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Behavior of 2',4',5',7'-Tetrabromofluorescein on a Platinum Electrode at Anodic Polarization in Aqueous Solution, Simulating Electrolytic Breakdown of Dioxins

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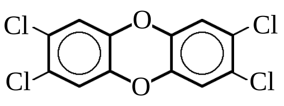
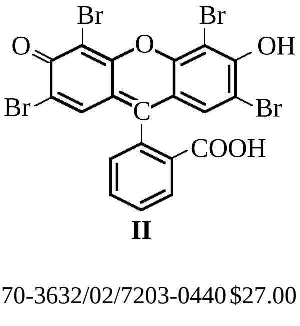
Abstract—Electrocatalytic systems are effective means for breakdown of pollutants in aqueous solution. 2',4',5',7'-Tetrabromofluorescein (eosin) is a convenient model compound for simulation of electrocatalytic oxidation of dioxins. Adsorption of eosin on platinum at potentials exceeding the oxygen evolution potential was discovered. The adsorbate orientation on platinum is presumably planar. The kinetics of electrocatalytic oxidation of eosin in aqueous solution were studied; the reaction orders, rate constants, half-lives, and activation energy were determined. Eosin is oxidized to mineral products (carbonates, bromates). Schemes of the electrocatalytic oxidation of the substrates were suggested.

The problem of removing toxicants is very urgent because of growing environmental pollution hazard. Among the most hazardous pollutants are dioxins and related compounds. Possible pollution sources are chemical enterprises and incineration plants. The toxic effect of dioxins is based on formation in a human body of an iron porphyrin complex [1]. Toxic dioxin-like substances are often rendered harmless by physicochemical (in particular, electrochemical) reductive dehalogenation. However, this reaction is not accompanied by complete breakdown of the molecule and decomposition of the aromatic system. Electrochemical oxidation ensures more efficient degradation, because it is accompanied by cleavage of not only C–Cl (as in electrochemical reduction), but also C–O and C–C bonds.

It was interesting to study electrocatalytic oxidation as a way of rendering dioxins harmless. Electrocatalytic transformations of dioxins have not yet been studied. We expected that electrocatalytic oxidation of the toxicants would be more efficient and selective than a noncatalytic electrochemical process.

In this work, we simulated the heterogeneous electrocatalytic oxidation of a typical dioxin (2,3,7,8-tetrachlorodibenzo-*p*-dioxin, **I**) using a structurally related compound, 2',4',5',7'-tetrabromofluorescein (eosin, **II**).


I


II

Substantiation of the model. Low solubility of dioxins, low precision of their quantitative determination (~50% error), and their high toxicity complicate direct experimental study of dioxin degradation mechanism. We believe that the use of a suitable simulator will be appropriate. Such a simulator, firstly, should be a structural analog of dioxin, i.e., it should contain halogenated polyaromatic fragments. Secondly, for the convenient process monitoring, the simulator should be readily soluble in the reaction medium. In this case, either appropriate organic solvent should be used (e.g., benzene), or the simulator molecule should contain hydrophilic substituents providing sufficiently high solubility in water. Thirdly, of course, the simulator should be less toxic than dioxins.

Taking into account these criteria, for simulation of dioxins we chose eosin (**II**). Molecules of dioxins and **II** have similar size and structure. The molecule of **II** contains halogen atoms, a polyaromatic structure, and an oxygen-containing heteroring. Furthermore, eosin is sufficiently soluble in water and nontoxic.

Adsorption measurements. Adsorption of **II** was studied on a platinized platinum electrode. Typical cyclic potentiodynamic curves in 0.5 M KOH are shown in Fig. 1. As seen from the figure, $Q_H^R < Q_H^0$, which is due to adsorption of **II** on the surface of the catalyst electrode. In the potential range 0.7–1.6 V in the presence of adsorbed species, the curve passes above that taken in the eosin-free supporting electro-

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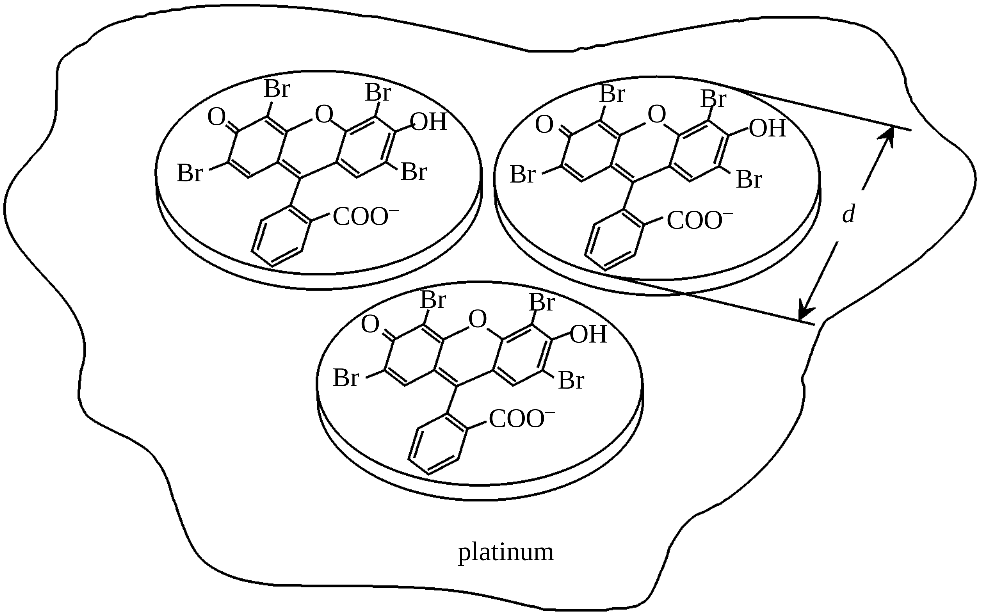
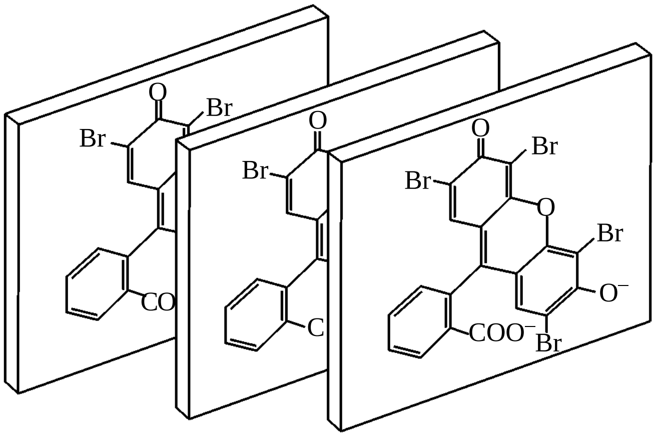
lyte. This is due to oxidation of the adsorbed species. In the course of cycling, $Q_{\mathrm{H}}^{\mathrm{R}}$ increases, and starting from the third cycle it becomes equal to Q_{H}^{0}, and the curve as a whole becomes coincident with the background curve. This fact is indicative of complete oxidation of **II** and removal of adsorbed species at these potentials.

From these data, we calculated the degree of filling of the catalyst electrode surface θ_{R} with the adsorbed species. We found that $\theta_{\mathrm{R}} = 0.4$.

It is known [2] that the orientation of aromatic fragments on platinum largely depends on the initial concentration of the substrate in solution. On the one hand, planar multicentered adsorption of such species is more probable from more dilute adsorbate solutions. On the other hand, vertical orientation of adsorbate molecules is also possible; it is characteristic of high concentrations. For example, the planar orientation of the benzene molecule was proved by in situ FT–RAS studies [3]. With increasing potential, the adsorbed aromatic fragments with planar orientation underwent oxidation to mineral products.



A



B

In the case of planar orientation (**A**), the surface area of the catalyst electrode occupied with a molecule of **II** is about 1.2 nm^2 (d ~1.1 nm). Thus, for θ_{R} 0.4 the number of molecules of **II** that can be accommodated on the free electrode surface is 9.3×10^{14} (~1×10^{-9} mol). At vertical orientation of the molecules of **II** (**B**), the number of adsorbed molecules increases to 9.3×10^{15} (1×10^{-8} mol). The eosin content in the

Table 1. Optical densities (*D*) and molar extinction coefficients [log ε ε, l mol^{-1} cm^{-1})] of aqueous eosin solutions

Concentration, mg l^{-1}	Optical density in absorption maxima							
	255 nm		300 nm		350 nm		520 nm	
	D	log ε	*D*	log ε	*D*	log ε	*D*	log ε
				0.5 M KOH				
10	0.44	4.48	0.2	4.14	0.06	3.61	1.15	4.90
5	0.23	4.5	0.1	4.14	0.03	3.62	0.56	4.89
2.5	0.1	4.44	0.05	4.14	0.02	3.74	0.24	4.82
				0.5 M K_2SO_4				
25	1.21	4.52	0.56	4.18	0.22	3.78	>1.4	—
10	0.51	4.54	0.24	4.22	0.10	3.84	1.26	4.94
7.5	0.38	4.55	0.18	4.22	0.07	3.81	0.92	4.93
5	0.25	4.54	0.12	4.22	0.05	3.84	0.61	4.93
2.5	0.12	4.52	0.06	4.21	0.03	3.92	0.28	4.89

volume taken in the experiment (0.1 l) is as low as 7×10^{-7}, and in this case the planar orientation is apparently preferable. Otherwise a decrease in the bulk concentration of eosin due to adsorption would be noticeable. Furthermore, the planar orientation of **II** is also preferable because in alkali solutions eosin exists as a negatively charged ion.

Kinetic measurements. Electrocatalytic oxidation of adsorbed species of **II** starts at a potential of 0.7 V (Fig. 1). The oxidation rate evaluated from the increase in the current at a given potential is relatively low up to the oxygen evolution potential (1.6 V). To intensify electrocatalytic oxidation of **II**, the process was performed at constant $I = 100$ mA and $E = 1.88$ V.

The absorption bands in the visible range agree with published data [4]. The reaction kinetics was studied *in situ* by monitoring the variation of the optical density of **II** in absorption maxima at its various initial concentrations in KOH and K_2SO_4 solutions (Table 1). Table 1 shows that the variation of the optical density *D* in the examined range of eosin concentrations obeys the Lambert–Beer law: The maximal deviation of log ε is within 2%.

In the course of electrocatalytic oxidation of eosin solutions in both supporting electrolytes, their optical density decreases. Spectrophotometric measurements show that at anodic polarization for 100 min (*Q* 5400 C) in the chosen supporting electrolytes eosin undergoes complete degradation. This is illustrated by data for KOH electrolyte in Table 2.

The plots of log*D* of **II** vs. time in 0.5 M KOH and K_2SO_4 solutions (Fig. 2) show that the reaction is described by a first-order kinetic equation. The supporting electrolyte has no effect on the reaction order,

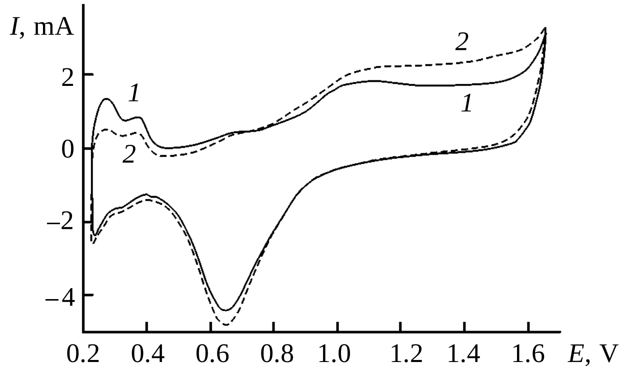


Fig. 1. Cyclic potentiodynamic curves of a Pt/Pt electrode (*1*) in eosin-free supporting electrolyte (0.5 M KOH) and (*2*) in the presence of adsorbed eosin on the electrode surface. Rate of potential sweeping 100 mV s^{-1}.

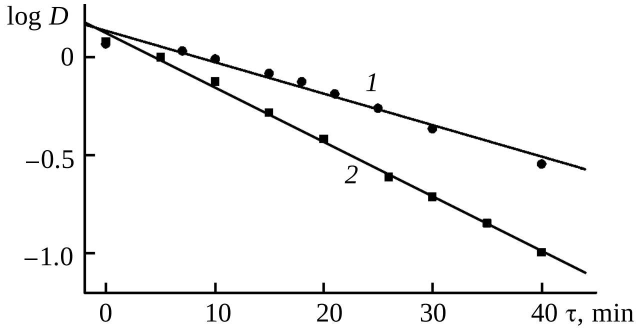


Fig. 2. Variation of log*D* of eosin solutions in (*1*) 0.5 M K_2SO_4 and (*2*) 0.5 M KOH with time in the course of anodic polarization. Initial concentration c_0 10 mg l^{-1}; catalyst electrode Pt/Pt gauze; *I* 500 mA (*i* 0.25 mA cm^{-2}); *E* 1.82 V; solution volume 100 ml.

but in the KOH solution the rate of electrocatalytic degradation of **II** is higher by a factor of 1.8 than in the K_2SO_4 solution.

We also studied the temperature dependence of the reaction rate for solutions of **II** in aqueous KOH (Fig. 3). The activation parameters of the process are given in Table 3. The half-lives of **II** coincide with data obtained previously for degradation of **I** under UV irradiation [5]. Thus, our results are described by the following equation for the apparent rate of electrocatalytic oxidation of **II** (r_{app}) on platinum in alkali solutions:

$$r_{app} = (2.5 \pm 0.8) \times 10^4 \exp[-(5.1 \pm 0.2) \times 10^3/T][\mathbf{II}].$$

Here, r_{app} is expressed in mol s^{-1}, and [**II**] is the current concentration of **II**.

Mechanism of electrocatalytic degradation of II and I. It is known that the spectra of substances containing conjugated π-electron systems and incorporating benzene rings are characterized by visible absorption bands ($\log \varepsilon \geq 4$) originating from electronic transitions in the conjugated π system as a whole and by UV absorption bands ($\log \varepsilon \geq 3$) originating from electronic transitions in aromatic fragments with various degrees of substitution. Absorption of **II** in neutral and alkali solutions is typical for this class of compounds.

In the course of electrocatalytic degradation of **II**, its absorption bands (255, 300, 350, and 520 nm) are not shifted but decrease in intensity in a strict proportion with their molar extinction coefficients (Table 2). Figure 4a shows typical patterns of the decrease with time of the optical density of eosin solutions at 255 and 520 nm. As seen from Fig. 4b, for both wavelengths the $\log(D/\varepsilon)$ values fall on a common straight line. The strict correlation between the decreases in the intensities of the absorption bands characteristic of the eosin molecule as a whole and of separate aromatic fragments shows that in the course of electrocatalytic oxidation of **II** the aromatic intermediates are fully broken down to form as the only products mineral substances and nonaromatic compounds. Thus, electrocatalytic oxidation of **II** essentially differs from the electrochemical oxidation of dioxins [6], which yields intractable organochlorine compounds and is therefore of little use.

Table 2. Variation of the optical density (*D*) of eosin solutions in 0.5 M KOH in the course of electrocatalytic oxidation[a]

τ, min	Optical density in absorption maxima			
	255 nm	300 nm	350 nm	520 nm
0	0.25	0.12	0.04	0.64
5	0.17	0.08	0.03	0.33
10	0.10	0.06	0.02	0.16
15	0.045	0.02	0.01	0.08
30	0.04	0.01	0	0
100	0	0	0	0

[a] Initial concentration c_0 5 mg l^{-1}; Pt/Pt gauze anode; *I* 900 mA (*i* 0.45 mA cm^{-2}); *E* 1.88 V; solution volume 30 ml.

Table 3. Apparent rate constants (*k*), half-lives ($\tau_{1/2}$), and activation energies (E_a) of electrocatalytic degradation of **II**

T, K	$k \times 10^7$, s^{-1}	$\tau_{1/2} \times 10^{-6}$, s
303	1.4±0.1	4.9±0.5
308	2.0±0.1	3.5±0.4
313	2.4±0.1	3.1±0.3
	E_a 43±2 kJ mol^{-1}	

Electrocatalytic oxidation of various organic pollutants ensures their complete breakdown to mineral products [7]. As noted previously [8], heterogeneous catalytic oxidation of a dioxin-like toxicant, 2-chlorobiphenyl, yields acetic and formic acids and ultimately CO_2 and H_2O. The reaction occurs via successive formation of such intermediates as aromatic aldehydes, ketones, and benzoic or chlorobenzoic acid. In the case of eosin, we could expect intermediate formation of phthalates, aromatic bromo derivatives, benzoates, and mineral products. However, the UV spectra of aqueous solutions of **II** after anodic treatment show

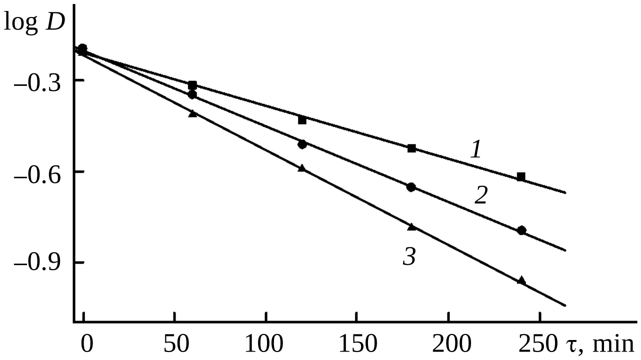


Fig. 3. Variation of log D of eosin solutions in 0.5 M KOH with time in the course of anodic polarization. Temperature, K: (*1*) 303, (*2*) 308, and (*3*) 313. Initial concentration c_0 5 mg l^{-1}; catalyst electrode Pt/Pt plate; *I* 100 mA (*i* 0.2 mA cm^{-2}); *E* 1.80 V; solution volume 100 ml.

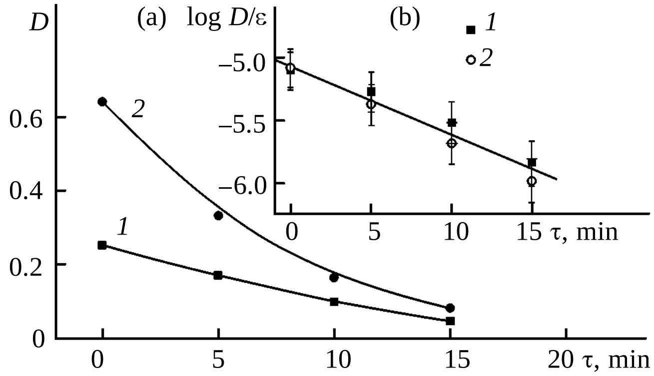


Fig. 4. Variation with time of (a) the optical density D and (b) $\log(D/\varepsilon)$ in the course of anodic polarization of eosin solutions in 0.5 M KOH. Initial concentration c_0 5 $\mathrm{mg\,l^{-1}}$; catalyst electrode Pt/Pt gauze; I 900 mA (i 0.45 $\mathrm{mA\,cm^{-2}}$); E 1.88 V; solution volume 30 ml. λ, nm: (*1*) 520 and (*2*) 255.

no absorption bands characteristic of phthalates, benzoates, and aromatic bromo derivatives. For example, the spectrum of a specially prepared mixture of these substances contains bands in the range from 200 to 280 nm whose extinction coefficients are an order of magnitude higher than those of **II**. This fact unambiguously shows that these compounds are absent in the reaction solution; it confirms our assumption that the organic intermediates fully decompose to mineral products (CO_3^{2-} and BrO_3^-) having no characteristic absorption bands in the range 200–800 nm.

According to the spectra, electrocatalytic oxidation for 5 h of more concentrated (500 $\mathrm{mg\,l^{-1}}$) eosin solutions also results in complete breakdown of fragments with the conjugated π system. On the other hand, treatment of solutions obtained after complete breakdown of **II** with an aqueous solution containing Ba^{2+} ions results in precipitation of $BaCO_3$, and in solution bromate ions are detected by volumetric titration.

Our results allow us to suggest Schemes 1 and 2 for electrocatalytic oxidation of **II** and **I**, respectively, with atomic oxygen adsorbed on platinum. In accordance with these schemes, the processes can be described by the following overall equations:

$$C_{20}H_6Br_4O_5^{2-} + 140OH^- - 98e$$
$$= 20CO_3^{2-} + 73H_2O + 4BrO_3^-,$$

$$C_{12}H_4Cl_4O_2 + 96OH^- - 68e = 12CO_3^{2-} + 50H_2O + 4ClO_3^-.$$

Thus, electrocatalytic oxidation of **I** and **II** is effected by adsorbed active atomic oxygen, which is formed in the electrocatalytic stage of oxidation of OH^- ions:

$$2OH^- - 2e = O_{ads} + H_2O.$$

It should be noted in conclusion that a doubtless advantage of electrocatalytic oxidation of dioxin-like substances is generation of the oxidant (adsorbed atomic oxygen) directly from the solvent (water), without specially adding oxidants and without using additional physicochemical procedures (extraction, concentrating, etc.).

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord UV-Vis spectrophotometer.

The electrochemical installation consisted of a PI-50-1 potentiostat interfaced with a computer, a P-5848 potentiostat, a U-2C thermostat, and a YaSE-2 three-electrode glass cell with separated cathode and anode compartments. As catalyst electrode we used a platinized platinum plate (S 3 $\mathrm{cm^2}$) and a platinized platinum (Pt/Pt) gauze. Platinum plating was performed for 2 h from 2% H_2PtCl_6 at a constant potential $E = -0.01$ V vs. silver chloride electrode. The true surface area of the catalyst electrodes was determined from the potentiodynamic curves. Calculation was performed using the hydrogen section of the anodic curve, measured in 0.5 M H_2SO_4 at a potential sweep rate of 10 $\mathrm{mV\,s^{-1}}$ [9]. The true surface areas of the Pt/Pt plate and Pt/Pt gauze were 490 ± 20 and 2000 ± 100 $\mathrm{cm^2}$, respectively. Electrocatalytic oxidation was performed at constant I 900 mA (i 0.45 $\mathrm{mA\,cm^{-2}}$) and the catalyst electrode potential E 1.88 V (here and hereinafter, all the potentials are given vs. reversible hydrogen electrode). The eosin concentration in 0.5 M KOH (30 ml) was c_0 5 $\mathrm{mg\,l^{-1}}$.

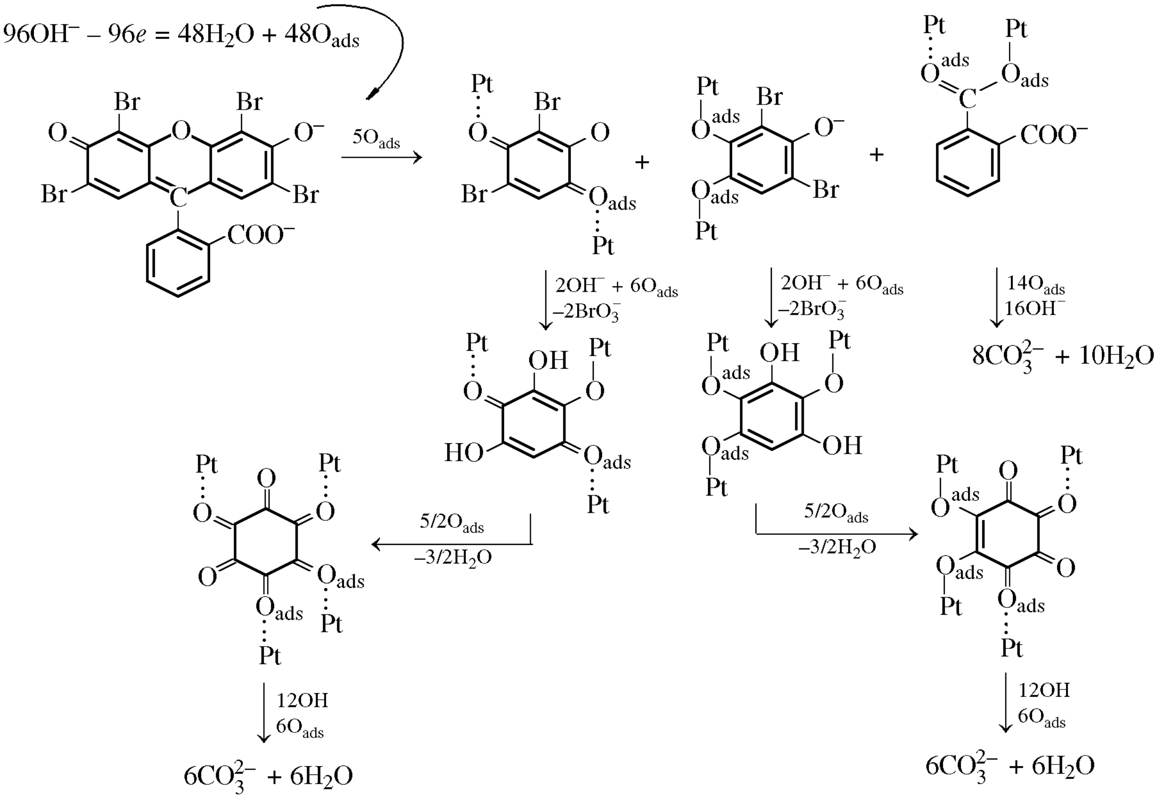
For kinetic study of electrocatalytic oxidation of **II**, we used platinized platinum plate. Measurements were performed under the following conditions: I 100 mA (i 0.2 $\mathrm{mA\,cm^{-2}}$), catalyst electrode potential E 1.88 V, initial concentration of **II** c_0 5 $\mathrm{mg\,l^{-1}}$. The reaction kinetics were studied at 303, 308, and 313 K.

Adsorption of **II** was studied by the method of potentiodynamic curves. Cyclic potentiodynamic curves were obtained in 0.5 M KOH at a constant potential sweep rate, 100 $\mathrm{mV\,s^{-1}}$. The degree of filling (θ_R) of the catalyst electrode surface with adsorbate molecules was calculated from the amount of the electricity passed in the presence (Q_H^R) and in the absence (Q_H^0) of the substrate.

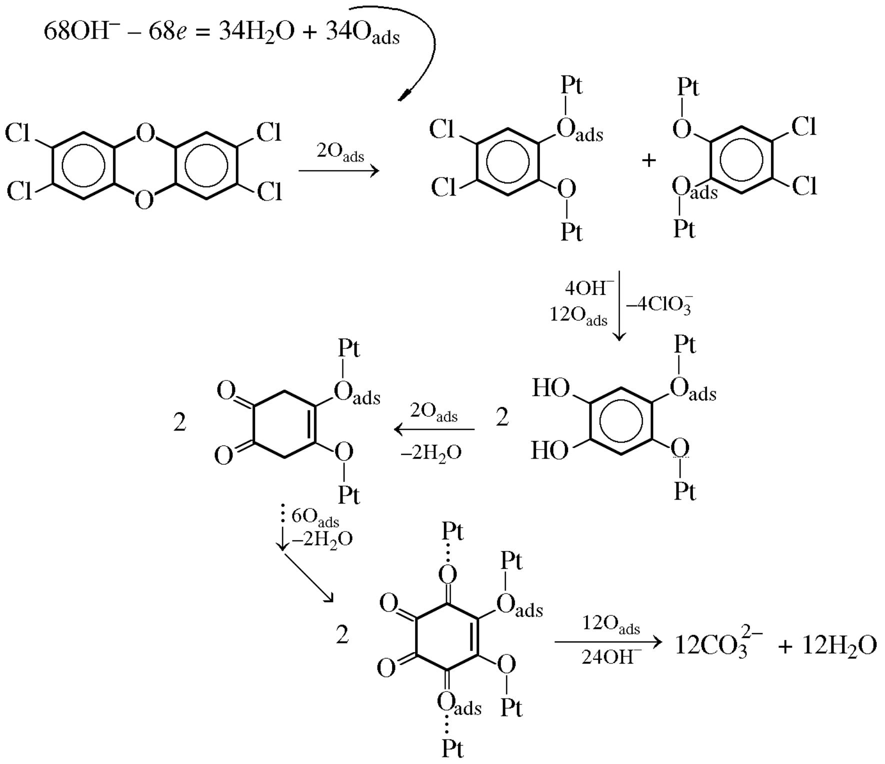
$$\theta_R = 1 - \frac{Q_H^R}{Q_H^0}, \quad Q_H^R = -\int_{E_1}^{E_2} C_H^R dE, \quad Q_H^0 = -\int_{E_1}^{E_2} C_H^0 dE.$$

Here, E_1 and E_2 are the potentials of the beginning of the hydrogen and double-layer regions, and C_H^R and

Scheme 1.



Scheme 2.



C_H^0 are the total polarization capacities in the presence and in the absence of the organic substance, respectively.

After keeping the Pt/Pt electrode in an eosin solution for 15 min at a potential of 1.8 V, it was placed in a 0.5 M KOH solution containing no eosin. The potentiodynamic curves were measured and recorded under computer control by a special program. Before each measurement, the catalyst electrode was reduced electrochemically in the hydrogen region to clean the platinum surface. All experiments with eosin were performed with stirring using a magnetic stirrer.

Commercial eosin, KOH, and K_2SO_4 were used without additional purification. Solutions were prepared in double-distilled water.

ACKNOWLEDGMENTS

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