Influence of H_2O_2 on a Chloride-Dependent Reaction Path to Chlorine Dioxide

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Reaction paths governing chlorine dioxide formation from solutions of sodium chlorate, sulfuric acid, hydrogen peroxide and sodium chloride at 25°C were examined. Chlorine dioxide was formed by two paths: the reduction of chlorate by hydrogen peroxide and the reduction of chlorate by chloride. At conditions of this study, the rate of the chloride-chlorate path predominated and was enhanced by hydrogen peroxide, reaching an upper limit as hydrogen peroxide concentration was increased. A mechanism was proposed that explains the observed behavior. It is based on existing theory, but includes a new step: the rapid reaction of hydrogen peroxide with an intermediate, Cl_2O_2*. It was shown also that chloride was not required to sustain chlorine dioxide formation in the hydrogen peroxide-chlorate path.*

Introduction

Chlorine dioxide is an oxidizing gas used in aqueous solution for water purification, and for bleaching wood pulp. It is produced by reducing sodium chlorate in acidic solution with sulfur dioxide, sodium chloride, methanol, or hydrogen peroxide. With hydrogen peroxide, the process is

$$2H^+ + 2ClO_3^- + H_2O_2 \rightarrow 2ClO_2 + 2H_2O + O_2 \qquad (1)$$

and is of commercial interest (Sokol and Conkle, 1993; Tenney et al., 1997). Burke et al. (1993) studied the rate. Yamasaki et al. (1977) proposed a free radical mechanism.

Reaction solutions in commercial reactors contain a small concentration of chloride: some entering as an impurity in commercial sodium chlorate, and some forming by stepwise reduction of chlorate. A chloride-dependent path may also occur, because chloride reduces chlorate to chlorine dioxide and chlorine in the absence of hydrogen peroxide (Lenzi and Rapson, 1962)

$$4H^+ + 2ClO_3^- + 2Cl^- \rightarrow 2ClO_2 + 2H_2O + Cl_2 \qquad (2)$$

Hydrogen peroxide rapidly converts chlorine to chloride (Makeower and Bray, 1933)

$$Cl_2 + H_2O_2 \rightarrow 2H^+ + 2Cl^- + O_2 \qquad (3)$$

Reactions 2 and 3 are a two-step path to chlorine dioxide that sum to reaction 1.

This path may not be efficient, because commercial reactor conditions favor rapid degassing that would cause some unreacted chlorine to escape into the ClO_2 product. For this reason, high levels of chloride are undesirable in a commercial process. A better understanding of this path is important.

The rate of reaction 1 was studied in the absence of added chloride (Burke et al., 1993), and the rate of reaction 2 in the absence of hydrogen peroxide (Hong et al., 1967). This work reports a study of the rate of chlorine dioxide formation in acidic solutions of chlorate containing both hydrogen peroxide and chloride. The objective was to focus on the chloride-dependent path, and to explain how hydrogen peroxide affects it. The work was conducted at 25°C as was the previous work of Hong et al. (1967). Most of the results were presented at a recent AIChE meeting (Crump, 1997).

Theoretical Studies

Chloride-chlorate reaction

Hong et al. (1967) studied reaction 2 and observed second-order dependence in chloride, variable-order dependence in chlorate (first- to second-order dependence), and thirteenth- fourteenth-order dependence in sulfuric acid. Chlorine inhibited the rate. They proposed that reaction 2

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takes place in two steps

$$3H^+ + ClO_3^- + 2Cl^- \leftrightarrow Cl_2 + HClO_2 + H_2O \quad (4)$$

$$HClO_2 + H^+ + ClO_3^- \rightarrow 2ClO_2 + H_2O \quad (5)$$

and derived a rate expression by applying the steady-state approximation to $HClO_2$

$$\text{Rate}_{ClO_2} = 2k_4k_5[H^+]^4[ClO_3^-]^2[Cl^-]^2/\{k_{-4}[Cl_2] + k_5[H^+][ClO_3^-]\} \quad (6)$$

Equation 6 is consistent with observations except for acid order. They attributed the unusually high (13th- to 14th-order) acid dependence to variation in activity coefficients with acid concentration. To reconcile theory and experiment, they substituted molal activity of sulfuric acid a_H+, (Shankman and Gordon, 1939) for $[H^+]$ and found an order of about 4.5. They reported $k_4 = 0.18\ M^{-5}\cdot min^{-1}$, $k_5 = 1.8\times10^4\ M^{-2}$, and $k^{-4} = 1.1\times10^7\ M^{-1}$.

The maximum rate predicted by Eq. 6 occurs at zero chlorine concentration, where

$$\text{Rate}_{ClO_2} = 2k_4[H^+]^3[ClO_3^-][Cl^-]^2 \quad (7)$$

Substituting values of rate constants, and substituting a_H+, the equation becomes

$$\text{Rate}_{ClO_2} = 0.36(a_H+)^3[ClO_3^-][Cl^-]^2 \quad (8)$$

In developing Eq. 6, Hong et al. (1967) did not explain how they arrived at Eq. 4, or explain why they treated the two reactions as elementary steps. A mechanism previously proposed by Edwards (1952) provides possible insight into Hong's development. Edwards (1952) proposed general mechanisms that explain reactions of inorganic oxyanions catalyzed by hydrogen ions with donor ions (bases in the Lewis sense). When applied to the chloride-chlorate system, the steps are

$$H^+ + ClO_3^- \leftrightarrow HClO_3 \quad (9)$$

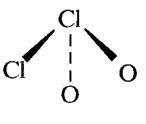
$$H^+ + HClO_3 \leftrightarrow H_2ClO_3^+ \quad (10)$$

$$Cl^- + H_2ClO_3^+ \leftrightarrow Cl_2O_2 + H_2O \quad (11)$$

$$Cl^- + Cl_2O_2 \leftrightarrow Cl_2 + ClO_2^- \quad (12)$$

$$H^+ + ClO_2^- \leftrightarrow HClO_2 \quad (13)$$

The equilibrium protonation of chlorite ions, not discussed by Edwards, is important at high acid concentrations. The intermediate Cl_2O_2 was suggested by Taube and Dodgen (1949), and extensive evidence summarized by Edwards (1952). Of the three isomers of formula Cl_2O_2, the one of pyramidal structure (isoelectronic with ClO_3^-)



is most reasonable from mechanistic considerations. It has been synthesized in the gas phase (Müller and Willner, 1992), and structure determined by IR and submillimeter spectroscopy (Müller and Cohen, 1997).

The above steps are consistent with Hong et al. (1967) and sum to reaction 4. If reaction 5 is included, the steps sum to reaction 2. A rate expression derived from these steps is identical to Eq. 6 except $[H^+]$ in the denominator is raised to the second power. The derivation assumes pseudo-equilibrium for reactions 9, 10, 11 and 13, and applies the steady-state approximation to the sum $\{[ClO_2^-]+[HClO_2]\}$. The discrepancy in the denominator does not arise if reactions 12 and 13 are combined and the resulting reaction assumed to be elementary. It is unlikely that reaction 5 is elementary; however, details of this step are unimportant since we will deal only with experimental conditions at which earlier steps in the mechanism are rate determining.

As chlorine concentration approaches zero, the forward rate of reaction 12 becomes rate determining, and the rate expression becomes

$$\text{Rate}_{ClO_2} = 2k_{12}K_9K_{10}K_{11}[H^+]^2[ClO_3^-][Cl^-]^2 \quad (14)$$

Acid dependence differs from that of Eq. 7, because reactions 12 and 13 were treated as separate steps.

In an earlier study, Skrabal and Schreiner (1935) established the maximum rate of the first three steps of this mechanism by incorporating arsenious oxide in reaction solutions. (There is some confusion in the literature regarding the time unit of the rate coefficient presented in Skraber and Schreiner (1935). The article, written in German, reports the time unit in minutes, whereas later authors who cite this article report the same numerical value but with units in seconds. We have assumed that the original authors correctly stated the units.) It rapidly destroyed Cl_2O_2 and eliminated the reverse of reaction 11. They observed first-order dependence in chloride and chlorate, and second-order dependence in acid, which is consistent with the first three steps of the mechanism, assuming steps 9 and 10 are in equilibrium, and step 11 is irreversible. They determined the rate expression

$$-R_{ClO_3^-} = k_{11}K_9K_{10}[H^+]^2[ClO_3^-][Cl^-] \quad (15)$$

with a fourth-order rate constant $k_{11}K_9k_{10} = 4.5\times10^{-5}\ M^{-3}\cdot min^{-1}$.

Skrabal and Schreiner (1935) conducted these experiments using hydrochloric acid and potassium chlorate at relatively dilute concentrations ~0.2 M, at which $[H^+]$ equals molar concentration of HCl. Our work involved sulfuric acid at higher concentrations, 1.5 to 3 M, where acidity functions better approximate proton-donating ability than do acid concentrations. H_- and H_0 (Hammett) acidity scales apply to equilibrium reactions 9 and 10, respectively. The H_- scale is a measure of the ability of an acid to protonate an ionic base; the H_0 scale is a measure of the ability of an acid to protonate a neutral base (Rochester, 1970; Lowry and Richardson, 1987; Cox and McTigue, 1964). In terms of acidity functions, the rate law of Skrabal and Schreiner becomes

$$-R_{ClO_3^-}(M/min) = 4.5\times10^{-5}h_-h_0[Cl^-][ClO_3^-] \quad (16)$$

Hydrogen peroxide-chlorate reaction

Yamasaki et al. (1977) studied reaction 1 in the absence of chloride. They proposed that the reaction was first-order in chlorate and in hydrogen peroxide. They demonstrated the presence of the perhydroxyl radical HO_2^* but did not measure the effect of acidity. Burke et al. (1993) measured the rate in the absence of chloride. They correlated all of the experimental data in terms of an empirical expression,

$$R_{ClO_2} = 1.5 \times 10^{10} \exp(-10{,}505/T)[h_-]^{1.9}[H_2O_2]^{0.7}[ClO_3^-]^{1.3} \quad (17)$$

Effect of mercuric salts

Indu et al. (1997) used mercuric ion as a diagnostic tool in studies of chlorine dioxide formation. Mercuric ions: (1) remove chloride from solution by forming soluble $HgCl_2$; (2) rapidly decompose chlorite ions in solution; and (3) do not react with chlorine dioxide in solution, unless chlorite ions are present. This latter property can be exploited to indicate whether chlorite is present in a reacting solution; a sudden decrease in chlorine dioxide concentration after addition of mercuric ions indicates that chlorite ions are present. No change in chlorine dioxide concentration indicates that chlorite is not present, or is present in very low concentration. Indu et al. (1997) referred to the work of Gordon and Emmenegger (1966) who suggested that chlorite and chlorine dioxide form a complex in solution

$$ClO_2 + ClO_2^- \rightarrow Cl_2O_4^- \quad (18)$$

Indu et al. speculated that mercuric decomposes chlorine dioxide in this complex form.

Experimental Studies

In this work, we focused attention on the rate of chlorine dioxide formation in the chloride-dependent mechanism (Eqs. 5 and 9–13) by performing experiments at conditions where that process predominated. Relatively high chloride concentrations were studied in order to enhance the chloride-dependent path.

The equipment consisted of a UV spectrophotometer (Milton Roy Spectronic 1201) with a 0.4 cm^3 flow cell of 1 cm path length. The reaction vessel was a 250-mL stirred flask, partially submerged in a constant-temperature water bath (+/−0.5 K). Total volume of the reaction solution was 200 mL in each experiment. Liquid was continuously pumped at 100 mL/min from the flask through the flow cell, and back to the flask. Residence time in the recycle tubing and flow cell was about 6 s.

In a typical experiment, an aqueous solution of all reagents except one was placed in the flask, rapidly agitated with a magnetic stirrer and circulated through the UV flow cell. The reaction was initiated by adding the appropriate volume of the final reagent and monitoring the absorbance at 370 nm as a function of time. The concentration of chlorine dioxide was determined from the absorbance based on the extinction coefficient $\epsilon_{370} = 1{,}040\ cm^{-1}\ M^{-1}$. All experiments were conducted at 25°C.

Results

Analysis of reaction paths by mercuric ion addition

Figure 1 shows chlorine dioxide concentration-time profiles observed in two reaction experiments involving 2-M sulfuric acid, 2-M sodium chlorate, 0.1-M hydrogen peroxide, and 0.01-M sodium chloride. For the first 11 min, the rate was approximately constant, as shown by the uniform slope. At 11 min, a few milliliters of concentrated mercuric nitrate solution were added at a concentration of 0.01 M in one experiment and 0.02 M in the other. These concentrations were respectively 1 and 2 times the chloride concentrations in the reaction mixture, and were sufficient to completely sequester all chloride ions. After the mercuric nitrate was added, the concentration of chlorine dioxide in each experiment decreased suddenly for a few seconds, and then resumed increasing, but at a slower rate.

The purpose of these experiments was to observe the rate of chlorine dioxide formation when both chloride and hydrogen peroxide were present, and the rate after all free chloride had been sequestered by mercuric ions. The slower rate following the addition of mercuric nitrate was attributed to the hydrogen peroxide-chlorate reaction (Eq. 1). These results confirm that this latter reaction does not depend upon chloride.

In Figure 1, the sudden small decrease in chlorine dioxide concentration following mercuric nitrate addition was attributed to dilution of the reaction mixture, and not to de-

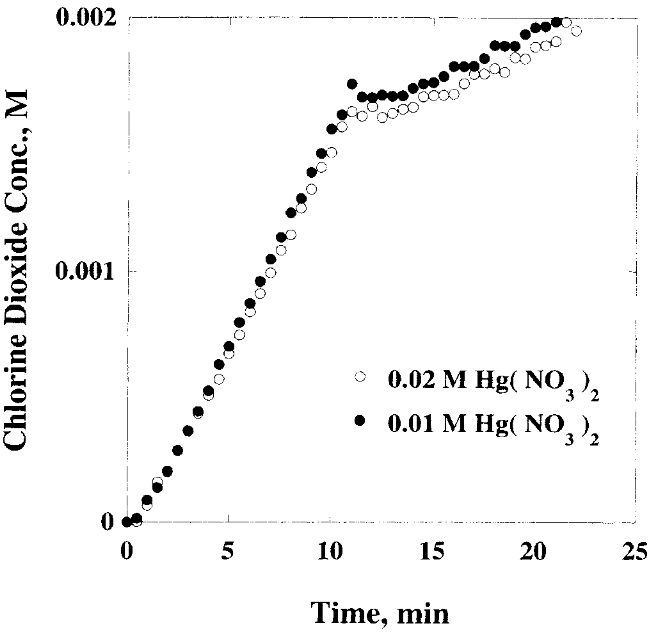


Figure 1. Influence of chloride sequestering on reaction rate.

Conditions: 25°C; 2-M H_2SO_4; 2-M $NaClO_3$, 0.1-M H_2O_2; 0.01-M NaCl; $Hg(NO_3)_2$ added at 11 min.

composition of a chlorous acid-chlorine dioxide complex produced in reaction 18. The concentration of this complex prior to mercuric nitrate addition could not have exceeded the steady-state chlorous acid concentration, which we estimated from the model of Hong et al. (1967) to have been ~10^{-8}M.

Hydrogen peroxide addition to reactions in progress

Figure 2 shows chlorine dioxide concentration-time profiles observed in three reaction experiments involving 2-M sulfuric acid, 2-M sodium chlorate, and 0.15-M sodium chloride. The decreasing slope of each profile illustrates the inhibiting effect of chlorine reported by Hong et al. (1967). According to reaction 2, the chlorine concentration in the reaction solutions equals one-half of the chlorine dioxide concentration. At a point in time in each experiment, a few milliliters of hydrogen peroxide solution were added to produce a final concentration of 0.001-M, 0.01-M or 0.1 M H_2O_2. Figure 2 shows that the rate suddenly increased after these additions. The steepness of the slope increased with the concentration of added hydrogen peroxide.

A sudden increase in rate following hydrogen peroxide addition was expected since hydrogen peroxide reacts rapidly with chlorine (Eq. 3) eliminating chlorine inhibition. However, based on the discussion following Eq. 8, the rate after hydrogen peroxide addition should have been equal to the initial rate in each experiment. Figure 2 shows, however, that the rate following hydrogen peroxide addition at 0.01 M and 0.1 M was greater than the rate at $t = 0$. This observation shows that hydrogen peroxide also increased the rate by another means.

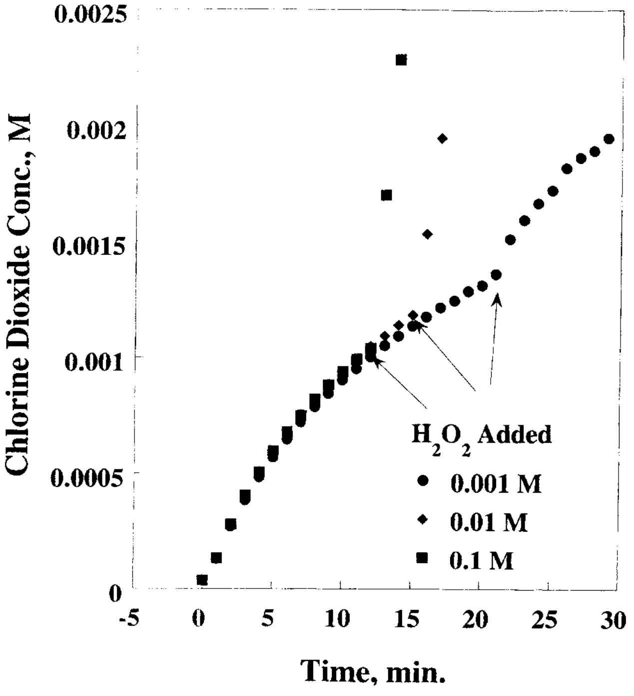


Figure 2. Effect of adding hydrogen peroxide to a reacting chloride-chlorate-sulfuric acid solution.
Conditions: 25°C; 2-M H_2SO_4; 2-M $NaClO_3$; 0.15-M NaCl.

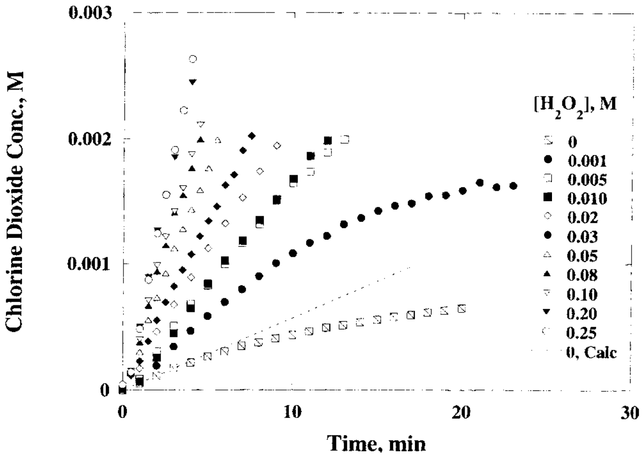


Figure 3. Influence of hydrogen peroxide on chlorine dioxide-time profiles.
Conditions: 25°C; 2-M H_2SO_4; 2-M $NaClO_3$; 0.1-M NaCl.

Hydrogen peroxide addition to initial reaction mixtures

Figure 3 provides further evidence that the rate-enhancing effect of hydrogen peroxide cannot be explained solely by its ability to eliminate chlorine inhibition. Figure 3 shows chlorine dioxide-time profiles for reactions involving 2-M sulfuric acid, 2-M sodium chlorate, and 0.1-M sodium chloride and various initial concentrations of hydrogen peroxide. At hydrogen peroxide concentrations greater than about 0.005 M, the slopes of the profiles were relatively constant with time, indicating that there was no chlorine inhibition. In one experiment, no hydrogen peroxide was added. The initial rate of the experiment is the slope of the dotted line, and has a value of 6×10^{-5} M/min. The most significant qualitative features of Figure 3 are that the slopes of all other profiles exceed the slope of the dotted line, and that the rate represented by these profiles increased with increasing hydrogen peroxide concentration.

As a test of the predictive capability of the model of Hong et al. (1967), we compared the initial rate, represented by the dotted line, with the rate calculated using Eq. 8. A value of molal activity, $a_{H^+} = 0.262$, which corresponds to 2-M sulfuric acid, was obtained from Shankman and Gordon (1939). The model predicted a rate of 1.3×10^{-4} M. Although the predicted value was about twice the experimental value, the agreement was sufficient for purposes of this study.

Figure 3 also shows another important feature of the influence of hydrogen peroxide concentration. At low concentration, the incremental effect on the chlorine dioxide rate was great, but at higher concentrations, the incremental effect diminished.

Analysis of the chloride-chlorate reaction path enhanced by hydrogen peroxide

Table 1 shows chlorine dioxide formation rates measured in one series of reaction experiments at constant sodium chloride concentration (Column 2). The series was conducted at 2-M sulfuric acid, 2-M sodium chlorate, 0.026-M sodium chloride, and various concentrations of hydrogen peroxide.

Table 1. Experimental Data and Rate Analysis: 25°C; 2-M H_2SO_4; 2-M $NaClO_3$ and 0.026-M NaCl

H_2O_2 (M)	ClO_2 Rate (M/min) Experimental	ClO_2 Rate (M/min) H_2O_2/Chlorate Path (Eq. 17)	ClO_2 Rate (M/min) Cl-/Chlorate Path (by Difference)
0.010	4.69×10^{-5}	1.10×10^{-5}	3.59×10^{-5}
0.025	6.64×10^{-5}	2.08×10^{-5}	4.56×10^{-5}
0.051	1.21×10^{-4}	3.43×10^{-5}	8.67×10^{-5}
0.095	1.91×10^{-4}	5.30×10^{-5}	1.38×10^{-4}
0.10	2.00×10^{-4}	5.50×10^{-5}	1.45×10^{-4}
0.14	3.17×10^{-4}	6.95×10^{-5}	2.47×10^{-4}
0.19	3.34×10^{-4}	8.61×10^{-5}	2.48×10^{-4}
0.19	3.58×10^{-4}	8.61×10^{-5}	2.72×10^{-4}
0.24	4.03×10^{-4}	1.01×10^{-4}	3.02×10^{-4}
0.38	3.78×10^{-4}	1.40×10^{-4}	2.38×10^{-4}
0.45	4.04×10^{-4}	1.57×10^{-4}	2.47×10^{-4}

Table 1 shows contributions to the overall rates from the hydrogen peroxide-chlorate reaction (Column 3) and from the chloride-chlorate reaction (Column 4). The experimental rates were determined from slopes of chlorine dioxide-time profiles such as those in Figure 3. The rates in Column 3 were shown by Figure 1 to represent the slower, hydrogen peroxide-chlorate path, and were calculated using the empirical equation of Burke et al. (1993), Eq. 17. Rates in Column 4 were determined by subtracting values in Column 3 from those in Column 2 and represent the chloride-chlorate reaction rate enhanced by hydrogen peroxide. (We ran several experiments such as those shown in Figure 1 to test Eq. 17 and found it predicted within ±25% the experimental rates measured following mercuric ion addition. Because these rates (shown in Column 3) were relatively small, an error of ±25% would affect the values in Column 4 on the average of about ±6%.)

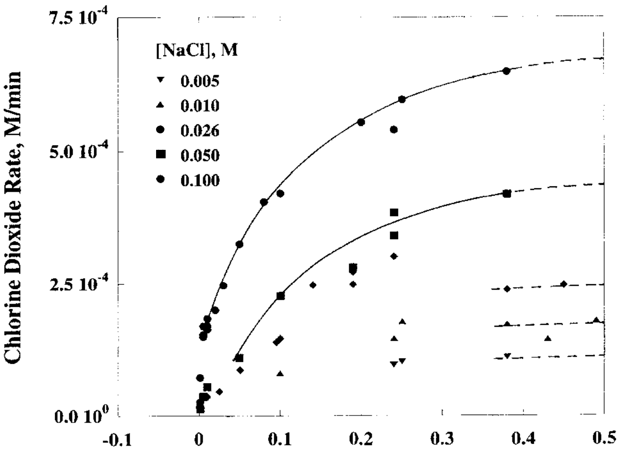


Figure 4. Influence of hydrogen peroxide on the chloride-chlorate reaction rate.

Conditions: 25°C; 2-M H_2SO_4.

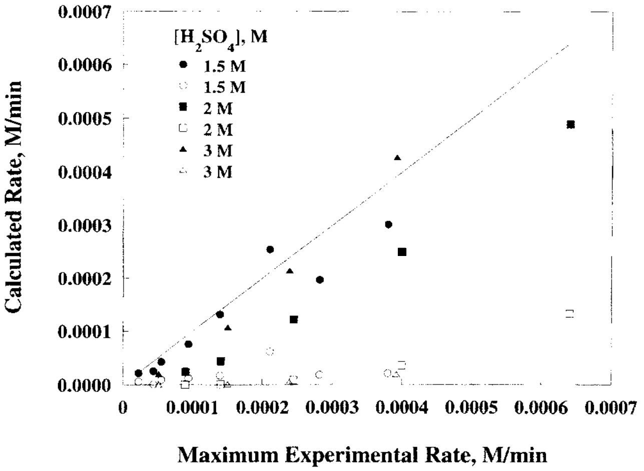


Figure 5. Parity plot.

Legend: filled symbols, calculated by Eq. 16; empty symbols, calculated by Eq. 8.

Figure 4 is a plot of rates from Column 4 (and from four other series of runs at other constant chloride concentrations) vs. hydrogen peroxide. At each constant chloride concentration, the rates were enhanced by hydrogen peroxide, and approached an upper, asymptotic limit with increasing hydrogen peroxide concentration.

Figure 5 compares these asymptotic rates with rates calculated using the rate expression (Eq. 16) reported by Skrabal and Schreiner (1935), and Eq. 8, reported by Hong et al. (1967). The plot also includes asymptotic rates determined in two additional series of runs at 1.5- and 3-M sulfuric acid. In applying Eq. 16, values of the Hammett function h_0 were obtained from Rochester (1970). Values of h_- were obtained from Indu et al. (1991). For the present study, the pertinent values of h_0 and h_- are, respectively, 3.63 and 1.48 for 1.5-M H_2SO_4, 7.08 and 2.38 for 2-M H_2SO_4, and 23.44 and 10.96 for 3-M H_2SO_4. To account for the increase in effective acidity by the dehydrating effect of sodium ions, each of the acidity functions was multiplied by the factor $10^{0.12[Na^+]}$, where the sodium concentration equals the sum of sodium chlorate and sodium chloride concentrations in the reacting solutions. Indu et al. (1991) showed that this factor accounts for the effect of sodium ions on h_- for sodium ion concentrations up to 3 M. Indu et al. also showed that there is an approximately linear relationship between the values of h_0 and h_-. For this reason, we made the assumption that sodium ions have the same enhancing effect on h_0 as on h_-. For example, a 2-M concentration of sodium chlorate in sulfuric acid enhances h_0 and h_- of the acid, each by a factor of $10^{0.24}$, or 1.73.

Figure 5 shows that the asymptotic rates are in reasonably good agreement with the predictions of Eq. 16. On average, the calculated rates are lower than experimental rates by a factor of about 1.6. The best fit of the data would be achieved if the rate constant in Eq. 16 were 7.2×10^{-5} instead of 4.5×10^{-5}. By comparison, Eq. 8 predicts much lower rates. On average, the calculated rates are lower than experimental rates by a factor of 107. The best fit of the data would be achieved if the rate constant in Eq. 8 were 38.5 instead of 0.36.

These results underscore our earlier observation that hydrogen peroxide enhanced the chlorine dioxide rate to a much greater extent than we could attribute to the elimination of chlorine inhibition. The fact that there was reasonable agreement between the experimental rates and Eq. 16 suggests that hydrogen peroxide intruded into the chloride-chlorate mechanism at the same step as arsenious oxide intruded in the experiments of Skrabal and Schreiner (1935); however, in contrast to arsenious oxide, the intrusion by hydrogen peroxide created a new pathway to chlorine dioxide. (In Figure 5, we cannot explain why the calculated and experimental rates at 1.5- and 3-M sulfuric acid are in better agreement than those at 2-M sulfuric acid; we will point out, however, that a small error, say 0.1, in the value of an acidity function, H_0 and H_-, would affect the calculated rate by 25%.)

These results suggest that hydrogen peroxide reacted rapidly with the intermediate Cl_2O_2 produced in reaction 11 by one or more steps that sum to the overall stoichiometry

$$2Cl_2O_2 + H_2O_2 \rightarrow 2ClO_2 + O_2 + 2H^+ + 2Cl^- \qquad (19)$$

The new path includes reactions 9, 10, 11 and 19, which sum to the stoichiometry of reaction 1.

Figure 6 is a logarithmic plot of the asymptotic rates vs. chlorate concentration that shows a chlorate order of 1.1, in agreement with Eq. 16. In developing Figure 6, it was necessary to conduct all experiments at the same effective acidity. Hong et al. (1967) have shown that the dehydrating effect of sodium ions changes the effective acidity of solutions. To correct for this effect, all solutions were adjusted to the same sodium ion concentration by adding sodium nitrate. The total sodium ions from sodium chlorate, sodium chloride, and sodium nitrate in these runs was constant at 2.1 M. Hong et al. (1967) also reported that nitrate anions had no effect on effective acidity.

Figure 7 is a logarithmic plot of the asymptotic rates vs. chloride concentration, showing that chloride order is about 0.7. This order is also in approximate agreement with Eq. 16, but is sufficiently different to suggest that there may be other factors influencing the kinetics that were not identified in this study.

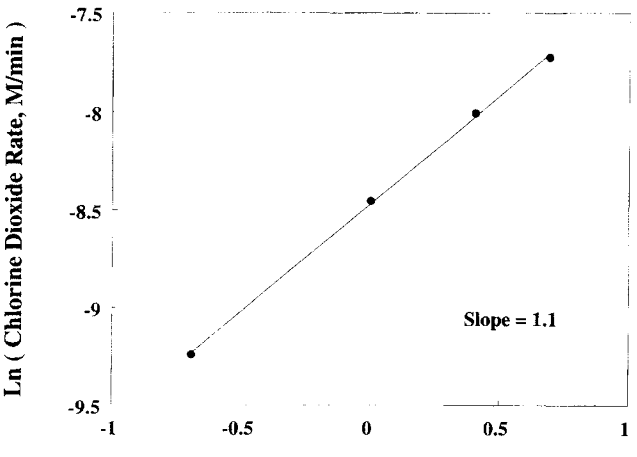


Figure 6. Chlorate reaction order.

Conditions 25°C; 2-M H_2SO_4; 0.05 M NaCl; 0.47-M H_2O_2; sodium ion concentration adjusted to 2.1 M with $NaNO_3$.

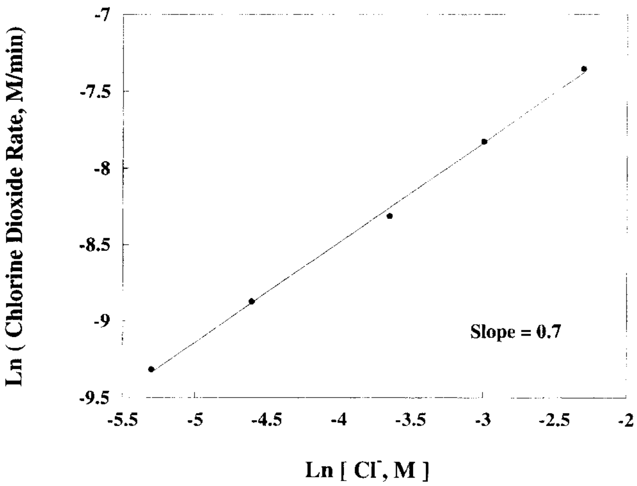


Figure 7. Chloride reaction order.

Conditions: 25°C; 2-M H_2SO_4; 2-M $NaClO_3$.

Speculation on mechanism of reaction of hydrogen peroxide and Cl_2O_2

Cahill and Taube (1952) studied hydrogen peroxide reaction mechanisms in both oxidizing and reducing environments using O^{18}. When hydrogen peroxide reacted as a reducing agent, they found that all O_2 was derived from H_2O_2, and drew the general conclusion that the O-O bond in H_2O_2 was not severed by any oxidizing agent. Baer and Stein (1953) studied the reaction of hydrogen peroxide with ceric salts and proposed the following mechanism to account for their observations

$$H_2O_2 + Ce^{4+} \rightarrow HO_2^* + H^+ + Ce^{3+} \qquad (20)$$

$$HO_2^* + Ce^{4+} \rightarrow O_2 + H^+ + Ce^{3+} \qquad (21)$$

This mechanism agrees with the statements of Cahill and Taube (1952) in that hydrogen peroxide is stepwise oxidized to oxygen via the perhydroxyl radical.

Applying this reasoning, the following is a plausible mechanism for the reaction of Cl_2O_2 with H_2O_2

$$H_2O_2 + Cl_2O_2 \rightarrow ClO_2 + HO_2^* + H^+ + Cl^- \qquad (22)$$

$$HO_2^* + Cl_2O_2 \rightarrow ClO_2 + O_2 + H^+ + Cl^- \qquad (23)$$

which gives the overall stoichiometry of reaction 19.

Conclusions

In a reaction solution consisting of sulfuric acid, sodium chlorate, hydrogen peroxide, and sodium chloride at 25°C chlorine dioxide forms by two reaction paths—(1) reduction of chlorate by hydrogen peroxide, and (2) reduction of chlorate by chloride. Based on earlier work, the first path is believed to occur by a free radical mechanism. We have confirmed that the path is not dependent upon chloride ions, and is also independent of the second path. The second path was explained by a six-step mechanism that involves the intermediate Cl_2O_2. In the absence of hydrogen peroxide, previous workers showed that the rate is inhibited by chlorine. We have shown that hydrogen peroxide increases the rate not only by reacting with chlorine and eliminating the inhibition, but by intruding in an early step of the mechanism, rapidly reducing Cl_2O_2 to chlorine dioxide. Although hydrogen peroxide enhances the rate, there is an upper rate limit that is reached with increasing hydrogen peroxide concentration. This maximum rate agrees reasonably well with predictions of a rate expression based on earlier studies of the chloride-chlorate reaction in the presence of arsenious oxide-$R_{ClO_2} = 4.5 \times 10^{-5}\ h_-\ h_0[Cl^-][ClO_3^-]$. This equation predicts rates that are about a factor of 1.6 below the experimental values. The best fit of this equation occurs when the rate constant is 7.2×10^{-5}.

Acknowledgments

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