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Electrochemical Oxidation Decomposition of Benzene by Intermediates

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Abstract

Indirect electrochemical oxidation of benzene by intermediates has been studied. The intermediates were generated *in situ* from O_2, H_2O, and H_2O_2 with the use of anodes from platinum, lead dioxide, and ruthenium-titanium oxide anode in water solutions with various pH. Schemes with *in situ* generated H_2O_2 from O_2 and with H_2O_2 adding to electrolyte have been implemented. It was found that hydroxylation of benzene to produce phenol with a gas diffusion cathode from commercial-grade carbon that generates H_2O_2 from O_2 *in situ* is ineffective because of the cathode passivation. On H_2O_2 addition into the electrolyte, oxidation of benzene occurred with mineralization to yield CO2 and H2O; the oxidation state could amount from 94.8 % (Pb/PbO_2, pH 2) to 63.5 % (Pt-anode, pH 2.8, $C_{Fe^{2+}} = 7.1 \cdot 10^{-6}$ mg/L). Efficiency of oxidation drops owing to the formation difficult-to-oxidize carboxylated complexes of iron.

INTRODUCTION

Interest in the technologies that are directed to decontaminate commercial sewage by means of environmentally sound reagents, namely, by chemically linked, active forms of oxygen, increases in recent years. It is common knowledge that it is possible to generate *in situ* intermediates with various oxidizing capacity ($HO^•$, HO_2^-, $HO_2^•$) from O_2, H_2O_2, and H_2O with the use of electrochemical methods [1–3]. It is common knowledge that indirect disruptive oxidation of difficultly biodestroyed aromatic compounds by means of the electrogenerated Fenton's reagent (pH 2.8–3, H_2O_2, in the presence of Fe^{2+} salts), photoelectro-Fenton, and peroxycoagulation proceeds with mineralization to yield CO_2, H_2O, and inorganic compounds [1–6]. Complications that appear in destruction of stable carboxylated complexes of iron can be eliminated by means of UV irradiation (photoelectro-Fenton).

It is common knowledge that it is possible to generate $HO^•$ radicals during the anodic oxidation of water with the use of oxides of metals of variable valence (oxides of titanium, lead, ruthenium, nickel, manganese, *etc.*) as anodes. These radicals show the highest oxidizing capacity in reactions of disruptive oxidation and mineralization of organic compounds [7, 8].

Resistance of benzene to reactions of homolytic oxidation by hydrogen peroxide is caused by its structure, and replacement reactions are more typical for it. Contrary to alternative hydrocarbons, it is not prone to generate hydroperoxide compounds that have capacity to break up to free radicals and to initiate further running chain reaction. Reaction of hydroxylation of benzene to phenol by Fenton's reagent has been reported [9, 10], and that in a fuel cell, with the use of $Cu^+ + H_2O_2$ system [11]. A one-stage oxidation occurs in the process. Oxidizing reaction of benzene on a platinum anode in acidic medium to yield CO_2, benzoquinone, and α,β-nonsaturated ethers has been reported too [12]. Under the alkaline condition, anodic oxidation is followed by benzene ring disruption and by the formation of CO_2 and salts of carboxylic acids [12, 13]. Electrochemical oxidation of benzene on an anode from carbon-glass in acidic medium occurs to form benzoquinone and hydroquinone [14].

The purpose of this work is to study the process of indirect electrochemical oxidation of benzene by intermediates that are generated *in situ* from O_2, H_2O, H_2O_2 in cells with various anodic materials.

EXPERIMENTAL

Experiments were conducted in electrochemical cells of two types (two- and three-chambered) with the use of a gas-diffusion cathode that generated H_2O_2 from O_2, and in a standard electrochemical cell with a filtrating diaphragm.

To yield H_2O_2 and to conduct electrolysis with its involvement, temperature-controlled cells of two types were used: those with non-separated cathodic and anodic space (the two-chamber cell) and with the space that was separated by an ion-exchange MK-40 membrane (the three-chambered cell). The gas-diffusion cathode consisted in a flat disk (the total pore space of 65–70 %, the thickness of 0.8–0.9 mm) from a mixture of carbon black A 437-E (60 mass %) and FP-4D (40 mass %). The construction of a like cell is described in the work [15]. A platinum plate (4 × 25 mm) served as the anode.

Potential of an electrode was monitored on the frontal side of the gas-diffusion cathode with reference to a silver-chloride reference electrode. Current density was calculated per unit of a visible frontal surface, 5 cm^2 in area; the volume of the electrolyte chamber comprised 20 mL. A standard electrochemical cell with a glass filtrating diaphragm and with anodes from ruthenium-titanium oxide anode (50 × 58 mm), dioxide of lead (10 × 58 mm), and platinum was used for electrolysis with a graphite cathode (a rod of diameter 10 mm, the length 30 mm). A PbO_2 layer on the surface of the lead anode was generated by the procedure described in [16].

Concentration of H_2O_2 was determined by permanganate method [17], and the concentration of phenol, by the procedure described in [18]. A variation in chemical oxygen demand (COD) that determines the content of organic compounds in water was monitored by the procedure described in [19].

RESULTS AND DISCUSSION

Electrolysis with the use of a gas-diffusion oxygen cathode

The efficiency of a gas-diffusion electrode that generates H_2O_2 from O_2 could be inferred from the curves of H_2O_2 accumulation in two- and three-chambered cells (Fig. 1). It is evident that the concentration of H_2O_2 in the 0.5 M NaOH solution at the current density of 20 mA/cm^2 in two- and three-chambered cells comprises 1.1 and 11.6 g/L, respectively.

A reaction of reduction of oxygen to perhydroxide ion proceeds on the cathode [20]:

$$O_2 + 2e^- + H_2O \rightarrow HO_2^- + OH^- \quad (1)$$

A reaction of water oxidation with the formation of $HO^\bullet$ radicals as intermediates proceeds on the anode, these radicals showing a strong oxidative action on organic substrate [21]:

$$2H_2O \rightarrow 2HO^\bullet_{\text{адс}} + 2H^+ + 2e^- \quad (2)$$

Lower concentrations of H_2O_2 in the cell with non-separated space are caused by processes of oxidation of H_2O_2 that is being generated on the anode:

$$H_2O_2 \rightarrow HO_2^\bullet + H^+ + e^- \quad (3)$$

$$HO_2^\bullet \rightarrow O_2 + H^+ + e^- \quad (4)$$

and by the interaction of H_2O_2 that is generated on the cathode with $HO^\bullet$ radicals that are formed on the anode [21]:

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (5)$$

Table 1 gives results of benzene hydroxylation to yield phenol in the two-chambered cell (the main hydroxylating agents are $HO^\bullet$, $HO_2^\bullet$ intermediates) and in the cathodic chamber of

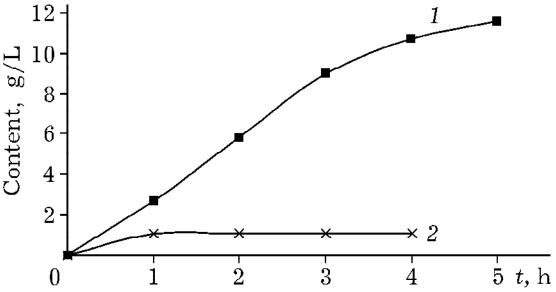

Fig. 1. Curves of H_2O_2 accumulation in 0.5 M NaOH solution (current density of 200 A/m^2): *1* – in the cathodic chamber of a three-chambered electrolytic cell, *2* – in the electrolyte chamber of a two-chambered electrolytic cell.

TABLE 1

Content of phenol in cells with a gas-diffusion oxygen cathode

Experiment number	Current density, mA/cm^2	Potential with reference to SCE, V	Q, A · h	C_{phen}, 10^6 mol/L	C_{benz}, mol/L	Cell type
1	4	0.5	0.04	3.4	0.57	Three-chambered
2	9	0.8	0.090	3.8	0.57	»
3	2	0.78	0.25	5.0	0.57	Two-chambered
4	10	0.8	0.10	7.2	0.57	»
5	16	0.8	0.25	4.8	0.57	»
6	10	0.8	0.25	17.8	1.14	»
7	10	0.8	0.105	11.0	1.14	»

the three-chambered cell ($HO_2^{\bullet}$ radicals are involved in the hydroxylation [11], the radicals being formed in cathodic reduction of O_2). Electrolysis was conducted in the range of potentials to reduce O_2 to H_2O_2.

Low concentrations of phenol are explainable in terms of data in Fig. 2, which gives cathodic curves of O_2 reduction in the gas-diffusion cathode in the supporting electrolyte (solution of 0.5 M NaOH) and in the presence of benzene. It is evident that the activity of the gas-diffusion cathode from commercial-grade carbon in the reaction of O_2 reduction sharply drops in the presence of benzole (see Fig. 2, curves *1*, *2*). The so low activity of the cathode and thus a low yield of phenol (C_{phen} = 10^{-5}–10^{-6} mol/L) are determined, apparently, by passivation of the cathode surface as a result of benzene adsorption on the carbon surface, which leads to blockage of active sites that are involved in the reaction of O_2 reduction. We failed to restore the activity of electrodes after the electrolysis (see Fig. 2, curve *3*). Oxidation in the two-chambered cell with the gas-diffusion cathode and anodes from platinum and dioxide of lead (*i.e.* enhancing the generation of $HO^{\bullet}$ radicals on the anode) did not result in substantial improvement of oxidation indices. It appears that an increase in the concentration of the produced phenol (see Table 1, exp. 6, 7) is related to an increase in benzene concentration, while the low yield of phenol is most likely to be determined by the capability of phenol to further oxidation. Oxidation of phenol (C_{phen} = $1.06 \cdot 10^{-3}$ mol/L) [22] under these conditions in the two-chambered cell has led its concentration to decrease by 70 %. In view of low performance of the process of benzene hydroxylation that is reached in electrolysis, and in view of passivation, the process with the use of the gas-diffusion oxygen cathode that is in direct contact to benzene appeared to be ineffective.

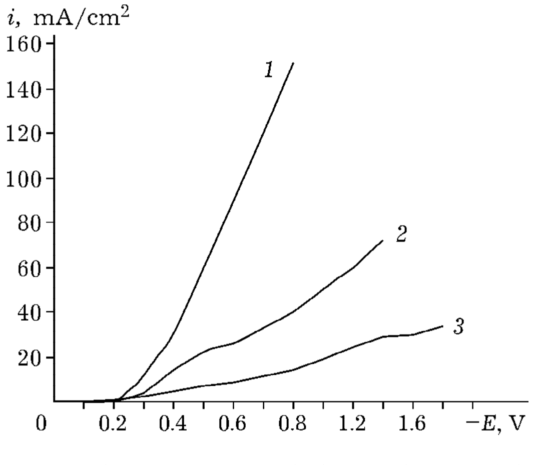

Fig. 2. Polarization curves of electroreduction of O_2 in a gas-diffusion cathode: *1* – in 0.5 M NaOH solution, *2* – the same + benzene (0.57 mol/L), *3* – the same after electrolysis and the subsequent activation of the electrode.

Electrolysis with adding hydrogen peroxide

To level the unproductive work of the cathode, the disruptive oxidation of benzole was conducted in a cell with a filtrating diaphragm that isolated the graphite cathode. The process of oxidation in this case occurs in the anodic chamber of the electrolytic cell, wherein H_2O_2 ($C_{H_2O_2}$ = 0.2 mol/L) was added to increase the concentration of highly reactive radicals (see the equations (3)–(5)). Platinum, ruthenium-titanium oxide anode, and lead dioxide were used as anodes. Oxidation was conducted in acidic (the electrolyte was the 0.1 M Na_2SO_4 solution with H_2SO_4 added to reach pH 3) and alkaline (solutions of 0.1–0.5 M NaOH) media at the current intensity of 0.6 A.

It is common knowledge that depending on the material of the anode, two mechanisms of oxidation are possible [23, 24]. A direct oxidation by way of substrate adsorption on the anode proceeds on anodes from platinum with high electrocatalytic activity [12, 13, 23]. On metal oxide electrodes, an indirect electrochemical oxidation proceeds by way of the formation of superficial mediators, namely, $HO^•$ radicals, according to the equation (2). Upon hydrogen peroxide is added into the solution, $HO_2^•$ radicals are formed additionally according to the equations (3)–(5). Oxidation may proceed also following a combined route that adds together the direct anodic and the indirect oxidation. According to data [1, 3, 5–8, 22, 25], a series of intermediate compounds of aromatic and aliphatic structure is formed in the indirect oxidation. In this relation, the index of chemical oxygen demand (according to dichromate oxidizability) is used as the key parameter to determine the efficiency of oxidation. Mineralization data of various products are presented in Table 2.

Upon Fe^{2+} salts are introduced in the solution ($C_{Fe^{2+}} = 7.1 \cdot 10^{-6}$ mol/L, $C_{H_2O_2} = 0.2$ mol/L, pH 2.8), the electro-Fenton scheme is realized and the oxidizing capacity of H_2O_2 increases owing to additional formation of $HO^•$ radicals:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^• \quad (6)$$

However, a lower efficiency of oxidation with the electro-Fenton scheme in a cell with a platinum anode is related, apparently, to the formation of difficult-to-oxidize oxalate complexes with Fe^{3+} [25], the availability of which is confirmed by results of UV spectroscopy.

The spectra were taken when carrying out the electrolysis in a galvanostatic regime after 1 and 4 h of work of the cell (Q = 0.6 and 2.4 A · h, respectively). Along with a changing magnitude of the chemical oxygen demand, the ratio of the received products of electrolysis also varied. No absorption lines that correspond to benzene were observed upon the oxidation of benzene on platinum under the alkaline condition after 1 h of electrolysis. Phenol and quinone were identified among the oxidates. The intensity of absorption lines for easier to oxidize phenol drops upon the further oxidation; quinone is more difficult to be oxidized. In the course of oxidation, the solution from colourless gets into colour that is typical for quinone derivatives. The solution becomes colourless again later.

UV spectroscopy data on the oxidation by the electro-Fenton method bear witness to the formation of a carboxylated complex of iron upon the oxidation. A height of its peak drops during the electrolysis; however, it remains the main oxidation product.

Spectra that relate to the processes of oxidation on anodes from oxide-ruthenium-titanium anode and lead dioxide in acidic and alkaline media do not have absorption bands that relate to aromatic structures even after 1 h of the cell operation. According to these spectra, only aliphatic oxygen-containing compounds, namely, ketones, acids (most likely, maleic acid), are present from intermediates, *i.e.* open-

TABLE 2

Results of mineralization of benzene and its oxidation products on various anodic materials

Anode material	Electrolyte	COD_{rem}	Efficiency of oxidation, %
Oxide-ruthenium-	0.1 M NaOH	0/122.0	100.0/90.2
titanium anode	0.1 M Na_2SO_4+ H_2SO_4, pH 2.8	15.4/96.3	87.7/92.3
Pt	0.1 M NaOH	29.4/195.0	75.5/84.4
	0.1 M Na_2SO_4 + H_2SO_4 + Fe^{2+}, pH 2.8	72.3/456.4	42.16/63.5
Pb/PbO_2	0.1 M Na_2SO_4 + H_2SO_4, pH 2	15.4/65.2	87.7/94.8
	0.1 M NaOH	15.0/131.3	88.0/89.5

Note. First value at COD_{ini} = 120 mg/L, Q = 2.4 A · h and second one at COD_{ini} = 1250 mg/L, Q = 3.3 A · h.

ing of the benzene ring is responsible for the oxidation. No any coloured solutions throughout the process of electrolysis are an indirect indication of this fact. Terminal products of benzene oxidation represent CO_2 and H_2O with all routes:

$$C_6H_6 + 30HO^{\bullet} \rightarrow 6CO_2 + 18H_2O$$

The obtained experimental and literary data allow the suggestion that depending on the material of the anode, oxidation of benzene to yield phenol and further, up to its complete mineralization by way of benzene ring opening, is possible.

CONCLUSION

It was found that the use of a gas-diffusion carbon-graphite cathode to generate *in situ* hydrogen peroxide from O_2 with indirect oxidizing methods may appear to be ineffective because of passivating adsorption of substrate (benzene) on them, which leads to blockage of active sites that are responsible for H_2O_2 generation. Consequently, it is necessary to eliminate possible direct contact between these sites.

It has been demonstrated that application of the electrolysis scheme with the use of a filtrating diaphragm that isolates the cathode makes it possible to conduct effective oxidation decomposition of benzene with a complete mineralization to yield CO_2 and H_2O in the presence of H_2O_2 and with anodes from oxides of metals that generate *in situ* $HO^{\cdot}$ radicals through water oxidation.

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