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Oxidation of Formic and Oxalic Acids in an Electrodeless Electrochemical Reaction

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Abstract—Decomposition of formic and oxalic acid and of sodium formate and sodium oxalate (~0.1 M solutions) in an electrodeless electrochemical reaction was studied. The oxidation kinetics was analyzed in terms of the previously developed model. The decomposition yields of formic acid and sodium formate are ~0.5 and ~1 molecule/(100 eV), respectively, which is comparable with the radiation-chemical decomposition yield, taking into account the installation efficiency.

Electrodeless electrochemical reactions were considered in [1] as a possible process for decomposing impurities dissolved in water. The reactions chiefly occur as oxidation [2]. Simple organic acids including formic and oxalic acids frequently arise from decomposition of more complex organic compounds; furthermore, these acids are oxidized with ozone slowly. Karpel Vel Leitner and Dore studied decomposition of these acids under the action of UV radiation and OH radicals [3–5] and considered the effect of ozone; Dzhe Chul Kim *et al.* studied radiation-chemical oxidation of formic acid [6]. Formic and oxalic acids exist in aqueous solution in the dissociated and nondissociated forms; their oxidation rates are different. Therefore, it is interesting to analyze the oxidation kinetics of various formic and oxalic acid species in an alternative process, electrodeless electrochemical reaction, in which the active species are OH radicals and ozone.

Variation of the concentrations of oxalic acid and sodium oxalate with the time of electrochemical treatment is illustrated in Fig. 1. It is seen that the time in which the concentration decreases by a factor of 100 is similar for both compounds: ~40 h. The chemical oxygen demand measured for these solutions agreed within the measurement error (~5%) with the concentrations of oxalic acid and sodium oxalate. It should be emphasized that determination of the chemical oxygen demand of the sodium oxalate solution involved its acidification, so that actually sodium oxalate was preliminarily converted to oxalic acid; in neutral solutions, sodium oxalate is not oxidized with potassium dichromate.

The chemical oxygen demand of formic acid and sodium formate solutions is plotted in Fig. 2 vs. treatment time. The time in which the chemical oxygen demand decreases by a factor of 100 is ~14.5 h for formic acid and ~5.5 h for sodium formate. It is known that the intermediate oxidation product of formic and oxalic acids is hydrogen peroxide [3–5]. The H_2O_2 concentration in solutions in the course of the process is plotted in Fig. 3. In oxidation of sodium oxalate and formate, no hydrogen peroxide was detected; the possible H_2O_2 concentration did not exceed 10^{-6} M. Oxidation of formic acid may also yield oxalic acid [4]; however, in this work it was not detected (the possible $H_2C_2O_4$ concentration did not exceed 5×10^{-6} M).

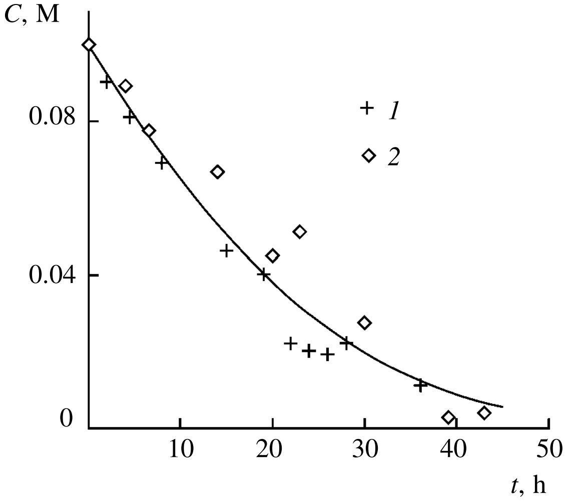

Fig. 1. Variation of the concentration of (*1*) oxalic acid and (*2*) sodium oxalate with time *t* of the electrodeless reaction at a discharge current of 0.5 mA. (Solid line): Calculation.

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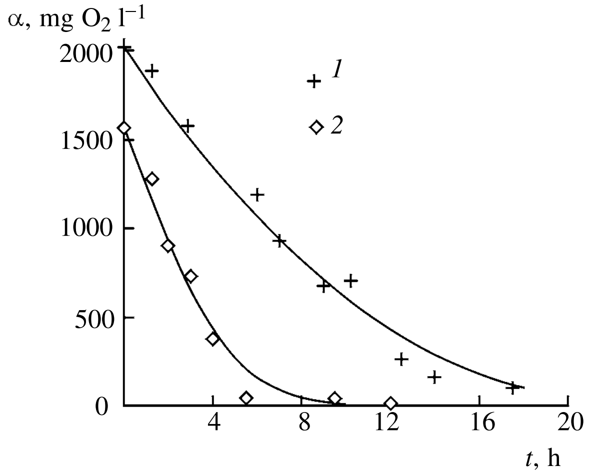

Fig. 2. Chemical oxygen demand α of solutions of (*1*) formic acid and (*2*) sodium formate as a function of treatment time. (Solid lines): Calculation.

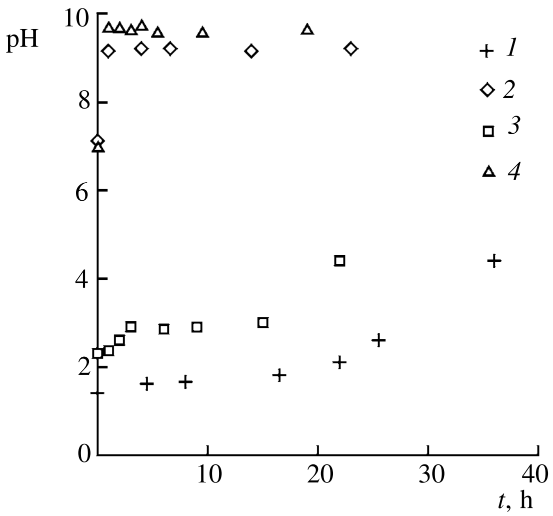

Fig. 4. Variation of the solution pH in the course of the electrodeless reaction: (*1*) oxalic acid, (*2*) sodium oxalate, (*3*) formic acid, and (*4*) sodium formate.

Variation of the solution pH in the course of the treatment is illustrated in Fig. 4. The initial pH was 1.6 for oxalic acid, 2.4 for formic acid, and ~7 for sodium oxalate and formate. During decomposition of the acids, the pH of their solution grows, reaching 4.4 in both cases. This is the limiting value, apparently determined by accumulation of carbonic acid. The presence of carbonic acid is qualitatively confirmed by vigorous gas evolution on adding 1 M H_2SO_4. It is known [7] that, at pH < 4.0, carbonic acid decomposes to CO_2 and water. In solutions of sodium oxalate and formate, the pH values initially grow, reaching within 1 h 9.2 and 9.7, respectively, and then remain unchanged. In both cases, sodium carbonate and hydroxide are formed. The difference between the pH values in decomposition of sodium oxalate and formate solutions may be due to the higher yield of sodium carbonate from sodium oxalate.

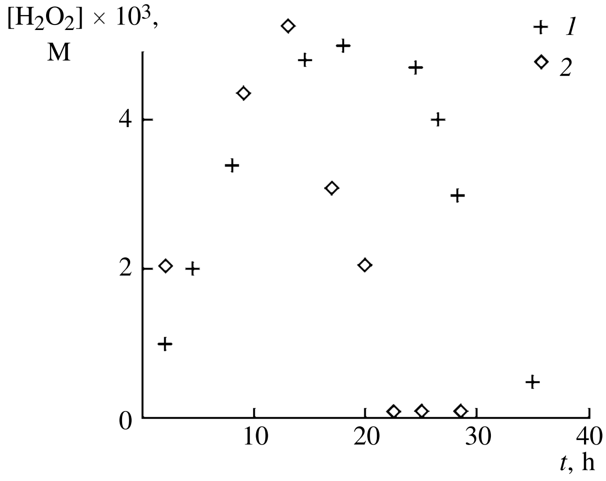

Fig. 3. Variation of the H_2O_2 concentration in solutions of (*1*) oxalic and (*2*) formic acids in the course of the electrodeless reaction.

The ozone concentration in the gas phase of the reaction vessel as a function of treatment time in the experiments with HCOOH, NaHCOO, $H_2C_2O_4$, $Na_2C_2O_4$, and distilled water is plotted in Fig. 5. In the initial period, which is not reflected in the figure, the ozone concentration smoothly increases from zero to the steady-state value.

Oxidation of formic acid with OH radicals and ozone can be described by the reaction scheme given in the table. Oxidation with ozone yielding no radical products is described by overall reactions (6) and (11).

All the oxidation steps can be traced only with molecular products, starting from the nondissociated formic and oxalic acid species. The dissociated species of these acids react with OH radicals at different rates [reactions (1a), (1b), and (7a)–(7c) in the table], which should affect the overall process kinetics. Let us analyze the oxidation kinetics in terms of the reaction pattern given in the table.

Oxalic acid. The experimentally observed oxidation rates of oxalic acid and sodium oxalate are similar. The initial rate of oxalic acid decomposition is 22 ± 3 mol/(mol electrons). In sodium oxalate solutions, oxalic acid exists in the form of $(COO)_2^{2-}$ ions. In oxalic acid solutions, the prevailing species are the $(COOH)(COO)^-$ ions, since pK_a^{I} 1.23, whereas pK_a^{II}

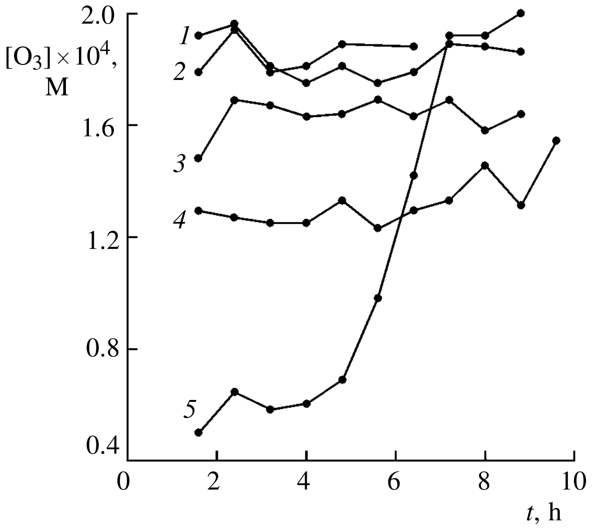

Fig. 5. Variation of the ozone concentration in the gas phase of the reaction vessel in the course of the electrodeless reaction: (*1*) distilled water, (*2*) sodium oxalate, (*3*) oxalic acid, (*4*) formic acid, and (*5*) sodium formate.

4.27. The rate constant of the reaction of OH radicals with monodeprotonated oxalic acid is almost an order of magnitude higher than the rate constant of the reaction with oxalate dianions; therefore, presumably, the reaction with the oxalate dianions will be the limiting step of the process. The calculation of the oxidation kinetics using the electrodeless reaction model described in [8] correctly reproduces the oxalic acid consumption at the rate constant of the reaction of the oxalate dianion with OH radicals k_{7c} 7.7 × 10^6 l mol^{-1} s^{-1} (solid line in Fig. 1). However, the calculated concentrations of H_2O_2 formed in the reaction appear to be an order of magnitude lower than the experimental values. This means that hydrogen peroxide is mainly formed by side reactions with ions and radical ions, not included in the scheme given in the table.

Formic acid. The rates of decomposition of formic acid and sodium formate, determined from the slopes of the plots in Fig. 2, are 48 ± 5 and 97 ± 10 mol/(mol electrons), respectively. This large difference may be due to the pH dependence of the rate constant of the reaction with ozone [reaction (6) in the table] {k_6 5 l mol^{-1} s^{-1} at pH ~2 and 100 l mol^{-1} s^{-1} at pH ~6 [9]}, and also to the different rate constants of the reactions of OH radicals with formic acid (which is weakly dissociated) and formate ion [reactions (1a) and (1b) in the table].

The oxidation kinetics was calculated in terms of model [8] and reaction pattern in the table using the constants k_6 for the actual solution pH and the rate constants of the reactions of OH radicals with nondissociated formic acid [reaction (1a), for oxidation of formic acid] and formate ion [reaction (1b), for oxidation of sodium formate]. The results (solid lines in Fig. 2) are in agreement with the experimental data. The calculated concentration of oxalic acid formed by decomposition of formic data is ~10^{-4} M, which is reasonably consistent with the experiment. The calculated hydrogen peroxide concentration is underestimated by more than an order of magnitude, suggesting, as in the case of oxalic acid, the major contribution of radical ion reactions not included in the scheme (see table).

Scheme of oxidation of formic and oxalic acids[a]

No.	Reaction	Rate constant, l mol^{-1} s^{-1}
1a	$HCOOH + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}COOH$	1.3×10^8
1b	$HCOO^- + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}COO^-$	3.2×10^9
2	${}^{\cdot}COOH + O_2 \rightarrow {}^{\cdot}HO_2^w + CO_2$	2×10^9
3	${}^{\cdot}COOH + {}^{\cdot}COOH \rightarrow (COOH)_2$	4×10^8
4	${}^{\cdot}COOH + {}^{\cdot}COOH \rightarrow CO_2 + HCOOH$	5×10^8
5	$HOOC{-}COO^{\cdot} + {}^{\cdot}COOH \rightarrow 2CO_2 + HCOOH$	5×10^6
6	$HCOOH + O_3 \rightarrow CO_2 + H_2O$	5 (pH ~2) 1×10^2 (pH > 6)
7a	$(COOH)_2 + {}^{\cdot}OH \rightarrow HOOC{-}COO^{\cdot} + H_2O$	1.4×10^6
7b	$HOOC{-}COO^- + {}^{\cdot}OH \rightarrow {}^{\cdot}OOC{-}COO^- + H_2O$	4.7×10^7
7c	${}^-OOC{-}COO^- + {}^{\cdot}OH \rightarrow$ Products	7.7×10^6
8	$HOOC{-}COO^{\cdot} + O_2 \rightarrow {}^{\cdot}HO_2^w + 2CO_2$	1.0×10^8
9	$HOOC{-}COO^{\cdot} + H_2O_2 \rightarrow {}^{\cdot}OH + H_2O + CO_2$	1.0×10^4
10	$HOOC{-}COO^{\cdot} + {}^{\cdot}OOC{-}COOH \rightarrow (COOH)_2 + 2CO_2$	7.7×10^6
11	$2COOH + O_3 \rightarrow CO_2 + H_2O$	1×10^{-2}
12	${}^{\cdot}OH^w + {}^{\cdot}OH^w \rightarrow H_2O_2$	5.5×10^9
13	${}^{\cdot}OH^w + {}^{\cdot}HO_2^w \rightarrow O_2 + H_2O$	1.4×10^{10}
14	${}^{\cdot}HO_2^w + {}^{\cdot}HO_2^w \rightarrow H_2O_2 + O_2$	8.3×10^5
15	${}^{\cdot}OH^w + O_3 \rightarrow {}^{\cdot}HO_2^w + O_2$	4.0×10^7
16	${}^{\cdot}HO_2^w + O_3 \rightarrow {}^{\cdot}OH^w + 2O_2$	1.2×10^6
17	${}^{\cdot}OH^w + H_2O_2 \rightarrow {}^{\cdot}HO_2^w + H_2O$	4.06×10^7

[a] Data of [3–5] are used. Superscript ^{w} denotes secondary active species generated in the liquid [reactions (2) and (8)]. Reactions (12)–(17) are the reactions between the active species in the liquid. The full scheme of reactions of the active species in the gas phase is given in [8].

The contribution of reactions with ozone is illustrated by Fig. 5. In ozonation of distilled water, when ozone is not consumed for oxidation of impurities, the steady-state ozone concentration is established at a level of $(1.9 \pm 0.1) \times 10^{-4}$ M. In the initial stage of oxalic acid concentration, the ozone concentration is lower, $(1.6 \pm 0.1) \times 10^{-4}$ M, suggesting its consumption for oxalic acid oxidation, whereas the concentration of ozone over the sodium oxalate solution is the same as that over distilled water, i.e., ozone is not consumed for sodium oxalate oxidation. In treatment of HCOOH, in the initial period, $[O_3] = (1.3 \pm 0.1) \times 10^{-4}$ M, and the ozone concentration grows as formic acid is consumed. The ozone consumption for the sodium formate oxidation is higher (the ozone concentration over the solution is lower), but, after complete oxidation of the formate ions (treatment time >5.5 h), the ozone concentration increases to the level characteristic of distilled water.

It is known that, in alkaline solutions, ozone reacts with OH^- ions to form OH radicals; the rate constant of this reaction is 210 $l\,mol^{-1}\,s^{-1}$ [10]. This process could accelerate the decomposition of oxalate and formate, but the generated OH radicals can be scavenged by carbonate ions; the rate constant of this reaction is $4.2 \times 10^8\ l\,mol^{-1}\,s^{-1}$ [10].

Dzhe Chul Kim *et al.* [6] studied the radiation-chemical decomposition of formic acid. In the process simulation, they mainly took into account the reactions of neutral radicals. The kinetic model developed in [6] and mainly including neutral species adequately described the experimental data. Among decomposition products, Dzhe Chul Kim *et al.* detected oxalic and some other organic acids in concentrations of 5–20% of the initial HCOOH concentration. The complex composition of the intermediates is due to the occurrence of both oxidative (with atomic oxygen and OH radicals) and reductive (with atomic hydrogen and hydrated electrons) processes.

Let us compare the product yields as functions of energy in various processes. In the radiation-chemical process, the radiation dose required for virtually complete decomposition of HCOOH is 60 kGy [6]; at the acid concentration of 10^{-2} M, the yield of the acid decomposition products is 1.6 molecules/(100 eV). The efficiency of a radiation-chemical installation (ratio of the energy transmitted to accelerated electrons to the energy consumed from the mains) is 10–20%.

In decomposition of formic acid by the electrodeless electrochemical reaction, the yield of decomposition products is ~0.5 molecule/(100 eV) [48 mol/(mol electrons)]; the voltage drop between the electrodes and liquid surface is 10 kV. In decomposition of sodium formate, the yield of decomposition products is ~1 molecule/(100 eV). The efficiency of an installation for the electrodeless reaction, determined by the efficiency of the high-voltage rectifier and the energy loss in ballast resistors, is about 85–90%.

In decomposition of formic acid under the action of OH radicals generated by UV photolysis of H_2O_2 [3–5], the yield of decomposition products varied from 0.2 to 2 molecules/(100 eV) depending on the H_2O_2 concentration; the efficiency of the UV lamp was ~30%. Thus, all the three processes exhibit comparable overall efficiency, taking into account the efficiency of the installations. Therefore, the electrodeless reaction has certain application prospects and deserves more detailed study.

EXPERIMENTAL

The reaction was performed in a 2.5-l glass vessel equipped with a fluoroplastic stopper [2]. The stopper had holes for seven aluminum discharge electrodes and for tubes for purging with oxygen. Before switching on the high voltage, the vessel was purged with oxygen for 14–16 h at a rate of 0.6 $l\,h^{-1}$. The high voltage (10 kV) was fed to the discharge electrodes through 11-MΩ ballast resistors. The total discharge current from all the electrodes was 0.5 mA. The contact electrode connecting the liquid to be treated with the positive pole of the power source was arranged on the vessel bottom. The liquid volume in the vessel was 100 ml. The concentrations of the solutions being treated were as follows (M): oxalic acid, sodium oxalate, and sodium formate, 0.1; formic acid, 0.13. The cp grade chemicals and distilled water were used.

The concentrations of oxalic acid and sodium oxalate in the initial and treated solutions were determined by titration with a potassium permanganate solution. One of the products of $H_2C_2O_4$ decomposition is H_2O_2, which is also titrated with permanganate; therefore, hydrogen peroxide was determined independently by iodometric titration (addition of a KI solution followed by titration of the released iodine with a sodium thiosulfate solution). For formic acid and sodium formate solutions, the chemical oxygen demand was determined by refluxing for 2 h with potassium dichromate in acid solution, followed by titration with Mohr's salt. The content of oxalic acid and hydrogen peroxide in the treated solutions was estimated by permanganate and iodometric titrations. The ozone concentration in the gas phase of the reaction vessel was estimated by trapping ozone from the outflowing gas with a KI solution.

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