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1963

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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE NATURE OF THE MINIMUM IN POTENTIAL-SHIFT CURVES OF A PLATINIZED PLATINUM ELECTRODE UPON INTRODUCTION OF ORGANIC SUBSTANCES

When organic substances are brought into contact with platinized and palladized electrodes depolarized to potentials of the "double-layer region," many authors ([1]-[4]) observed, after an initial rapid shift of the potential in the negative direction, a shift of the potential toward more positive values. This phenomenon was explained either by oriented adsorption of the substance after a potential drop caused by direct electron transfer from molecules of the organic substance to the electrode without preliminary adsorption ([1]), or by a change in the character of adsorption ([2]), or by reorientation of adsorbed molecules ([3], [4]). The experimental data obtained by us make it possible to propose another cause of the phenomenon.

The experimental procedure and the characteristics of the electrode are described in the paper ([5]). The gaseous products of the processes occurring on Pt/Pt (a platinized platinum electrode) without passage of current were collected in a special cell with a large Pt/Pt mesh having a visible surface area of 500 cm^2 (the true surface was 20-100 m^2). Acetaldehyde (pure grade) was distilled over a dephlegmator before the experiment. Propanol (chemically pure grade) and butanol (analytically pure grade) were distilled on a 1-meter rectification column with glass packing. The values of the potential φ_r are given relative to the reversible hydrogen electrode in the same solution.

Fig. 1. Dependence of the potential-shift curves of a Pt/Pt electrode upon introduction of acetaldehyde ($0.5\,M$ CH_3CHO + $0.1\,N$ H_2SO_4) on the initial potential.
1—60 mV, 2—112 mV, 3—205 mV, 4—505 mV.

As can be seen from Fig. 1, when CH_3CHO is introduced into $0.1\,N$ H_2SO_4 at φ_r of the Pt/Pt electrode below +80 ($\pm$10) mV (curve 1), only a shift of the electrode potential in the positive direction is observed, which indicates hydrogenation of acetaldehyde by adsorbed hydrogen*. Mass-spectrometric analysis

Figure 2

Figure 2: Figure 2

showed that the gaseous products of the hydrogenation of acetaldehyde in the adsorption layer of hydrogen are ethane (46%) and methane (54%).

When CH_3CHO is introduced at higher φ_r, after the initial rapid shift of φ_r in the negative direction, a shift of it toward more positive values is observed (curves 2, 3, 4 in Fig. 1). In this case the ascending branch of curve 3 runs almost parallel to curve 1, while the ascending branch of curve 2 practically coincides with curve 1. Such a change in φ_r is apparently caused by a transition from the process of dehydrogenation of CH_3CHO, which causes a shift of the electrode potential in the cathodic direc-

* The ability of CH_3CHO to be hydrogenated by hydrogen adsorbed on the Pt surface was noted earlier as well ([6]).

ron ([7]), to the process of its hydrogenation, the latter process beginning with a certain delay*.

Halide anions inhibit both the dehydrogenation ([7]) and hydrogenation of CH_3CHO (curves 1, 2, 3, 4 in Fig. 2), and the effect of their action increases in the series $(SO_4^{2-}) \ll Cl^- < Br^- < J^-$. This, apparently, explains why the effect of the initial shift of φ_r into the region of more negative values relative to the finally established potential decreases in the presence of Cl^- anions and disappears completely in the presence of Br^- anions (Fig. 2, curves 5, 6, 7).

Fig. 2. Potential-shift curves of a Pt/Pt electrode upon introduction of acetaldehyde (0.5 M) into solutions: 1, 5 –0.1 N H_2SO_4; 1, 6 –0.1 N HCl; 3, 7 – 0.09 N KBr + 0.01 N HCl; 4 –0.09 N KJ + 0.01 N HCl

We found that the potential-shift curves of a Pt/Pt electrode upon introduction of propanol and butanol, under certain conditions, can also pass through a minimum. Meanwhile, in reviews on catalytic hydrogenation, for example ([8-11]), we found no indications of the ability of C_3H_7OH and C_4H_9OH to undergo hydrogenation in the liquid phase in the presence of solid catalysts at room temperature, and according to works ([12], [13]) propanol and butanol are not hydrogenated on Pt/Pt. In view of the contradiction that arose, an additional investigation was carried out.

The investigation showed that upon introduction of C_3H_7OH and C_4H_9OH at +60 mV, a shift of the electrode φ_r is observed in the positive direction (curves 1, 3 in Fig. 3 and curve 1 in Fig. 4) and the evolution of gas bubbles. This effect, in our opinion, could be explained only by hydrogenation of the alcohols with formation of gaseous products, since displacement of gaseous hydrogen from the electrode surface at $\varphi_r > 0$ is thermodynamically impossible. Indeed, when hydrogen was passed through solutions containing C_3H_7OH and C_4H_9OH, the Pt/Pt electrode acquired zero potential. Analysis of the gaseous products

Figure 3

Figure 3: Figure 3

evolved upon introduction of C_3H_7OH and C_4H_9OH at φ_r of the Pt/Pt electrode close to 0 (30-60 mV) fully confirmed the above point of view. Upon introduction of C_3H_7OH, propane is evolved (more than 75%), ethane, and a small amount of ethylene (semquantitative chromatographic analysis); upon intro-

Fig. 3. Potential-shift curves of a Pt/Pt electrode upon introduction of C_3H_7OH into 0.1 N H_2SO_4. 1, 2 –0.6 M C_3H_7OH; 3, 4 –3 M C_3H_7OH; the dotted curve (0.6 M C_3H_7OH) corresponds to samples of propanol purified on a Pt/Pt gauze in a stream of hydrogen from hydrogenatable impurities**

* Elucidation of the cause of this delay requires further investigation of the mechanism of the hydrogenation and dehydrogenation processes of CH_3CHO.

** However, since one of the reasons for the difference between this curve and curve 1 may be the accumulation, in the sample, of liquid products of hydrogenation of C_3H_7OH, the formation of which is not excluded, such purification was not carried out in the remaining experiments.

introduction of C_4H_9OH—butane (76%), propane (23%), ethane, ethylene, and methane (1%) (mass-spectrometric analysis)*.

Pochekaeva [14], upon introducing C_3H_7OH (1.3 M) into 0.1N H_2SO_4 at φ_r of a Pt/Pt electrode close to 0, observed a shift of φ_r to 626 mV and the evolution of gas bubbles, which was identified as pure hydrogen. In the present work Pochekaeva' s data were not confirmed.

According to the data of analysis of the hydrogenation products of C_3H_7OH and C_4H_9OH, the $> C - O$ bond is predominantly hydrogenated, the $> C_2 - C_1 <$ bond much less so**, while cleavage of the other $> C - C <$ bonds practically does not occur. The result obtained shows that the presence of the OH group lowers the strength of the $> C - C <$ bond. For the hydrogenation process to proceed, it is apparently also necessary that the alcohol molecule be oriented either with the OH group toward the surface or "lying" on the Pt surface (the latter, in our opinion, is more probable).

Comparison of the results of the study of hydrogenation of propyl and allyl alcohols [12,15] shows that the rate of the process and the composition of the hydrogenation products differ markedly for these two alcohols. It is possible that hydrogenation of C_3H_5OH proceeds not through the intermediate formation of propanol, but through propylene. On the other hand, even if the process proceeds through the formation of propanol, differences may arise in the energy state and, consequently, in the rate and mechanism of hydrogenation of the C_3H_7OH molecules formed from adsorbed C_3H_5OH molecules as compared with molecules adsorbed from the bulk of the solution.

Fig. 4. Dependence of the potential-shift curves of a Pt/Pt electrode upon introduction of butanol ($0.5M$ $C_4H_9OH + 0.1N$ H_2SO_4) on the initial potential. 1 −60 mV; 2 −109 mV; 3 −196 mV; 4 −505 mV.

Figure 4: Fig. 4. Dependence of the potential-shift curves of a Pt/Pt electrode upon introduction of butanol ($0.5M$ $C_4H_9OH + 0.1N$ H_2SO_4) on the initial potential. 1 −60 mV; 2 −109 mV; 3 −196 mV; 4 −505 mV.

Fig. 4. Dependence of the potential-shift curves of a Pt/Pt electrode upon introduction of butanol ($0.5M$ $C_4H_9OH + 0.1N$ H_2SO_4) on the initial potential. 1 −60 mV; 2 −109 mV; 3 −196 mV; 4 −505 mV.

Upon introducing C_3H_7OH at +500 mV at a concentration of $0.5M$ (curve 2, Fig. 3), φ_r of the electrode does not reach values at which hydrogenation of the alcohol proceeds at a noticeable rate, which apparently explains the absence of a minimum on curve 2. The rate of hydrogenation of C_3H_7OH increases markedly with increasing alcohol concentration (curve 3, Fig. 3). Considering that the rate of dehydrogenation must also increase with increasing concentration, at sufficiently high concentrations one should expect the appearance of a minimum on the potential-shift curves upon introduction of C_3H_7OH, which is confirmed by curve 4 in Fig. 3.

The final value of φ_r, established approximately one hour after introduction of C_4H_9OH at 60 mV (curve 1, Fig. 4), is 120 ± 5 mV. Upon intro-

* Small amounts of hydrogen found in all samples (0.5–1.5%) were not taken into account in calculating the percentage composition, since they could have entered the gas phase from the solution. The possible relative error of the mass-spectrometric data is 5%.

** In the destructive hydrogenation of $C_{nH_{2n+1}}OH$ [9], cleavage of the $> C_1 - C_2 <$ bond also occurs, and the hydrogenation products are $C_{n-1}H_{2n}$ and CH_4. The absence of CH_4 among the products of hydrogenation of C_3H_7OH and C_4H_9OH by hydrogen adsorbed on Pt can apparently be explained only after analysis of the liquid hydrogenation products.

introduction of C_4H_9OH at φ_r in the double-layer region, the electrode potential is established 20–30 mV more anodic than these values, and the minimum on the corresponding curve (curve 4, Fig. 4) is absent. With a decrease in the initial value of φ_r, the minimum value of φ_r reached in the course of its displacement decreases somewhat (these changes, however, are small compared with the change in the initial values of φ_r), and a minimum appears on the φ_r, t-curves (curves 2 and 3, Fig. 4).

Since the effect of the appearance of a minimum on the φ_r, t-curves is determined by the ratio of the rates of the hydrogenation and dehydrogenation processes, the shape of the φ_r-displacement curve upon introduction of organic substances which can both be oxidized and reduced on a Pt/Pt electrode must depend

strongly on the temperature of the experiment. This is confirmed by data for CO obtained by Sokolsky, Fasman, and Padyukova ([2]). When CO is introduced at φ_r about 500 mV at 15° and 30°C, there is no minimum on the φ_r, t-curves; at 50° φ_r, after a rapid shift to approximately 50 mV, slowly rises to 200 mV. Only at the latter temperature, when CO is introduced at values of φ_r close to 0, is a shift of φ_r in the positive direction observed, i.e., apparently, reduction of CO begins to proceed at an appreciable rate.

The experimental material presented above shows that, in considering the nature of the stationary potentials of a Pt/Pt electrode established in the presence of organic substances, one must take into account not only the reactions of hydrogen ionization and oxidation of the organic compound, but also the hydrogenation reaction of the organic substance, which under certain conditions, for a number of substances, can proceed at an appreciable rate at $\varphi_r > 0$. In the present work, apparently for the first time, it has been established that C_3H_7OH and C_4H_9OH belong to the number of such substances.*

In conclusion, we consider it our pleasant duty to express our deep gratitude to Prof. A. V. Kiselev (Adsorption Laboratory, Faculty of Chemistry, Moscow State University), Prof. V. L. Tal' roze (Institute of Chemical Physics, Academy of Sciences of the USSR), and their colleagues, who kindly undertook the work of gas analysis.

Received
20 VIII 1963

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* It is possible that at sufficiently high concentrations ethanol is also hydrogenated at an appreciable rate; this is currently being investigated by us.

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