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Catalysis of the Reaction of Ozone with Chloride Ions by Metal Ions in an Acidic Medium

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Abstract—It was found that VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions catalyze the reaction of O_3 with Cl^- in an acidic medium. The dependence of the rate of Cl_2 liberation in the reaction of O_3 with Cl^- on the concentrations of H^+, VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions in the reaction solution was studied. A reaction scheme was proposed to explain the experimentally found catalytic effects of these ions. The constants that characterize the steps of the proposed scheme were determined.

INTRODUCTION

The catalytic effects of various metal ions in the reaction of ozone with the chloride ion are of interest from the standpoint of atmospheric chemistry. Marine aerosol, which contains various transition metal salts along with main components, is the main source of atmospheric chloride ions. A great amount of chlorine leaves the aerosol; however, the mechanism of this process has not been conclusively established [1]. On the other hand, the concentration of molecular chlorine in the marine boundary layer cannot be explained by currently known chemical reactions [2]. It is likely that these phenomena are due to the rapid reaction of ozone with the chloride ion, catalyzed by various metal ions and hydrogen ions.

The aim of this work was to study the catalytic effects of various metal ions in the reaction of ozone with the chloride ion in acidic solutions and to examine the effect of catalyst concentration on the kinetics of this reaction.

Determination of the conditions under which the reaction of O_3 with Cl^- is accelerated will furnish insights into general methods for increasing the reactivity of ozone toward inert substrates.

EXPERIMENTAL

The reaction between ozone and acidic solutions containing chloride ions was performed in a bubbling reactor at room temperature (20°C). The experimental setup was described previously in [3]. The experimental procedure was analogous to that described elsewhere [3]. In all the experiments, the flow rate of ozonized oxygen was 21 l/h and the concentration of ozone at the reactor inlet was equal to 10.0 g/m^3. Before the experiment, ~170 ml of a test solution was placed in the reactor; the true volume of the solution was determined by preliminary density measurement and weighing. The test solutions contained 0.01–0.8 M HCl and NaCl ([HCl] + [NaCl] = 1 mol/l) and various metal salts whose concentration was no higher than 0.1 mol/l. To prepare the solutions, we used the following: distilled water; hydrochloric acid standard titrimetric substance (1 mol/l); chemically pure sodium chloride; potash alum and iron(II) sulfate heptahydrate of analytical grade; chromic potassium alum, potassium dichromate, iron(III) chloride hexahydrate, cobalt(II) sulfate heptahydrate, nickel nitrate hexahydrate, copper sulfate pentahydrate, zinc chloride, and tin(II) chloride dihydrate of reagent grade; and vanadyl sulfate trihydrate and cerium nitrate hexahydrate, which were prepared from available reagents and recrystallized.

In our experiments, we determined the ratio of the rate of Cl_2 release from the reactor to the volume of the test solution, $\frac{1}{V}\frac{dn_{Cl_2}}{dt}$ (henceforth, the rate of chlorine release), as a function of the concentrations of various metal ions and hydrogen ions in the reaction solution. The rate of chlorine release was related to the apparent rate constant of the $O_3 + Cl^-$ reaction (k_{app}) by the equation $\frac{1}{V}\frac{dn_{Cl_2}}{dt} = k_{app}[Cl^-][O_3]$. The current concentration of the chloride ion in the reaction solution was virtually equal to the initial concentration (1 mol/l) because the amount of chlorine released from the reactor during the experiment time was negligibly small, compared to the initial amount of chloride ions. We did not determine the concentration of ozone in the reaction solution because almost all of the metal compounds used in our experiments exhibited considerable absorption in the region of the spectrum used for the determination of dissolved ozone in accordance with a previously proposed procedure [3]. Taking into account that metal ions were present in low concentrations in solution and are relatively inert with respect to ozone (except for reducing metals), the concentration of dissolved ozone in solution can be estimated based on previous data [3].

According to these data, the concentration of ozone is equal to 49 μmol/l in an aqueous solution containing HCl and NaCl ([HCl] + [NaCl] = 1 mol/l) at 20°C and a 10.0 g/m^3 concentration of ozone in the initial gas mixture. This estimate of the concentration of dissolved oxygen is true only when there are no substances in the solution that rapidly react with ozone.

RESULTS AND DISCUSSION

In experiments on the effect of the nature of metal ions on the rate of the reaction of O_3 with Cl^-, the test solution contained 0.4 M HCl, 0.6 M NaCl, and a metal salt. In the absence of metal salts, the rate of chlorine release was equal to 17–18 μmol l^{-1} min^{-1}. The presence of $KAl(SO_4)_2$, $KCr(SO_4)_2$, $Ni(NO_3)_2$, $CuSO_4$, $ZnCl_2$, and $Ce(NO_3)_3$ in a concentration of 0.01 mol/l or $K_2Cr_2O_7$ in a concentration of 0.005 mol/l did not result in a change in the rate of chlorine release. Upon the addition of $VOSO_4$, $FeCl_3$, or $CoSO_4$ in a concentration of 0.01 mol/l to the test solution, the rate of chlorine release increased to 22, 23, or 115–120 μmol l^{-1} min^{-1}, respectively. At a concentration of H^+ in the reaction solution higher than 0.4 mol/l, the addition of 0.01 M $CuSO_4$ also resulted in an increase in the rate of chlorine release. In the presence of $SnCl_2$ or $FeSO_4$ in a concentration of 0.01 mol/l in the reaction solution, the oxidation of Sn^{2+} ions to Sn^{4+} (or Fe^{2+} to Fe^{3+}) with ozone occurred initially; in this case, chlorine was not liberated. After oxidation was complete, the reaction of ozone with the chloride ion began and chlorine was released. The presence of tin ions in the solution did not increase the rate of chlorine release. In the presence of iron ions, the rate of chlorine release increased to 20 μmol l^{-1} min^{-1}. In the case of the addition of a salt to a Fe^{2+} salt solution, the rate of chlorine release was somewhat lower than that with the addition of Fe^{3+}; this was likely due to the fact that only a portion of Fe^{2+} was converted into a catalytically active species. Thus, VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions catalyze the reaction of O_3 with Cl^- in an acidic medium, whereas Al^{3+}, Cr^{3+}, $Cr_2O_7^{2-}$, Ni^{2+}, Zn^{2+}, Sn^{4+}, and Ce^{3+} ions do not have a catalytic effect. Note that the catalytic effects of the above ions can be affected under changes in the acidity of the test solution.

We studied the effect of the concentration of catalysts (VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+}), as well as hydrogen ions in the presence of each of the above ions, on the rate of chlorine release in the reaction of O_3 with Cl^- in an acidic medium. Figures 1–6 illustrate the experimental results.

The catalytic effect of metal ions in the reaction of ozone with chloride ions in an acidic medium can be explained as described below: First, in oxidation with ozone, metal ions in a higher oxidation state can be formed; these are capable of oxidizing the chloride ion (charge-transfer catalysis). Second, a catalytic complex that decomposes with the liberation of chlorine (coordination catalysis) can be formed.

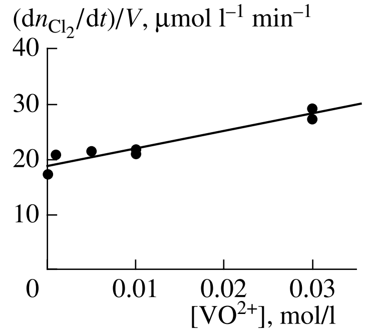

Fig. 1. Dependence of the rate of chlorine release on the concentration of VO^{2+} in the reaction solution. Solution composition: 0.4 M HCl + 0.6 M NaCl + $VOSO_4$. Points and lines correspond to experimental data and model calculations, respectively.

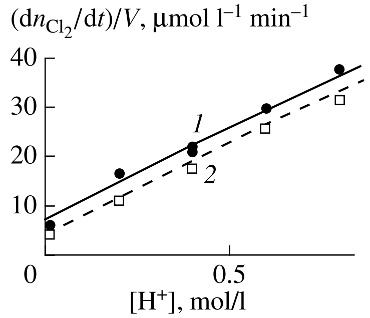

Fig. 2. Dependence of the rate of chlorine release on the concentration of H^+ in the reaction solution. Solution composition: [HCl] + [NaCl] = 1 mol/l. (*1*) 0.01 M $VOSO_4$ was present in solution; (*2*) blank experiment ($VOSO_4$ was absent). Points and lines correspond to experimental data and model calculations, respectively.

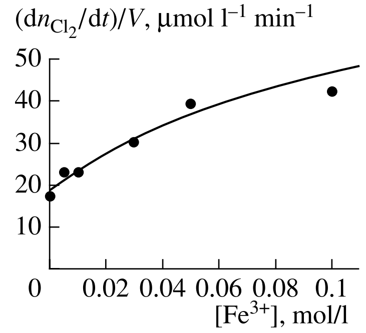

Fig. 3. Dependence of the rate of chlorine release on the concentration of Fe^{3+} in the reaction solution. Solution composition: 0.4 M HCl + 0.6 M NaCl + $FeCl_3$. Points and lines correspond to experimental data and model calculations, respectively.

The interactions of VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} with

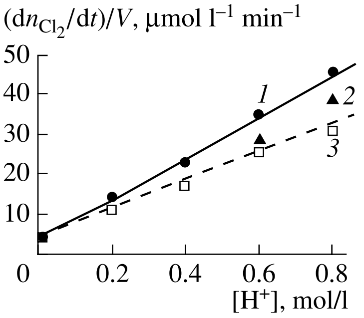

Fig. 4. Dependence of the rate of chlorine release on the concentration of H^+ in the reaction solution. Solution composition: [HCl] + [NaCl] = 1 mol/l. (*1*) 0.01 M $FeCl_3$ was present in solution; (*2*) 0.01 M $CuSO_4$ was present in solution; (*3*) blank experiment ($FeCl_3$ or $CuSO_4$ was absent). Points and lines correspond to experimental data and model calculations, respectively.

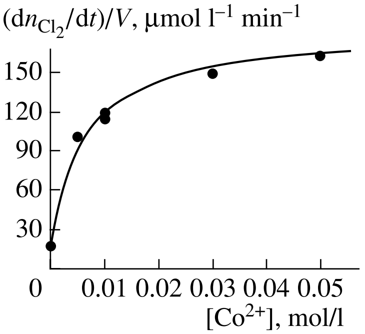

Fig. 5. Dependence of the rate of chlorine release on the concentration of Co^{2+} in the reaction solution. Solution composition: 0.4 M HCl + 0.6 M NaCl + $CoSO_4$. Points and lines correspond to experimental data and model calculations, respectively.

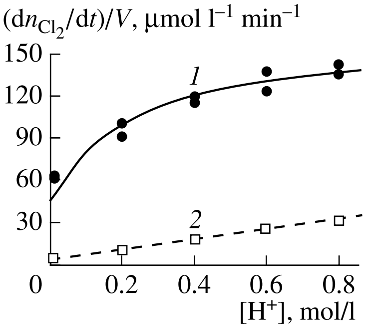

Fig. 6. Dependence of the rate of chlorine release on the concentration of H^+ in the reaction solution. Solution composition: [HCl] + [NaCl] = 1 mol/l. (*1*) 0.01 M $CoSO_4$ was present in solution; (*2*) blank experiment ($CoSO_4$ was absent). Points and lines correspond to experimental data and model calculations, respectively.

ozone and of VO^{2+} and Co^{3+} with the chloride ion were studied experimentally. The progress of the reaction was monitored by measuring the absorption spectra of reaction solutions in the UV and visible regions.

The spectroscopic data indicated that VO_2^+ was formed on passing ozonized oxygen through a 0.02 M $VOSO_4$ solution in 1 M H_2SO_4. The resulting solution of pentavalent vanadium did not react with HCl (concentration to 4 mol/l).

Based on a study of the spectra, we can conclude that trivalent cobalt compounds were formed on the treatment of 0.001–0.1 M $CoSO_4$ solutions in 0.1–6 M H_2SO_4 with ozonized oxygen. On mixing the resulting Co^{3+} solutions with HCl or NaCl solutions, a rapid reaction occurred, during which Co^{2+} and molecular chlorine were formed. After mixing, the reaction was complete in a few seconds.

The Fe^{3+} (0.005 M $Fe_2(SO_4)_3$ in 4.8 M H_2SO_4) and Cu^{2+} (0.01 M $CuSO_4$ in 4.8 M H_2SO_4) ions did not react with ozone. This is consistent with the published data [4].

Thus, only coordination catalysis can occur in the case of VO^{2+}, Fe^{3+}, and Cu^{2+} ions. Generally speaking, both charge-transfer and coordination catalysis can occur in the case of the Co^{2+} ion.

To explain the experimental dependence of the rate of chlorine release on the concentration of a catalyst (VO^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, or H^+ ions), we performed a simplified simulation of the kinetics of chlorine release.

To perform model calculations, we used the fact that steady-state conditions were established in the course of our experiments; that is, the rate of chlorine release and the composition of the reaction solution, particularly the concentration of dissolved ozone, did not depend on time. The steady-state conditions were due to the facts that the system was open, ozone was supplied at a constant rate, and the amount of chlorine released from the reactor was negligibly small, compared to the initial amount of chloride ions. Previously [3], we substantiated the occurrence of steady-state conditions in a similar case. We estimated the concentration of ozone in solution (49 μmol/l under conditions of our experiments) based on previously published data [3].

The following processes that lead to the release of chlorine into a gas phase were taken into consideration: First, the reaction of ozone with chloride ions catalyzed by H^+ ions (in the absence of transition metal ions). The kinetics of this reaction was studied in detail previously [3]. Second, coordination catalysis by metal ions. Third, charge-transfer catalysis (only for Co^{2+} ions).

Thus, the entire set of chemical processes leading to the release of Cl_2 in the reaction of ozone with chloride ions in an acidic medium in the presence of metal salts that exhibit a catalytic effect can be represented as the reaction scheme given below (the constants at 20°C are given):

$$Cl^- + O_3 \longrightarrow ClO^- + O_2, \qquad k_1 = 0.088\ \mathrm{l\ mol^{-1}\ min^{-1}}; \tag{I}$$

$$H^+ + O_3 + Cl^- \rightleftarrows HO_3Cl, \qquad K_2 = 0.079\ \mathrm{l^2/mol^2}; \tag{II}$$

$$HO_3Cl \longrightarrow HOCl + O_2, \qquad k_3 = 9.9\ \mathrm{min^{-1}}; \tag{III}$$

$$ClO^- + Cl^- + 2H^+ \rightleftarrows Cl_2 + H_2O \quad \text{or} \quad HOCl + Cl^- + H^+ \rightleftarrows Cl_2 + H_2O, \qquad \text{rapidly established equilibria}; \tag{IV}$$

$$M^{m+} + O_3 + nH^+ + xCl^- \rightleftarrows H_nMO_3Cl_x, \qquad \text{the equilibrium constant } K_5 \text{ is determined based on experimental data}; \tag{V}$$

$$H_nMO_3Cl_x \longrightarrow M^{m+} + O_2 + Cl_2 + H_2O + (n-2)H^+ + (x-2)Cl^-, \qquad \text{the rate constant } k_6 \text{ is determined based on experimental data}; \tag{VI}$$

$$Co^{2+} + O_3 \dashrightarrow Co^{3+} + O_2, \qquad w_7 = k_7[Co^{2+}][O_3], \ \text{the rate constant } k_7 \text{ is determined based on experimental data}; \tag{VII}$$

$$Co^{3+} + Cl^- \dashrightarrow Co^{2+} + Cl_2, \qquad \text{the specific rate is high.} \tag{VIII}$$

Notation: M^{m+} is a metal ion; $H_nMO_3Cl_x$ is a catalytic complex containing the metal ion, ozone, H^+ ions, and chloride ions, which can decompose with the formation of chlorine and the regeneration of the M^{m+} metal ion (for simplicity, the charge of the complex is not shown).

According to [3], the reaction of O_3 with Cl^- in an acidic medium in the absence of transition metal ions occurs via steps (I)–(III). The kinetic characteristics of these steps were taken from [3]. The formation of molecular chlorine and its release into a gas phase results from rapidly established equilibria (IV).

Coordination catalysis by metal ions occurs via steps (V) and (VI) of the formation and decay of a catalytic complex, respectively. We assumed that the catalytic complex of only a certain composition is formed and its decomposition occurs in a single step. A quasi-equilibrium approximation was used for the step of complex formation and was characterized by the equilibrium constant K_5 (the stability constant of the catalytic complex). The step of complex degradation was characterized by the rate constant k_6. We believe that the catalytic complex necessarily contained a metal ion, and that ozone, a chloride ion, and (possibly) a H^+ ion participated in its formation and/or degradation. The degradation of the complex results in the regeneration of the metal ion and in the formation of ClO^-, HOCl, or Cl_2; in an acidic medium, this is equivalent to the formation of molecular chlorine (Cl_2) due to equilibria (IV).

Note that it is impossible to obtain information on the effect of chloride ions on the kinetics of the test reaction based on our experimental data, since they were obtained at the same concentration of chloride ions in the reaction solution, which was equal to 1 mol/l. In particular, it is impossible to determine whether the catalytic complex contains chloride ions or if it reacts with them at the stage of degradation.

We believe that the charge-transfer catalysis by Co^{2+} ions occurs via the steps of Co^{3+} formation in reaction (VII) between O_3 and Co^{2+} and in reaction (VIII) of the oxidation of chloride ions with trivalent cobalt to result in the liberation of Cl_2 in an acidic medium as a consequence of equilibria (IV). According to published data [5], the rate of the reaction of O_3 with Co^{2+} is proportional to the product of the concentrations of these substances. Our data indicate that the interaction of O_3 with Co^{2+} is much slower than the interaction of Co^{3+} with the chloride ion. This suggests that step (VII) of the interaction of O_3 with Co^{2+} is a rate-limiting step in charge-transfer catalysis and a steady-state approximation is applicable to Co^{3+}. Therefore, the rate of chlorine formation in reaction (VIII) between Co^{3+} and the chloride ion is equal to the rate of reaction (VII) between O_3 and Co^{2+}. Thus, the rate of chlorine release due to charge-transfer catalysis is proportional to the product of the concentrations of O_3 and Co^{2+}, and the rate constant k_7 of the reaction of O_3 with Co^{2+} is a kinetic characteristic of charge-transfer catalysis.

The constants K_5, k_6, and k_7 were unknown parameters of the model; they were determined by comparing data obtained by simulation and experimental results. The desired values of the unknown parameters were those at which the functional of the relative difference between the experimental and calculated rates of chlorine release reached a minimum.

All of the constants were calculated with the use of the total concentration of a metal ion in solution. This was reasonable, since estimates based on published data [6] demonstrated that varying the concentrations of H^+ and metal ions (over the range used in our experiments) at constant ionic strength and the concentration of chloride ions had practically no effect on the concentration ratio between various metal species in solution.

As a result of our calculations, we obtained the following constants and data on the composition of complexes:

Ion	Complex composition	K_5	k_6, min^{-1}	k_7, l mol^{-1} min^{-1}
VO^{2+}	Does not contain H^+	$<10^{-2}$	$k_6K_5 = 6.5$	0
Fe^{3+}	Contains two H^+ and one O_3	50	1.7	0
Co^{2+}	Contains one H^+ and one O_3	400	3.23	85

Note: Ionic strength, 1 mol/l; concentration of chloride ions, 1 mol/l; temperature, 20°C. The values of the stability constant K_5 are given on a mol/l concentration scale; however, the units are not specified because the true composition of the complexes is unknown.

The values of the rates of chlorine release were obtained with the use of the above constants in model calculations. A comparison between these values (lines) and experimental data (points) is illustrated in Figs. 1–6.

Let us consider the characteristics of the catalytic effects of VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions in the reaction of ozone with chloride ions in acidic solutions.

As can be seen in Fig. 2, the difference between the rates of chlorine release in the presence and in the absence of VO^{2+} is independent of the concentration of H^+ ions and proportional to the concentration of VO^{2+}. This can be explained based on the assumption that a catalytic complex free from H^+ ions is formed, whose stability constant is low. This complex reacts with the formation of Cl_2 and the regeneration of the vanadyl ion. The following versions are indistinguishable: the complex contains VO^{2+}, Cl^-, and O_3 and decomposes in a first-order reaction; the complex contains VO^{2+} and Cl^- and reacts with O_3; and the complex contains VO^{2+} and O_3 and reacts with Cl^-.

In the catalysis by trivalent iron ions (Fig. 4), the catalytic effect of Fe^{3+} increases with the concentration of hydrogen ions. At sufficiently low concentrations of H^+, the catalytic effect of Fe^{3+} does not manifest itself. Thus, the H^+ ions take part in the catalysis by Fe^{3+} ions. The catalysis by trivalent iron ions can be explained based on the assumption that a catalytic complex is formed that contains Fe^{3+}; ozone; two H^+ ions; and (possibly) chloride ions; this complex decomposes with the formation of chlorine and the regeneration of the iron ion. The calculated and experimental curves of the rate of chlorine release (the rate as a function of $[H^+]$ or $[Fe^{3+}]$ is represented by a somewhat concave or convex curve, respectively) coincide only on the assumption that the complex contains two H^+ ions and one ozone molecule and decomposes in a (pseudo-)first-order reaction. Thus, in this case, simulation allowed us to draw conclusions on the composition of the catalytic complex. The dependence of the rate of chlorine release on $[H^+]$ and $[Fe^{3+}]$ in this system can be explained by considering the release of chlorine without the participation of metal ions (reactions (I)–(IV)) and the steps of complex formation and degradation (reactions (V) and (VI), respectively).

The catalytic effect of Cu^{2+} ions is analogous to that of Fe^{3+}; however, it comes into play at higher concentrations of H^+ (Fig. 4).

In the case of catalysis by Co^{2+} ions (reaction (II)) (Fig. 6), the catalytic effect increased with the concentration of H^+; however, it also appeared at low concentrations of H^+ ions. Hence, it follows that catalysis by cobalt ions occurs via two reaction paths; H^+ ions participate in one of these and do not participate in the other.

The reaction path in which the H^+ ions do not participate occurs either through the formation of trivalent cobalt (reaction (VII)) and the oxidation of the chloride ion by the trivalent cobalt (reaction (VIII)), or through the formation of a particular catalytic complex (that does not contain H^+) and the degradation of this complex, which results in the release of Cl_2. These versions are indistinguishable, given the condition that the stability constant of the catalytic complex is small. Note that, although the formation of trivalent cobalt and its capability to oxidize the chloride ion were supported experimentally despite the catalytic complex being a hypothetic species, it is impossible to exclude this complex based on our experimental data.

The effects of the concentrations of H^+ and Co^{2+} on the rate of chlorine release in catalysis by bivalent cobalt ions can be explained on the assumption that catalysis with the participation of H^+ ions occurs through the formation of a catalytic complex containing Co^{2+}, ozone, one H^+ ion, and (possibly) chloride ions. This complex decomposes with the formation of chlorine and the regeneration of Co^{2+}. Coincidence between the shapes of calculated and experimental curves of the rate of chlorine release, plotted as a function of $[Co^{2+}]$ and $[H^+]$ (both of these curves are convex and tend toward saturation), is seen only upon the assumption that the complex contains exactly one H^+ ion and one ozone molecule and decomposes in a (pseudo-) first-order reaction. In this case, simulation allows one to draw conclusions on the composition of the catalytic complex.

Thus, the concentration dependence of the rate of chlorine release in the test system can be explained by considering the processes of chlorine liberation without the participation of metal ions (reactions (I)–(IV)); a catalytic reaction path without the participation of H^+ (it is most likely that this path occurs via steps (VII) and (VIII)); and a catalytic reaction path with the participation of H^+, which occurs via steps (V) and (VI) of complex formation and decomposition, respectively.

Yeatts and Taube [7] were the first to find the catalytic effect of Co^{2+} ions in the reaction of ozone with chloride ions in an acidic medium. However, Yeatts and Taube [7] did not study the dependence of the catalytic effect on the concentration of H^+ ($[H^+]$ was equal to ~0.1 mol/l), and the concentration of Co^{2+} was varied over a narrow range. Therefore, in contrast to this work, Yeatts and Taube [7] revealed only partially the effect of Co^{2+} on the occurrence of the reaction of ozone with the chloride ion. Our data (Fig. 6) suggest that, at $[H^+] = 0.1$ mol/l, the catalysis by Co^{2+} ions mainly occurs without the participation of hydrogen ions. That is, the increase in the rate of chlorine formation that was found by Yeatts and Taube [7], ($39.3[Co^{2+}][O_3]$ mol l^{-1} min^{-1} at 0°C), corresponds to catalysis by Co^{2+} ions via a reaction path without the participation of H^+. The result given in this work ($85[Co^{2+}][O_3]$ mol l^{-1} min^{-1} at 20°C) is consistent with the above value, as well as with the rate constant of the reaction of Co^{2+} with O_3 (37 l mol^{-1} min^{-1} at 0°C) determined by hill [8].

According to the available information, the catalytic effects of VO^{2+}, Fe^{3+}, and Cu^{2+} ions in the $O_3 + Cl^-$ reaction in an acidic medium have not been not reported previously.

Thus, in this work, we for the first time performed systematic studies on the catalytic activity various metal ions in the reaction of ozone with chloride ions in an acidic medium and determined the kinetic characteristics of catalytic reactions.

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