THE NATURE OF THE MINIMUM ON THE POTENTIAL DISPLACEMENT CURVES FOR A PLATINIZED PLATINUM ELECTRODE WHEN ORGANIC SUBSTANCES ARE ADDED

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Translated from Doklady Akademii Nauk SSSR, Vol. 153, No. 2,
pp. 379-382, November, 1963
Original article submitted August 20, 1963

Many authors [1-4] have observed a displacement of potential to more positive values after the initial rapid displacement of potential to more negative values when organic substances are brought into contact with platinized and palladized electrodes polarized to the potentials of the "double-layer region". This phenomenon has been attributed either to the orientated adsorption of the substance after the potential drop produced by the direct transfer of electrons from the molecules of the organic substance to the electrode without preliminary adsorption [1], or to a change in the nature of the adsorption [2], or reorientation of the adsorbed molecules [3, 4]. The experimental data which we have obtained make it possible to suggest another cause of this phenomenon.

The experimental procedure and the characteristics of the electrode have been described earlier [5]. The gaseous products of the processes taking place on the Pt/Pt (platinized platinum) electrode without the passage of current were collected in a special cell with a large Pt/Pt-gauze with a visible surface area of 500 cm^2 (the true surface area amounted to 20-100 m^2). The acetaldehyde (pure grade) was distilled on a fractionating column before the experiment. The propanol (chemically pure grade) and butanol (analytical reagent grade) were redistilled on a 1-meter fractionating column with glass packing. The values of the potential φ_r are given relative to a reversible hydrogen electrode in the same solution.

It can be seen from Fig. 1 that when CH_3CHO is added to 0.1 N H_2SO_4 at φ_r for the Pt/Pt-electrode less than +80 (±10) mV (curve 1), the electrode potential is displaced only to more positive values, indicating that hydrogenation of the acetaldehyde by adsorbed hydrogen takes place.* Mass-spectrometric analysis showed that the gaseous products of the hydrogenation of acetaldehyde in the adsorbed layer of hydrogen are ethane (46%) and methane (54%).

When CH_3CHO is added at higher values of φ_r, the latter is displaced to more positive values after its initial rapid displacement to more negative values (curves 2, 3 and 4 in Fig. 1). The ascending branch of curve 3 is almost parallel to curve 1 and the ascending branch of curve 2 almost coincides with curve 1. This change in φ_r is apparently due to a change from the process of CH_3CHO dehydrogenation, producing a displacement of the electrode potential in the cathodic direction [7], to a process involving its hydrogenation, which begins after some delay.†

Halide ions retard both the dehydrogenation [7] and the hydrogenation of CH_3CHO (curves 1, 2, 3 and 4 in Fig. 2), their effect increasing in the order $(SO_4^{2-}) \leq Cl^- < Br^- < I^-$. This apparently also explains the fact that the effect of initial displacement of φ_r towards more negative values relative to the final established potential decreases in the presence of Cl^- anions and disappears completely in the presence of Br^- anions (curves 5, 6, and 7 in Fig. 2).

We found that the potential displacement curves for the Pt/Pt-electrode when propanol and butanol are added may also pass through a minimum under certain conditions. At the same time, review articles on catalytic hydrogenation, e.g., [8-11], contain no references to the ability of C_3H_7OH and C_4H_9OH to undergo hydrogenation in the liquid phase in the presense of solid catalysts at room temperature, and according to [12, 13] propanol and butanol do not undergo hydrogenation on Pt/Pt. We carried out further studies to examine this contradiction.

* The ability of CH_3CHO to undergo hydrogenation by hydrogen adsorbed on a Pt surface was noted earlier [6].
† The reason for this delay requires further study of the mechanism of the hydrogenation and dehydrogenation of CH_3CHO.

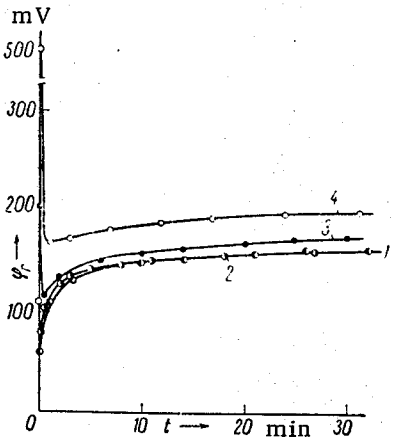

Fig. 1. Dependence of the potential displacement curves for the Pt/Pt-electrode when acetaldehyde is added (0.5 M CH_3CHO + 0.1 N H_2SO_4) on the original potential. 1) 60 mV, 2) 112 mV, 3) 205 mV, 4) 505 mV.

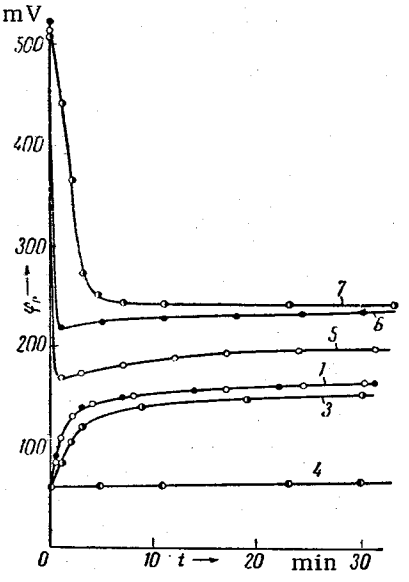

Fig. 2. Curves for the displacement of the potential of the Pt/Pt-electrode when acetaldehyde (0.5 M) is added to the solution. 1,5) 0.1 N H_2SO_4; 1, 6) 0.1 N HCl; 3, 7) 0.09 N KBr + 0.01 N HCl; 4) 0.09 N KI + 0.01 N HCl.

The studies showed that when C_3H_7OH and C_4H_9OH are added at +60 mV, φ_r for the electrode is displaced to more positive values (curves 1 and 3 in Fig. 3 and curve 1 in Fig. 4) and bubbles of gas are liberated. This effect, in our opinion, can be due only to hydrogenation of the alcohols with the formation of gaseous products, since the displacement of gaseous hydrogen from the electrode surface at $\varphi_r > 0$ is thermodynamically impossible. When hydrogen is passed through solutions containing C_3H_7OH and C_4H_9OH, the Pt/Pt-electrode in fact acquires zero potential. Analysis of the gaseous products liberated when C_3H_7OH and C_4H_9OH are added at φ_r for the Pt/Pt-electrode close to 0 (30-60 mV) confirmed completely the above viewpoint. When C_3H_7OH is added, propane (more than 75%), ethane, and some ethylene are liberated (semiquantitative chromatographic analysis) and when C_4H_9OH is added, butane (76%), propane (23%), ethane, ethylene, and methane (1%) are liberated (mass spectrometric analysis).*

Pochekaeva [14] added C_3H_7OH (1.3 M) to 0.1 N H_2SO_4 at φ_r for the Pt/Pt-electrode close to 0 and observed a displacement of φ_r to 626 mV and the liberation of bubbles of gas, which were identified as pure hydrogen. Pochekaeva's data was not confirmed in the present work.

According to the data obtained in the analysis of the products of hydrogenation of C_3H_7OH and C_4H_9OH, the $>C-O$ bond undergoes hydrogenation to the greatest extent, the $-C_2-C_1-$ bond to a much smaller extent†, while almost no rupture of other $-C-C-$ bonds takes place. This result shows that the presence of the OH group decreases the strength of the $-C-C-$ bond. For the hydrogenation process to take place, it is also apparently necessary that the alcohol molecule either is orientated by the OH group towards the surface, or "lies" on the Pt surface (in our view the latter is more probable).

* The small quantities of hydrogen detected in all specimens (0.5-1.5%) were not taken into account in the calculation of the percentage composition, since they may enter the gaseous phase from the solution. The possible relative error in the mass spectrometric data amounts to 5%.

† In the destructive hydrogenation of $C_nH_{2n+1}OH$ [9] rupture of the $-C_1-C_2-$ bond also takes place and the hydrogenation products are $C_{n-1}H_{2n}$ and CH_4. The fact that no CH_4 is found in the products of the 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.

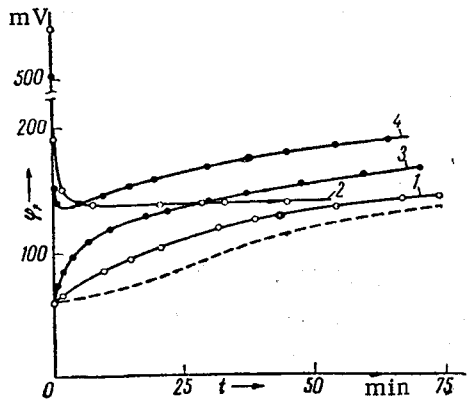

Fig. 3. Potential displacement curves for the Pt/Pt-electrode when C_3H_7OH is added to 0.1 N H_2SO_4. 1,2) 0.6 M C_3H_7OH; 3,4) 3 M C_3H_7OH; the broken curve (0.6 M C_3H_7OH) corresponds to propanol specimens purified in a current of hydrogen on Pt/Pt-gauze from impurities undergoing hydrogenation.*

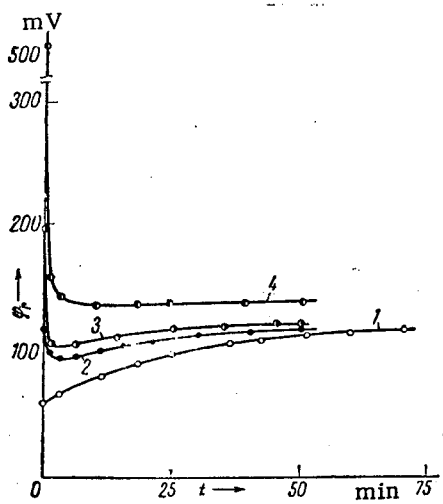

Fig. 4. Dependence of the potential displacement curves for the Pt/Pt-electrode when butanol is added (0.5 M C_4H_9OH + 0.1 N H_2SO_4) on the original potential. 1) 60 mV; 2) 109 mV; 3) 196 mV; 4) 505 mV.

Comparison of the results of a study of the hydrogenation of propyl and allyl alcohols [12, 15] shows that the rate of the process and the composition of the hydrogenation products differ considerably for these two alcohols. It is possible that the hydrogenation of C_3H_5OH takes place not via the intermediate formation of propanol but via propylene. On the other hand, it is probable that even if the process takes place via the formation of propanol, differences may arise in the energetic state and hence, in the rate and mechanism of hydrogenation of the C_3H_7OH molecules formed from adsorbed C_3H_5OH molecules, compared with molecules adsorbed from the bulk of the solution.

When C_3H_7OH is added at +500 mV at a concentration of 0.5 M (curve 2 in Fig. 3), φ_r for the electrode does not reach values at which hydrogenation of the alcohol takes place at an appreciable rate; this apparently also explains the absence of a minimum on curve 2. The rate of hydrogenation of C_3H_7OH increases considerably with increase in the alcohol concentration (curve 3 in Fig. 3). Since the rate of dehydrogenation should also increase with increase in concentration, we should expect that, at sufficiently high concentrations, a minimum should appear on the curves for the potential displacement when C_3H_7OH is added, and this is confirmed by curve 4 in Fig. 3.

The final value of φ_r established approximately one hour after the addition of C_4H_9OH at 60 mV (curve 1 in Fig. 4) amounts to 120 ±5 mV. When C_4H_9OH is added at a value of φ_r in the double-layer range, the established electrode potential is 20-30 mV more anodic then these values, and the corresponding curve (curve 4 in Fig. 4) shows no maximum. Decrease in the original value of φ_r leads to a slight decrease in the minimum value of φ_r reached during its displacement (these changes however are small compared with the change in the original values of φ_r) and the φ_r, t-curves show a minimum (curves 2 and 3 in Fig. 4).

Since the appearance of the minimum on the φ_r, t-curves is determined by the ratio of the rates of the processes of hydrogenation and dehydrogenation, the shape of the curve for the displacement of φ_r when organic substances which may be oxidized or reduced on a Pt/Pt-electrode are added should depend to a marked extent on the temperature of the experiment. This is confirmed by data for CO obtained by Sokol'skii, Fasman, and Padyukova [2]. When CO is added at φ_r equal to approximately 500 mV at 15° and 30°C, the φ_r, t-curves show no minimum; at 50°, φ_r is first rapidly displaced to approximately 50 mV and then rises slowly to 200 mV. Only at the last temperature in the addition of CO at values of φ_r close to 0 is φ_r displaced to more positive values, i.e., the reduction of CO apparently begins to take place at an appreciable rate.

The above experimental material shows that in the examination of the nature of the stationary potentials of a Pt/Pt-electrode, established in the presence of organic substances, it is necessary to make allowance not only for the

*Since one of the reasons for the difference between this curve and curve 1 may be the accumulation, in the specimen, of liquid products of the hydrogenation of C_3H_7OH, whose formation is not excluded, this purification was not carried out in the other experiments.

ionization of hydrogen and the oxidation of the organic compound but also for the hydrogenation of the organic substance, since under certain conditions, for a number of substances, this reaction may take place at an appreciable rate at $\varphi_r > 0$. In the present work, apparently for the first time, it has been established that this group of substances includes C_3H_7OH and C_4H_9OH.*

In conclusion we wish to thank Prof. A. V. Kiselev (Adsorption Laboratory, Chemistry Department, Moscow State University), Prof. V. L. Tal'roze (Institute of Chemical Physics, Academy of Sciences of the USSR) and their coworkers, who kindly undertook the work involved in the analysis of the gases.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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*It is possible that at sufficiently high concentrations ethanol is also hydrogenated at an appreciable rate and we are at present studying this question.