. Fig. 2 demonstrates the adsorption of acetaldehyde, butyl alcohol, and their mixture (calculated on the assumption that all the ether has hydrolyzed) on a degassed platinum electrode. The analogy between curves III (Fig. 2) and I (Fig. 1) is evident. Hydrogenation of acetaldehyde in a monolayer of hydrogen proceeds analogously to the curves for the hydrogenation (curve I, Fig. 2) of vinyl butyl ether, especially at higher temperatures (40 and 60°).

Fig. 1. Change in catalyst potential with time upon contact with vinyl butyl ether. *I, II, III*—on a degassed surface at 20, 40, and 60° in 0.1 N H_2SO_4. *1, 2, 3*—on a surface covered with a monomolecular layer of hydrogen at the same temperatures.

Electrohydrogenation was carried out by the usual procedure; i.e., vinyl butyl ether was introduced onto the degassed surface of a platinized electrode at a potential of +0.6 V. After a constant potential had been established, the cathodic polarization current was switched on. Electrohydrogenation was carried out at $i = 1$ mA; moreover, throughout the entire electrohydrogenation time no con-

Fig. 2. Change in catalyst potential with time upon contact with acetaldehyde (I, 1), with butyl alcohol (II), and with a mixture of butyl alcohol and acetaldehyde (III) at 20° in 0.1 N H_2SO_4. I, II, III—on a degassed surface. 1—on a surface covered with a monomolecular layer of hydrogen.

Figure 2: Fig. 2. Change in catalyst potential with time upon contact with acetaldehyde (I, 1), with butyl alcohol (II), and with a mixture of butyl alcohol and acetaldehyde (III) at 20° in 0.1 N H_2SO_4. I, II, III—on a degassed surface. 1—on a surface covered with a monomolecular layer of hydrogen.

Fig. 3. Electrohydrogenation of vinyl butyl ether on platinum in 0.1 N H_2SO_4 at 20° (I) and 40° (II)

Figure 3: Fig. 3. Electrohydrogenation of vinyl butyl ether on platinum in 0.1 N H_2SO_4 at 20° (I) and 40° (II)

stancy whatever was observed in the values of the catalyst-electrode potential (Fig. 3). At $E = 120$ mV, the evolution of gas bubbles from the surface of the platinum electrode was observed visually. Chromatographic analysis showed that the evolved gas was a mixture of methane, ethylene, and butane (whether hydrogen was present could not be established, since the presence of argon interfered). Similar data were obtained in the electrohydrogenation of allyl—

Fig. 2. Change in catalyst potential with time upon contact with acetaldehyde (*I, 1*), with butyl alcohol (*II*), and with a mixture of butyl alcohol and acetaldehyde (*III*) at 20° in 0.1 N H_2SO_4. *I, II, III*—on a degassed surface. *1*—on a surface covered with a monomolecular layer of hydrogen.

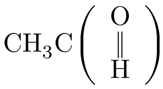
alcohol (^{5}). The probable reason here lies in the very method of electrohydrogenation with preliminary adsorption of an unsaturated compound on the degassed electrode surface. There are reports in the literature showing that, on a catalyst completely freed of gases adsorbed on it, an introduced organic substance undergoes a change (^{6}).

Fig. 3. Electrohydrogenation of vinyl butyl ether on platinum in 0.1 N H_2SO_4 at 20° (I) and 40° (II)

A. I. Shlygin and G. A. Bogdanovskii (^{7}) showed that the electrooxidation of certain organic compounds, including acetaldehyde, on platinized platinum in a sulfuric-acid medium begins at potentials of $(+0.4) - (+0.6)$ V relative to the reversible hydrogen electrode in the same solution. Probably vinyl butyl ether also decomposes upon adsorption into its constituent parts

$$CH_2{=}CH\,O\,C_4H_9$$

Analysis of the liquid phase was not carried out, but it probably contains products of ether hydrolysis, i.e. C_4H_9OH and



$$CH_3C\left(\begin{array}{c} O \\ \| \\ H \end{array}\right)$$

hydrogenated forms, and possibly CH_3COOH (^{7}).

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