ELECTRO-OXIDATION OF ORGANIC SUBSTANCES ON PLATINIZED PLATINUM IN THE HYDROGEN ADSORPTION POTENTIAL REGION

Khira Lal, O. A. Petrii, and B. I. Podlovchenko

M. V. Lomonosov Moscow State University
(Presented by Academician A. N. Frumkin, July 3, 1964)
Translated from Doklady Akademii Nauk SSSR, Vol. 158, No. 6,
pp. 1416-1419, October, 1964
Original article submitted June 3, 1964

Electro-oxidation of organic substances on a platinum electrode in the double-layer and oxygen regions has been the object of numerous investigations (see for example [1, 2]).

We have demonstrated that by suitable choice of experimental conditions one can obtain appreciable electro-oxidation rates for various organic substances in the hydrogen-adsorption potential region. The electronic potentiostat used was based on a TsLA PO-5122 oscillographic polarograph and could change the electrode potential at speeds v from 1.8 to 120 mV/sec. Experiments were performed with both sawtooth and triangular scanning.

The measurements were made at room temperature (20 ± 2°) on rotating platinized platinum (Pt/Pt) electrodes with apparent surfaces of 1.78, 0.2 and 0.07 cm^2. The true electrode surfaces, calculated in the hydrogen region from the potentiostatic i-φ curve in 0.1 N H_2SO_4 varied from 150 to 750 cm^2 per cm^2 apparent surface. The current densities were calculated per 1000 cm^2 true surface. The potentials φ_r were measured with respect to a hydrogen electrode in the same solution.

The organic substance was brought into contact with the Pt/Pt electrode, whose potential was maintained at +50 mV by means of the potentiostat. The potentiostatic curve was then recorded for the first sweep from 0.05 V on the anode side, followed by the curves for successive anode pulses after the potential had returned to its original value of 0.05 V, either unevenly or by reverse scanning.

Figure 1 shows results obtained in methanol solutions. In solutions of alcohols, formic acid and formate ions, the potentiostatic curve for the first sweep lies not only above the curves for subsequent sweeps but also above those for the base electrolyte, owing to the electro-oxidation of the organic substances.

The shapes of the curves for the subsequent sweeps depend on the final φ_r of the sweep (as observed in [1, 2]) and on the form of the applied potential. For example, with sawtooth scanning from 0.05 to 0.9-1.5 V in methanol solutions, the i-φ curve lies close to that obtained during the first sweep, but a little below it (Fig. 1, curve 2). For sawtooth scanning with final φ_r below 0.8 V, and for triangular scanning with any final φ_r, practically no electro-oxidation of methanol was observed (Fig. 1, 2, 3); the initial part of the curves corresponds to ionization of adsorbed hydrogen. To obtain curves which do not vary with time it is here generally necessary to carry out several sawtooth sweeps in the interval $0.05 \leq \varphi_r \leq 0.8$ V. In formate solutions the first and subsequent sawtooth scans practically coincide, even with final $\varphi_r \geq 0.65$ V, whereas in HCOOH solutions the subsequent curves lie somewhat below the first, for any final φ_r during sawtooth scanning.

The differences between the curves for the first anode pulse and those for subsequent sawthooth sweeps to a low φ_r (or with triangular scanning) are caused by accumulation on the electrode surface of the chemisorption products of organic substances at low anode φ_r (or, in the case of triangular scanning, during the cathode sweep). In fact, if the potential is maintained at 0.05 V 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 system being subsequently washed free from alcohol and the i-φ curve measured in a pure solution of 1 N H_2SO_4, the curve displayes a maximum due to oxidation of the chemisorbed substance. The adsorption coefficient, f, calculated from this curve [3] is ~0.6. With a sawtooth voltage (other conditions remaining constant) the amount of chemisorbed substance is nearly zero ($f \sim 0.05$). It follows that the choice of potential for introducing an organic substance before the first scan should be close to the reversible hydrogen potential. At these

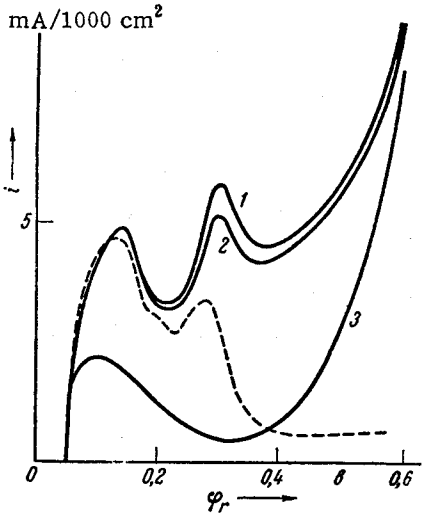

Fig. 1. Potentiostatic curves in solutions of 0.1 N H_2SO_4 + 0.05 M CH_3OH. 1) First scan; 2) with sawtooth scanning from 0.05 to 1.5 V; 3) anode curve for triangular scanning (v = 5.4 mV/sec). Broken line: curve for base electrolyte solution.

φ_r values methanol is hardly adsorbed at all on Pt/Pt, as shown in [4], and ethanol, HCOOH and $HCOO^-$ are also scarcely adsorbed before the sweep. On the other hand, for acetaldehyde and formaldehyde, which are chemisorbed on platinum even at φ_r values near to zero, owing to the occurrence of appreciable hydrogenation, dehydrogenation and molecular decomposition rates [5], no difference is observed between the first and subsequent sweep and between measurements with applied sawtooth and triangular potentials.

The first-sweep curves for electro-oxidation of organic substances have a complex form and different maximum currents. The number and height of the maxima depends on the nature and concentration of the organic substance, the pH and the solution composition. The oxidation current increases with the concentration of the substance. For oxidation to begin a number of the sites occupied by adsorbed hydrogen must be vacated; this is especially noticeable at low substance concentrations. On increasing the sweep frequency the current maxima are displaced towards the anode and become less marked.

If we suppose that, to a first approximation, electro-oxidation of organic substances does not affect the ionization of hydrogen adsorbed on the platinum,* the first-sweep curves can be corrected for the base-electrolyte current. The corrected curve in 1 N H_2SO_4 (Fig. 2a) has one maximum which coincides approximately in potential with the ionization maximum of adsorbed hydrogen. On increasing the pH another maximum begins to appear at more anodic potential (Fig. 2a). In 1 N H_2SO_4 this maximum evidently conceals the main methanol oxidation peak, which gradually moves in the anode direction with increasing pH. The rate of oxidation decreases considerably during the first sweep when Cl^- ions are present. In alkaline solutions only one maximum is observed before the main peak; its height increases with the pH, and in 1 N KOH is about three times that of the analogous maximum in acid solutions (Fig. 2b).

As seen from Fig. 2a, b, in the hydrogen region of φ_r the methanol oxidation current is nearly independent of the pH, especially in acid solutions. This supports the hypothesis that at low φ_r values electro-oxidation takes place by dehydrogenation [6]. To explain the relation between the process rate and the pH in the more anodic φ_r region – especially its increase with the pH in alkaline solutions – we need an additional hypothesis. It may be that, in alkaline solutions, dehydrogenation is facilitated by an increase in energy of the bond between the adsorbed hydrogen and the platinum surface. It is, however, also possible that in such solutions hydroxyl ions take part in the slowest stage of the process.

Assuming that the occurrence of dehydrogenation does not affect the ionization of hydrogen adsorbed on the platinum, we can plot Q_H, the quantity of electricity obtained by electrolysis of methanol during the first sweep, and Q_M, the quantity of electricity used in oxidizing the substance undergoing chemisorption. To construct this graph we used sawtooth scanning from 0.05 V to various φ_r; on return of φ_r to its initial value, the electrode was washed free of methanol and the oxidation curve of the chemisorbed substance was measured. Q_H was determined from the first-sweep curve, Q_M from the curve after washing. The results are shown in Fig. 3. In acid solution there is a linear relation between Q_H and Q_M with gradient 45° up to ~ 400 mV. This implies that all the current during the first sweep is expended on forming a chemisorbed product of composition HCO, as suggested in [4]. The deviation at higher φ_r (which begins earlier in alkaline solutions) is evidently due to the fact that the current does not only form the chemisorbed product but also oxidizes it further, also oxidizing methanol to stable non-chemisorbable products.

*This assumption is only approximately true, as shown by measurements of the current-time curve after introducing the organic substance at φ_r in the hydrogen region, and also by analysis of the charging curves for chemisorption of methanol [4].

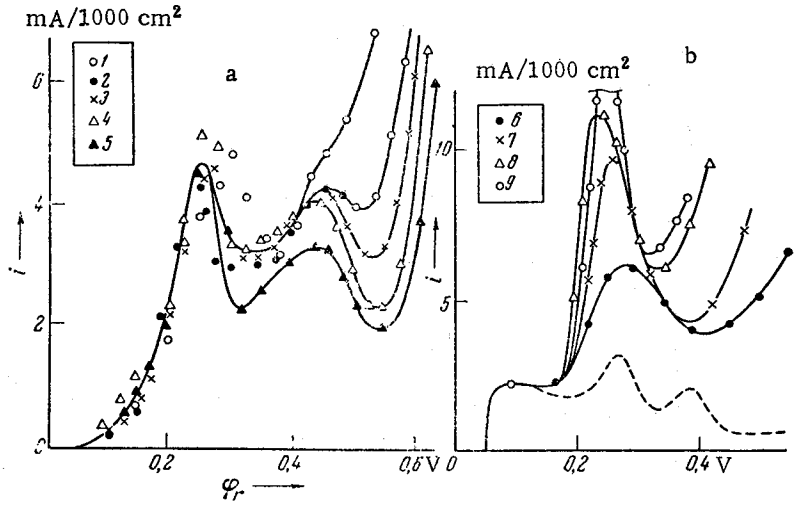

Fig. 2. Potentiostatic curves in solutions of (a) 1 N (H_2SO_4 + K_2SO_4) and (b) 1 N (KOH + K_2SO_4) with 0.5 M CH_3OH, for the first sweep at different pH values: 1) 0.37; 2) 1.19; 3) 1.67; 4) 2.33; 5) 2.96; 6) 12.13; 7) 12.85; 9) 13.75; 8) in 0.3 M KOH. The curves measured in acid solution are corrected for the base-electrolyte current. Dotted line: base-electrolyte curve in 1 N KOH. v = 5.4 mV/sec.

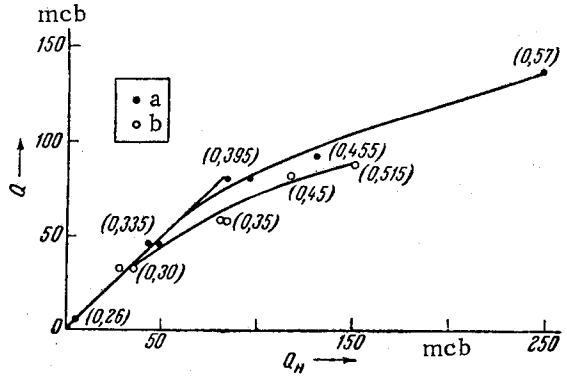

Fig. 3. Q_H versus Q_M: a) in 0.1 N H_2SO_4 + 0.05 M CH_3OH; b) in 0.1 N KOH + 0.05 M CH_3OH. Figures in brackets are the final φ_r values of the sweep (in volts). Points for one φ_r value refer to different experiments. Apparent electrode surface = 1.78 cm^2.

The authors wish to thank Academician A. N. Frumkin for his constant guidance, valuable advice and comment, and I. E. Bryksin, who constructed the potentiostat.

LITERATURE CITED

1. M. Breiter and S. Gilman, J. Electrochem. Soc., 109, 622, 1099 (1962); 110, 449 (1963); Electrochim. acta, 8, 447, 973 (1963).
2. A. Juliard and H. Salit, J. Electrochem. Soc., 110, 1002 (1963); J. Giner, Electrochim. acta, 9, 63 (1964); W. Vielstich and A. Kutschker, Electrochim. acta, 8, 985 (1963).
3. B. I. Podlovchenko, and Z. A. Iofa, ZhFKh, 38, 211 (1964).
4. B. I. Podlovchenko and E. P. Gorgonova, DAN, 156, No. 3 (1964).
5. B. I. Podlovchenko, O. A. Petrii, and A. N. Frumkin, DAN, 153, 379 (1963).
6. A. N. Frumkin and B. I. Podlovchenko, DAN 150, 349 (1963).

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.