

## Indirect Oxidation of Maleic Acid by Fenton's Reagent with Electrochemical Generation of Hydrogen Peroxide upon Oxygen Reduction

NATALIA V. CHAENKO, VASILY L. KORNIENKO and NINA I. PAVLENKO

*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)*

*E-mail: kvl@icct.ru*

(Received June 5, 2003)

### Abstract

Indirect oxidation of maleic acid by Fenton's reagent with electrochemical generation of hydrogen peroxide from oxygen in a carbon hydrophobized electrode in 1 M Na<sub>2</sub>SO<sub>4</sub> solution is studied. It is established that the process goes on destructively through a number of intermediates with mineralization to CO<sub>2</sub> and H<sub>2</sub>O. Succinic, malic, oxalic acids and anhydrides of ketoacids were detected among the intermediates. The rate of mineralization depends on the current density and on the concentration of Fe<sup>2+</sup> ions.

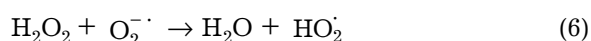
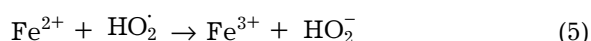
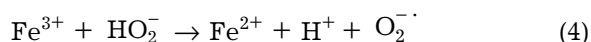
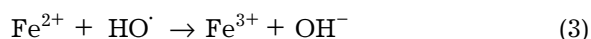
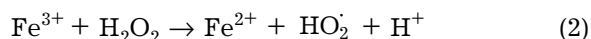
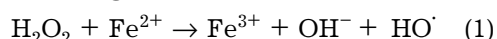
### INTRODUCTION

It is necessary to take into account the modern requirements of ecology when solving the problem of utilization of maleic acid, which is a by-product of large-scale production of phthalic and maleic anhydrides [1] and at intermediate product of oxidation of many aromatic compounds [2].

Development of modern chemical technological processes of oxidation of organic compounds, both for the purpose of obtaining new products and for decomposition of the organics, an increasing importance is held by the use of chemically bound forms of oxygen (O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) and principles of conjugated processes [3]. N. M. Emanuel [4, 5] was the first to formulate the concept of radical forms of conjugation of chemical reactions: «...radicals generated in one of the chemical reactions proceeding in the system stand as active reagents for another reaction which almost does not proceed under the given conditions by itself». This statement is a basis of the mechanism of indirect oxidation of organic and inorganic substrates by hydrogen peroxide [6, 7]. It is known that the active compound is

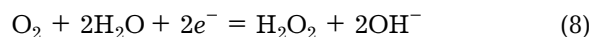
not hydrogen peroxide itself but intermediates based on it; HO· radical is among the most active ones.

A classical method of obtaining HO· radical proposed by Fenton [8] involves catalytic decomposition of H<sub>2</sub>O<sub>2</sub> in acid medium in the presence of Fe<sup>2+</sup> and is described by the following mechanism:



Under indirect electrochemical oxidation, the process of obtaining these reactive species can be carried out using two electrolysis schemes: directly in an electrochemical cell without a membrane, involving the anode process of water oxidation (electro-Fenton) [10], and in the cathode chamber of electrolyzer with a

membrane involving the addition of  $\text{Fe}^{2+}$  ions into the solution [11]. Both schemes assume the formation of  $\text{H}_2\text{O}_2$  at the cathode under reduction of oxygen to be the main reaction:



The process goes through the formation of intermediates  $\text{O}_2^{\cdot-}$ ,  $\text{HO}_2^{\cdot}$  which are able to additionally oxidize organic compounds.

The use of gas diffusion electrodes (GDE) made of technical-grade carbon for the reduction of  $\text{O}_2$  allows one to intensify the process of  $\text{H}_2\text{O}_2$  formation substantially [12].

It is necessary to stress that the presence of  $\text{Fe}^{2+}$  in the solution causes adsorption of a part of these ions on the carbon surface of the electrode, which allows obtaining a system operating as a carrier catalyst. It is known that the reduction of  $\text{Fe}^{3+}$  to form  $\text{Fe}^{2+}$  proceeds on the carbon cathode almost at the same potential as the reduction of  $\text{O}_2$  to form  $\text{H}_2\text{O}_2$  [13]. In addition, oxidation of organic substrate takes place in a solution saturated with oxygen, which may affect the course of oxidation [14].

In the previous work, we described oxidation of maleic acid in a cell without a membrane involving the anode process of water oxidation to obtain  $\text{HO}^{\cdot}$  radicals [15]. It was established that under these conditions the oxidation of maleic acid proceeds destructively to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through an intermediate formation of malic acid with the conversion about 76 %.

The goal of the present work is investigation of the process of maleic acid oxidation by Fenton's reagent ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) on the basis of hydrogen peroxide generated electrochemically *in situ* from oxygen in gas diffusion carbon electrode in cells with membranes.

## EXPERIMENTAL

In order to obtain hydrogen peroxide  $\text{H}_2\text{O}_2$  and to carry out electrolysis with its participation, we used a thermostated cell, which was electrolyzer with the separated cathode and anode spaces. The cell was composed of three chambers: gas chamber into which  $\text{O}_2$  was supplied from gas cylinder, cathode and anode chambers separated with an ion exchange mem-

brane MK-40. The design of a similar cell was described in [4]. A 1 M  $\text{Na}_2\text{SO}_4$  solution was used as a catholyte, while 1 M  $\text{H}_2\text{SO}_4$  solution was anolyte. A platinum plate was the anode.

The electrode potential was monitored at the from face of the gas diffusion cathode with respect to the silver chloride comparison electrode. The current density was calculated per unit visible front surface of the electrode, which was 5  $\text{cm}^2$ ; the volume of electrolyte chamber was 25 ml. For preparative electrolysis, we used weighed portions of maleic acid  $\text{C}_4\text{H}_4\text{O}_4$  ("ch. d. a." grade) with a mass 0.1–1 g, which corresponds to the concentration of 0.0344–0.344 mol/l.

Analysis for maleic acid content in solution was carried out using standard procedures of determination of unsaturated organic compounds: iodometry [16] and permanganatometry [17]. The concentration of  $\text{H}_2\text{O}_2$  was determined permanganatometrically [18]. The  $\text{CO}_2$  evolved during electrolysis was blown with oxygen supplied in excess to the electrode, and gathered in a trap containing  $\text{CaCl}_2$  solution. The precipitated calcium carbonate was analyzed for  $\text{CO}_2$  and  $\text{Ca}^{2+}$  content using the procedure described in [19]. Determination of the concentration of maleic acid was carried out taking into account the consumption of potassium permanganate for the interaction with hydrogen peroxide. After electrolysis, water was evaporated from the solutions under analysis at a temperature of 30–40 °C. The dry residue was analyzed with the IR Fourier spectrometer Vector 22 (Bruker) within the wavenumber range 400–4000  $\text{cm}^{-1}$ ; the spectra data were processed using OPUS.3 software, version 22. The samples for recording were prepared in KBr matrix; weighed portions of the substance to be analyzed and the matrix were constant. The compounds were identified with the help of the corresponding standards.

## RESULTS AND DISCUSSION

In order to establish the possibility of efficient generation of hydrogen peroxide in the presence of ferrous ions, we recorded the voltage-current curves of  $\text{O}_2$  reduction and carried out preparative electrolysis for obtaining

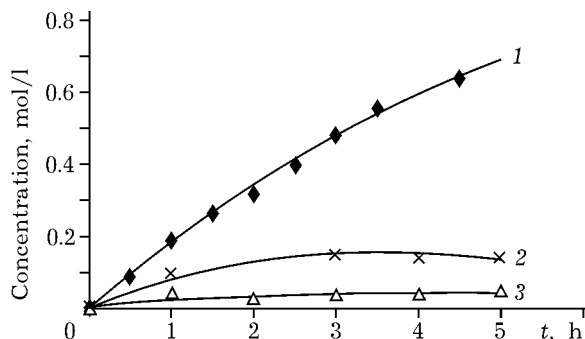


Fig. 1. Curves of hydrogen peroxide accumulation in the cathode chamber of electrolyzer in 1 M Na<sub>2</sub>SO<sub>4</sub>: 1 - without Fe<sup>2+</sup> added; 2, 3 - concentration of Fe<sup>2+</sup>: 1.36 and 5.35 mmol/l, respectively. Temperature: 20 °C.

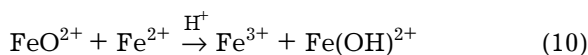
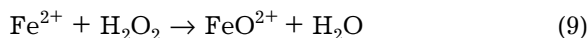
H<sub>2</sub>O<sub>2</sub>. It was established that the introduction of Fe<sup>2+</sup> ions into the system does not affect the behaviour of the polarization curve of O<sub>2</sub> reduction and does not cause any decrease in the efficiency of the GDE.

The yield of H<sub>2</sub>O<sub>2</sub> as a function of current at the current density of 500 A/m<sup>2</sup> in the electrolyte containing no Fe<sup>2+</sup> for 1 h operation was 90–92 % (Fig. 1, curve 1). In the presence of Fe<sup>2+</sup> ions (curves 2, 3) the yield of H<sub>2</sub>O<sub>2</sub> decreases because of an increase in the rate of its catalytic decomposition according to reactions (1), (2). An increase in pH occurs in the solution during electrolysis due to reaction (8), which causes the formation of iron hydroxides after electrolysis for a long time.

Preparative oxidation of maleic acid was carried out in non-buffered solutions at pH 2.1–3.0. The kinetic curves showing a decrease in the concentration of maleic acid *versus* time of electrolysis indicate that conversion of maleic acid increases in the presence of Fe<sup>2+</sup> ions (curves 2, 3) but is almost independent of the current density within the range 500–1000 A/m<sup>2</sup>. The absence of such dependence may be explained by the existence of the limiting stage of the process, namely, formation of a number of intermediates [20].

In addition to the unreacted maleic acid in the sample, analysis of the IR spectra indicated the presence of a complicated mixture of organic compounds, which are intermediates of the oxidation of maleic acid. Among them, we identified succinic, oxalic and malic acids; we also observed absorption bands which we assume to belong to anhydrides of keto acids. In our opinion, such a composition of the products of

electrolysis can be explained by the presence of Fe<sup>2+</sup> ions in the solution. Along with reaction (1) involving the formation of HO· radicals that hydroxylate the double bonds in maleic acid leading to the formation of organic radical, which is further protonated to give malic acid, two-electron oxidation of iron is possible, resulting in the formation of ferryl ion [21]; the latter acts stereospecifically:



Unlike HO· radical, the interaction of maleic acid with ferryl ion leads to the formation of carboxyl radical HOOCHC=CHCOO· [21]. Oxidation of the organic substrate in aerated system does not exclude participation of O<sub>2</sub> in this process [14] and can lead to the formation of organic compounds containing ketone group.

Comparison of the kinetic curves of oxidation of maleic acid (see Fig. 2) and its most probable intermediate, *i. e.* malic acid (Fig. 3), by hydrogen peroxide and by Fenton's reagent shows that the rate of oxidation of malic acid increases with an increase in current density, that is, depends on the rate of hydrogen peroxide generation. The process is most efficient at the current density of 1000 A/m<sup>2</sup>. It involves mineralization of the acid to form CO<sub>2</sub> and H<sub>2</sub>O, which was confirmed by the results of chemical analysis and IR spectroscopy.

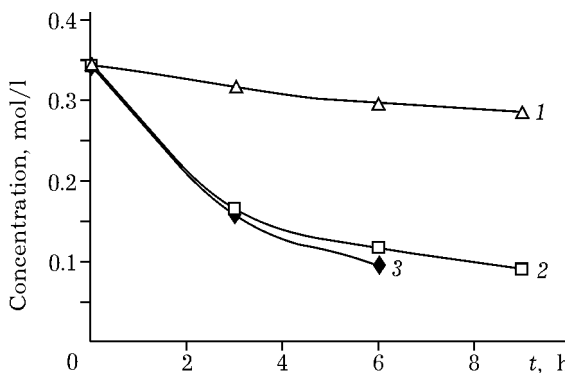


Fig. 2. Changes in the concentration of maleic acid depending on time of electrolysis. Current density, A/m<sup>2</sup>: 500 (1, 2), 1000 (3); concentration of Fe<sup>2+</sup>, mmol/l: 0 (1), 3.2 (2, 3); temperature: 35 °C.

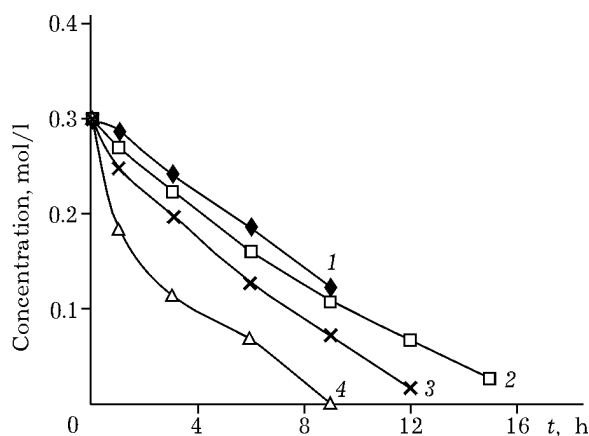
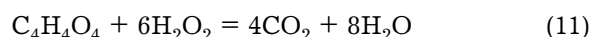


Fig. 3. Changes in the concentration of malic acid depending on time of electrolysis. Current density, A/m<sup>2</sup>: 500 (1, 2), 1000 (3, 4); concentration of Fe<sup>2+</sup>, mmol/l: 0 (1, 4), 3.2 (3, 4); temperature: 35 °C.

The overall equation of mineralization of maleic acid can be written down as follows:



It is necessary to stress that the selectivity of mineralization of maleic acid into CO<sub>2</sub> and H<sub>2</sub>O in the presence of Fe<sup>2+</sup> ions increases with an increase in the current density and time of electrolysis (Fig. 4, Table 1). However, the highest efficiency of the process is observed for  $I = 200 \text{ A/m}^2$  and  $Q = 3600 \text{ C}$ . The corresponding mineralization into CO<sub>2</sub> and H<sub>2</sub>O is 30 %, while the yield as a function of current is 33.2 %. Passing the electrolyte containing the substrate to be oxidized through electrolytic

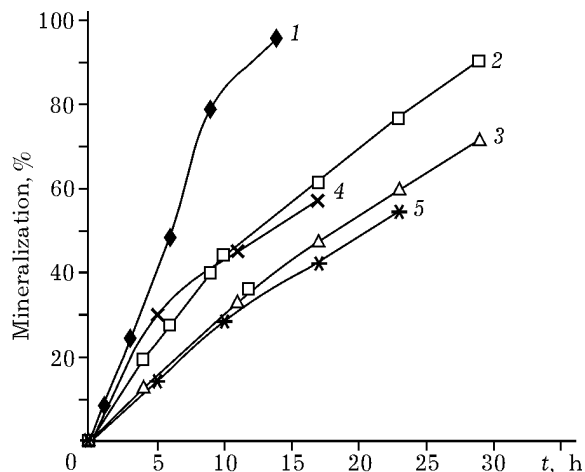


Fig. 4. Dependence of mineralization of maleic acid (0.136 mol/l) on time of electrolysis. Current density, A/m<sup>2</sup>: 1000 (1, 4), 500 (2, 5), 200 (3); concentration of Fe<sup>2+</sup>, mmol/l: 8.9 (1–3), 17.8 (4, 5); temperature: 35 °C.

cells connected in series can likely increase the productivity of the process.

It was established experimentally that an optimal concentration of Fe<sup>2+</sup> ions in the solution is 8.9 mmol/l. An increase in Fe<sup>2+</sup> ion content to 17.8 mmol/l causes a decrease in the efficiency of mineralization (see Fig. 4). Oxidation of maleic acid proceeds through the intermediate formation of oxalic acid, which is known to form a difficultly oxidized complex with ferric ions [22].

The comparison of the results of conversion of maleic acid, obtained by different methods (Table 2), shows that the methods of oxidation

TABLE 1

Results of mineralization of maleic acid by Fenton's reagent

$I$ , A/m <sup>2</sup>	$Q$ , C	Time, h	Mass of maleic acid, g	Mass of the formed CO <sub>2</sub> , g	Mineralization of the acid, %	Yield as a function of current, %
500	3600	4	0.1	0.059	38.9	10.8
1000	3600	2	0.1	0.062	40.9	11.3
500	3600	4	0.2	0.506	49.7	27.4
1000	3600	2	0.2	0.129	42.6	23.5
1000	4500	2.5	0.2	0.162	53.6	29.6
1000	3600	2	0.3	0.099	21.9	18.3
1000	4500	2.5	0.3	0.124	27.3	18.2
1000	7200	4	0.3	0.171	37.8	15.6
200	3600	10	0.4	0.182	30.0	33.2
500	3600	4	0.4	0.117	19.3	21.3
1000	3600	2	0.4	0.099	16.4	18.2

TABLE 2

Comparison between the results on the conversion of maleic acid

Time, h	Conversion of maleic acid, %				
	Cell with membrane without $\text{Fe}^{2+}$	Cell with membrane, $[\text{Fe}^{2+}] = 8.9 \text{ mmol/l}$		Cell without membrane	
	1000 $\text{A/m}^2$	500 $\text{A/m}^2$	1000 $\text{A/m}^2$	500 $\text{A/m}^2$	1000 $\text{A/m}^2$
3	8.13	52.2	54.1	16.7	34.9
6	14.2	66.3	72.1	37.7	61.4
9	17.1	74.1	76.8	65.4	74.5

with Fenton's reagent and electro-Fenton are close to each other in efficiency.

For electrolysis in non-separated cell [15], where the cathode reduction of  $\text{O}_2$  into peroxide is combined with the anode generation of  $\text{HO}^\cdot$  radical, the oxidation of maleic acid is participated by  $\text{HO}^\cdot$  radicals and intermediates of  $\text{O}_2$  reduction; difficultly oxidized oxalate complexes are not formed. The authors of [22] increased the efficiency of oxidation of the oxalate complex of iron by means of additional generation of  $\text{HO}^\cdot$  radicals due to photo-Fenton process.

It should also be noted that the use of cation exchange membrane in a three-chamber cell causes an increase in voltage at the electrolyzer.

## CONCLUSION

Indirect oxidation of maleic acid by Fenton's reagent with electrolytic generation of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  in gas diffusion electrode proceeds destructively to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  according to a mixed mechanism participated by  $\text{HO}^\cdot$  radicals and ferryl ions, having different oxidative abilities.

The presence of  $\text{Fe}^{2+}$  ions in solution decreases the efficiency of destructive oxidation due to the formation of difficultly oxidized intermediates, *i. e.*, oxalate complexes of iron.

Comparison of the indirect oxidation of maleic acid by Fenton's reagent with membrane-free electrolysis scheme shows that oxidation with Fenton's reagent gets more difficult due to the formation of difficult-to-oxidize intermediate oxalate complexes of iron

and goes on with less efficiency because of an increase in Ohmic losses accompanying the use of the cation exchange membrane.

## REFERENCES

- 1 A. A. Pashayan, O. S. Shchetinskaya, *Zhurn. prikl. khimii*, 71 (1998) 1151.
- 2 B. Boye, E. Brillas, M. M. Dieng, *J. Electroanal. Chem.*, 540 (2003) 25.
- 3 T. M. Nagiev, *Uspekhi khimii*, 54 (1985) 1654.
- 4 N. M. Emanuel, *Gorenie i vzryv*, Nauka, Moscow, 1972, 608 p.
- 5 N. M. Emanuel, *Khim. fizika*, 1 (1982) 91.
- 6 V. L. Kornienko, G. A. Kolyagin, I. S. Vasilieva, *Khimiya v interesakh ustoychivogo razvitiya*, 7 (1999) 681.
- 7 D. Pletcher, *Acta Chem. Scand.*, 53 (1999) 745.
- 8 H. S. Fenton, *J. Chem. Soc.*, 65 (1894) 899.
- 9 N. Hri, *Chem. Rev.*, 50 (1952) 375.
- 10 B. E. Brillas, R. M., Bastida, E. Llosa, J. Casado, *J. Electrochem. Soc.*, 142 (1995) 1733.
- 11 E. Brillas, E. Mur, J. Casado, *Ibid.*, 143 (1996) L 49.
- 12 N. V. Chaenko, G. V. Kornienko, T. L. Pustovalova, V. L. Kornienko, *Zhurn. prikl. khimii*, 64 (1991) 2297.
- 13 M. A. Oturan, *J. Appl. Electrochem.*, 30 (2000) 475.
- 14 N. K. Vel Leitner, M. Dore, *J. Photochem. and Photobiology A: Chem.*, 99 (1996) 137.
- 15 N. V. Chaenko, N. I. Pavlenko, V. L. Kornienko, *Khimiya v interesakh ustoychivogo razvitiya*, 10 (2002) 497.
- 16 R. Poludek-Fabini, T. Beirik, *Organicheskiy analiz*, Khimiya, Leningrad, 1981.
- 17 I. M. Kolthof, R. Belcher, V. A. Stenger, D. Matsuyama, *Obyemnyy analiz*, vol. III, Moscow, 1961.
- 18 *Perekis' vodoroda i perekisnye soyedineniya*, Leningrad-Moscow, 1951.
- 19 *Unifitsirovannyye metody analiza vod*, Pod red. Yu. Lurie, Khimiya, Moscow, 1971.
- 20 M. A. Oturan, N. Oturan, C. Lahitte, S. Trevin, *J. Electroanal. Chem.*, 507 (2001) 96.
- 21 A. Ya. Sychev, S. O. Travin, G. G. Duka, *Kataliticheskiye reaktsii i okhrana okruzhayushchey sredy*, Shtiintsa, Kishinev, 1983, p. 271.
- 22 E. Brillas, J. Calpe, J. Casado, *Wat. Res.*, 8 (2000) 2253.