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Oxidation of Oxalic Acid in the Ozone–Chloride–Ion Reaction System in an Aqueous Solution

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Abstract—It is shown that the rate of oxidation of oxalic acid $H_2C_2O_4$ during the ozonation of its solutions grows considerably if sodium chloride is added to the solution. Based on the kinetics of evolution of molecular chlorine during ozone treatment of solutions of $H_2C_2O_4$ and NaCl, the mechanism of reaction of oxalic acid with chlorine is clarified, and the rate constant of this reaction is determined.

Keywords: ozone, chloride ion, oxalic acid, molecular chlorine, kinetics, bubble column reactor **DOI:** 10.1134/S0036024420010173

INTRODUCTION

Oxalic acid and its salts (i.e., oxalates) are water pollutants and are present in the wastewater of different industries [1]. Removing oxalates from solutions of various compositions is of great importance in the industrial processing of aluminum ores [2] and liquid radioactive waste [3]. Ozone is widely used in human activities in various types of water treatment [4], and the final product of ozonolysis of many organic impurities is oxalic acid or its anions [5]. They barely undergo oxidative degradation. For these reasons, studying the oxidation of oxalic acid and oxalates in ozonation processes is an important task. The aim of this was to study the kinetics of oxalic acid oxidation during the ozonation of aqueous solutions containing high concentrations of chloride ions, and to determine the mechanism and rate constant of the reaction between oxalic acid and chlorine.

EXPERIMENTAL

Our experimental setup and technique were similar to those described in [6–8]. Aqueous solutions of oxalic acid with acidimetric concentrations of 0.02– 0.1 M oxalic acid, 0.02–0.1 M oxalic acid and 1 M NaCl, and 0.06 M oxalic acid and 0.4–1 M NaCl were ozonated. Once-distilled water, chemically pure sodium chloride, and titrimetric standards of oxalic acid were used for their preparation. The pH index before and after ozonation was monitored using an Expert-001 pH meter equipped with an ESK-10601/7 glass electrode and an EVL-1M3.1 silver chloride electrode. The process was conducted in a bubble column reactor at room temperature ($21 \pm 1^{\circ}C$), keeping

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the flow rate of the initial gas mixture (ozonized oxygen) equal to v = 21 L/h (standard conditions for temperature and pressure), the concentration of ozone at the reactor inlet equal to $C^{\circ}(O_3) = 20$ g/m³, and the volume of the reaction solution equal to $V_L = 220$ mL in most experiments.

The gases leaving the reactor were passed through a furnace for the destruction of ozone, and then the carbon dioxide CO_2 and molecular chlorine Cl_2 in them were determined in the steady-state operating mode of the reactor. The content of carbon dioxide was determined via IR spectroscopy on an EQUINOX 55/S infrared Fourier spectrometer (Bruker) with a resolution of 0.5 cm⁻¹ and averaging over 50 scans. A 10-cm-long optical cell with CaF₂ windows was filled with effluent gases and placed in the spectrometer's cell compartment. The device and cell compartment were purged with nitrogen gas to eliminate the influence of atmospheric CO_2 .

Molecular chlorine was determined via photometric iodometry with the preliminary thermal destruction of ozone [9]. In this work, the furnace temperature was 500–550°C, which ensured the almost complete removal of ozone and a constant concentration of Cl₂. After passing through the furnace, the gas mixture was sent to a trap filled with 100 mL of an aqueous solution of 50 g/L KI. A quantitative reaction between chlorine and KI produced triiodide ion I_3^- , the concentration of which was determined using a KFK-3 photometer. Rate $r(Cl_2)$ of chlorine evolution was found from the slope of the final linear segment of the

Table 1. Optical density at the absorption line maximum near 2360 cm⁻¹ in the IR spectrum of the gases leaving the reactor (the volume of the reaction solution is 200–220 mL)

$C^{\circ}(O_3), g/m^3$	Composition of reaction solution	D ₂₃₆₀
57	$0.1 \text{ M H}_2\text{C}_2\text{O}_4$	0.40
57	$0.1 \text{ M H}_2\text{C}_2\text{O}_4 + 1 \text{ M NaCl}$	0.78
10	$0.02 \text{ M H}_2\text{C}_2\text{O}_4$	0.06
10	$0.02 \text{ M H}_2\text{C}_2\text{O}_4 + 1 \text{ M NaCl}$	0.14
20	$0.02 \text{ M H}_2\text{C}_2\text{O}_4$	0.03
20	$0.02 \text{ M H}_2\text{C}_2\text{O}_4 + 1 \text{ M NaCl}$	0.19
20	$0.06 \text{ M H}_2\text{C}_2\text{O}_4$	0.12
20	$0.06 \text{ M H}_2\text{C}_2\text{O}_4 + 1 \text{ M NaCl}$	0.32

time dependence of the amount of I_3^- using the formula

$$r(\mathrm{Cl}_2) \equiv \frac{1}{V_L} \frac{dn(\mathrm{Cl}_2)}{dt} = \frac{1}{V_L} \frac{\Delta n(\mathrm{I}_3^-)}{\Delta t},$$

where V_L is the volume of the solution in the reactor. A blank experiment was performed to consider the possible contribution from different side processes to the oxidation of iodide in the trap. A 0.1 M solution of oxalic acid was ozonized without sodium chloride (all other conditions being similar to real experiments). The rate of formation of triiodide was in this case a negligible value of 0.03 µmol L⁻¹ min⁻¹ not exceeding 1% of the measured value of the rate of chlorine evolution.



Fig. 1. Dependences of the rate of chlorine evolution during the ozonation of a solution of 1 M NaCl and oxalic acid on the acidimetric concentration of acid ($C^{\circ}(O_2) =$

 20 g/m^3). The points show experimental data: (1) results calculated for a model that includes the oxidation of oxalic acid with chlorine; (2) results calculated by assuming there was no reaction between chlorine and oxalic acid.

RESULTS AND DISCUSSION

When ozonating ($C^{\circ}(O_3) = 10-57 \text{ g/m}^3$) aqueous solutions of 0.02–0.1 M oxalic acid (pH 1.3–1.9), the characteristic vibrational-rotational structure of the absorption band of CO₂ with a center at about 2350 cm⁻¹ was observed in the IR spectrum of effluent gases, along with strong absorption bands of water vapor; no contributions from absorption bands of other substances to the spectrum were found. With a constant flow rate of ozonized oxygen, the intensity of the absorption bands of CO₂ in the spectrum of effluent gases was proportional to the rate of its release from the reactor. To measure changes in the concentration of CO_2 , we compared the intensities of the line of the vibrational-rotational structure with the maximum at 2360 cm⁻¹. The intensities of this line under different experimental conditions are given in Table 1.

The formation of CO_2 is a result of the oxidation of oxalic acid or its anions by ozone. This reaction is very slow; the apparent rate constant determined from the intensity of CO_2 signals in the IR spectrum of effluent gases and the concentrations of ozone and oxalic acid in the solution was around $10^{-3}-10^{-2}$ L mol⁻¹ s⁻¹ as an estimate of their orders of magnitude.

When sodium chloride was added to the reaction solution at a concentration of 1 M, the rate of carbon dioxide evolution grew by 2-6 times (see Table 1). On the other hand, rate $r(Cl_2)$ of the evolution of molecular chlorine, which formed as a result of the reaction between chloride ions and ozone, became notably lower in the presence of oxalic acid (Fig. 1). These phenomena were due to the oxidation of oxalic acid with active chlorine in solution.

It should be noted that the primary products of the reaction of O_3 with $Cl^-(aq)$ are hypochlorous acid HOCl and/or hypochlorite ion ClO^- . They react in reversible reactions

$$HOCI \rightleftharpoons CIO^{-} + H^{+}, \qquad (1)$$

$$Cl_2(aq) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-,$$
 (2)

$$\operatorname{Cl}_2(\operatorname{aq}) + \operatorname{Cl}^- \rightleftharpoons \operatorname{Cl}_3^-,$$
 (3)

in which equilibrium is established quickly. As a result, chlorine compounds in the oxidation states of +1 and 0 (i.e., ClO⁻, HOCl, and Cl₂) are present in the solution, the quantitative ratios between which are determined from the values of the corresponding equilibrium constants and the concentrations of H⁺ and Cl⁻ in the reaction solution. Particles of ClO⁻, HOCl, and Cl₂ can be considered different forms of a single set of chemicals, the so-called "active chlorine." If at least one of these forms participates in any chemical reaction, the concentrations of the other forms change proportionally.

It is well known that oxalic acid and oxalates react quickly with active chlorine (but virtually do not interact with chlorine compounds in higher oxidation states, e.g., CIO_2^- , CIO_2^- , and CIO_3^-) [10]. The subsequent sections of this work are devoted to determining the mechanism of this reaction based on experimental data on the evolution of Cl_2 during the ozonation of solutions of oxalic acid and NaCl (Figs. 1 and 2). We therefore constructed a mathematical model of the kinetics of the process, the desired parameters of which were the shape of the dependence and the rate constant of the reaction between chlorine and oxalic acid. We determined the parameters from the condition of minimal discrepancy between the calculated and experimental dependences of rate $r(Cl_2)$ of chlorine evolution on the concentrations of oxalic acid and chloride ions.

We describe the bubble column reactor as an ideal mixing reactor containing two phases, liquid and gaseous, and consider the steady-state mode of its operation. We write the material balance equation (the equality of the rates of formation and consumption) for active chlorine:

$$k_{O_3+Cl^-}[Cl^-][O_3] = r_{O_X} + \frac{V}{V_L}C(Cl_2).$$
 (4)

Here, $k_{O_3+Cl^-}$ is the rate constant of the primary reaction between O₃ and Cl⁻(aq) with the formation of HOCl or ClO⁻, and r_{Ox} is the rate of the reaction between one form of active chlorine (HOCl, ClO⁻, Cl₂, or Cl₃⁻) and any form of oxalic acid (with acid H₂C₂O₄ itself, hydrooxalate HC₂O₄⁻, or oxalate C₂O₄²⁻). The reactions between hypochlorite ions and ozone can be ignored, since using oxalic acid results in fairly high acidity of the reaction solution (pH 1.1–1.7 in all experiments). The concentration of molecular chlorine in the effluent gases is denoted *C*(Cl₂). The *v*(C(Cl₂)/*V_L* term describes the loss of active chlorine due to the removal of Cl₂ from the reactor with a gas flow. Constant $k_{O_3+Cl^-}$ (L mol⁻¹ s⁻¹) is determined by the expression

$$k_{\rm O_3+Cl^-} = \frac{2.44 \times 10^{-3} + 0.0212[\rm H^+]}{1 + 0.0707[\rm H^+][\rm Cl^-]}$$
(5)

under conditions where the ionic strength of the reaction solution I = 1 M and the temperature is 21°C, according to [6]. The presence of the concentration of H⁺ in Eq. (5) reflects that the reaction of O₃ with Cl⁻(aq) is catalyzed by hydrogen ions. The concentration of ozone in solution, [O₃] is determined by the formula

$$[O_3] = L_{O_3} C^{\circ}(O_3), \tag{6}$$

where $C^{\circ}(O_3)$ is the concentration of ozone in the gas flow at the inlet to the reactor. The value of the solubility coefficient (the apparent Henry constant) is

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Fig. 2. Dependence of the rate of chlorine evolution during the ozonation of a solution of 0.06 M oxalic acid and sodium chloride on the concentration of NaCl ($C^{\circ}(O_3) = 20 \text{ g/m}^3$). The points show experimental data (for solutions of 0.06 M H₂C₂O₄ and 0.4 M NaCl + 0.6 M KNO₃, 0.8 M NaCl, 1 M NaCl), and the line shows the results calculated for models (solutions of 0.06 M H₂C₂O₄ with an ionic strength of 1 M and concentrations of chloride ions in the range of 0–1 M).

 $L_{O_3} = 0.151$ (at an ionic strength of 1 M and a temperature of 21°C), as was determined in [6] for solutions of sodium chloride in the same reactor under similar experimental conditions.

If we assume there is a chemical reaction between only one of the forms of active chlorine and one form of oxalic acid, we can write twelve different expressions for rate r_{Ox} :

$$r_{Ox} = k_{Ox_A} [Cl_2] [H_2C_2O_4],$$

$$r_{Ox} = k_{Ox_B} [Cl_2] [HC_2O_4^-],$$

$$r_{Ox} = k_{Ox_C} [Cl_2] [C_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_D} [HOCl] [H_2C_2O_4],$$

$$r_{Ox} = k_{Ox_E} [HOCl] [HC_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_F} [HOCl] [C_2O_4^{2-2}],$$

$$r_{Ox} = k_{Ox_B} [ClO^-] [H_2C_2O_4],$$

$$r_{Ox} = k_{Ox_H} [ClO^-] [HC_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_I} [ClO^-] [C_2O_4^{2-2}],$$

$$r_{Ox} = k_{Ox_I} [ClO^-] [HC_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_I} [ClO^-] [HC_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_L} [Cl_3^-] [HC_2O_4^{-2}],$$

$$r_{Ox} = k_{Ox_L} [Cl_3^-] [C_2O_4^{-2}].$$

(7)

To derive formulas for calculating concentration $C(Cl_2)$ of Cl_2 in the effluent gases and rate $r(Cl_2)$ of the evolution of chlorine from the reactor using Eq. (4), we must express the concentrations of Cl_2 , HOCl, ClO^- , and Cl_3^- in Eqs. (7) through $C(Cl_2)$, and the concentrations of H^+ , $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ through the acidimetric concentration of oxalic acid, $C(H_2C_2O_4)$. Using the quasi-equilibrium approximation for different forms of active chlorine, we obtain

$$[Cl_{2}] = H_{Cl_{2}}C(Cl_{2}),$$

$$[HOCl] = \frac{K_{Cl_{2}}H_{Cl_{2}}}{[H^{+}][Cl^{-}]}C(Cl_{2}),$$

$$[Cl0^{-}] = \frac{K_{HOCl}K_{Cl_{2}}H_{Cl_{2}}}{[H^{+}]^{2}[Cl^{-}]}C(Cl_{2}),$$

$$[Cl_{3}^{-}] = K_{Cl^{-}}[Cl^{-}]H_{Cl_{2}}C(Cl_{2}).$$
(8)

Here, H_{Cl_2} is the Henry constant of molecular chlorine, K_{HOCl} is the constant of hypochlorous acid dissociation (reaction (1)), K_{Cl_2} is the constant of Cl_2 hydrolysis (reaction (2)), and K_{Cl_2} is the constant of

 Cl_3^- ion stability (reaction (3)).

The concentrations of H^+ ions, undissociated oxalic acid molecules $H_2C_2O_4$, hydroxalate anions $HC_2O_4^-$, and oxalate anions $C_2O_4^{2^-}$ in the reaction solution were calculated by solving a system of algebraic equations that included expressions of the equilibrium constants of acid dissociation in an aqueous solution, and the material-balance and charge-conservation equations

$$K_{a1} = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]}, \quad K_{a2} = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]},$$
$$C(H_2C_2O_4) = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}], \quad (9)$$
$$[H^+] = [HC_2O_4^-] + 2[C_2O_4^{2-}].$$

The calculations using Eqs. (4)-(9) were performed for a temperature of 21° C and a reaction solution ionic strength of 1 M, which corresponded to the experimental conditions. The equilibrium constants under these conditions had the values

$$H_{\text{Cl}_2} = 1.51 [11], \quad K_{\text{Cl}_2} = 7.50 \times 10^{-4} \text{ M}^2 [12],$$

 $K_{\text{Cl}_3} = 0.18 \text{ M}^{-1} [13], \quad K_{\text{HOCl}} = 3.92 \times 10^{-8} \text{ M} [14],$ (10)

$$K_{a1} = 0.151 \text{ M} [15], \quad K_{a2} = 3.18 \times 10^{-4} \text{ M} [15].$$

It was believed that the acidimetric concentration of oxalic acid, $C(H_2C_2O_4)$, and the concentration of chloride ions, $[Cl^-]$, in the reaction solution did not change during ozonation, since the real drop in these concentrations during our experiments was negligible.

In the range of oxalic acid concentrations used in the experiments of this work ($C(H_2C_2O_4) = 0.02-$ 0.1 M), the ratio of the concentrations of hydroxalate anions and H⁺ ions is almost constant: $[HC_2O_4^-]/[H^+] =$ 0.97–0.99. It is therefore convenient to express rates (7) through this ratio, and through the concentration of H⁺; the [H⁺] values are determined by solving Eqs. (9).

It turns out that the theoretical expressions for the chlorine evolution rate obtained from Eq. (4) correspond to the experimental dependences shown in Figs. 1 and 2 only when rate r_{Ox} does not depend on

the concentration of H^+ (only the $[HC_2O_4^-]/[H^+]$ ratio is included in the expression for r_{Ox}) and is inversely proportional to the concentration of Cl⁻. This can be only in two cases that correspond to when the reaction between oxalic acid and chlorine is the chemical interaction between either a hypochlorous acid molecule and a hydroxalate ion according to the scheme

$$HOCl + HC_2O_4^- \rightarrow H_2O + Cl^- + 2CO_2 \qquad (11)$$

or a hypochlorite ion with a molecule of undissociated oxalic acid by scheme

$$ClO^{-} + H_2C_2O_4 \rightarrow H_2O + Cl^{-} + 2CO_2.$$
 (12)

In addition, rate r_{Ox} is determined by the corresponding equations

$$r_{\text{Ox}} = k_{\text{Ox}_E}[\text{HOCl}][\text{HC}_2\text{O}_4^-]$$

= $k_{\text{Ox}_E} \frac{K_{\text{Cl}_2}H_{\text{Cl}_2}}{[\text{Cl}^-]} \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]} C(\text{Cl}_2),$ (13)

$$r_{\text{Ox}} = k_{\text{Ox}_{G}} [\text{ClO}^{-}] [\text{H}_{2}\text{C}_{2}\text{O}_{4}]$$

= $k_{\text{Ox}_{G}} \frac{K_{\text{HOCl}}K_{\text{Cl}_{2}}H_{\text{Cl}_{2}}}{K_{\text{al}}[\text{Cl}^{-}]} \frac{[\text{HC}_{2}\text{O}_{4}^{-}]}{[\text{H}^{+}]} C(\text{Cl}_{2}).$ (14)

In light of Eqs. (4), (6), (8), (13), and (14), the concentration of chlorine in the gas phase at the outlet of the reactor is determined by the equations

$$C(Cl_{2}) = \frac{k_{O_{3}+Cl^{-}}[Cl^{-}]L_{O_{3}}C^{\circ}(O_{3})}{\frac{V}{V_{L}} + k_{O_{X}}E} \frac{K_{Cl_{2}}H_{Cl_{2}}[HC_{2}O_{4}^{-}]}{[Cl^{-}]},$$

$$C(Cl_{2}) = \frac{k_{O_{3}+Cl^{-}}[Cl^{-}]L_{O_{3}}C^{\circ}(O_{3})}{\frac{V}{V_{L}} + k_{O_{X}}G} \frac{K_{HOCl}K_{Cl_{2}}H_{Cl_{2}}}{K_{al}[Cl^{-}]}[HC_{2}O_{4}^{-}]}.$$

Rate $r(Cl_2)$ of the evolution of chlorine from the reactor is associated with concentration $C(Cl_2)$ by the formula

$$r(\mathrm{Cl}_2) = \frac{V}{V_L}C(\mathrm{Cl}_2),$$

where v is the volumetric flow rate of the gas mixture and V_L is the volume of the reaction solution. The theoretical expressions of the rate of chlorine evolution in our model, in which the chemical reactions between chloride ions and ozone and oxalic acid with chlorine take place, are thus

$$r(\text{Cl}_{2}) = \frac{k_{\text{O}_{3}+\text{Cl}^{-}}[\text{Cl}^{-}]L_{\text{O}_{3}}C^{\circ}(\text{O}_{3})}{1 + k_{\text{O}_{X}_\text{E}}}\frac{K_{\text{Cl}_{2}}H_{\text{Cl}_{2}}[\text{HC}_{2}\text{O}_{4}^{-}]V_{L}}{[\text{Cl}^{-}][\text{H}^{+}]}$$
(15)

or

$$r(\text{Cl}_{2}) = \frac{k_{\text{O}_{3}+\text{Cl}^{-}}[\text{Cl}^{-}]L_{\text{O}_{3}}C^{\circ}(\text{O}_{3})}{1 + k_{\text{O}_{x}_{G}}\frac{K_{\text{HOCl}}K_{\text{Cl}_{2}}H_{\text{Cl}_{2}}}{K_{\text{al}}[\text{Cl}^{-}]}\frac{[\text{HC}_{2}\text{O}_{4}^{-}]V_{L}}{[\text{H}^{+}]}}.$$
 (16)

These formulas can be rewritten as one:

$$r(\text{Cl}_{2}) = \frac{k_{\text{O}_{3}+\text{Cl}^{-}}[\text{Cl}^{-}]L_{\text{O}_{3}}C^{\circ}(\text{O}_{3})}{1 + \kappa \frac{[\text{HC}_{2}\text{O}_{4}^{-}]}{[\text{Cl}^{-}][\text{H}^{+}]}\frac{V_{L}}{v}},$$
(17)

where

$$\kappa = k_{\mathrm{Ox}_{\mathrm{E}}} K_{\mathrm{Cl}_{2}} H_{\mathrm{Cl}_{2}} \tag{18}$$

for reaction (11) or

$$\kappa = k_{\text{Ox}_E} K_{\text{HOCl}} K_{\text{Cl}_2} H_{\text{Cl}_2} / K_{\text{al}}$$
(19)

for reaction (12). Coefficient κ is an unknown parameter of expression (17), since rate constants $k_{\text{Ox}_{\text{E}}}$ and $k_{\text{Ox}_{\text{G}}}$ of reactions (11) and (12) are unknown.

The value of the κ parameter was determined from the condition of the minimum discrepancy between the $r(Cl_2)$ values obtained in the experiment (Figs. 1 and 2) and calculated with formula (17):

$$\kappa = 0.0342 \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

at 21°C.

Constants $k_{Ox_E} = 30.2 \text{ L mol}^{-1} \text{ s}^{-1}$ or $k_{Ox_G} = 1.17 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ correspond to this value. They are obtained using formulas (18) and (19), allowing for equilibrium constants H_{Cl_2} , K_{Cl_2} , K_{HOCl} , and K_{a1} given in Eq. (10).

It should be noted that the experimental data obtained in this work did not allow us to determine which of the reactions, (11) or (12), actually occurs during the chemical interaction between oxalic acid and active chlorine in an aqueous solution. However, it is well known (see [16]) that rate constants of around $10^7 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ are typical only of reactions between $H_2C_2O_4/HC_2O_4^{-}/C_2O_4^{2-}$ and active free radicals (e.g., hydroxyl radical OH⁻), and the rate constants of reactions between different forms of oxalic acid and less active reagents are much smaller. A relatively high rate constant of reaction (12) ($k_{Ox G} = 1.17 \times 10^8 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$)

is therefore extremely improbable. We may therefore conclude that the reaction between oxalic acid and active chlorine is the chemical interaction between hydroxalate ions hypochlorous acid molecules according to scheme (11), with a rate constant of $k_{\text{Ox}_{\text{E}}} = 30.2 \text{ L mol}^{-1} \text{ s}^{-1} (21^{\circ}\text{C}).$

Let us determine the error of the obtained k_{OX_E} value. The relative error of the experimental values of rate $r(Cl_2)$ of chlorine evolution is less than 5%. This means a relative error of coefficient κ equal to 9%. If we assume that equilibrium constants H_{Cl_2} and K_{Cl_2} given in Eq. (10) are known with an accuracy of $\pm 5\%$, the estimate of the relative error for $k_{OX_E} = 30.2 \text{ L mol}^{-1} \text{ s}^{-1}$ is 20%:

$$k_{\text{Ox} \text{E}} = 30 \pm 6 \text{ mol } \text{L}^{-1} \text{ s}^{-1}.$$

The reaction between oxalic acid and active chlorine was studied earlier only in [17] (1932). The authors of [17] came to the conclusion that reaction (11) takes place in the range of $10-20^{\circ}$ C with the rate constant equal to $k = 3.659 \times 10^{12} \exp(-7787/T)$ at 21° C, i.e., $k = 12 \text{ L mol}^{-1} \text{ s}^{-1}$. The correctness of the rate constant values found in [17] is doubtful, since the values of equilibrium constants K_{HOCl} , K_{Cl_2} , and $K_{\text{Cl}^{3-}}$, which differ substantially from the current data, were used to calculate it. Our value of the rate constant of reaction (11) would seem to be more reliable and accurate.

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