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Electrochemical Oxidation of Hydrocarbons on a Platinum Electrode

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A number of studies have shown that on a platinum electrode in aqueous electrolyte solutions the electrochemical oxidation of ethylene, ethane, and other hydrocarbons to CO_2 takes place ([1]-[7]). According to the ideas developed by Bockris et al. ([1]), adsorbed ethylene molecules on the platinum surface interact with adsorbed OH groups:

$$C_2H_4 + OH_{ads} = C_2H_4OH, \tag{1}$$

and then complete oxidation occurs according to equation (2):

$$C_2H_4OH + ... \to 2CO_2 + 11H^+ + 11e. \tag{2}$$

In this case reaction (1) is the limiting stage. Meanwhile, from studies on the chemisorption of hydrocarbons on metals of the platinum group, it is known that in the process of chemisorption dehydrogenation of hydrocarbons occurs and hydrocarbon molecules of a different composition are formed ([8]-[10]). Thus, for example, chemisorption of ethane on rhodium leads to the formation of considerable amounts of methane, while during chemisorption of ethylene, ethane and methane are formed. In the works of Frumkin, Podlovchenko, and Petria ([11]-[13]) it was shown that dehydrogenation and self-hydrogenation of saturated alcohols on platinum take place in aqueous electrolyte solutions, and that the first stage of the oxidation process, at least at not too positive potentials, is dehydrogenation. Processes of dehydrogenation and self-hydrogenation are also observed during adsorption of hydrocarbons ([14]).

In the present work the nature of the chemisorption of ethane and ethylene on the surface of platinum in acidic and alkaline solution was studied by the charging-curve method. This method was used in works ([11]-[13]) in the investigation of the mechanism of alcohol oxidation.

The apparatus in which the measurements were carried out was connected by ground joints to units for purifying ethylene, ethane, and argon, and to a reservoir containing the electrolyte under investigation, freed of oxygen and kept

Figure 1

Figure 1: Figure 1

in an argon atmosphere. The experiments were performed with an electrode made of platinized platinum with an area of 4 cm^2. The roughness coefficient of the electrodes R in different experiments was $3800 \div 1000$. Determination of the roughness coefficient was carried out from the hydrogen charging curve (from $\varphi = 0$ to the end of the hydrogen delay), assuming that desorption of a monolayer of hydrogen from 1 cm^2 requires an expenditure of 0.21 μC. After recording the hydrogen charging curve in an argon atmosphere, the electrode potential was brought to 400 mV relative to the hydrogen electrode in the same solution, and then ethane or ethylene was passed through. When hydrocarbons were passed through, the potential shifted in the negative direction. After a constant value of the potential had been established, the electrolyte was replaced in an argon atmosphere, and then the charging curve was recorded on the platinum electrode that had chemisorbed ethylene or ethane, both in 1 N H_2SO_4 solution and in 1 N KOH solution. The charging curves were recorded at a current of 0.25 mA/cm^2 at 20 and 97°. All potentials are given 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 expressing the dependence of potential on time, both when the experiment is carried out at 20° and at 97° (Fig. 1b, curves 3, 4), passes through a minimum corresponding to 230-240 mV. The minimum value of the potential is established in 10-15 min. Then the potential shifts slightly in the positive direction. The shift of the potential in the negative

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

The shift of the potential in the negative direction is associated with adsorption of hydrogen appearing in the dehydrogenation process, while the shift of the potential in the positive direction is associated with hydrogenation leading to the formation of ethane and methane. These phenomena are analogous to the kinetics of potential establishment observed in the presence of alcohols (13). In an acidic solution in an atmosphere of ethane at 20° (Fig. 1*a*, curve 3), approximately the same potential value is established as in ethylene, but the potential is established more slowly and the curve ϕ-t has no minimum. A similar course of the potential-establishment curve occurs at 97° (Fig. 1*a*, curve 4), but in this case the stationary potential has a more negative value and corresponds to 200 mV, which is associated with an increase in the amount of adsorbed hydrogen. In alkaline solution in an atmosphere of ethylene and ethane, the potential is established more slowly than in acidic solution.

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

On the charging curves of a platinum electrode in 1 N H_2SO_4 and 1 N KOH solutions, recorded at 20°, there are clearly expressed arrests in the region of potentials 500-700 mV, corresponding to the oxidation of chemisorbed ethylene and ethane (curves 2, Fig. 2*a, b, v, g*). It should be noted that the charging curves at 20° also show an arrest corresponding to hydrogen adsorption. In Figs. 2 and 3, hydrogen curves (curves 1) are given for comparison and for calculation of the surface.

Fig. 2. Charging curves. *a*—ethane in 1 N KOH, *b*—ethane in 1 N H_2SO_4, *v*—ethylene in 1 N KOH, *g*—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 $t = 97°$.

The character of the charging curves at 97° (curves 4, Fig. 2) for the indicated systems differs substantially from the charging curves at 20°. From the data presented it is evident that, both in the case of chemisorption of ethylene and of ethane, in alkaline solution the charging curves show only a barely noticeable arrest at a potential of 650-800 mV, corresponding to oxidation of the organic substances. In the case of chemisorption of ethylene, the charging curve at 97° also shows a hydrogen arrest. On the charging curves—

after adsorption of ethylene and ethane, recorded in 1 N H_2SO_4 and 1 N KOH solution at 97°, hydrogen arrests are observed (curves 4, Fig. 2). At a potential of 320-400 mV the slope of the charging curve changes. At these potentials, along with oxidation of H_2, oxidation of some hydrocarbon residue may possibly occur. The presence of chemisorbed hydrogen is especially clearly seen on curve 3 in Fig. 2. The experiments corresponding to curves 3 were carried out as follows. After chemisorption of ethylene and ethane at 20° and establishment of a stationary potential, the electrolyte solution saturated with hydrocarbon was drained off and an electrolyte solution saturated with argon and having a temperature of 97° was poured in. The potential of the electrode in argon then shifts in the negative direction, in ethane to 190 mV, and in ethylene to 155 mV.

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

From the data presented in curve 3 of Fig. 2 and in Table 1, it is evident that, both in the case of adsorption of ethylene and of 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 the hydrocarbons is manifested more distinctly. As was shown above, with more prolonged heating of the

Figure 4 graph

Figure 4: Figure 4 graph

platinum electrode at 97° (curve 2, Fig. 3), the adsorption of hydrogen on the electrode surface was considerably smaller. The latter is apparently connected with the fact that chemisorbed hydrogen hydrogenates the radicals formed upon rupture of C–C and C=C bonds, with methane being formed, which at elevated temperatures desorbs from the platinum surface. In this connection, however, it should be assumed that a residue of organic substance remains on the platinum surface, the oxidation of which, in experiments conducted at elevated temperatures, is not observed on the charging curves. It is possible that in this case the oxidation process proceeds not by an electrochemical mechanism. It should be noted that after experiments with chemisorbed ethylene in alkaline solution, a change in the platinum surface was detected, expressed in a significant decrease in its ability to adsorb hydrogen. This phenomenon is possibly connected with the presence on the surface of a difficultly oxidizable organic residue or carbon. From the data given in Table 1 it follows that the amount of hydrogen from the experiments shown in curves 3, Fig. 2 b, c (20-97°), is even greater than can be obtained from chemisorbed ethylene on the basis of charging curves recorded at 20°. This compels one to assume that ethylene molecules chemisorbed on the less active portions of the surface are not oxidized completely at 20°. This question requires further clarification. The processes observed on the charging curves are seen more distinctly in Fig. 3, where some of the investigated curves are presented in differencial form. The maximum on 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 on curves 1, 2, and 3 correspond to the adsorption of hydrogen on the hydrogen curve, after adsorption of ethane at 20° and after heating at 97° (Fig. 3).

Table 1

t, °C	Ethane, in 1 N H_2SO_4, R	Ethane, in 1 N H_2SO_4, θ_e	Ethane, in 1 N H_2SO_4, θ_H	Ethane, in 1 N KOH, R	Ethane, in 1 N KOH, θ_e	Ethane, in 1 N KOH, θ_H	Ethylene, in 1 N H_2SO_4, R	Ethylene, in 1 N H_2SO_4, θ_e	Ethylene, in 1 N H_2SO_4, θ_H	Ethylene, in 1 N KOH, R	Ethylene, in 1 N KOH, θ_e	Ethylene, in 1 N KOH, 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. 4. Polarization curves in 1 N H_2SO_4: 1, 2 –ethane; 3, 4 –ethylene; 1, 3 –21°; 2, 4 –97°

From the charging curves of platinized electrodes that had chemisorbed ethylene and ethane, one can approximately determine the fraction of the surface occupied by hydrocarbon, θ_{u}, and by hydrogen, θ_{H}. Since at 20° the decomposition of ethylene and ethane molecules during chemisorption proceeds very slowly, it may be assumed that the principal amount of electricity corresponding to the delay at 500–700 mV goes toward the oxidation of chemisorbed hydrocarbons.

Assuming that oxidation of an ethylene molecule yields 12 electrons, and of an ethane molecule 14 electrons, and taking it that during adsorption one molecule occupies 4 sites on the surface, we obtain the values for surface coverage by ethylene and ethane at different temperatures given in Table 1. For the hydrocarbon residue, in accordance with (9), the ratio $H/C = 1.5$ was adopted, which corresponds to 5.5 electrons.

As follows from the data of Table 1, the greatest surface coverage at 97° occurs during chemisorption of ethylene in a solution of 1 N H_2SO_4. In experiments in which chemisorption of ethane was carried out at 20°, and oxidation at 97°, the surface coverage, mainly by hydrogen, in 1 N H_2SO_4 and 1 N KOH is 0.5, whereas in the case of ethylene in 1 N H_2SO_4 and 1 N KOH it is 0.90.

For the indicated systems, polarization curves were also studied (Fig. 4). The highest oxidation rate was observed for ethylene at 97° (curve 4). The higher reaction rate in this case, compared with the others, is due to the higher adsorption rate, the larger amount of chemisorbed gas on the surface, and, as is evident from the data presented in Fig. 2 (curve 3), the higher rate of dehydrogenation, manifested in substantial filling of the surface with adsorbed hydrogen. It is possible that oxidation of hydrocarbons at high current densities follows mechanisms (1) and (2). However, at low current densities, when oxidation proceeds at more negative potentials, the first stage of the process is apparently dehydrogenation. Analysis of the polarization curves will be presented in the following communication.

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