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Abstract

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THE EFFECT OF X-RAY RADIATION ON THE ELECTROCHEMICAL OXIDATION OF FORMIC ACID ON A Pt ANODE

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The electrochemical oxidation of many organic compounds on a Pt anode proceeds with kinetic delays, which manifest themselves in the appearance of current drops at definite values of the anode potential. It is assumed that the current drops are caused by inhibition of the reaction at certain degrees of oxidation of the Pt electrode or upon adsorption of intermediate electrolysis products on the surface of the anode ([1,2,5]). It is of interest to elucidate both the causes of such inhibition in various cases and possible ways of removing it.

It is known that under the action of ionizing radiation on not very concentrated aqueous solutions, the principal products formed are the products of water radiolysis: molecular products—hydrogen and hydrogen peroxide—as well as short-lived products—hydrogen atoms and OH radicals. It may be expected that the kinetics of an electrode process on a platinum electrode immersed in an irradiated solution may be affected either by the products of water radiolysis, or by direct irradiation of the electrode, or by both of these factors together. For this purpose we undertook an investigation of the influence of X-ray radiation on the anodic oxidation reaction, on a rotating Pt electrode, of the simplest representative of fatty carboxylic acids—formic acid, for whose electrochemical oxidation data are available ([1,2]).

The anodic oxidation of formic acid was carried out on a smooth platinum rotating microelectrode, which was the end face of a Pt wire 0.5 mm in diameter sealed into glass. The rotation speed in all experiments was 3000 rpm. The investigation was conducted by the polarographic method on a PE-312 polarograph with automatic recording of polarograms. The rate of potential application was 10 mV/sec.

For the work, twice-distilled formic and sulfuric acids were used. The solutions were prepared with twice-distilled water. Solutions of 1 N H_2SO_4 with various concentrations of HCOOH were employed. Irradiation was carried out with an X-ray tube operating at 90 kV and 20 mA, and also with a sealed short-focus tube of type 11-BXV-3, operating at 80 kV and 200 mA. The dose rate, determined by the ferrosulfate method, was $5.04 \cdot 10^{16}$ eV/cm$^3 \cdot$min and $5.02 \cdot 10^{17}$

Fig. 1

Figure 1: Fig. 1

eV/cm^3 · min, respectively. Polarograms were usually recorded directly during irradiation of the solution. In all experiments the temperature was maintained at 26–27°. In the electrochemical oxidation of an unirradiated solution of formic acid we obtained on the polarogram (Fig. 1) three maxima and three current minima. The potentials of the maxima were 0.55, 0.9, and 1.5 V; the potentials of the minima were 0.8, 1.1, and 1.6 V (N.H.E.).

Upon irradiation of a 3 N HCOOH solution saturated with air, an increase in the current of the first maximum is observed with increasing dose (Fig. 2), but at a dose of $\sim 0.5 \cdot 10^{19}$ eV/cm^3 a certain stationary state is reached, which persists up to doses of $\sim 1 \cdot 10^{19}$ eV/cm^3. When the solution is saturated with nitrogen, the height of the first maximum in the unirradiated solution is appreciably higher than when saturated with air. This is associated with the reaction of oxygen reduction

in a solution saturated with air, occurring at the same potentials; in this case the oxygen reduction current is subtracted from the formic-acid oxidation current.

The rise of the current of the first maximum under irradiation in an air atmosphere is apparently associated with the oxidation, at the electrode, of molecular hydrogen formed during radiolysis, since, when molecular hydrogen was added to the solution, an increase in current was observed in the region of the first maximum. In this case the ionization current of H_2 is superimposed on the oxidation current of HCOOH. The H_2 used for this purpose was obtained electrolytically in the cell on a Pt auxiliary cathode (with the anode external). Immediately after hydrogen evolution had been stopped, a polarogram was recorded in the potential region of the first maximum. An increase in current was observed, which decreased with time because of the escape of hydrogen from the solution. It should be noted that the HCOOH oxidation currents in the region of the first maximum and the H_2 ionization currents in HCOOH solutions are very sensitive to preliminary treatment of the electrode surface. The reproducibility of current values in the region of the first maximum is considerably lower than the reproducibility of polarograms at higher potentials.

Fig. 1. Polarogram of oxidation of 3 N HCOOH

Upon irradiation of the solution in a nitrogen atmosphere, the magnitude of the current in the first maximum decreases. This may be explained as follows. Hart ([3]) and Harrison ([4]) found that, during radiolysis of formic-acid solutions in the absence of air, especially in concentrated solutions, formaldehyde is formed. It is known that aldehydes strongly poison the surface of a Pt electrode, even at very low concentrations ([5]), and the decrease in current in the first maximum upon irradiation of a nitrogen-saturated solution is apparently connected with the fact that the oxidation of hydrogen and formic acid on the poisoned surface

Fig. 2

Figure 2: Fig. 2

Fig. 3 and Fig. 4: polarograms of formic acid oxidation

Figure 3: Fig. 3 and Fig. 4: polarograms of formic acid oxidation

is slowed.

No effect of the radiation on the electrode itself was observed in this potential region. This is natural, since at a potential of about 0.5 V there is only the lowest surface oxide of platinum on the surface, in which energy absorption is negligibly small. The magnitude of the current in the second maximum decreases only very slightly under irradiation, which is probably connected with a change in the state of the electrode surface and a decrease in the rate of the electrochemical reaction. The minimum after the second maximum decreases with increasing dose and, upon reaching a certain dose, disappears. On the polarogram, a plateau appears instead of the maximum and minimum. This phenomenon arises, as will be shown below, from the superposition of effects associated with the oxidation of hydrogen peroxide.

Fig. 2. Polarograms of oxidation of 3 N HCOOH in the potential region of the first current maximum under the action of radiation: 1 –without irradiation; 2 –dose $0.15 \cdot 10^{19}$; 3 –$0.45 \cdot 10^{19}$; 4 –$0.60 \cdot 10^{19}$; 5–7 –above $0.75 \cdot 10^{19}$ eV/cm^3

The dependence of the current in the third maximum on dose was investigated for 0.005, 0.10, and 0.5 N HCOOH solutions. Figure 3 presents the polarogram of oxidation of a 0.1 N HCOOH solution under irradiation. For all the indicated

for the given concentrations the current at the 3rd maximum increases in proportion to the dose. For low concentrations of HCOOH, at a dose of $\sim 1 \cdot 10^{19}$ eV/cm^3, a slowing of the increase in the current of the 3rd maximum with dose is observed. This is connected with the fact that during radiolysis formic acid is consumed, and since the height of the maximum is in proportional dependence on the concentration of HCOOH, a decrease in the latter causes a decrease in the current. At potentials

Fig. 3. Polarograms of the oxidation of 0.1 N HCOOH (region of the 2nd and 3rd maxima).
1–without irradiation; 2–dose $0.31 \cdot 10^{19}$; 3–dose $0.9 \cdot 10^{19}$; 4–dose $1.06 \cdot 10^{19}$ eV/cm^3.

Fig. 4. Polarogram of the oxidation of 0.1 N HCOOH in the presence of H_2O_2.
1–without H_2O_2; 2–after addition of $2.29 \cdot 10^{-4}$ mol/l H_2O_2.

of the 3rd maximum, oxidation of hydrogen peroxide may occur on the electrode. Superposition of the H_2O_2 oxidation current should produce an effect similar to that observed upon irradiation. To verify this assumption, a graphical subtrac-

tion was made of the polarogram of oxidation of unirradiated formic acid (Fig. 3, 1) from the polarogram of oxidation of irradiated HCOOH (Fig. 3, 4). As a result of the subtraction, a wave is obtained with $\varphi_{1/2} = 1.08$ V, which coincides with the half-wave potential of hydrogen peroxide oxidation in an acid solution on a Pt anode ([6]). The concentration of hydrogen peroxide in this case (dose $1.06 \cdot 10^{19}$ eV/cm^3), according to the calibration curve from the value of the limiting current, is $1.4 \cdot 10^{-4}$ mol/l. Thus, it may be considered that the increase in the current of the 3rd maximum is connected with oxidation of hydrogen peroxide appearing as a result of radiolysis. Additions of hydrogen peroxide to an unirradiated HCOOH solution cause an analogous increase in the current of the 3rd maximum (Fig. 4). For exact modeling, the accumulation of hydrogen peroxide as a function of dose was determined in a 0.1 N HCOOH solution. The concentration of hydrogen peroxide obtained at a dose of $1.06 \cdot 10^{19}$ eV/cm^3, for which the polarographic determination was carried out, proved to be $1.25 \cdot 10^{-4}$ mol/l.

Comparison of the dependence of the current of the 3rd maximum on the concentration of H_2O_2 formed upon irradiation at different doses, and in model experiments with addition of H_2O_2 to an unirradiated solution, showed that in the first case the current is higher by ~20%; i.e., in addition to the oxidation of hydrogen peroxide under irradiation, there is also an additional process that increases the current.

To check the possibility of an effect of the radiation directly on the electrode surface, the dependence of the current of the 3rd maximum was determined for a shielded and an unshielded electrode. Shielding of the electrode was carried out by placing in the solution, at a distance of ~2 mm from the electrode, a platinum screen (thickness 0.5 mm, diameter 5 mm). It was found that in the first case the currents are appreciably lower. For a dose of $0.75 \cdot 10^{19}$ eV/cm^3 the difference is ~20%. This effect cannot be caused by a decrease in the concentration of hydrogen peroxide, since the volume of the shielded part of the solution relative to the total volume is no more than 1%. Moreover, rotation of the electrode produced intensive stirring of the solution. Consequently, the additional increase in current at the 3rd maximum is caused by the direct action of the radiation on the electrode. This conclusion is also confirmed by experiments on irradiation of the solution with ultraviolet radiation of wavelength 300–400 mμ. Photolysis of formic acid does not occur in this case; i.e., there is only the action of electromagnetic radiation on the electrode ([7]). Under ultraviolet irradiation the current rapidly increases by ~20%, and then does not change during irradiation. In the case where the electrode is shielded, no changes in the magnitude of the current are observed.

In 0.1 N HCOOH solution, the post-radiation effect was determined. Immediately after the irradiation was switched off, a rapid drop in the current of the 3rd maximum by ~10% was observed, followed by its slow decrease with time. Thus, experiments with a shielded electrode and with ultraviolet radiation, as well as the presence of a post-radiation effect, showed that approximately 20%

of the effect of the increase in current in the region of the 3rd maximum is associated with the direct action of the radiation on the electrode. The increase in current in this case can be explained by excitation of the photoconductivity of the surface oxide formed at a potential of ~1.5 V.

The principal effects of radiation in the electrooxidation of HCOOH are associated with the oxidation reactions of the molecular products of water radiolysis: H_2 and H_2O_2. No participation of atomic products of radiolysis in electrode reactions was detected.

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