Electrocatalitic oxidation of 2,7-dichlorofluorescein and 2,3,7,8-(tetrabromo)fluorescein by platinum-adsorbed oxygen

Marina Silaeva, Galina Vidovich, Olga Lebedeva, and Dmitry Kultin
Department of Chemistry, Moscow State University, Moscow, 119899, Russia

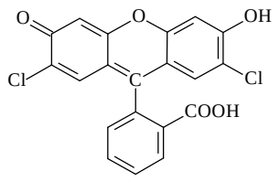
The kinetics of electrocatalytic oxidation of 2,7-dichlorofluorescein (I) and 2,3,7,8-(tetrabromo)fluorescein (II) both at constant current (200 and 500mA) and at cycling of potentials (0 – 0.95 V) was carried out. The substrates I and II were dioxin (III) substitute. Their electrocatalytic oxidation was modeling heterogeneous catalytic oxidation of dioxin in nature [1].

The oxidation was carried out on platinized platinum electrode (~ 1000 cm^2). The volume of cell was 10 mL. The surface of supporting electrode (platinized platinum) was about three times more than that of working electrode. It was necessary for elimination secondary reactions on supporting electrode by cycling of potentials. All the potentials referred to a reversible hydrogen electrode. Concentrations of I and II was determined according to the electronic absorption spectra. Solutions of I ($5 \cdot 10^{-6}$M) and II ($3 \cdot 10^{-6}$M) was used. Supporting electrolyte was 1M KOH.

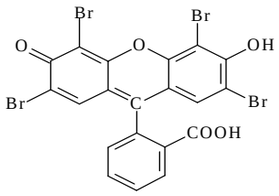
There were no oxidation's peaks and oxygen-gas evolution at potential range. Reversible platinum-adsorbed oxygen was oxidative agent [2].

The results presented in table. The reaction constants were comparable. The electric mass at cycling of potentials method reduces progressively than at constant current method. Therefore, the cycling of potentials method is more effective.

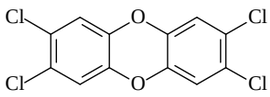
Mass spectrometry was the main method of identification of the products. The electrocatalytic oxidation of I and II happened yielding only low-molecular acids fragments and those containing no aromatic fragments.



I



II



III

Substrate	Experimental	k[s^{-1}]	Q [C]
I	I=500mA	$(5.5\pm0.5)\cdot10^{-7}$	150
	I=200 mA	$(1.0\pm0.1)\cdot10^{-7}$	168
	V=50 mV·s^{-1}	$(1.9\pm0.2)\cdot10^{-8}$	62.2
	V=100 mV·s^{-1}	$(9.1\pm0.2)\cdot10^{-9}$	59.3
II	I=500 mA	$(5.3\pm0.5)\cdot10^{-7}$	360
	I=200 mA	$(1.0\pm0.1)\cdot10^{-7}$	180
	V=500 mV·s^{-1}	$(1.3\pm0.2)\cdot10^{-8}$	60.5

Table. Effective reaction constant and electric mass (for 20% conversion of substrates) for both methods of oxidation.

1. G.A. Bogdanovsky, G.L. Vidovich, D.Yu. Kultin, O.K. Lebedeva, A.N. Zakharov. Chemical model for dioxin destruction in aqueous medium. Electrocatalytic oxidation of dioxin-like substance simulating natural pollutant. Applied Catalysis A: General 232. (2002) 137-145.
2. M. Silaeva, G. Vidovich, O. Lebedeva, and D. Kultin. Electrocatalytic oxidation of 2',7'-dichlorofluorescein by platinum-adsorbed oxygen. Proc. of the 204th ECS Meeting. Orlando. USA. Time Abs. # 1247.