ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 5, pp. 682–685. © MAIK "Nauka/Interperiodica" (Russia), 2006.
Original Russian Text © A.V. Levanov, I.V. Kuskov, K.B. Koiaidarova, E.I. Antipenko, V.V. Lunin, 2006, published in Kinetika i Kataliz, 2006, Vol. 47, No. 5, pp. 705–708.

Interaction between Ozone and the Chloride Ion in Sulfuric Acid Solutions up to 6-M Concentration

A. V. Levanov, I. V. Kuskov, K. B. Koiaidarova, E. I. Antipenko, and V. V. Lunin

Department of Chemistry, Moscow State University, Moscow, 117234 Russia
e-mail: levanov@kge.msu.ru

Received June 15, 2005

Abstract—The effect of sulfuric acid concentration on Cl_2 evolution in the reaction between O_3 and Cl^- has been investigated. The catalytic effects of metal ions in this reaction have been studied as a function of solution acidity. The chlorine evolution rate increases markedly with increasing acid concentration. At acid concentrations below 4 mol/l, the most effective catalyst is Co^{2+}. The catalytic activities of Fe^{3+} and Cu^{2+} peak at $C_{H_2SO_4} = 4.8$ mol/l. In passing to highly acidic solutions ($C_{H_2SO_4} > 5$ mol/l), the catalytic activity of the metal ions decreases, but the chlorine evolution rate remains high owing to the high acidity. Kinetics of VO^{2+} oxidation with ozone in acid media have been studied, and the ozone solubility in aqueous sulfuric acid has been measured.

DOI: 10.1134/S0023158406050053

The interaction between O_3 and Cl^- is of significance in the design of various processes in which ozone is used and chloride ions may be present, and is of interest to atmospheric chemists. Furthermore, determination of the conditions favorable for the reaction between O_3 and Cl^- would show general ways of enhancing the reactivity of ozone towards inert substrates.

Our previous studies demonstrated that the reaction between O_3 and Cl^-, which is slow under ordinary conditions, can be markedly accelerated by raising the H^+ ion concentration or by adding the VO^{2+}, Fe^{3+}, Co^{2+}, or Cu^{2+} ion as a catalyst [1, 2].

This study is devoted to the reaction between O_3 and Cl^- in strongly acidic media. Its purpose is to elucidate the effect of acidity on the kinetics of the reaction and to see whether this reaction can be catalyzed by metal ions at various acidities.

EXPERIMENTAL

The experimental setup and experimental procedure used in this study are described in our earlier publications [1, 2]. The reaction between ozone and acid solutions of the chloride ion was carried out in a bubbler at room temperature (20°C). In all runs, the flow rate of ozonized oxygen was 21 l/h, the inlet ozone concentration was 10.0 g/m^3 (unless otherwise stated), and the volume of the reaction solution was 100 ml. Ozone was produced from special-purity-grade oxygen.

The solutions to be examined contained 0.25 M HCl, 0–6 M H_2SO_4, and 0.01 mol/l of a metal salt. The solutions were prepared from distilled water; reagent- or special-purity-grade hydrochloric and sulfuric acids; analytical-grade potash alum; pure-grade chromic potash alum, iron(III) chloride hexahydrate, cobalt(II) sulfate heptahydrate, nickel(II) hexahydrate, and copper sulfate pentahydrate; and vanadyl sulfate trihydrate and cerium(III) nitrate hexahydrate synthesized from readily available chemicals and then recrystallized.

In kinetic experiments, we determined the Cl_2 evolution rate divided by the solution volume and by the chloride ion concentration $\left(\frac{1}{V[Cl^-]}\frac{dn_{Cl_2}}{dt}\right)$ as a function of the sulfuric acid concentration. This quantity is related to the effective rate constant of the reaction between O_3 and Cl^- (k_1):

$$\frac{1}{V[Cl^-]}\frac{dn_{Cl_2}}{dt} = k_1[O_3]. \quad (1)$$

The current chloride ion concentration in the reacting solution can be taken to be equal to the initial chloride ion concentration (0.25 mol/l), since the amount of chlorine released by the solution over the measurement time is small as compared to the initial amount of chloride ions. The ozone concentration in the reacting solution was not determined. It was estimated from the solubility of ozone in aqueous solutions of sulfuric acid.

The O_3 solubility in H_2SO_4 solutions was derived from the extinction coefficient at 260 nm ($\varepsilon_{260}(O_3) = 3000$ l mol^{-1} cm^{-1}). Spectra were recorded on an Agilent 8453 UV–vis spectrophotometer. Special-purity sulfuric acid was used in the preparation of solutions to minimize the impurity-induced decomposition of O_3.

Table 1. Apparent Henry constant of ozone in aqueous H_2SO_4 as a function of acid concentration at 20–21°C

$[H_2SO_4]$, M	0	0.5	1	2	6
H	0.275	0.23	0.21	0.18	0.15

The experimental and data processing procedures used in this study are detailed elsewhere [3]. Ozone solubility was characterized in terms of the apparent Henry constant H, which was determined as the ratio of ozone concentrations in the solution and gas phase expressed in the same units: $H = [O_3]/C_{O_3}$. The experimental data are presented in Table 1. Furthermore, we determined ozone solubilities in aqueous solutions of sulfuric acid containing 0.01 M $CuSO_4$. These solubilities are nearly equal to the solubilities listed in Table 1.

The reaction between VO^{2+} and O_3 was carried out in a bubbler at room temperature (20°C). Ozonized oxygen was fed into the reactor at a rate of 21 l/h. The inlet ozone concentration was 30.0 g/m^3. The reaction was monitored by measuring the absorption intensity due to the VO^{2+} in the reacting solution ($\lambda_{max} = 765$ nm, $\varepsilon_{765} = 18$ l mol^{-1} cm^{-1}). Absorption spectra were recorded on an Agilent 8453 UV–vis spectrophotometer.

RESULTS AND DISCUSSION

In the study of the effect of the nature of the metal ion on chlorine evolution in the reaction between O_3 and Cl^-, we examined solutions containing 0.25 M HCl, 6 M H_2SO_4, and 0.01 M metal salt. In the absence of a metal salt, the specific chlorine evolution rate is (165–185) × 10^{-6} min^{-1}. $KAl(SO_4)_2$, $KCr(SO_4)_2$, $Ni(NO_3)_2$, and $ZnCl_2$ exert no effect on the chlorine evolution rate.

In the presence of $VOSO_4$, the specific chlorine evolution rate has a lower value of 124 × 10^{-6} min^{-1}. This finding will be discussed below.

$FeCl_3$, $CoSO_4$, $CuSO_4$, and $Ce(NO_3)_3$ raise the chlorine evolution rate to 200 × 10^{-6}, 190 × 10^{-6}, 230 × 10^{-6}, and 190 × 10^{-6} min^{-1}, respectively. Thus, the Fe^{3+}, Co^{2+}, Cu^{2+}, and Ce^{3+} ions are catalytically active in strongly acidic media.

We demonstrated in earlier works [1, 2] that the H^+ ion concentration (acidity) is the determining factor in the rate of the reaction between O_3 and Cl^- in aqueous solutions. The H^+ ion catalyzes this reaction [1] and exerts an effect on the catalytic activity of metal ions (the VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions have been examined) [2]. For this reason, in the study reported here, we investigated the effect of high acid concentrations on the rate of the reaction between O_3 and Cl^- and the catalytic activity of the VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions as a function of acidity. The acidity of the reaction solution was varied by adding sulfuric acid.

In the presence of transition metal ions, the chlorine evolution rate increases monotonically with increasing H_2SO_4 concentration (Figs. 1, 2, curves *1*). The reaction catalyzed by the H^+ ion proceeds via the formation of the HO_3Cl complex [1], whose decomposition results in Cl_2 evolution. The concentration of this complex increases with increasing acidity, resulting in a higher chlorine evolution rate.

Note that, according to Eq. (1), the chlorine evolution rate depends on the ozone concentration in the reaction solution. The ozone solubility decreases with increasing H_2SO_4 concentration (Table 1). However, in the acid concentration range examined here, this factor has a weaker effect on the chlorine evolution rate than catalysis by the H^+ ion. Indeed, as the sulfuric acid concentration is raised from 0 to 8 mol/l, the effective rate constant $\left(k_{app} = \frac{dn_{Cl_2}}{dt}\frac{1}{[O_3][Cl^-]V}\right)$ of the reaction between O_3 and Cl^- increases monotonically [1].

A specific feature of the dependences of the chlorine evolution rate on the sulfuric acid concentration in the presence of the VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions is that these dependences have a maximum (Figs. 1, 2). This finding is in agreement with the mechanism suggested

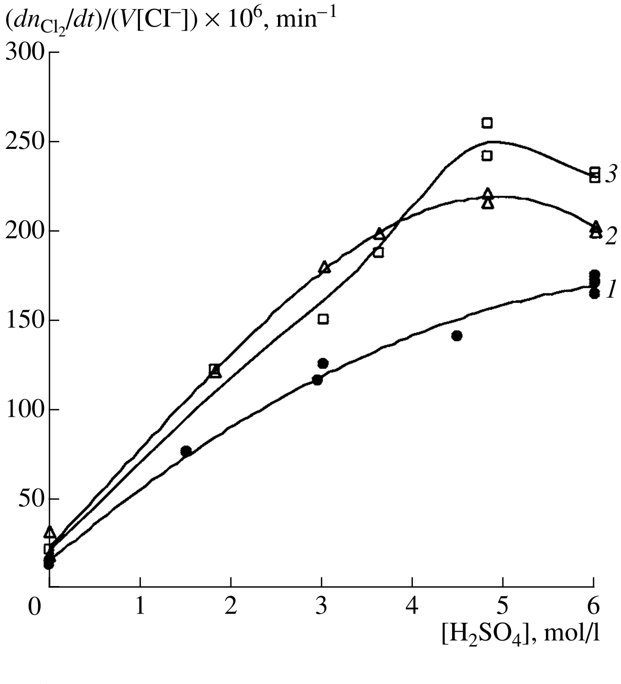

Fig. 1. Specific chlorine evolution rate as a function of the sulfuric acid concentration in the reaction solution. Solution composition: (*1*) 0.25 M HCl + H_2SO_4, (*2*) 0.25 M HCl + H_2SO_4 + 0.01 M $FeCl_3$, and (*3*) 0.25 M HCl + H_2SO_4 + 0.01 M $CuSO_4$.

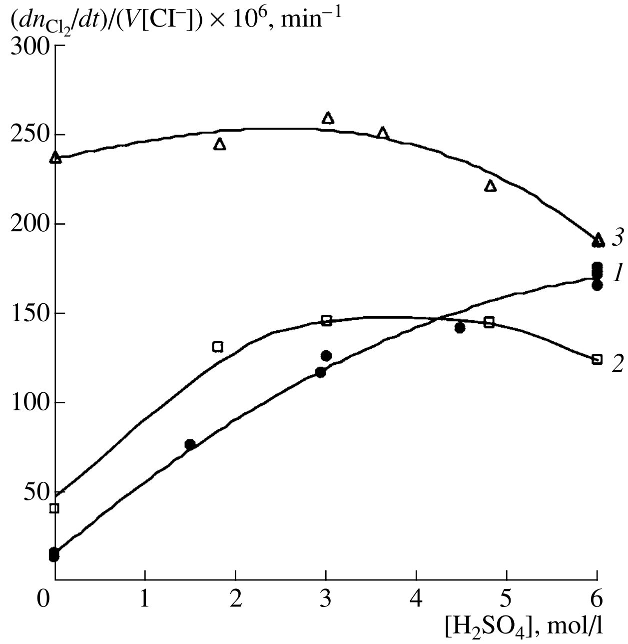

Fig. 2. Specific chlorine evolution rate as a function of the sulfuric acid concentration in the reaction solution. Solution composition: (*1*) 0.25 M HCl + H_2SO_4, (*2*) 0.25 M HCl + H_2SO_4 + 0.01 M $VOSO_4$, and (*3*) 0.25 M HCl + H_2SO_4 + 0.01 M $CoSO_4$.

earlier for the catalytic effect of the H^+, VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions in the reaction between O_3 and Cl^- [2]. Here, it is necessary to take into account that, in the sulfuric acid medium, the VO^{2+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions can be bound into relatively stable sulfate complexes, which cannot participate in the catalysis of the reaction between O_3 and Cl^- by the coordination mechanism (through the formation of a catalytically active complex). On the one hand, increasing the H_2SO_4 concentration causes an increase in the H^+ concentration, thereby accelerating the reaction between O_3 and Cl^-. On the other hand, this raises the HSO_4^- and SO_4^{2-} concentrations, reducing the catalytic activity of the metal ions.

The catalytic effects of the Fe^{3+} and Cu^{2+} ions are explained by the formation of a complex containing a metal ion, H^+, Cl^-, and ozone. This complex decomposes to release chlorine [2]. In the presence of 0.01 M Fe^{3+} or Cu^{2+} (Fig. 1, curves *2*, *3*, respectively), the specific chlorine evolution rate increases with increasing H_2SO_4 concentration, passes through a maximum, and then falls off. This behavior of the chlorine evolution rate is explained by the competition between the formation of catalytically active complexes containing H^+ and the formation of catalytically inactive sulfate complexes.

Table 2. Dependence of the effective rate constant of the reaction between VO^{2+} and O_3 on the nature and concentration of the acid

Initial composition of the reaction solution	k_2, l mol^{-1} min^{-1}
0.02 M $VOSO_4$, 1 M HCl	30
0.02 M $VOSO_4$, 1 M H_2SO_4	300
0.02 M $VOSO_4$, 6 M H_2SO_4	1000

At low acid concentrations, Co^{2+} causes a marked increase in the chlorine evolution rate (Fig. 2, curve *3*). This finding is in agreement with the fact that the reaction between O_3 and Cl^- catalyzed by Co^{2+} can take place without involving H^+ ions, via the oxidation of Co^{2+} to Co^{3+} with ozone and subsequent Cl^- oxidation with trivalent cobalt [2]. As the acidity of the solution is increased, the chlorine evolution rate first increases slightly and then decreases. In 6 M H_2SO_4 solutions, Co^{2+} causes only a slight increase in the chlorine evolution rate (Fig. 2, curve *3*). This is explained by the fact that, along with favoring the formation of catalytically active complexes containing H^+, Co^{2+}, ozone, and Cl^- [2], an increase in sulfur acid concentration causes a buildup of catalytically inactive Co^{2+} sulfate complexes.

As distinct from the above metal ions, 0.01 M VO^{2+} in 6 M H_2SO_4 causes a decrease, not an increase, in the chlorine evolution rate (Fig. 2, curve *2*). A possible explanation of this finding is that the VO^{2+} ion reacts with ozone.

In order to understand the effect of the VO^{2+} ion on the chlorine evolution rate, we studied the dependence of the rate of the reaction between VO^{2+} and O_3 on the nature and concentration of the acid and carried out experiments to see whether VO^{2+} can react with Cl^-. Most ozone–substrate reactions are characterized by an overall reaction order of 2 and are first-order with respect to the substrate and O_3 [5]. For this reason, the effective rate constant of the reaction between VO^{2+} and O_3 was calculated using the rate equation

$$-\frac{d[VO^{2+}]}{dt} = k_2[VO^{2+}][O_3]. \qquad (2)$$

The ozone concentration in H_2SO_4 solutions was estimated from the data listed in Table 1; the ozone concentration in aqueous HCl, from data presented in [1]. The calculated values of the effective rate constant k_2 are listed in Table 2.

As follows from the data presented in Table 2, the rate of the reaction between VO^{2+} and O_3 is much higher in the sulfuric acid medium than in the hydrochloric acid medium and increases with increasing H_2SO_4 concentration. It was demonstrated by absorption spectroscopy and qualitative analysis [6] that the product of this reaction is the pentavalent vanadium ion VO^{2+}. Note that, in our experiments on the reaction between O_3 and Cl^- catalyzed by VO^{2+} in hydrochloric acid ([HCl] ≤ 0.8 mol/l), which are discussed in [2], the reaction between VO^{2+} and O_3 can be neglected.

In order to study the reaction between VO^{2+} and Cl^-, we prepared a 0.005 M VO^{2+} + 0.015 M VO^{2+} + 1 M HCl and a 0.01 M VO^{2+} + 0.25 M HCl + 3 M H_2SO_4 solution. According to absorption spectroscopy data, the composition of these solutions was unchanged after 24 h. Therefore, the VO^{2+} ion does not oxidize the chloride ion under our experimental conditions.

The reaction between O_3 and Cl^- catalyzed by the VO^{2+} ion proceeds via the formation of a catalytic complex involving no H^+ ion [2]. As a consequence, the chlorine evolution rate versus sulfuric acid concentration curves in the presence and absence of VO^{2+} (Fig. 2, curves *2*, *1*, respectively) are parallel at low acidities. As the H_2SO_4 concentration is raised, the proportion of catalytically inactive vanadium(IV) sulfate complexes increases, reducing the catalytic effect of VO^{2+}. Furthermore, the rate of the reaction between VO^{2+} and O_3 increases markedly (Table 2), resulting in a noticeable decrease in the ozone concentration in the solution. As a consequence, at high H_2SO_4 concentrations, the chlorine evolution rate is lower in the presence of VO^{2+} than in the absence of this ion.

Thus, we have for the first time investigated the chlorine evolution kinetics in the reaction between O_3 and Cl^- in sulfuric acid solutions with acid concentrations of up to 6 mol/l. Furthermore, the catalytic activity of various metal ions in this process has been studied. The most significant factor in this process is acidity, which is responsible for the increase in the chlorine evolution rate. At low acid concentrations, a high catalytic activity in the reaction between O_3 and Cl^- is shown by Co^{2+}.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 04-03-32915) and through the Support to Leading Scientific Schools RF State Program (grant NSh 1275.2003.3).

REFERENCES

1. Levanov, A.V., Kuskov, I.V., Zosimov, A.V., Antipenko, E.E., and Lunin, V.V., *Kinet. Katal.*, 2003, vol. 44, no. 6, p. 810 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 6, p. 740].
2. Levanov, A.V., Kuskov, I.V., Koiaidarova, K.B., Zosimov, A.V., Antipenko, E.E., and Lunin, V.V., *Kinet. Katal.*, 2005, vol. 46, no. 1, p. 147 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 1, p. 138].
3. Levanov, A.V., Kuskov, I.V., Zosimov, A.V., Antipenko, E.E., and Lunin, V.V., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2002, vol. 45, no. 5, p. 286.
4. Martell, A.E. and Smith, R.M., *Critical Stability Constants*, vol. 4: *Inorganic Complexes*, New York: Plenum, 1976.
5. Hoigne, J., Bader, H., Haag, W.R., and Staehelin, J., *Water Res.*, 1985, vol. 19, no. 8, p. 993.
6. Feigel, F. and Anger, V., *Spot Tests in Inorganic Analysis*, Amsterdam: Elsevier, 1972.