

# Indirect Electrochemical Oxidation of Maleic Acid by Hydrogen Peroxide Generated *in situ* from Oxygen in the Gas-Diffusion Electrode

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## Abstract

Indirect oxidation of maleic acid by hydrogen peroxide electrochemically generated *in situ* from oxygen in the gas-diffusion electrode in 1 M Na<sub>2</sub>SO<sub>4</sub> has been studied. The oxidation of substrate in divided cell with cation-exchange membrane is shown to proceed to malic acid, and in undivided cell destructive oxidation occurs to CO<sub>2</sub> and H<sub>2</sub>O.

## INTRODUCTION

The strengthening of ecological safety requirements of existing chemical manufactures causes the necessity for refining the old and for the development of the new technologies by the use of ecologically pure reagents, for example hydrogen peroxide, and electric current both for target synthesis processes, and for disinfecting of sewage containing organic substrates [1, 2]. The utilisation of maleic acid involved in the industrial waters of the maleic and phthalic anhydrides production plants, presents an ecological problem. Nowadays, some part of these wastes is processed to difficultly soluble fumaric acid, but the main part of them remains dead and is directed to burial places in the underground chinks or arrives at the biological cleansing structures after preliminary neutralisation [3].

The literature analysis shows that maleic acid can be converted to malic acid by means of Fenton's reagent (Fe (II) + H<sub>2</sub>O<sub>2</sub>) [4, 5]. Here, the limiting stage is the formation of OH<sup>•</sup> rad-

icals, and not their interaction with organic substrate. Use of vanadate or tungstate ions as catalysts for maleic acid conversion into tartaric or malic acids [6, 7] is well known. The reaction, in this case, proceeds through formation of epoxide. Both ways use H<sub>2</sub>O<sub>2</sub> as an oxidiser.

The procedure of indirect oxidation of organic substrate by hydrogen peroxide, electrochemically generated *in situ* from molecular oxygen in the gas-diffusion carbon-black electrode, has been reported [8–14]. This procedure may be realized in the electrolysis cells of two types: with a cation-exchange membrane or without it, that allows to obtain high-reactive intermediates OH<sub>2</sub><sup>-</sup>, OH<sub>2</sub><sup>•</sup>, OH<sup>•</sup>, differing by 5–6 orders in their reactivity [2, 10].

The purpose of the present work is the investigation of the possibility of the indirect oxidation of maleic acid with hydrogen peroxide, using the oxygen diffusion cathode in the divided and undivided cells.

## EXPERIMENTAL

For  $\text{H}_2\text{O}_2$  production and the electrolysis performance with it, the temperature-controlled cells – electrolyzers with separated and unseparated cathode and anode area have been used. The divided cell consisted of three chambers: the gas one, where  $\text{O}_2$  was fed to from a cylinder, the cathode and anode ones, divided by the ion-exchange membrane MK-40. Between the cathode and gas chambers, in Teflon holder, the oxygen gas-diffusion cathode was the flat disks of the total porosity of 65–70 % and the thickness of 0.8–0.9 mm, made of the mixture of A 437-E (60 % mass) and PFTE-4d dispersion (40 % mass). Prior to the experiments, the energised electrodes were impregnated by the electrolyte. The delivery of oxygen in the electrode was effected in a continuous regime from the rear side of the electrode under the atmospheric pressure in a moderate excess, which was drained off in the atmosphere. The 1 M  $\text{Na}_2\text{SO}_4$  solution served as a catholyte. 1 M  $\text{H}_2\text{SO}_4$  solution was used as an anolyte. The design of a similar cell is presented in the work [15]. The undivided cell consisted of two chambers: the gas and electrolyte. 1 M solution of  $\text{Na}_2\text{SO}_4$  was used as an electrolyte. The platinum plate served as an anode.

The electrode potential was monitored on the frontal side of the gas-diffusion cathode with reference to the chlorine-silver electrode of comparison. Current density was calculated for the unit of a visible frontal surface comprising  $5 \text{ cm}^2$ , the electrolyte chamber volume was 20 ml. For preparation electrolysis, the weighted samples of maleic acid  $\text{C}_4\text{H}_4\text{O}_4$  (analytically pure) were used, 0.5 and 1 g in weight, which corresponds to the concentrations of 0.215 and 0.43 mol/l.

The analysis of the maleic acid content in a solution was performed by the standard determining methods for unsaturated organic compounds: an iodometric [16] and a permanganatometric [17] ones. Concentration of  $\text{H}_2\text{O}_2$  was determined with  $\text{TiCl}_3$  following the procedure [18], since the literature analysis and preliminary experiments have shown that its application makes it possible to determine selectively the hydrogen peroxide in the pres-

ence of organic compounds. The determining of maleic acid concentration was performed with regard to the expenditure of the potassium permanganate solution for the reaction of interaction with hydrogen peroxide. Water was vaporised from the analysed solutions after electrolysis at the temperature of 30–40 °C. The dry residue was analysed by IR Fourier spectrometer Vector 22 of Bruker Co. in the field of  $400\text{--}4000 \text{ cm}^{-1}$ . The spectral information has been processed by the OPUS.3 programme, version 22. Samples for spectral investigations were prepared in a potassium bromide matrix, the substance batches and matrix being constant. Identification of the compounds was performed with the appropriate standards.

To perform the electrolysis, an indifferent neutral  $\text{Na}_2\text{SO}_4$  electrolyte was chosen. For the purpose of making possible the efficient generation of hydrogen peroxide in the given electrolyte, the preparation electrolyses for hydrogen peroxide production in the gas-diffusion electrode were carried out. The form of a polarizing curve of reduction of oxygen in the 1 M solution of  $\text{Na}_2\text{SO}_4$ , and the range of operation potentials (0.2–0.6 V) were identical with the ones presented in [19] for 0.5 M  $\text{K}_2\text{SO}_4$ .

## RESULTS AND DISCUSSION

In Fig. 1 there are the curves of  $\text{H}_2\text{O}_2$  accumulation in the divided and undivided cells,

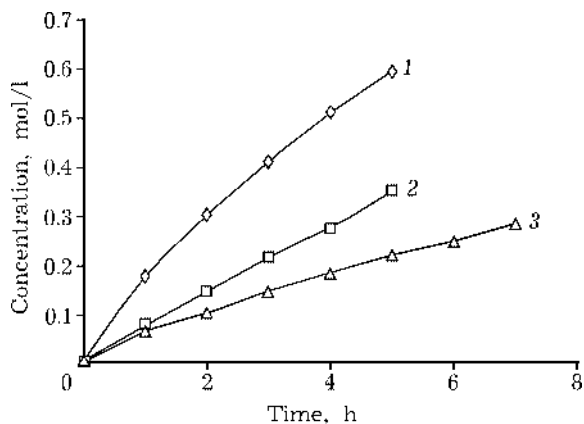
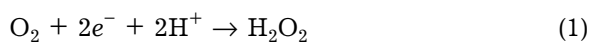
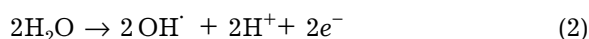


Fig. 1. Curves of hydrogen peroxide accumulation in 1 M  $\text{Na}_2\text{SO}_4$ : 1 – in the cathode chamber of divided cell, 2 – in undivided cell, 3 – in oxidation of maleic acid in a cathode chamber of divided cell.

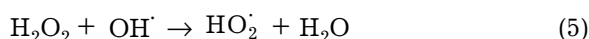
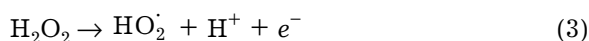
whence it follows that the process of  $\text{H}_2\text{O}_2$  generation proceeds rather effectively for both electrolysis schemes. The current yield of  $\text{H}_2\text{O}_2$  comprised for the first hour 76 and 33 % respectively at current density of  $50 \text{ mA/cm}^2$  and the temperature of  $25^\circ\text{C}$ , the achieved concentration being 0.18 and 0.08 mol/l in the process. The reaction of two-electronic reduction of oxygen to hydrogen peroxide [8, 9] is effected at the cathode:



At the anode, the reaction of water oxidation proceeds to form the  $\text{OH}^\cdot$  radicals as the intermediates [8, 9]:



The decrease of the current yield of  $\text{H}_2\text{O}_2$  in respect to current and the lower  $\text{H}_2\text{O}_2$  concentration in the electrolyzer with the undivided area are caused by the oxidation of the produced  $\text{H}_2\text{O}_2$  at the anode and by the reaction of interaction between  $\text{H}_2\text{O}_2$  generated at the cathode and  $\text{OH}^\cdot$  radicals produced at the anode [8, 9]:



It is worth noting that these high-reactive intermediates have the higher oxidizing properties, than  $\text{HO}_2^\cdot$  ion [20].

#### Electrolysis in the divided cell

Relationships, characterizing the efficiency of maleic acid oxidation by hydrogen peroxide generated *in situ* from oxygen in gas-diffusion cell, are presented in Fig. 2. Electrolysis was carried out at the current density of 50 and  $100 \text{ mA/cm}^2$  and the temperatures of 12 and  $25^\circ\text{C}$ .

The comparison of curves of the decrease of maleic acid concentration shows that the increase of current density, as well as temperature, has practically no influence on the rate of oxidation. The conversion of maleic acid after 12 h of electrolysis comprised 56–58 %. Parallel with determining of the maleic

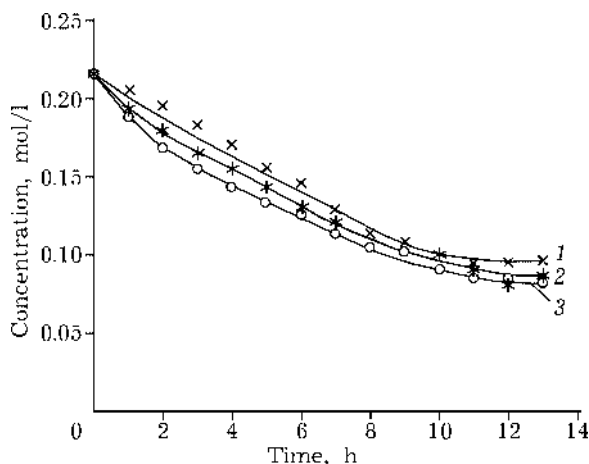


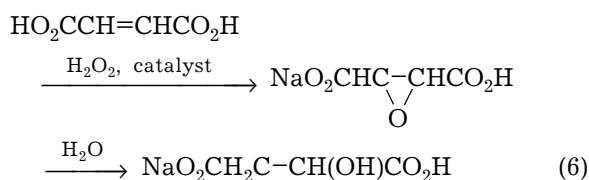
Fig. 2. Kinetic curves of maleic acid oxidation by hydrogen peroxide in the cell with a membrane. Current density,  $\text{mA/cm}^2$ : 50 (1, 2), 100 (3); the temperature,  $^\circ\text{C}$ : 12 (1), 25 (2, 3).

acid content, the concentration of  $\text{H}_2\text{O}_2$  in the solution was determined. The comparison of the curves of hydrogen peroxide accumulation presented in Fig. 1, during the  $\text{H}_2\text{O}_2$  synthesis in  $\text{Na}_2\text{SO}_4$  solution (curve 1) and in the presence of maleic acid (curve 3), indicates that the produced hydrogen peroxide does not fully enter the reaction with substrate. The  $\text{H}_2\text{O}_2$  excess demonstrates that the reaction rate in the given interval of temperatures does not depend on concentration of the produced  $\text{H}_2\text{O}_2$ .

The examined batches were identified by IR spectroscopy method after oxidation using the standards. The analysis has shown that the obtained product represents the mixture of sodium salt of malic acid ( $\text{NaC}_4\text{H}_5\text{O}_5$ ) as the basic substance, and unreacted maleic acid. Besides these compounds, the product contains insignificant amount of epoxide. The circumstantial confirmation of the last-mentioned is the presence of the absorption bands in the area of about  $3020, 1720, 1260, 840 \text{ cm}^{-1}$  in the spectra of the product. We attributed these bands to the vibrations of the appropriate functional groups. The reported way of the obtaining of tartaric acid [3, 21] from the maleic one is realized by the formation of epoxide in the presence of tungstate ions as the catalyst. As  $\text{H}_2\text{O}_2$  is rather stable in acid solutions, it should be expected that, in absence of the catalyst, the oxidation of an organic substrate would be ineffective under the given condi-

tions. The assumption is possible that under our experimental conditions, the role of the catalyst in maleic acid oxidation, apparently, is fulfilled by either the hydrophobic black-carbon electrode, or by the cation-exchange membrane. In the works [22, 23] it has been shown that the nature of the coal and modifiers, ions of metals, has the essential impact on the catalytic oxidation of the hydrocarbons by oxygen. The authors of the work [24] on ethane oxidation by hydrogen peroxide point to the probable catalytic influence of a cation-exchange membrane (Nafion).

The assumption is possible that the additional introduction of the catalyst (tungstate or vanadate ions) in this system would allow to increase the rate of the process of maleic acid hydroxylation by the reaction:



Thus, the method of indirect oxidation of aqueous solutions of maleic acid in a membrane-supplied cell can supplement the available methods of obtaining of the malic acid and its salts.

#### Electrolysis in the undivided cell

The well-known reaction of maleic acid oxidation by means of Fenton's reagent proceeds with  $\text{OH}^\cdot$  radicals involved to form the malic acid [4, 5]. The process in undivided cell combining the reaction of hydrogen peroxide generation from oxygen at the cathode with  $\text{OH}^\cdot$  radicals generation from water at the anode, may serve as an electrochemical analogue of this system.

In Fig. 3 there are the kinetic curves of maleic acid oxidation in the cell without a membrane. It is evident that the rate of oxidation of maleic acid increases with growth of temperature and current density. For example, after 1 h of cell operation, the maleic acid concentration comprised 0.385 mol/l at current density of 50 mA/cm<sup>2</sup>, and 0.32 mol/l at current density of 100 mA/cm<sup>2</sup> (see Fig. 3, b). The

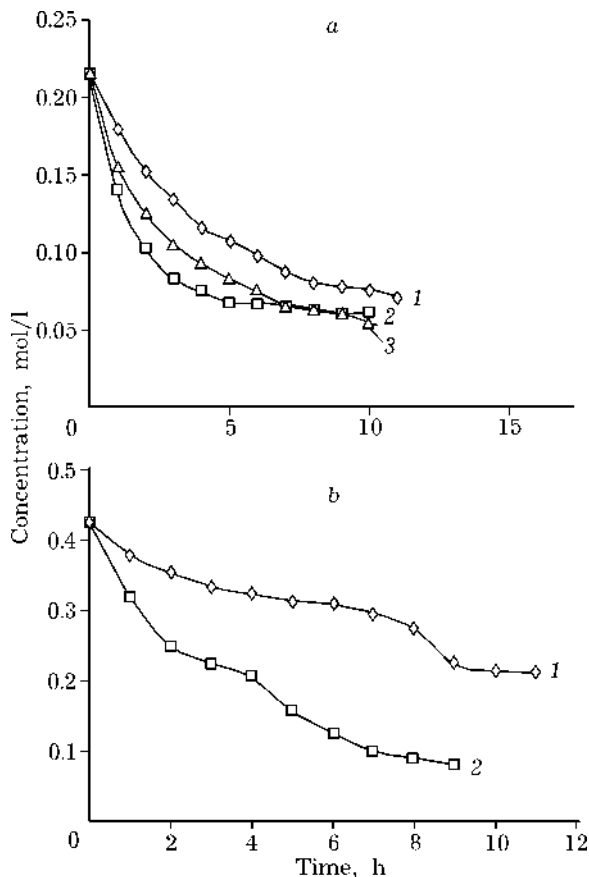
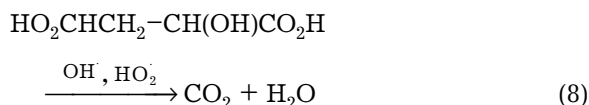
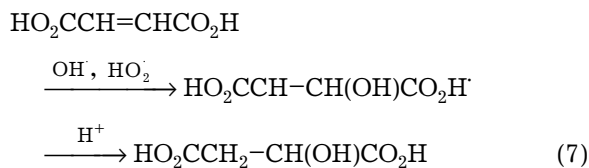


Fig. 3. Kinetic curves of maleic acid oxidation (0.215 mol/l) in the undivided cell electrolyzer in the presence of  $\text{H}_2\text{O}_2$ . Current density, mA/cm<sup>2</sup>: 50 (1), 100 (2, 3); a - temperature, °C: 25 (1, 2), 38 (3), concentration of maleic acid, 0.215 mol/l; b - temperature, 38 °C, concentration of maleic acid, 0.43 mol/l.

hydrogen peroxide content in the electrolyte in the process did not exceed 0.01 g/l during 8 h of electrolysis. The conversion of maleic acid comprised 68 %.

Identification of the products of electrolysis was performed on the basis of IR spectra. IR spectrum of a sample represented a superposition of spectra of maleic acid (of the residue),  $\text{Na}_2\text{SO}_4$  and, namely, the product of electrolysis. Upon deduction the spectra of maleic acid and  $\text{Na}_2\text{SO}_4$  from it, we got the spectrum of the electrolysis products. The comparison of the differential spectrum with the spectrum of malic acid and its sodium salt has allowed us to make the conclusion that both these substances are in the sample composition. Here, the yield of the malic acid does not exceed 6 %. The intensive absorption bands in the field of 2300–2400 cm<sup>-1</sup> are also observed

in the spectrum, which correspond to  $\nu_{\text{CO}}$  vibrations of the  $\text{CO}_2$  molecule. The mechanisms of possible reactions are as follows:



The obtained results make it possible to assume that the destructive oxidation of maleic acid to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  occurs in this case. Thus, the oxidation of maleic acid proceeds through the stage of formation of malic acid followed by its destruction to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . According to [25], malic acid is oxidized by hydroxyl radicals substantially easier than the maleic one. Under the conditions of the electrode process, when the high-reactive intermediates arrive at the reactionary mix continuously at the certain rate, the malic acid, being produced and more easily oxidizable, first of all becomes the object of the  $\text{HO}_2^\cdot$  and  $\text{OH}^\cdot$  attack.

To estimate the possible influence of anode process (the oxidation of substrate at the anode) the direct oxidation of maleic acid was also performed at current density of  $100 \text{ mA/cm}^2$  in the anode chamber of divided cell with Pt anode, followed by the analysis of the obtained product. The analysis of IR spectra has shown that the product of electrolysis is the acid of much more complex structure than maleic, malic, succinic or paratartaric ones. As it has been known, anode oxidation of organic acids occurs by the Kolbe reaction [26].

The dissimilarity of the electrolysis products, obtained through indirect oxidation in the no-membrane cell in the presence of hydrogen peroxide and through the direct anode oxidation, demonstrates that the presence of  $\text{H}_2\text{O}_2$  in the anode chamber changes the route of maleic acid oxidation. In the undivided cell, the oxidation of maleic acid occurs in a destructive way to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

## CONCLUSIONS

The obtained results give evidence that ecologically pure method of indirect oxidation of maleic acid by hydrogen peroxide, electrochemically generated *in situ* from  $\text{O}_2$  in the gas-diffusion electrode, may be used in the divided cell for the synthetic purposes (obtaining of the malic acid), and in the undivided cell, for destruction to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . To intensify the suggested patterns, the further investigations on optimization of electrolysis conditions are called for.

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