

Acid Catalysis in Reaction of Ozone with Chloride Ions¹

A. V. Levanov, I. V. Kuskov, A. V. Zosimov, E. E. Antipenko, and V. V. Lunin

Department of Chemistry, Moscow State University, Moscow, 119899 Russia

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Abstract—The kinetics of the interaction of ozone with aqueous solutions of chlorides resulting in Cl_2 evolution to the gas phase was studied. The reaction of O_3 with Cl^- is accelerated by H^+ ions. The effects of the concentrations of H^+ and Cl^- , the ionic strength, and temperature (ranged from 7 to 60°C) on the reaction rate were studied. A mechanism explaining the experimental kinetics was proposed. The acid catalysis is due to the formation of the HO_3Cl complex, which is in equilibrium with H^+ , O_3 , and Cl^- . The constants of reactions involved in the proposed mechanism were determined.

INTRODUCTION

Studies of the interaction between ozone and chloride ions in aqueous solutions are of current interest in the light of the problem of changes in the concentration of atmospheric ozone, as well as of the processes of water preparation and purification. The reaction $\text{O}_3 + \text{Cl}^-$ is believed to be slow, and only rough estimates of its rate constant at room temperature are known [1]. However, our experimental findings showed that under certain conditions the rate of this reaction can be considerably increased. The aim of this work is to study the effect of various experimental parameters (concentrations of H^+ and Cl^- , the ionic strength, and temperature) on the reaction between ozone and chlorine ions in aqueous solutions and its kinetic features.

EXPERIMENTAL

Experiments were carried out using a setup whose schematic is shown in Fig. 1. The reaction between ozone and chlorine ions was performed in a temperature-controlled bubble-column reactor (2). The main part of the reactor represented a glass cylinder (inner diameter, 2.5 or 3 cm) with a sintered glass filter sealed into its bottom for feeding the initial gas mixture. Before the experiment, a solution under study was placed in the reactor; the height of the liquid was 25–30 cm. The exact volume of the solution in the reactor was calculated from the previously measured density of solution and the weight in the reactor.

In most runs, solutions under study contained NaCl and 0.01–1 M HCl, and $[\text{NaCl}] + [\text{HCl}] = 1$ M. In some experiments, NaClO_4 was added to vary the ionic strength of solutions. An additional series of runs was carried out with solutions containing 0.25 M HCl and 0–8 M H_2SO_4 . Distilled water, standard solution of hydrochloric acid (1 M), chemically pure sodium chlo-

ride, sodium perchlorate monohydrate of analytical purity grade (Merck), and concentrated sulfuric acid of chemical purity grade were used in the preparation of solutions.

Ozone was prepared by passing special purity oxygen through a barrier discharge in an ozonizer 1. The ozone concentration at the reactor inlet was measured with a Medozon-254/5 photometer and normally was 10.0 g/m³. The flow rate of the initial gas mixture was 21 l/h in all experiments.

In the course of a run, we determined the concentration of Cl_2 in the gas mixture at the reactor outlet and the ozone concentration in the reaction solution; in some cases we measured the pH of the reaction solution.

The composition of the gas mixture evolved was analyzed on a Balzers PGM 407 mass spectrometer. Along with the components of the initial mixture, molecular Cl_2 was found in the outgoing gas. Other gaseous reaction products were not found.

The concentration of Cl_2 in the evolved gas mixture was estimated by photometric iodometry. The gas mixture passed through an oven (3) to decompose O_3 and then through a trap (4) with a solution of KI to absorb Cl_2 and to form the equivalent amount of I_2 , whose concentration was measured using a KFK-3 photometer. The amount of chlorine n_{Cl_2} entering the trap was calculated as a function of time t from the known iodine concentration and solution volume. The rate of the

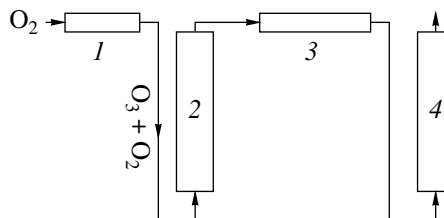


Fig. 1. Schematic of the experimental setup: (1) ozonizer, (2) bubble-column reactor, (3) oven for ozone decomposition, (4) trap with a KI solution.

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chlorine inflow in the trap dn_{Cl_2}/dt was estimated from a tangent slope of the linear portion of the plot n_{Cl_2} vs. t . The procedure for estimating Cl_2 in the ozone-containing gas mixture was reported in detail in our previous paper [2].

Estimation of the Concentration of Dissolved Ozone

To selectively determine the concentration of dissolved ozone in the presence of chlorine, we developed a method based on the use of an alkaline solution of a Cr(III) salt. In alkaline solutions ozone rapidly and completely oxidizes Cr(III), which mainly exists in the form of hydroxochromite $[\text{Cr}(\text{OH})_6]^{3-}$ [3], to chromate CrO_4^{2-} . This reaction was proposed for the determination of ozone in air [4]. We found that under these conditions chlorine reacts slowly, and under certain conditions one can neglect the formation of chromate via the reaction of $[\text{Cr}(\text{OH})_6]^{3-}$ with ClO^- . Chromate CrO_4^{2-} has a well-resolved absorption band with a maximum at 373 nm (the molar absorbance is $4610 \text{ l mol}^{-1} \text{ cm}^{-1}$) [5]. Therefore, the chromate concentration and hence the ozone concentration can be measured by the absorbance at 373 nm using an alkaline Cr(III) solution without ozone as a reference solution. To determine the ozone concentration in the reaction solution, we used the following procedure. A portion of the solution from the reactor was mixed with an equal volume of an alkaline Cr(III) solution containing $0.005 \text{ M KCr}(\text{SO}_4)_2 + ([\text{HCl}] = 0.5 \text{ M}) \text{ NaOH}$, where $[\text{HCl}]$ is the HCl molar concentration in the initial solution. Immediately after mixing, the absorbance at 373 nm of the solution formed was measured on a KFK-3 photometer. An alkaline Cr(III) solution of the same composition diluted with an equal volume of distilled water was used as a reference solution. The ozone concentration was determined from a calibration plot.

The concentrations of dissolved ozone found with the above method are shown in Table 1 and Figs. 2 and 3. We found that under experimental conditions, the concentration of dissolved ozone is determined by the ionic strength only and is independent of the nature of the supporting electrolyte (HCl, NaCl, or NaClO_4) (Fig. 2).

Under our experimental conditions (a flow reactor and a constant ozone concentration in the initial gas mixture), dissolved ozone is present in a steady-state concentration determined by the equality of the rates of its dissolution and decay:

$$[\text{O}_3] = \frac{H}{1 + k_{\text{O}_3}/\kappa} C_{\text{O}_3}, \quad (1)$$

where H is Henry's constant (the ratio between the equilibrium ozone concentrations in the solution and gas phase), k_{O_3} is the apparent rate constant of decay

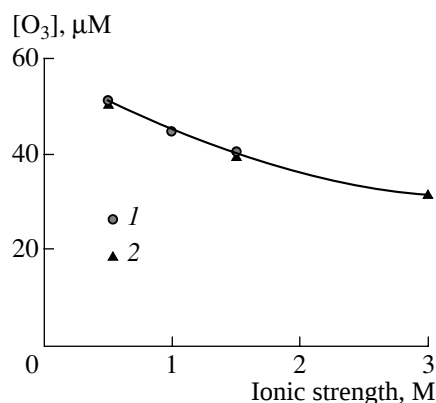


Fig. 2. Concentration of dissolved ozone vs. ionic strength at room temperature (24°C). $C_{\text{O}_3} = 10 \text{ g/m}^3$. The composition of solution: (1) $0.5 \text{ M HCl} + \text{NaCl}$; (2) $0.5 \text{ M HCl} + \text{NaClO}_4$.

(ozone decay in solution is a first-order reaction), κ is the rate coefficient of ozone dissolution, and C_{O_3} is the ozone concentration in the initial gas mixture. At room temperature, the following estimates are made: $\kappa \sim 500 \text{ min}^{-1}$ [6] and $k_{\text{O}_3} < 10 \text{ min}^{-1}$, and, therefore, Henry's law $[\text{O}_3] = HC_{\text{O}_3}$ is practically fulfilled.

The plot $\ln[\text{O}_3]$ vs. $1/T$ is linear at temperatures $7\text{--}41.5^\circ\text{C}$ (see Fig. 3), since the concentration of dissolved ozone is determined by Henry's law due to a relatively low value of k_{O_3} . The concentration of dissolved ozone at 60°C deviates from the linear plot in the $\ln[\text{O}_3] - 1/T$ coordinates because of a significant increase in the k_{O_3} value.

Table 1. Concentrations of dissolved ozone vs. the $[\text{HCl}]/[\text{NaCl}]$ ratio and temperature

[HCl], M	[O ₃], μM			
	7°C	24°C	41.5°C	60°C
0.01	—	—	27.3	11.5
0.1	73.1	42.3	—	11.9
0.3	—	44.9	—	11.1
0.4	74.5	—	27.1	—
0.5	—	44.5	—	—
0.7	71.8	45.6	—	—
1	73.7	44.9	—	—
Average value [O ₃]	73	44	27	11.5

Note: In the initial solution $[\text{HCl}] + [\text{NaCl}] = 1 \text{ M}$ and $C_{\text{O}_3} = 10 \text{ g/m}^3$.

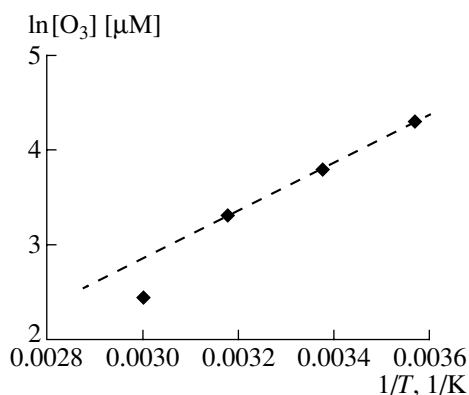


Fig. 3. The natural logarithm of the average concentration of the dissolved ozone vs. inverse temperature. $C_{O_3} = 10 \text{ g/m}^3$. The composition of solution: $[HCl] + [NaCl] = 1 \text{ M}$.

We found the heat of ozone dissolution to be 21 kJ/mol from the linear portion of the plot (Fig. 3), and this value is in good agreement with previously published data (17–24 kJ/mol) [7–9].

Measurement of Apparent Rate Constant of the Reaction $O_3 + Cl^-$

A flow-type bubbling reactor was used in our experiments. In this case, the following differential equation is applicable:

$$\frac{dS_{Cl}}{dt} = k_{app}[Cl^-][O_3] - (k_I + k_{II})[ClO^-][O_3] - \frac{v}{V_l}C_{Cl_2}, \quad (2)$$

where k_{app} is the apparent rate constant of the reaction $O_3 + Cl^- \rightarrow ClO^- + O_2$, k_I and k_{II} are the rate constants of the reactions $ClO^- + O_3 \rightarrow Cl^- + 2O_2$ and $ClO^- + 2O_3 \rightarrow ClO_3^- + 2O_2$, respectively (values of k_I and k_{II} are given in the work [10]), $[X]$ is the concentration of substance X in a solution, C_{Cl_2} is the concentration of Cl_2 in the gas phase (at the reactor outlet), $S_{Cl} = [ClO^-] + [HOCl] + [Cl_2] + [Cl_3^-] + C_{Cl_2} V_g/V_l$ is the amount of the active chlorine in the reactor divided by the volume of the liquid, v is the gas mixture flow rate (in all experiments $v = 21 \text{ l/h}$ (standard conditions)), V_l is the volume of the liquid in the reactor, and V_g is the volume of the gas phase. At $pH < 3$, when almost all the active chlorine is either molecular chlorine (Cl_2) or Cl_3^- ions in solution, the differential equation takes the form

$$\frac{dS_{Cl}}{dt} = k_{app}[Cl^-][O_3] - \frac{v}{V_l}C_{Cl_2}, \quad (3)$$

where $S_{Cl} = [Cl_2] + [Cl_3^-] + C_{Cl_2} V_g/V_l$.

The experimental and simulation results showed that a nearly steady-state regime is quickly reached when the concentrations of reactants in the reaction solution, and the chlorine concentration in the outgoing gas mixture remain almost constant. In the course of runs (duration was at most 1.5 h), the reaction solution was nearly of the same composition as the initial solution with the exception that ozone and chlorine appeared. This result is due to the relatively slow removal of chlorine from the reactor. Our flow system did not operate in a strictly steady-state regime because at least one of the reactants, chlorine ion, was not fed during the run but was present within the reaction system in a limited amount. In the case of a nearly steady-state regime, the differential equation takes the following form:

$$k_{app}[Cl^-][O_3] = \frac{v}{V_l}C_{Cl_2}. \quad (4)$$

We used this expression for the calculation of the constant k_{app} . The concentration of chlorine ions and the volume of solution placed in the reactor are set by experimentalist. The concentrations of ozone in the solution and chlorine in the outgoing gas were measured with the above procedures. The rate of chlorine evolution from the reactor, vC_{Cl_2} , is equal to the experimentally measured rate of the chlorine inflow to the trap: $vC_{Cl_2} = \frac{dn_{Cl_2}}{dt}$. Hence, the final expression for the calculation of k_{app} takes the form:

$$k_{app} = \frac{dn_{Cl_2}}{dt} \frac{1}{[O_3][Cl^-]V_l}. \quad (5)$$

Reaction Orders in Ozone and the Chloride Ion

The expression for the calculation of k_{app} was found assuming that the reaction has the first orders in ozone and chlorine ion. To determine the reaction order, we measured the rate of chlorine evolution from the reactor based on the unit liquid volume in the reactor and determined its dependence on the concentration of ozone in the initial gas mixture or on the concentration of chlorine ions in the reaction solution (Fig. 4).

The relative rate of chlorine evolution is proportional to the ozone concentration in the initial gas mixture (see Fig. 4a) and, therefore, to the ozone concentration in solution because, in our experiments at room temperature, the ozone concentration in solution obeys Henry's law.

The relative rate of chlorine evolution is also proportional to the concentration of chlorine ion in the reaction solution (Fig. 4b). In experiments of this series, we maintained a constant ionic strength and varied the ratio of the concentrations of chlorine and perchlorate ions. The ozone concentration in the initial gas

mixture was constant. Since the constant-temperature solubility of ozone in solutions used in our experiments is only determined by the ionic strength (see above), then in all the experiments of this series the ozone concentration in the reaction solutions was also constant. Therefore, the experimental reaction orders with respect to ozone and chlorine ions are unity.

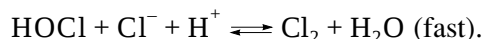
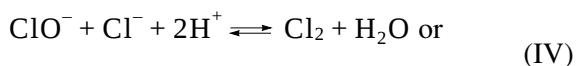
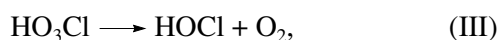
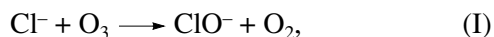
As shown below, the reaction under study is complex. Hence, the term *reaction order* is barely applicable to it. Nevertheless, the relative rate of chlorine evolution is in fact nearly proportional to the concentration of chlorine ions in the reaction solution.

DISCUSSION

The apparent rate constant for the reaction $\text{O}_3 + \text{Cl}^-$ increases with increasing $[\text{H}^+]$ (Fig. 5). In highly acidic media the rate of the reaction $\text{O}_3 + \text{Cl}^-$ considerably increases (Fig. 6). Hence, the H^+ ions are the catalyst of the reaction.

The apparent rate constant increases with an increase in the solution ionic strength (Fig. 7) except for the case when the ionic strength is created by NaCl. An increase in the chloride concentration results in some decrease in k_{app} (Fig. 7). A nonzero value of k_{app} at $[\text{H}^+] = 0$ (see Fig. 5) corresponds to a noncatalytic reaction route.

These features can be rationalized assuming the following mechanism of the reaction between ozone and chlorine ion in an aqueous solution:



The hydration of the species is not shown here for simplicity. According to the proposed mechanism, the reaction occurs via two parallel pathways. One of them, noncatalyzed reaction (I) includes the formation of hypochlorite ion in the reaction of chlorine ion with ozone.

The catalyzed reaction pathway includes the formation of the intermediate HO_3Cl from H^+ , O_3 , and Cl^- in a fast equilibrium step (II) followed by HO_3Cl decomposition to HOCl in step (III). Protonation of ClO^- and HOCl in acidic media due to the fast equilibration steps (IV) produces Cl_2 . The expression for the apparent rate constant under quasi-equilibrium approximation for HO_3Cl takes the form

$$k_{\text{app}} = \frac{k_1 + k_3 K_2 [\text{H}^+]}{1 + K_2 [\text{H}^+][\text{Cl}^-]}, \quad (6)$$

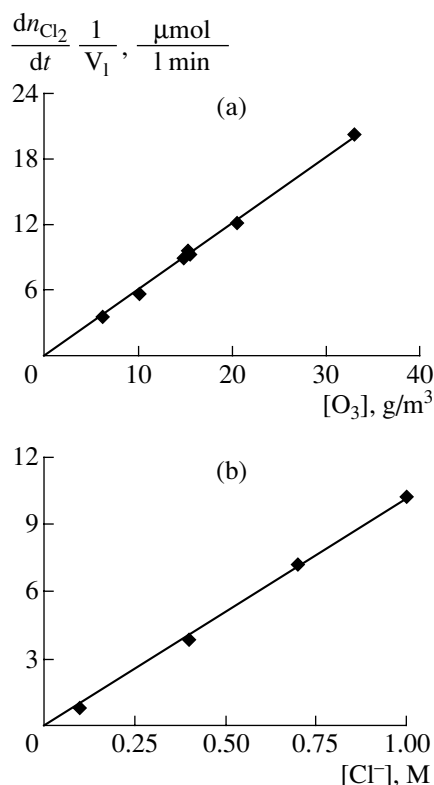


Fig. 4. The rate of Cl_2 evolution at room temperature (24°C) divided by the volume of the liquid in the reactor vs. (a) the ozone concentration in the initial gas mixture (composition of solution: 0.01 M HCl + 0.9 M NaCl) and (b) the concentration of chlorine ion in solution at $C_{\text{O}_3} = 10 \text{ g/m}^3$ (composition of solution: 0.1 M HCl, $[\text{NaCl}] + [\text{NaClO}_4] = 0.9 \text{ M}$).

where k_1 and k_3 are the rate constants of steps (I) and (III), respectively, and K_2 is the equilibrium constant of step (II). The quasi-equilibrium approximation for HO_3Cl implies that the concentration of dissolved ozone in our experiments is the sum of the concentrations of the O_3 and HO_3Cl species in solution. According to Eq. (6), the constant k_{app} is an increasing function of $[\text{H}^+]$ and K_2 for the nonnegative $[\text{H}^+]$ and $[\text{Cl}^-]$ values and positive k_1 , K_2 , and k_3 values (an additional condition should be $[\text{Cl}^-] < k_3/k_1$) and is a decreasing function of $[\text{Cl}^-]$. Thus, expression (6) explains catalysis by hydrogen ions and retardation by chlorine ions. The effect of the ionic strength is due to an increase in the concentration equilibrium constant K_2 with an increase in the ionic strength, while the rate constants k_1 and k_3 are independent of the ionic strength.

The effect of H^+ on the rate of ozone reactions in acidic media can be due to the formation of protonated ozone HO_3^+ , which is more reactive than normal ozone [11–15]. In our case, the assumption of the formation of HO_3^+ can explain catalysis by the H^+ ion but cannot explain the retardation by chlorine ions. Meanwhile,

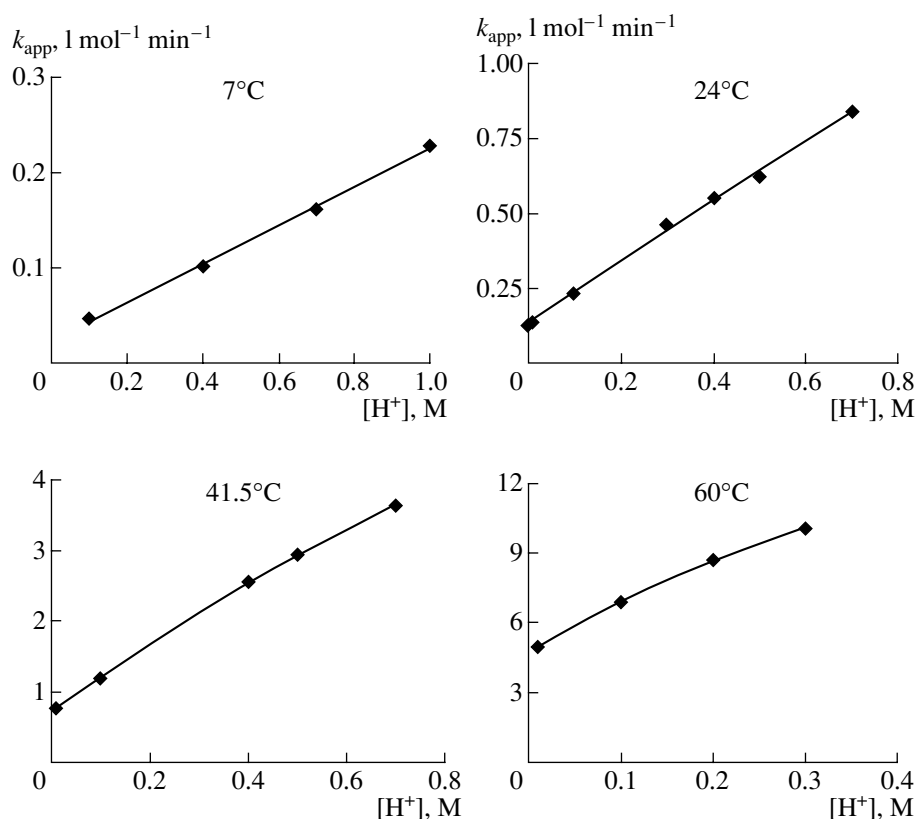


Fig. 5. The apparent rate constant of the reaction $\text{O}_3 + \text{Cl}^-$ vs. $[\text{H}^+]$ at various temperatures. The composition of solution: $[\text{HCl}] + [\text{NaCl}] = 1 \text{ M}$.

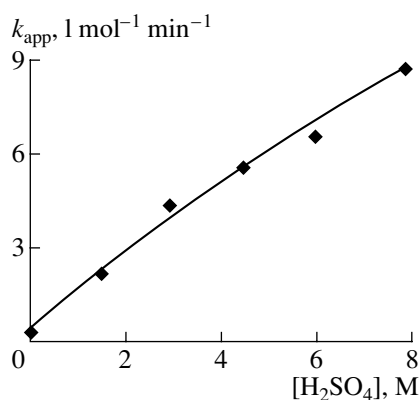


Fig. 6. The apparent rate constant of the reaction $\text{O}_3 + \text{Cl}^-$ vs. concentration of sulfuric acid in solution at room temperature (24°C). The composition of solution: 0.25 M HCl + H_2SO_4 . The concentration of dissolved ozone was evaluated on the basis of data presented in [11].

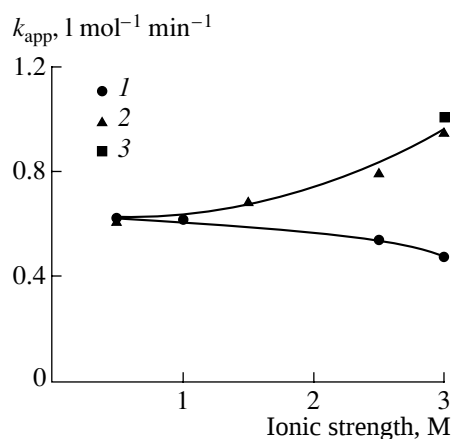


Fig. 7. The apparent rate constant of the reaction $\text{O}_3 + \text{Cl}^-$ vs. ionic strength at room temperature (24°C). The composition of solution: 0.5 M HCl , and either: (1) NaCl , (2) NaClO_4 , or (3) KNO_3 .

the assumption for the formation of HO_3Cl gives a reasonable explanation for all the experimental features of the kinetics of the reaction between O_3 and Cl^- in aqueous solutions. The intermediate HO_3Cl can be treated as a complex of protonated ozone with chlorine ion.

Based on experimental plots k_{app} vs. $[\text{H}^+]$ (Fig. 5) for solutions with the ionic strength of 1 M, we found the numerical values of the constants k_1 , K_2 , and k_3 and the characteristics of their temperature dependences (Table 2).

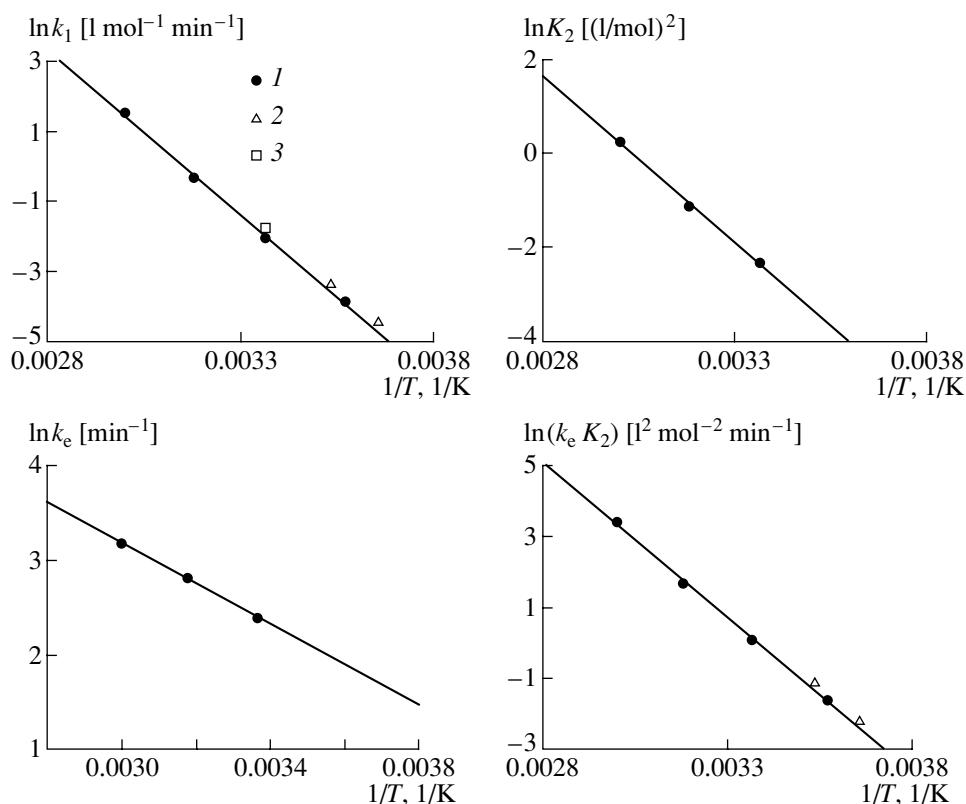


Fig. 8. The natural logarithm of the constants k_1 , K_2 , k_3 , and k_3K_2 vs. inverse temperature: (1) our data (ionic strength 1 M); (2) data of [16] (ionic strength, 0.3 M); 3, the upper limit of k_1 estimated in [1] (ionic strength, 1–4 M).

The experimental plot k_{app} vs. $[H^+]$ (Fig. 5) is linear at 7°C and, therefore, it is possible to estimate the product of constants $k_3K_2 = 0.21 \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}$ and the upper limit of K_2 (or the lower limit of k_3). The temperature dependences of the constants k_1 , K_2 , k_3 , and k_3K_2 are presented in Fig. 8.

The activation energy or the enthalpy of reaction steps are as follows:

Step (I)	Step (II)	Step (III)
79	55	18

Our experimental findings are in agreement with published data. For instance, data on the catalysis of the reaction of ozone with chlorine ion by H^+ ion were presented in [16], according to which the apparent rate constant linearly depends on $[H^+]$ and is independent of $[Cl^-]$. The authors of [16] only partly characterized the effect of $[H^+]$ on k_{app} because they only performed experiments at low temperatures and in a narrow range of H^+ concentrations: 0°C, $[H^+] = 0.01\text{--}0.2 \text{ M}$; 9.5°C, $[H^+] = 0.02\text{--}0.1 \text{ M}$. The parameters of the linear plot k_{app} vs. $[H^+]$ found in [16] (k_1 and k_3K_2 values in terms of the mechanism proposed by us) are in good agreement with our data.

In the work [1], the upper limit of the rate constant of the noncatalyzed pathway (k_1 in terms of the

proposed mechanism) at room temperature was found, which is also in good agreement with our data (Fig. 8).

The value $k_1 = 0.12 \text{ l mol}^{-1} \text{ min}^{-1}$ (room temperature, ionic strength 1 M) found in [17] practically coincides with the value presented in this work (see Table 2).

Thus, the findings of our work give the most accurate description of the kinetics and mechanism of interaction between ozone and chlorine ion in aqueous solutions and more adequately characterize the contribution of this interaction in the processes of atmospheric chemistry.

Table 2. Parameters of the reaction steps

$T, ^\circ\text{C}$	$k_1,$ $\text{l mol}^{-1} \text{ min}^{-1}$	$k_2,$ $(\text{l/mol})^2$	$k_3,$ min^{-1}
7	0.021	<0.05	>4
24	0.13	0.10	11
41.5	0.71	0.32	17
60	4.7	1.3	24

Note: Ionic strength, 1 M. The composition of the solution: $[HCl] + [NaCl] = 1 \text{ M}$.

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