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# Electrocatalytic Oxidation of 2,4,5,7-Tetrabromofluorescein and 2,7-Dichlorofluorescein by Oxygen Adsorbed on Platinum

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**Abstract**—The development of new catalytic systems based on environmentally safe components is of theoretical and practical importance because of increasing environmental contamination. Promising systems make it possible to decompose ecotoxicants to nontoxic products, which can be achieved by electrocatalytic oxidation with the use of platinum electrodes.

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Oxygen adsorption on platinum is believed to be irreversible [1]. This is due to that the oxygen bond to the platinum surface becomes stronger with an increase in the anode potential and residence time of oxygen on the electrode surface. This leads to a decrease in the reactivity of oxygen as the oxidant [2, 3].

2,4,5,7-Tetrabromofluorescein (TBF) and 2,7-dichloroflurescein (DCF) were subjected to electrocatalytic oxidation. These compounds were used as models for verifying the idea that organic compounds can be reversibly oxidized by adsorbed oxygen. They are of interest because they can serve as a model of 2,3,7,8-tetrachlorodibenzo-*p*-dioxine, a typical dioxine. They are similar to dioxine in composition, structure, and the presence of an oxygen-containing heterocycle, but they are readily soluble in an aqueous medium and nontoxic [4].

In studies of TBF adsorption, platinized platinum with the surface area $S = 1200$ cm$^2$ ($f = 600$) served as the working electrode, a platinum wire was the auxiliary electrode, and silver/silver chloride was the reference electrode. All potentials were recalculated against the reversible hydrogen electrode (RHE). Measurements were carried out in a YaSE-2 three-electrode cell in an argon atmosphere, with 1 M KOH as the supporting electrolyte. The TBF concentration was $2 \times 10^{-2}$ g/L ($3 \times 10^{-5}$ mol/L). Measurements were carried out by the potentiodynamic method at the potential sweep rate 10 mV/s as described in [5]. Adsorption was studied at the double-layer potential 0.45 V and the potential 0.9 V. It was shown that all adsorbed TBF particles on the electrode surface are in the strongly bound chemisorbed state (table). According to [6], chemisorption of TBF and DCF particles is due to the interaction of the π electrons of the benzene rings with the *d* orbitals of platinum. Chemisorbed TBF particles are completely oxidized in the range of potentials below the oxygen overvoltage: the oxygen section of the potentiodynamic curve after washing is located above the curve of the supporting electrolyte (Fig. 1). Subsequent anodic curves coincide with this curve. It was previously shown [7] that, upon adsorption of TBF and DCF at the anodic potential, the coverage of the surface ($\theta_R^H$) somewhat decreases (as compared with that at potentials where the hydrogen and oxygen adsorption is minimal). This can be explained by the competition between the organic compound and oxygen for adsorption sites at the surface or by the oxidation of chemisorbed particles [8].

The electrocatalytic oxidation of TBF and DCF was carried out at the oxygen evolution potentials, as well as in the range of potentials below the oxygen overvoltage. The oxidation at the oxygen evolution potentials was carried out under galvanostatic conditions. The kinetics of processes was studied in situ by spectrophotometry by measuring the decrease in the optical density *D* of solutions at the wavelengths of maximum absorption. Electronic absorption spectra were recorded on a Specord UV-Vis spectrophotometer. The spectra of TBF and DCF show four absorption bands at 245, 300, 350, and 500 nm for DCF and at 245, 300,

Adsorption of TBF on Pt/Pt (supporting electrolyte 1 M KOH) at different potentials, the TBF concentration is $2 \times 10^{-2}$ g/L ($3 \times 10^{-5}$ mol/L)

| *E*, V | Coverage $\theta_R^H$ | |
|---|---|---|
| | in the presence of TBF in the solution | after washing |
| 0.45 | 0.51 ± 0.05 | 0.50 ± 0.05 |
| 0.90 | 0.45 ± 0.04 | 0.44 ± 0.04 |

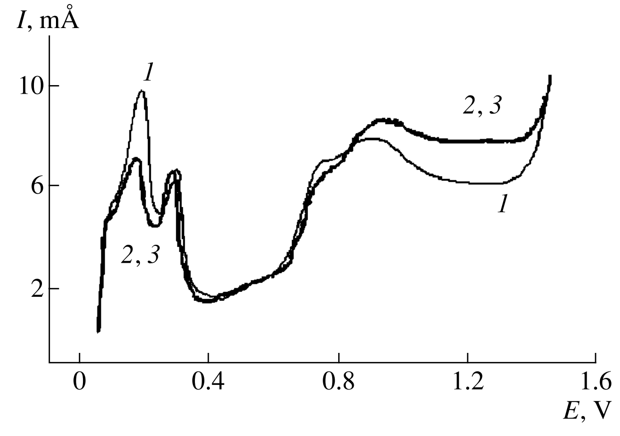

**Fig. 1.** Anodic potentiodynamic curves ($V_{\text{sweep}}$ = 10 mV/s): (*1*) supporting electrolyte 1 M KOH, (*2*) in the presence of $3 \times 10^{-5}$ M TBF, and (*3*) the first cycle after washing the electrode in 1 M KOH.

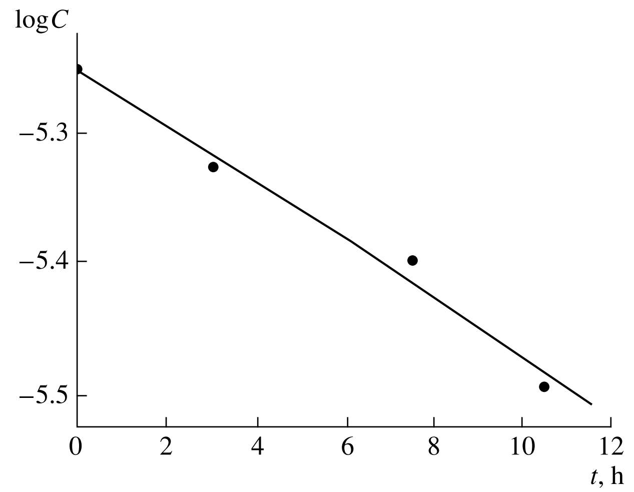

**Fig. 2.** Plot of log*C* vs. *t* for the oxidation of DCF. $C_0 = 5.6 \times 10^{-6}$ mol/L, $V_{\text{sweep}}$ = 50 mV/s, *E* = 0–0.95.

350, and 520 nm for TBF. The change in concentration was assessed by monitoring the most characteristic band in the visible range at 500 (DCF) and 520 nm (TBF). The optical density at these λ values obeys the Beer–Lambert law.

In the course of oxidation, the optical density *D* at the wavelengths of maximum absorption decreased with time to the values of the supporting electrolyte, which is evidence of the conversion of the initial compounds. The processes of electrocatalytic oxidation of TBF and DCF at the oxygen evolution potential are first-order reactions. The effective rate constants of galvanostatic oxidation processes at *I* = 500 mA ($E \approx 2$ V) were $(5.5 \pm 0.5) \times 10^{-7}$ and $(5.3 \pm 0.5) \times 10^{-7}$ s$^{-1}$ for DCF and TBF, respectively.

The electrocatalytic oxidation of TBF and DCF by oxygen adsorbed on platinum at potentials below the oxygen overvoltage was carried out by the cyclic voltammetry method using a PI-50.1.1 potentiostat. The anode was Pt/Pt with the surface area of about 1000 cm$^2$. Measurements were performed in a cell without separation of the anode and cathode spaces; therefore, the auxiliary electrode was also Pt/Pt ($S$ = 3000 cm$^2$), and its large surface served to avoid cathodic side processes. The volume of solutions to be studied was 10 mL. The working electrode was platinized before each experiment and its surface area was measured. The potential sweep rate was 50 mV/s.

At this potential sweep rate in the potential cycling range 0–0.95 V, oxygen adsorption was reversible. The potential cycling conditions used for the electrocatalytic oxidation of the TBF and DCF made it possible to carry out measurements with the constantly renewing surface of the electrode, which resulted in obtaining adsorbed oxygen, a reactive oxidant.

The linear plots of ln*C* versus *t* (Fig. 2) for TBF and DCF solutions indicate that the process is described by the first-order kinetic equation. The effective rate constants for electrocatalytic oxidation were $(1.9 \pm 0.2) \times 10^{-8}$ and $(1.5 \pm 0.2) \times 10^{-8}$ s$^{-1}$ for DCF and TBF, respectively.

DCF solutions after electrocatalytic oxidation by the cyclic voltammetry method and after oxidation at the oxygen evolution potential (according to the UV-Vis spectrum, the initial compound was absent in this solution) were studied by chromatography/mass spectrometry. The initial solution was shown to be free of impurities.

In the solution containing the products of electrocatalytic oxidation of the substrate by the cyclic voltammetry method, 13.6% of organic compounds without aromatic moieties and 0.31% of phthalates were found. We can conclude that $CO_2$ ($CO_3^{2-}$) and $H_2O$ constituted 86% of the products. The qualitative reaction for $CO_3^{2-}$ ions was carried out by introducing $Ba^{2+}$ ions. The resulting white precipitate of barium carbonate, after washing and drying, reacted with acetic acid to evolve a gas.

In the solution containing the products of the electrocatalytic oxidation of DCF at the oxygen evolution potential ($E \approx 2$ V), 73% of organic compounds was found (25% of them contained aromatic moieties), and the remaining 27% was $CO_2$ ($CO_3^{2-}$) and $H_2O$. Thus, the electrocatalytic oxidation of DCF under the potential cycling conditions used turned out to be more efficient for destruction of the studied compounds than the oxidation at the oxygen evolution potentials.

We demonstrated that TBF and DCF can be oxidized by oxygen adsorbed on platinum at potentials below the oxygen overvoltage by the potential cycling method.

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