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CHEMICAL KINETICS AND CATALYSIS

The Oxidation of Chlorine Ions under the Joint Action of Ozone and Permanganate Ions

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Abstract—The oxidation of chlorine ions in the system $O_3 + MnO_4^- + H^+ + Cl^-$ with the formation of Cl_2 in the gas phase was studied. The phenomenon of transfer catalysis of the reaction between O_3 and Cl^- by the MnO_4^- ion was observed (the products of the reduction of MnO_4^- by the chlorine ion are oxidized by ozone to recover MnO_4^-). The rate of the formation of Cl_2 in the $O_3 + MnO_4^- + H^+ + Cl^-$ system was higher than the sum of the corresponding rates in the oxidation of Cl^- by O_3 and MnO_4^- separately. A scheme explaining the trends observed experimentally for the formation of Cl_2 and changes in MnO_4^- concentration was suggested. The formation of MnO_4^- in the oxidation of Mn^{3+} with ozone in acid media was studied.

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INTRODUCTION

The shortcoming of ozone as an oxidizer is its low reactivity toward certain substances. The permanganate ion can interact with many compounds inactive with respect to ozone. It was, however, shown in [1] and this work (see below) that ozone can, in acid solutions, oxidize low-oxidation-degree manganese compounds formed in the reduction of MnO_4^- back to MnO_4^-. For this reason, joint use of MnO_4^- and O_3 in acid media may offer promise for the oxidation of substrates that weakly interact with ozone.

The chlorine ion is an example of substrates inert with respect to ozone. The interaction $O_3 + Cl^-$ is of interest for various processes where ozone is used and the presence of chlorine ions is possible. In addition, revealing the conditions under which the rate of the reaction between O_3 and Cl^- increases can contribute to developing general methods for increasing the reactivity of ozone toward inert substrates.

The purpose of this work was to study the oxidation of chlorine ions in the $O_3 + MnO_4^- + H^+ + Cl^-$ system with the formation of Cl_2 in the gas phase and the influence of significant experimental factors (acidity and the concentration of permanganate ions) on the rate of releasing chlorine.

EXPERIMENTAL

The reaction between O_3, MnO_4^-, and Cl^- was performed in a bubbler at ~20°C. Experiments were conducted on a unit described earlier [2]. In all experiments, the flow rate of ozonized oxygen was 21 l/h, and the concentration of ozone in the gas entering the reactor (C_{O_3}) was 10.0 g/m^3, unless otherwise specified. The solutions studied contained 0.01–0.08 M HCl and NaCl, [HCl] + [NaCl] = 1 M and 0–1.0 mM $KMnO_4$. In all experiments, the total ionic strength of solutions and concentration of chlorine ions were 1 M. The solutions were prepared from distilled water, hydrochloric acid of os. ch. (special purity) grade, sodium chloride of kh. ch. (chemically pure) grade, and pharmaceutical potassium permanganate.

We measured the rate of chlorine liberation from the reactor per unit reaction solution volume $\frac{1}{V}\frac{dn_{Cl_2}}{dt}$ (further "chlorine release rate") and the concentration of MnO_4^- in the solution. The permanganate ion has a light absorption maximum at 525 nm ($\varepsilon_{525} = 2300$ M^{-1} cm^{-1}), and its concentration was determined by optical density measurements at this wavelength. The absorption spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer.

The chlorine release rate was measured after a stationary concentration of MnO_4^- in the reaction solution was established. The amount of Cl_2 in outgoing gases was determined by photometric iodometry. A detailed description of the procedure for determining Cl_2 in a mixture of gases containing ozone can be found in our work [3]. As a result, we obtained the time t depen-

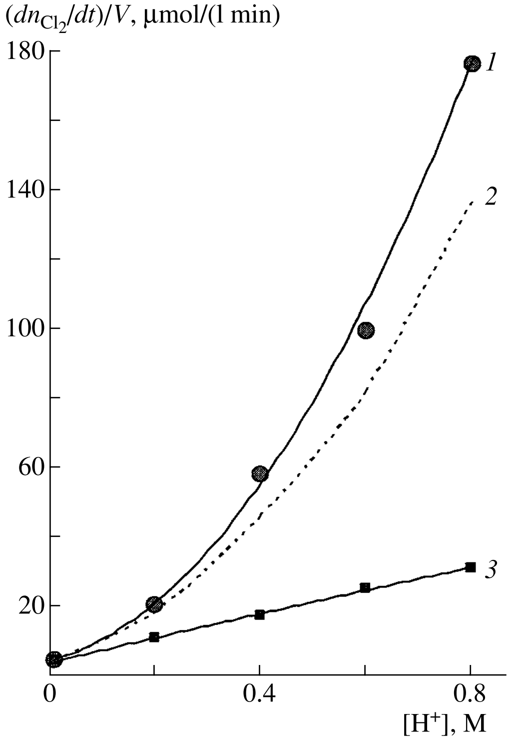

Fig. 1. Dependences of the rate of chlorine formation on reaction solution acidity. The sum of the concentrations of HCl and NaCl in reaction solutions is 1 M, the stationary concentrations of MnO_4^- are 1.0 mM ($[H^+]$ = 0.01 M), 0.96 mM ($[H^+]$ = 0.2 M), 0.93 mM ($[H^+]$ = 0.4 M), 0.78 mM ($[H^+]$ = 0.6 M), and 0.85 mM ($[H^+]$ = 0.8 M); (*1*) experimental data on the O_3–MnO_4^-–H^+–Cl^- system, (*2*) calculated sum of chlorine formation rates in the oxidation of Cl^- by ozone and permanganate ion separately, and (*3*) experimental data on the O_3–H^+–Cl^- system.

dence of the amount of chlorine n_{Cl_2} formed in the reactor; the dependence was rectilinear. The chlorine release rate $\frac{1}{V}\frac{dn_{Cl_2}}{dt}$ was determined as the slope of the linear dependence of n_{Cl_2} on t per unit reaction solution volume V. So far, the experimental procedure was similar to that used in [2].

An approximately stationary regime, when the concentrations of the reagents in the reaction solution and chlorine in outgoing gases remained virtually constant, was established during measurements. The regime was stationary because, first, ozone was supplied into the reaction system from the outside at a constant rate, second, the concentrations of Cl^- and H^+ in the reaction solution were virtually equal to their initial concentrations (the experimental conditions were selected such that the rates of Cl^- oxidation and Cl_2 formation were fairly small and the consumption of Cl^- and H^+ during measurements could be ignored), and, third, the equality of the rates of formation and consumption of manganese compounds in various degrees of oxidation was established because of constant concentrations of the oxidizer (ozone) and reducing agent (Cl^-) in the reaction solution. The chlorine release rate was time-independent under approximately stationary conditions.

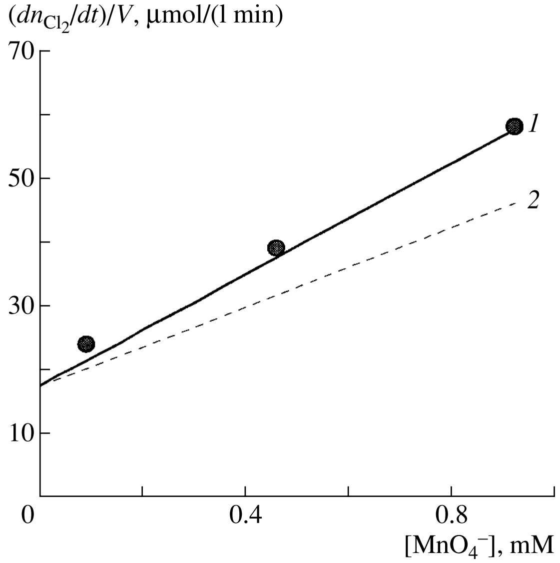

Fig. 2. Dependences of chlorine formation rate on the stationary concentration of MnO_4^- in the reaction solution. The initial solution contained 0.4 M HCl, 0.6 M NaCl, and potassium permanganate; (*1*) experimental data for the O_3–MnO_4^-–H^+–Cl^- system and (*2*) calculated sum of chlorine formation rates in the oxidation of Cl^- by ozone and permanganate ion separately.

RESULTS AND DISCUSSION

When ozone interacts with acid solutions of Cl^-, the presence of permanganate ions in the reaction solution considerably accelerates chlorine release (Figs. 1, 2).

Changes in the concentration of MnO_4^- in the reaction solution. Both O_3 and MnO_4^- can oxidize chlorine ions in the O_3–MnO_4^-–H^+–Cl^- system. Ozone is supplied into the reactor at a constant rate substantially higher than the rate of its decay as a result of various chemical reactions in the solution. It can therefore be expected that a stationary concentration of ozone is established in the reactor. Conversely, permanganate ions are contained in the reaction system in a limited amount and are used in the oxidation of chlorine ions. In order to characterize the processes responsible for the liberation of Cl_2 in the O_3–MnO_4^-–H^+–Cl^-system, it is important to know how the concentration of MnO_4^- changes during the reaction. According to Fig. 3, the concentration of MnO_4^- first decreases and then reaches a stationary value. The dependence of the stationary concentration of permanganate ions on experimental conditions is presented in the table. The ratio between the stationary and initial MnO_4^- concentrations does not depend on the initial concentration of permanganate ions; it decreases as solution acidity increases and increases as the concentration of ozone grows. It follows that, in the O_3–MnO_4^-–H^+–Cl^- system along with the consumption of permanganate ions in the oxidation of chlorine ions, MnO_4^- is regenerated by ozone from the products of its reduction. Note that small amounts of hydrated MnO_2 precipitates are formed at low reaction solution acidity.

The oxidation of Mn^{3+} with ozone. The final product of the reduction of permanganate ions with chlorine ions in an acid medium at ~20°C is Mn(III) compounds [4]. We therefore studied the products formed in the interaction of trivalent manganese ions with ozone and the kinetics of this interaction. The interaction of Mn^{3+} with O_3 was conducted in a bubbler at ~20°C in sulfuric acid solutions. The initial solutions contained 0.5, 1, or 2 M H_2SO_4 and 1 mM Mn^{3+}. Ozonized oxygen was supplied into the reactor at a rate of 21 l/h, and the concentration of ozone at the entrance to the reactor was 10.0 g/m^3.

We found that the oxidation of Mn^{3+} with ozone gave MnO_4^-. All trivalent manganese was converted into permanganate ions in 1 and 2 M H_2SO_4. In 0.5 M H_2SO_4, only 27 mol % of Mn^{3+} was converted into MnO_4^-, and the rest was oxidized to Mn(IV) and precipitated as hydrated MnO_2.

The kinetics of the reaction was controlled spectrophotometrically by measuring the intensity of absorption of MnO_4^- in the reaction solution. The overwhelming majority of ozone reactions with various substrates follow second-order kinetics and are first-order in the substrate and O_3 [5]. The effective rate constant for the reaction between Mn^{3+} and O_3 was therefore calculated by the equation

$$\frac{d[MnO_4^-]}{dt} = k_{eff}[Mn^{3+}][O_3].$$

The concentration of ozone in H_2SO_4 solutions was estimated using the data obtained by us in [6]. The effective constant values are given below:

$[H_2SO_4]$, M	0.5	1.0	2.0
k_{eff}, l/(mol min)	~2500	1350	630

It follows that the rate of the reaction of Mn^{3+} with O_3 substantially decreases as the concentration of the acid increases. This is in agreement with the observation that the stationary concentration of MnO_4^- in the O_3 + MnO_4^- + H^+ + Cl^- system decreases as solution acidity grows (see table).

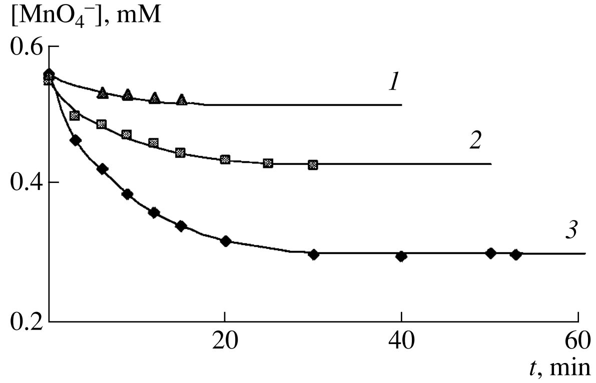

Fig. 3. Dependences of the concentration of MnO_4^- in reaction solutions on the duration of experiments. The initial solution composition: $[MnO_4^-]_0$ = 0.56 mM; $[Cl^-]$ = 1 M; and $[H^+]$ = (*1*) 0.4 M, (*2*) 0.6 M, and (*3*) 0.8 M.

A scheme of processes responsible for the formation of Cl_2. The release of chlorine in the O_3–MnO_4^-–H^+–Cl^- system occurs as a result of two parallel reactions, including, first, the interaction of MnO_4^- with Cl^- accompanied by the regeneration of MnO_4^- in the reaction between ozone and the products of MnO_4^- reduction and, second, the reaction between Cl^- and O_3 without permanganate ion participation. The kinetics of the reaction between Cl^- and O_3 in acid media (the O_3–H^+–Cl^- system) was studied in detail in our work [2].

We suggest the following scheme of interrelated processes of the interaction of MnO_4^- with Cl^- and regeneration of MnO_4^- with ozone that occur in the O_3 + MnO_4^- + H^+ + Cl^- system:

$$MnO_4^- + Cl^- \longrightarrow Mn(V) + Cl_2, \qquad (1)$$

$$Mn(V) + Cl^- \longrightarrow Mn(III) + Cl_2, \qquad (2)$$

Ratios between stationary and initial concentrations of permanganate ions ($[MnO_4^-]_\infty/[MnO_4^-]_0$) in the O_3–MnO_4^-–H^+–Cl^- system under various experimental conditions

c_{O_3}, g/m^3	$[H^+]$, M	$[MnO_4^-]_0$, mM	$[MnO_4^-]_\infty/[MnO_4^-]_0$
10.0	0.4	0.11	0.93
10.0	0.4	0.56	0.93
10.0	0.6	0.56	0.78
10.0	0.8	0.56	0.53
40	0.8	0.56	0.85

$$\mathrm{Mn(III)} + \mathrm{O_3} \longrightarrow \mathrm{Mn(V)} + \mathrm{O_2}, \quad (3)$$

$$\mathrm{Mn(V)} + \mathrm{O_3} \longrightarrow \mathrm{MnO_4^-} + \mathrm{O_2}. \quad (4)$$

The scheme is based on the data on permanganate ion concentration changes in the O_3–MnO_4^-–H^+–Cl^- system, data on the interaction of O_3 with Mn^{3+} (see above), and data on the kinetics of interaction between MnO_4^- and Cl^- in acid media (see our work [4]). The scheme only includes the main processes that lead to the formation of Cl_2 and, in particular, ignores the formation of hydrated MnO_2 precipitates at low acidities.

According to [4], the reaction between MnO_4^- and Cl^- in acid media involves two steps (steps (1) and (2) in the scheme given above). The reagent concentration dependence of the rate at stage (1) is given by the equation

$$w_1 = k_1[\mathrm{MnO_4^-}][\mathrm{H^+}]^2[\mathrm{Cl^-}]^2, \quad k_1 = 0.098\ \mathrm{l^4/(mol^4\ min)}\ [4]. \quad (5)$$

At stage (1), permanganate ions are consumed, and one Cl_2 molecule per MnO_4^- ion is formed; MnO_4^- is reduced to manganese compounds containing manganese in the oxidation degree intermediate between +7 and +3. Supposedly, Mn(V) is formed: this is our working hypothesis. At stage (2), the second Cl_2 molecule and Mn(III), which is the final MnO_4^- reduction product, are formed. It was shown in [4] that it was Mn(III) that was the final product of the reaction between MnO_4^- and Cl^- in acid media at room temperature.

The regeneration of MnO_4^- from the products of its reduction is described by stages (3) and (4). As has been shown above, the oxidation of Mn(III) with ozone does indeed produce MnO_4^-.

It is assumed that reactions (1)–(4) are first order in the concentrations of the corresponding manganese compounds. This is substantiated by the observation that the ratio between the stationary and initial MnO_4^- concentrations in the O_3–MnO_4^-–H^+–Cl^- system does not depend on the initial concentration of MnO_4^- (see table). The rate w_i of stage i is then equal to the product of the specific rate R_i by the concentration of the corresponding Mn compound. For instance, for reaction (1), we have $w_1 = R_1[MnO_4^-]$, where $R_1 = k_1[H^+]^2[Cl^-]^2$ and $k_1 = 0.098\ l^4/(mol^4\ min)$.

As has been mentioned above, stationary regime is established in the reactor as time passes. The rates of formation and consumption of manganese compounds in various oxidation states are then equal, that is,

$$R_1[\mathrm{MnO_4^-}]_\infty = R_4[\mathrm{Mn(V)}]_\infty, \quad (6)$$

$$R_2[\mathrm{Mn(V)}]_\infty = R_3[\mathrm{Mn(III)}]_\infty. \quad (7)$$

The concentrations in the stationary state are denoted by subscript ∞.

In our experiments, the chlorine formation rate was measured under stationary conditions. Chlorine is formed in reactions (1) and (2) and in the reaction between Cl^- and O_3 without permanganate ion participation. The following equation therefore follows from the above scheme for the experimentally determined chlorine release rate:

$$\frac{1}{V}\frac{dn_{\mathrm{Cl_2}}}{dt} = \frac{dn_{\mathrm{Cl_2}}}{Vdt}(\mathrm{O_3, Cl^-}) + R_1[\mathrm{MnO_4^-}]_\infty + R_2[\mathrm{Mn(V)}]_\infty. \quad (8)$$

Here, $\frac{dn_{Cl_2}}{Vdt}(O_3, Cl^-)$ is the rate of chlorine formation from Cl^- under the action of ozone only. This rate can be calculated using our data from [2]. Its dependence on acidity is shown in Fig. 1 (curve *3* was obtained in calculations based on the data from [2] and symbols are the experimental values). Using (6) to describe $[Mn(V)]_\infty$ through $[MnO_4^-]_\infty$ measured experimentally yields

$$\frac{1}{V}\frac{dn_{\mathrm{Cl_2}}}{dt} = \frac{dn_{\mathrm{Cl_2}}}{Vdt}(\mathrm{O_3, Cl^-}) + R_1[\mathrm{MnO_4^-}]_\infty\{1 + R_2/R_4\}. \quad (9)$$

Here, the $\frac{1}{V}\frac{dn_{Cl_2}}{dt}$, $\frac{dn_{Cl_2}}{Vdt}(O_3, Cl^-)$, and R_1 values are known (R_1 is calculated by (5)), and we can therefore calculate the ratio between the specific rates R_2/R_4 in each experiment. We found that this ratio was $R_2/R_4 \approx 1.8$ (at $c_{O_3} = 10\ g/m^3$) in all experiments. The chlorine formation rates calculated by (9) with the use of the ratio $R_2/R_4 = 1.8$ and the known $\frac{dn_{Cl_2}}{Vdt}(O_3, Cl^-)$ and R_1 values are shown in Figs. 1 and 2 (solid lines *1*). According to these figures, (9) is in agreement with the rates of chlorine formation observed experimentally. Equation (9) was obtained within the framework of Scheme (1)–(4), according to which the reduction of MnO_4^- to Mn(III) and the oxidation of Mn(III) to MnO_4^- proceed via the same intermediate compound. The conclusion that the consumption and regeneration of MnO_4^- in the O_3–MnO_4^-–H^+–Cl^- system involves the same intermediate compound is substantiated by the possibility of correctly describing the experimental chlorine release rates with the use of Eq. (9).

The opposite suggestion that the reduction of MnO_4^- and oxidation of Mn(III) proceed via different intermediate compounds is at variance with the experimental data. The rate of chlorine formation would then be $\frac{1}{V}\frac{dn_{Cl_2}}{dt} = \frac{dn_{Cl_2}}{Vdt}(O_3, Cl^-) + 2R_1[MnO_4^-]_\infty$. Here, all the values on the right-hand side are known from experiment or can be calculated. The rates of chlorine formation calculated this way (they are shown by dashed lines in Figs. 1, 2, curves *2*) noticeably differ from the experimental values.

To summarize, we for the first time studied the formation of chlorine in the oxidation of chlorine ions under the joint action of O_3 and MnO_4^- in acid media. Transfer catalysis of the reaction between O_3 and Cl^- by MnO_4^- ions was observed; the latter react with Cl^- to produce chlorine and are reduced to manganese compounds in low oxidation degrees. These compounds are oxidized back to MnO_4^- by O_3. Compared with the other systems studied by us [2, 6, 7], this one is characterized by the highest rate of chlorine ion oxidation. The permanganate ion can be used as a catalyst of ozone reactions with inactive substrates.

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