Effect of X-Radiation on the Electrochemical Oxidation of Ethyl Alcohol at a Pt Anode

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In the anodic oxidation of many organic compounds on a Pt electrode, decreases in current are observed at certain values of the anode potential; these indicate a slowing of the reaction in this range of potentials, and several current maxima and minima may be observed on the polarization curve $i - \varphi$ ($^{1-5}$). V. S. Bagotskii and Yu. B. Vasil' ev (^{5}) showed that the characteristic form of the polarization curves in anodic oxidation on a Pt electrode, and the approximate coincidence of the potentials of the current minima in the oxidation of the most diverse compounds (in $1N$ H_2SO_4, current minima are observed at potentials ~ 0.8; 1.1, and 1.6-1.7 V), are due to the fact that, simultaneously with the electrooxidation of the organic substance, the state of the electrode surface changes as a result of its oxidation; each decrease in current corresponds to a definite form of the surface compound of platinum with oxygen. It is also known that the product of the oxidation of ethyl alcohol—acetaldehyde—causes inhibition of the alcohol oxidation reaction (^{1}).

When carrying out the anodic oxidation reaction under the action of radiation in not very concentrated aqueous solutions, it is of particular interest to determine the influence of short-lived active products of water radiolysis on changes in the state of the electrode surface, since in this case one might expect acceleration of electrochemical reactions where kinetic retardations are observed. In addition, stable products of water radiolysis—H_2O_2 and H_2—and products of radiation-chemical transformations of the dissolved substance may participate in the electrode reaction (^{6}).

In order to clarify the role of the factors mentioned above in the electrode process, the present work investigated the effect of x-radiation on the anodic oxidation of ethyl alcohol at a Pt electrode. The electrooxidation reaction was carried out on a smooth platinum rotating microelectrode, which was the end face of a wire 0.3 mm in diameter. The rotation speed was 3000 rpm. The study was performed by the polarographic method on a PE-312 polarograph with automatic recording of polarograms. For irradiation, an x-ray tube was used with a maximum voltage of 90 kV and a current of 200 mA. The dose rate was $1.0 \cdot 10^{16}$ eV/cm$^3 \cdot$ sec. Irradiation of the solutions was carried out in the same cell in which the measurements were made.

Fig. 1. Polarograms of the oxidation of C_2H_5OH in a $0.35\,M$ solution ($0.72\,N\,H_2SO_4$) under X-ray irradiation without access of oxygen: 1 —unirradiated solution, 2 —dose $9 \cdot 10^{18}$ eV/cm^3, 3 —dose $1.44 \cdot 10^{20}$ eV/cm^3

Figure 1: Fig. 1. Polarograms of the oxidation of C_2H_5OH in a $0.35\,M$ solution ($0.72\,N\,H_2SO_4$) under X-ray irradiation without access of oxygen: 1 —unirradiated solution, 2 —dose $9 \cdot 10^{18}$ eV/cm^3, 3 —dose $1.44 \cdot 10^{20}$ eV/cm^3

On the polarogram of the unirradiated acidic alcohol solution we observed two current maxima at potentials of 0.85 and 1.25 V relative to the normal hydrogen electrode, and two minima at potentials of 1.1 and 1.5 V, which agrees well with the available literature data ([1,5]).

In our work, the dependence of the height of the first and second maxima on the concentration of ethyl alcohol in the absence of radiation was determined. It was found that the height of the first and second maxima increases linearly with the alcohol concentration in the range 0.17–1.0 M. With further increase in concentration, the growth of the heights of the maxima slows down, and at concentra-

acid $\sim 3\,M$ reaches a constant value. Increasing the concentration of sulfuric acid from 0.72 to $3.6\,N$ does not affect the height of the maxima. In what follows, polarograms are presented for solutions with an H_2SO_4 concentration of $0.72\,N$.

Irradiation of the solutions was carried out under two different conditions: 1) with a deficiency of oxygen (which was consumed from the solution in the first minutes of irradiation) and 2) with sufficient access of oxygen. In the first case, during irradiation the electrode was at rest and the solution was not stirred; after absorption of a certain dose, the irradiation was switched off and the polarogram was recorded on the rotating electrode.

Fig. 1. Polarograms of the oxidation of C_2H_5OH in a $0.35\,M$ solution ($0.72\,N\,H_2SO_4$) under X-ray irradiation without access of oxygen: 1 —unirradiated solution, 2 —dose $9 \cdot 10^{18}$ eV/cm^3, 3 —dose $1.44 \cdot 10^{20}$ eV/cm^3.

In the second case, rotation of the electrode was not stopped, and during irradiation of the solution the polarographic measurements were carried out without switching off the irradiation.

Irradiation of 0.17–3.5 M acidic alcohol solutions under oxygen deficiency causes a lowering of the entire polarogram (Fig. 1). The current decreases more strongly in the region of the maxima than of the minima; therefore, with increasing dose, the oxidation polarograms take the form of two waves with limiting currents (Fig. 1, curve 3). The oxidation currents decrease with increasing dose, but, beginning with doses of $\sim 5 \cdot 10^{19}$ eV/cm^3, the oxidation polarograms practically do not change. The magnitude of the greatest decrease in the current of the maxima increases in proportion to the alcohol concentration. When the

Fig. 2

Figure 2: Fig. 2

H_2SO_4 concentration is increased to $3.6\,N$, the magnitude of the decrease in current does not change.

When a solution is irradiated with sufficient access of oxygen, the current of the first maximum changes hardly at all, while the current at the second maximum increases (Fig. 2). This increase is proportional to the dose over the entire dose range (up to $3 \cdot 10^{19}$ eV/cm^3).

The results obtained cannot be due to the influence of radical products of radiolysis, since measurements carried out during the action of the radiation and after switching off the X-ray apparatus give identical results. At the same time, it is obvious that substances formed in the solution influence the process of electrochemical oxidation. This is indicated by the fact that the effects obtained increase in proportion to the growth of the dose. They depend very strongly on the presence of oxygen in the system. Moreover, when polarograms are recorded in the absence of oxygen on a stationary electrode, the current increases very strongly compared with the current on a rotating electrode. This increase in current may be caused by the slowing, when rotation is stopped, of the supply of substances formed in the solution as a result of radiolysis and inhibiting the oxidation reaction of ethyl alcohol. On the basis of these results it was suggested that the influence of irradiation on the electrooxidation of ethyl alcohol is associated with the formation and reactions of stable radiolysis products, namely: acetaldehyde and hydrogen peroxide.

To verify the correctness of this assumption, it was examined how additions of acetaldehyde and hydrogen peroxide to an unirradiated solution of ethyl alcohol affect the form of the polarogram. It turned out that additions of acetaldehyde in concentrations of $0.5\text{–}3.0 \cdot 10^{-4}\,M$ decrease the magnitude of the current at the first and second maxima. As in the irradiation of solutions under deficiency of O_2, the decrease of the current at the maxima is considerably stronger than at the minima. Therefore, at a sufficient concentration of acetaldehyde, two waves with limiting currents are observed on the polarogram.

When hydrogen peroxide is added to the C_2H_5OH solution at a concentration,

corresponding to conditions of absence of O_2 and to conditions of its sufficient supply, the magnitude of the current at the first maximum does not change, since the oxidation potential of H_2O_2 on Pt (1.08 V) has not yet been reached, while the magnitude of the second maximum increases in proportion to the peroxide concentration (Fig. 3).

Fig. 2. Polarograms of the oxidation of C_2H_5OH in a 0.35 M solution (0.72 N H_2SO_4) irradiated with X-rays with sufficient access of oxygen: 1 —unirradiated solution; 2 —dose $2 \cdot 10^{18}$ eV/cm^3; 3 —dose $9 \cdot 10^{18}$; 4 —dose $25 \cdot 10^{18}$ eV/cm^3

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 3. Polarograms of the oxidation of C_2H_5OH in a 0.35 M solution (0.72 N H_2SO_4) with additions of H_2O_2: 1 $-$initial solution; 2 $-H_2O_2$ concentration $5 \cdot 10^{-5}$ M; 3 $-H_2O_2$ concentration $1.2 \cdot 10^{-5}$ M

In order to carry out a more accurate modeling of the system formed upon irradiation, the accumulation of hydrogen peroxide and acetaldehyde was measured in a 0.35 M alcohol solution under the same conditions as those under which the electrochemical oxidation of the alcohol was carried out. Hydrogen peroxide was determined iodometrically (^{7}) on a spectrophotometer at a wavelength of 350 mμ. Acetaldehyde was determined by reaction with 2,4-dinitrophenylhydrazine. It was found that hydrogen peroxide accumulates linearly with dose until oxygen is present in the solution, with a yield of 4.4 mol/100 eV. When the oxygen in the solution has been consumed during irradiation, the concentration of hydrogen peroxide drops sharply to a value of $\sim 0.5 \cdot 10^{-4}$ M, which remains constant upon further irradiation.

Acetaldehyde is formed with a yield of 2.15 molecules/100 eV, both in the presence of oxygen and in its absence. The results for the formation of hydrogen peroxide and acetaldehyde agree well with literature data (^{8}). Addition to an unirradiated solution of ethyl alcohol of hydrogen peroxide and acetaldehyde in a ratio corresponding to their formation

Fig. 4. Increase in the current of the second maximum upon irradiation of a 0.35 M solution of C_2H_5OH (0.72 N H_2SO_4) and upon modeling of the irradiated solution by additions of H_2O_2 and acetaldehyde: 1 $-$model solution; 2 $-$irradiated solution

during the radiolysis of a solution containing oxygen produces almost the same effect as irradiation (the current in the simulation is lower than the current during irradiation of the solution by about 5-7%) (Fig. 4). In an analogous simulation of a solution irradiated in the absence of oxygen, an increase in current was found in comparison with the original solution, whereas under irradiation a decrease in currents is observed. This discrepancy is probably connected with the influence of products not taken into account in our experiments. In ethanol solutions that do not contain oxygen, besides hydrogen peroxide and acetaldehyde, hydrogen and butanediol are formed with comparable yields (ˆ7). The sum of all the processes occurring probably gives rise to the observed effect.

Thus, it has been shown that X-radiation affects the electrochemical oxidation of ethanol through stable radiolysis products formed in the solution. In an airsaturated solution these products are hydrogen peroxide and acetaldehyde; in a solution containing no oxygen, they are acetaldehyde, small concentrations of hydrogen peroxide, hydrogen, and, in all probability, butanediol. No influence of short-lived products of water radiolysis on the indicated reaction was detected.

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