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Abstract

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ELECTROOXIDATION OF ORGANIC SUBSTANCES ON PLATINIZED PLATINUM AT HYDROGEN ADSORPTION POTENTIALS

(Presented by Academician A. N. Frumkin, 3 VI 1964)

The electrooxidation of organic substances on a platinum electrode at potentials in the double-layer and oxygen regions has been the subject of numerous studies (see, for example, [1,2]).

We have found that, with an appropriate choice of experimental conditions, it is possible to obtain appreciable rates of electrooxidation of various organic substances in the region of hydrogen adsorption potentials. The electronic potentiostat used for the measurements was constructed on the basis of the TsLA PO-5122 oscillographic polarograph and made it possible to vary the electrode potential at rates v from 1.8 to 120 mV/sec. The experiments were carried out using sawtooth and triangular sweeps.

The measurements were performed at room temperature $20 \pm 2°$ on rotating platinized platinum (Pt/Pt) electrodes with visible surface areas of 1.78, 0.2, and 0.07 cm^2. The true surface area of the electrodes, calculated from the hydrogen region of the potentiostatic i, φ-curve in 0.1 N H_2SO_4, varied for different electrodes from 150 to 750 cm^2/cm^2 of visible surface. The values of current density are given per 1000 cm^2 of true surface. The potentials φ_r are given relative to the hydrogen electrode in the same solution.

The organic substance was brought into contact with the Pt/Pt electrode, the potential of which was maintained by means of the potentiostat at +50 mV. Then the potentiostatic curve was recorded during the first sweep from 0.05 V in the anodic direction, and the curves during subsequent anodic pulses after the potential had been returned to the initial value of 0.05 V, either stepwise or by reversing the direction of the sweep.

The results obtained in methanol solutions are presented in Fig. 1. The potentiostatic curve measured during the first sweep in solutions of alcohols, formic acid, and formate ion lies not only above the curves for subsequent sweeps, but also above the curves in background solutions, which is associated with the occurrence of electrooxidation of the organic substances.

Fig. 1

Figure 1: Fig. 1

The course of the curves during subsequent sweeps depends on the final φ_r during the sweep, as was also noted earlier in [1,2], and on the shape of the applied voltage. Thus, with a sawtooth sweep in the interval from 0.05 to 0.9–1.5 V in methanol solutions, the $i,\ \varphi$-curve is close to the curve obtained during the first sweep, although it lies somewhat below it (curve 2, Fig. 1). At a final φ_r of the sawtooth sweep below 0.8 V and with a triangular sweep (independently of the final φ_r), electrooxidation of methanol is practically not observed (Figs. 1, 2, 3), and the initial portion of the curves corresponds to the ionization of adsorbed hydrogen. In this case, in order to obtain curves that do not change with time, it is generally necessary to carry out several sawtooth sweeps in the interval $0.05 \leqslant \varphi_r \leqslant 0.8$ V. In formate solutions, the first and subsequent sawtooth swee –

the sweeps practically coincide even at a final $\varphi_r \geqslant 0.65$ V, whereas in HCOOH solutions the subsequent curves lie appreciably below the first curve at any final φ_r during the sawtooth sweep.

The differences between the curve measured with the first anodic pulse and the curves during subsequent sawtooth sweeps to low φ_r, or during a triangular sweep, are caused by the accumulation on the electrode surface of products of chemisorption of organic substances at low anodic φ_r (in the case of a triangular sweep, during the cathodic branch). Indeed, if after a triangular sweep from 0.05 to 1.5 V in a solution of 1 N $H_2SO_4 + 0.05\,M$ CH_3OH the potential is held at 0.05 V, the system is washed free of alcohol, and the i, φ-curve is measured in a pure 1 N H_2SO_4 solution, then a maximum of oxidation of the chemisorbed substance is found on it. The adsorption coefficient f ([3]), calculated on the basis of this curve, is found to be ~ 0.6. When a sawtooth voltage is used, under otherwise identical conditions, the amount of chemisorbed substance is close to 0 ($f \sim 0.05$). Hence the choice becomes clear of a potential for introducing the organic substance before the first sweep that is close to the reversible hydrogen potential. At such values of φ_r, methanol is practically not chemisorbed on Pt/Pt, as shown in ([4]), and chemisorption of ethanol, HCOOH, and $HCOO^-$ also practically does not occur during the time preceding the sweep. By contrast, for acetaldehyde (and also formaldehyde), which is chemisorbed on platinum even at φ_r close to 0, owing to hydrogenation, dehydrogenation, and molecular decomposition processes proceeding at an appreciable rate ([5]), it is not possible to observe differences between the first and subsequent sweeps, or between measurements with superposition of sawtooth and triangular voltage.

Fig. 1. Potentiostatic curves in a solution of 0.1 N $H_2SO_4 + 0.05\,M$ CH_3OH: **1** –during the first sweep; **2** –during a sawtooth sweep from 0.05 to 1.5 V; **3** –anodic curve during a triangular sweep ($v = 5.4$ mV/sec). Dashed line –curve in the background solution.

The electrooxidation curves of organic substances during the first sweep have a complex shape and are characterized by the presence of current maxima. The number of maxima and their height depend on the nature and concentration of the organic substance, the pH, and the composition of the solution. The oxidation current increases with increasing concentration of the substance. For oxidation to begin, it is necessary to liberate some number of sites occupied by adsorbed hydrogen, which is especially clearly noticeable at low concentrations of the substances. As the sweep rate is increased, the current maxima shift in the anodic direction and become less pronounced.

If it is assumed, as a first approximation, that the course of the electrooxidation process of organic substances during the sweep does not affect the ionization of hydrogen adsorbed on platinum,* then the curves for the first sweep can be corrected for the background current. On the corrected curve in 1 N H_2SO_4 (Fig. 2a) there is one maximum, approximately coinciding in potential with the maximum of ionization of adsorbed hydrogen. With increas– of pH, one more maximum begins to appear at more anodic potentials (Fig. 2a). Apparently, in 1 N H_2SO_4 this maximum is masked by the main methanol-oxidation wave, which, with increasing pH, is gradually shifted in the anodic direction. The rate of oxidation during the first sweep decreases noticeably in the presence of Cl^- ions. In alkaline solutions only one maximum is observed before the main wave; its height increases with increasing pH, exceeding in 1 N KOH the height of the analogous maximum in acid solutions by approximately a factor of three (Fig. 2b).

Fig. 2. Potentiostatic curves in solutions of 1 N (H_2SO_4 + K_2SO_4) (a) and 1 N (KOH + K_2SO_4) (b) in the presence of 0.5 M CH_3OH during the first sweep at different pH values: 1 –0.37; 2 –1.19; 3 –1.67; 4 –2.33; 5 –2.96; 6 –12.13; 7 –12.85; 9 –13.75; 8 –0.3 M KOH. Curves measured in acid solutions have been corrected for the background current. Dashed line –background curve in 1 N KOH. $v = 5.4$ mV/sec.

Fig. 3. Relationship between Q_H and Q_M in a solution of 0.1 N H_2SO_4 + 0.05 M CH_3OH (a) and in 0.1 N KOH + 0.05 M CH_3OH (b). The values of the final φ_r during the sweeps (in volts) are indicated in parentheses. Points at one φ_r refer to different experiments. Apparent electrode surface –1.78 cm^2.

As is evident from the data obtained (Fig. 2a, b), at φ_r in the hydrogen region the methanol-oxidation current depends little on the pH of the solution, which is observed especially well in acid solutions. This is consistent with the concept that the electrooxidation process in the low-φ_r region proceeds by the dehydrogenation mechanism (⁶). To explain the dependence of the process rate on pH in the more anodic region of φ_r, and especially to explain its increase

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* Such an assumption is fulfilled only approximately, as shown by the results of measurements of the time dependence of the current after introduction of the organic substance at φ_r in the hydrogen region, as well as by analysis of charging curves during chemisorption of methanol (⁴).

in alkaline solutions with increasing pH, further investigation is required. It is possible that in alkaline solutions the dehydrogenation process is facilitated as a result of an increase in the energy of the bond between adsorbed hydrogen and the platinum surface. It cannot be excluded, however, that in such solutions hydroxyl ions participate in the rate-determining stage of the process.

Assuming that the occurrence of the dehydrogenation process does not affect the ionization of hydrogen adsorbed on platinum, one can construct a dependence between the quantity of electricity Q_{H} obtained during the electrooxidation of methanol in the course of the first sweep and the quantity of electricity Q_{M} going to the oxidation of the substance chemisorbed in this process. To construct such a dependence, a sawtooth sweep was carried out from 0.05 V to various φ_r, and, upon returning φ_r to the initial value, the electrode was washed free of methanol and the oxidation curve of the chemisorbed substance was measured. From the curve during the first sweep the value Q_{H} was determined, and from the curve after washing, Q_{M}. The results obtained are presented in Fig. 3. In acidic solutions there is a linear dependence between Q_{H} and Q_{M}, with a slope of 45°, up to ~ 400 mV. This means that all the current obtained during the first sweep is spent only on the formation of a chemisorbed product of composition HCO, as was assumed earlier in (4). The deviation at higher φ_r, which begins earlier in alkaline solutions, is evidently due to the fact that the current goes not only to the deposition of the chemisorbed product, but also to its further oxidation and to the oxidation of methanol to stable, non-chemisorbing products.

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