ELECTROCHEMICAL OXIDATION OF HYDROCARBONS ON A PLATINUM ELECTRODE

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In a series of investigations it was shown that electrochemical oxidation of ethylene, ethane and other hydrocarbons to CO_2 takes place on a platinum electrode in aqueous electrolyte solutions [1-7]. According to the concepts developed by Bockris and co-workers[1], ethylene molecules adsorbed on the platinum surface react with absorbed OH groups:

$$C_2H_4 + OH_{ads} = C_2H_4OH, \quad (1)$$

and then complete oxidation occurs according to Eq. (2):

$$C_2H_4OH + \ldots \rightarrow 2CO_2 + 11H^+ + 11e. \quad (2)$$

In this case reaction (1) is the limiting step. Meanwhile, from the studies of chemisorption of hydrocarbons on metals of the platinum group it is known that in the chemisorption process dehydrogenation of hydrocarbons takes place with the formation of hydrocarbons of a different structure [8-10]. Thus, for example, chemisorption of ethane on rhodium results in the formation of significant amounts of methane, and in the chemisorption of ethylene—of ethane and methane. In the studies of Frumkin, Podlovchenko and Petrii [11-13] it was demonstrated that dehydrogenation and self-hydrogenation of saturated alcohols on platinum takes place in aqueous electrolyte solutions and that the first step of the oxidation, process, at least at not too positive potentials, is dehydrogenation. Dehydrogenation and self-hydrogenation are also observed in the adsorption of hydrocarbons [14].

In this work the nature of the chemisorption of ethane and ethylene on a platinum surface in acid and alkaline solution was studied by means of charging curves. This method was used in the studies [11-13] in investigating the mechanism of oxidation of alcohols.

The apparatus in which the measurements were performed was connected by means of ground-glass joints to the set-up for the purification of ethylene, ethane and argon, and to the reservoir containing the electrolyte being studied, which had been freed of oxygen and was in an argon atmosphere. The experiments were performed with a 4 cm^2 platinized platinum electrode. The roughness coefficient, R, of the electrodes was 3800-1000 in different experiments. The roughness coefficient was determined from the hydrogen charging curve (from $\varphi = 0$ to the end of the hydrogen arrest) on the basis that 0.21 mcoul. is required for the desorption of a monolayer of hydrogen of 1 cm^2. After recording the hydrogen charging curve in an argon atmosphere the electrode potential was brought to 400 mV relative to a hydrogen electrode in the same solution and then ethane or ethylene was bubbled in. On bubbling in the hydrocarbons the potential was displaced in the negative direction. After establishing a constant

t, °C	Ethane						Ethylene					
	in 1N H_2SO_4			in 1N KOH			in 1N H_2SO_4			in 1N KOH		
	R	θ_e	θ_H	R	θ_e	θ_H	R	θ_e	θ_H	R	θ_e	θ_H
20	2860	0,21	0,1	3060	0,27	0,16	1040	0,17	0,11	3720	0,50	0,23
20—97	2860	0,12	0,43	3060	0,0	0,52	1080	0,0	0,88	2790	0,0	0,91
97	2860	0,08	0,1	3060	0,0	0,04	1400	0,17	0,16	2790	0,0	0,16

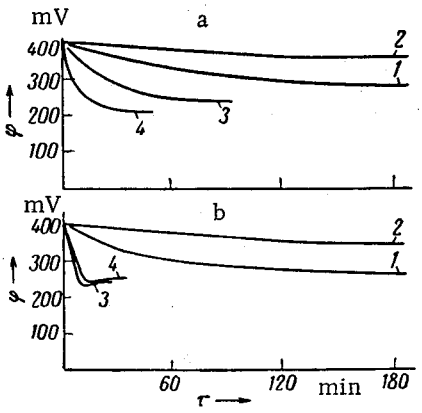

Fig. 1. Establishment of a stationary potential: a) ethane, b) ethylene. 1, 2) 1 N KOH; 3, 4) 1 N H_2SO_4; 1, 3) 21°; 2, 4) 97°.

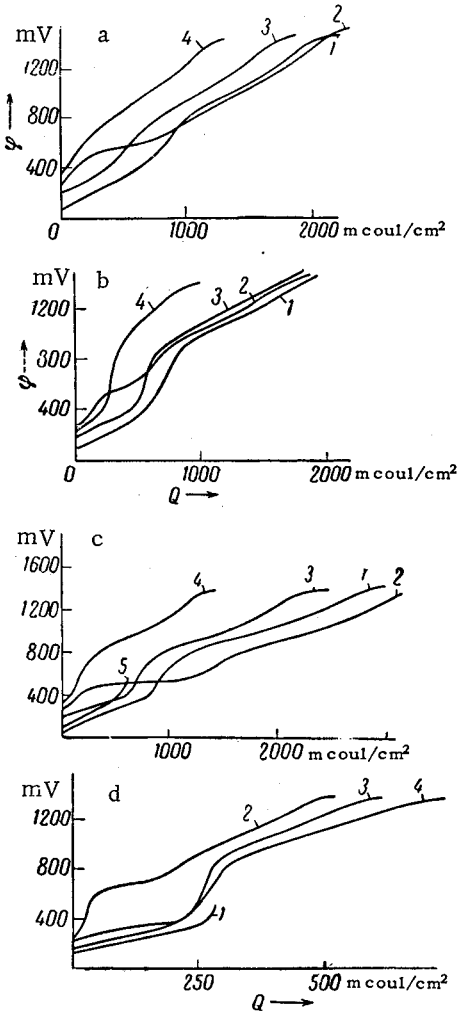

Fig. 2. Charging curves. a) Ethane in 1 N KOH, b) ethane in 1 N H_2SO_4, c) ethylene in 1 N KOH, d) ethylene in 1 N H_2SO_4. 1) H_2 (for comparison), 2) at 21°, 3) 21-97°, 4) 97°. For ethylene in KOH; 1) H_2 at t = 21°, 5) H_2 at t = 97°.

potential the electrolyte was changed in an argon atmosphere and the charging curve of a platinum electrode chemisorbed with ethylene or ethane was then obtained in both 1 N H_2SO_4 and 1 N KOH solutions. The charging curves were recorded with a current of 0.25 mA/cm^2 at 20 and 97°. All potentials are corrected relative to the hydrogen electrode in the same solution.

In the case of adsorption of ethylene on Pt in 1 N H_2SO_4 solution, the curve which shows the dependence of the potential on time of experiments performed both at 20 and 97° (Fig. 1b, curves 3 and 4) passes through a minimum at 230-240 mV. The minimum potential is established within 10-15 min. The potential then shifts somewhat in the positive direction. Displacement of the potential in the negative direction is due to the adsorption of hydrogen originating from the dehydrogenation process and a displacement in the positive direction is due to hydrogenation, resulting in the formation of ethane and methane. These phenomena are similar to the kinetics of establishing a potential in the presence of alcohols [13]. Approximately the same potential is established in an acid solution at 20° in an ethane atmosphere (Fig. 1a, curve 3) as in ethylene, although the potential is established more slowly and there is no minimum in the φ vs t curve. A similar dependence of the curve establishing a potential is observed at 97° (Fig. 1a, curve 4), but in this case the stationary potential has a more negative value corresponding to 200 mV due to the increase in the amount of hydrogen adsorbed. The potential is established more slowly in ethylene or ethane atmospheres in alkaline solution than in acid solution.

In the charging curves of a platinum electrode in 1 N H_2SO_4 and 1 N KOH solutions at 20° there is a distinct arrest in the 500-700 mV potential range which corresponds to the oxidation of chemisorbed ethylene and ethane (curves 2, Fig. 2a, b, c and d). It should be noted that there is also an arrest corresponding to hydrogen adsorption in the charging curves at 20°. In Figs. 2 and 3 hydrogen curves (curves 1) are presented for comparison and for calculating the surface area.

The nature of the charging curves at 97° (curves 4, Fig. 2) for the systems indicated is substantially different from the charging curves at 20°. From the data presented it can be seen that in the chemisorption of both ethylene and ethane in alkaline solution there is only a barely noticeable arrest in the charging curves at a potential of 650-800 mV which corresponds to oxidation of the organic substances. In the case of chemisorption of ethylene there is also a hydrogen arrest in the charging curve at 97°. In the charging curves obtained in 1 N H_2SO_4 and 1 N KOH at 97° there are hydrogen arrests after the adsorption of ethylene and ethane (curves 4, Fig. 2). At a potential of 320-400 mV the slope of the charging curve changes. It is possible that at these potentials oxidation of some hydrocarbon residue occurs together with the oxidation of H_2. The presence of chemisorbed hydrogen is

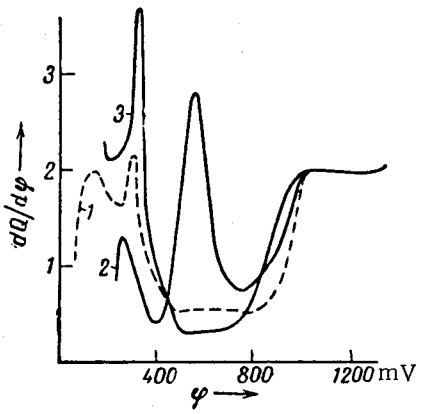

Fig. 3. Differential charging curves, Ethane, 1 N H_2SO_4. 1) H_2 (for comparison); 2) 21°; 3) 21-97°.

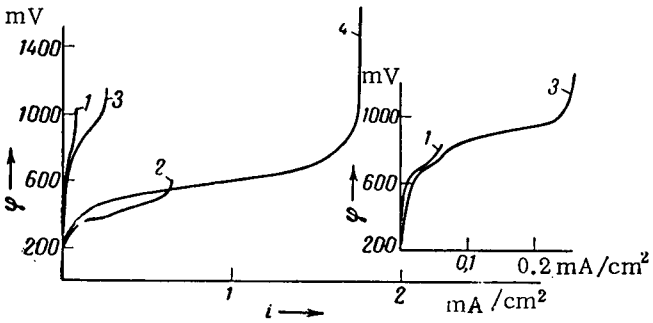

Fig. 4. Polarization curves in 1 N H_2SO_4. 1,2) Ethane; 3,4) ethylene; 1,3) 21°; 2,4) 97°.

obvious in curve 3 of Fig. 2. The experiments corresponding to curve 3 were performed as follows: After chemisorbing the ethylene and ethane at 20° and establishing the stationary potential, the electrolyte solution saturated with hydrocarbon was decanted and an electrolyte solution saturated with argon, having a temperature of 97°, was introduced. In so doing the potential of the electrode in argon is displaced in the negative direction to 190 mV in the case of ethane and to 155 mVin the case of ethylene.

It is evident from the data presented in curve 3 of Fig. 2 and in the table that in the adsorption of both ethylene and ethane in acid and alkaline solution there is a large amount of hydrogen on the platinum surface, i. e., in these experiments the process of dehydrogenation of hydrocarbons appears more distinctly. As was shown above, after prolonged heating of the platinum electrode at 97° (curve 2 of Fig. 3) there was significantly less adsorption of hydrogen on the electrode surface. The latter is apparently due to the fact that chemisorbed hydrogen hydrogenates the radicals formed from the rupture of the C−C and C = C bonds, and in this case methane is formed which is desorbed from the platinum surface at higher temperatures. However, it must be assumed here that an organic residue remains on the platinum surface and that its oxidation in the experiments performed at higher temperatures is not observed in the charging curves. It is possible that in this case oxidation does not proceed via an electrochemical mechanism. It should be noted that after performing the experiments with chemisorbed ethylene in alkaline solution a change in the platinum surface was found, as evidenced by the significantly decreased ability to adsorb hydrogen. This phenomenon may be due to the presence on the surface of a difficultly oxidizable organic residue or carbon. It follows from the data in the table that the amount of hydrogen from the experiments presented in curves 3 of Fig. 2 c and d (20 97°) is even greater than obtainable from chemisorbed ethylene on the basis of charging curves obtained at 20°. This compels us to assume that ethylene molecules chemisorbed on less active portions of the surface are not completely oxidized at 20°. This question requires further explanation. The processes observed in the charging curves are more clearly evident in Fig. 3 where some of the curves studied are presented in differential form. The maximum in curve 2 at 500 mV corresponds to the oxidation of ethane in H_2SO_4 at 20°. The maxima at a potential of 350 mV in curves 1,2 and 3 (the hydrogen curve, after adsorption of ethane at 20° and after heating at 97°, respectively) correspond to adsorption of hydrogen (Fig. 3).

From the charging curves of platinized electrodes chemisorbed ethylene and ethane can be determined approximately by the fraction of surface occupied by the hydrocarbon, θ_E, and by hydrogen, θ_H. Because in the chemisorption process the decomposition of ethylene and ethane proceed very slowly, it can be assumed that the total quantity of electricity, corresponding to the arrest at 500-700 mV, is consumed in the oxidation of chemisorbed hydrocarbons.

Assuming that 12 electrons are liberated in the oxidation of ethylene and 14 in the case of ethane, and considering that four surface sites are occupied in the adsorption of one molecule, a value is obtained for the surface coverage by ethylene and ethane at various temperatures (the table). In accordance with [9] an H/C ratio of 1.5 corresponding to 5.5 electrons is assumed for the hydrocarbon residue. From the data of the table it follows that the greatest surface coverage at 97° occurs in the chemisorption of ethylene in 1 N H_2SO_4. In experiments in which chemisorption of ethane was performed at 20° but oxidation at 97°, in general surface coverage by hydrogen in 1 N KOH amounts to 0.5, whereas for ethylene in 1 N H_2SO_4 and 1 N KOH it is 0.90.

The polarization curves were also investigated for these systems (Fig. 4). The fastest rate of oxidation was observed for ethylene at 97° (curve 4). The faster rate of reaction in this case in comparison with the others is due to the faster rate of adsorption, the larger amount of chemisorbed gas on the surface, and, as is evident from the data presented in Fig. 2 (curve 3), the greater rate of dehydrogenation as manifest in the significant surface coverage by adsorbed hydrogen. It is possible that oxidation of hydrocarbons at high current densities follows mechanism (1) and (2). However, at low current densities when oxidation occurs at more negative potentials the first step is apparently dehydrogenation. An analysis of the polarization curves will be presented in the next communication.

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