

Kinetics and Mechanisms of Aqueous Chlorine Reactions with Chlorite Ion in the Presence of Chloride Ion and Acetic Acid/Acetate Buffer

Jeffrey S. Nicoson and Dale W. Margerum*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

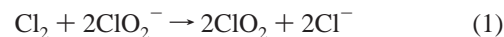
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The kinetics and mechanism of the reaction between Cl_2 and ClO_2^- are studied in acetate buffer by stopped-flow spectrometric observation of ClO_2 formation. The reaction is first-order in $[\text{Cl}_2]$ and $[\text{ClO}_2^-]$, with a rate constant of $k_1 = (5.7 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C. Nucleophilic attack by ClO_2^- on Cl_2 , with Cl^+ transfer to form ClOClO and Cl^- , is proposed as the rate-determining step. A possible two-step electron-transfer mechanism for Cl_2 and ClO_2^- is refuted by the lack of ClO_2 suppression. The yield of ClO_2 is much less than 100%, due to the rapid reactions of the metastable ClOClO intermediate via two competing pathways. In one path, ClOClO reacts with ClO_2^- to form 2ClO_2 and Cl^- , while in the other path it hydrolyzes to give ClO_3^- and Cl^- . The observed rate constant also is affected by acetate-assisted hydrolysis of Cl_2 . The rate of Cl_2 loss is suppressed as the concentration of Cl^- increases, due to the formation of Cl_3^- . In excess ClO_2^- , a much slower formation of ClO_2 is observed after the initial Cl_2 reaction, due to the presence of HOCl , which reacts with H^+ and Cl^- to re-form steady-state levels of Cl_2 .

Introduction

Reactions of oxochlorine species that involve a Cl_2O_2 intermediate were first discussed by Taube and Dodgen.¹ Emmenegger and Gordon² supported the existence of such an intermediate in their study of the reaction between ClO_2^- and $\text{HOCl}/\text{Cl}_2(\text{aq})$. The emergence of chlorine dioxide as an alternative oxidant in water treatment^{3,4} and pulp bleaching⁵ and the development of chlorite-based oscillating reactions^{6–11} has stimulated continued discussion about the formation and rapid reactions of XOCIO (or XClO_2) intermediates ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).^{12–16} The stoichiometry for the reaction between

Cl_2 and ClO_2^- is shown in eqs 1 and 2.^{1,2} Acidic conditions and high concentrations of ClO_2^- favor the formation of ClO_2 , while basic conditions and low concentrations of ClO_2^- favor the formation of ClO_3^- .



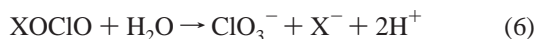
Jia et al.¹⁵ and Furman and Margerum¹⁴ have shown that the reactions of HOCl and HOBr with ClO_2^- form an XOCIO intermediate by halogen cation (X^+) transfer (eqs 3–4). These studies have also provided detailed schemes for the rapid reactions of ClOClO and BrOCIO to produce ClO_2 and ClO_3^- (eqs 5 and 6).



* Author to whom correspondence should be addressed. E-mail: margerum@purdue.edu.

- (1) Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330–3336.
- (2) Emmenegger, F.; Gordon, G. *Inorg. Chem.* **1967**, *6*, 633–635.
- (3) Aieta, E. M.; Roberts, P. V. In *Water Chlorination*; Jolley, R. L., Bull, R. J., Davis, W. P., Katz, S., Roberts, M. H., Jr., Jacobs, V. A., Eds.; Lewis Publishers: Chelsea, MI, 1985; Vol. 5, pp 783–794.
- (4) Vel Leitner, K. N.; De Laat, J.; Dore, M.; Suty, H. In *Disinfection By-Products in Water Treatment*; Minear, R. A., Amy, G. L., Eds.; CRC Press: Boca Raton, FL, 1996; pp 393–407.
- (5) Hart, P. W.; Hsieh, J. S. *AIChE Symp. Ser. No. 319* **1998**, *94*, 73–81.
- (6) Grant, J. L.; De Kepper, P.; Epstein, I. R.; Kustin, K.; Orban, M. *Inorg. Chem.* **1982**, *21*, 2192–2196.
- (7) Epstein, I. R.; Kustin, K. *J. Phys. Chem.* **1985**, *89*, 2275–2282.
- (8) Valdes-Aguilera, O.; Boyd, D. W.; Epstein, I. R.; Kustin, K. *J. Phys. Chem.* **1986**, *90*, 6696–6702.
- (9) Rabai, G.; Beck, M. T. *Inorg. Chem.* **1987**, *26*, 1195–1199.
- (10) Peintler, G.; Nagypal, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954–2958.
- (11) Rabai, G.; Orban, M. *J. Phys. Chem.* **1993**, *97*, 5935–5939.

- (12) Aieta, E. M.; Roberts, P. V. *Environ. Sci. Technol.* **1986**, *20*, 50–55.
- (13) Gordon, G.; Tachiyashiki, S. *Environ. Sci. Technol.* **1991**, *25*, 468–474.
- (14) Furman, C. S.; Margerum, D. W. *Inorg. Chem.* **1998**, *37*, 4321–4327.
- (15) Jia, Z.; Margerum, D. W.; Francisco, J. S. *Inorg. Chem.* **2000**, *39*, 2614–2620.
- (16) Fabian, I.; Gordon, G. *Inorg. Chem.* **1992**, *31*, 2144–2150.



The reaction between Cl_2 and ClO_2^- is much more rapid than the corresponding HOCl and HOBr reactions. Aieta and Roberts¹² estimated the rate constant for the $\text{Cl}_2/\text{ClO}_2^-$ reaction to be $k = 1.62 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (20 °C, $\mu = 0 \text{ M}$) using mass-transfer theory for the difference in absorption of $\text{Cl}_2(\text{g})$ into a ClO_2^- solution versus absorption into an HCl solution. However, in their experiments, impure NaClO_2 (78–96%) was used, there was no pH control, and the effect of Cl_3^- was ignored.

Historically, the reactions of Br_2 and Cl_2 with ClO_2^- have been assumed to follow the same general mechanism of HOBr and HOCl. However, Toth and Fabian¹⁷ have recently shown an alternative mechanism for the reaction between Br_2 and ClO_2^- that proceeds by electron transfer rather than Br^+ transfer. Detailed kinetic data are required to determine whether the Cl_2 reaction with ClO_2^- proceeds by Cl^+ transfer or electron transfer. The present work uses stopped-flow spectroscopy to study the $\text{Cl}_2/\text{ClO}_2^-$ reaction to obtain a more reliable rate constant and determine the mechanism of the reaction. Chlorine hydrolysis pathways that compete with the reaction are discussed, along with a comparison of the reactivity and mechanisms of ClO_2^- with Cl_2 , HOCl, HOBr, and Br_2 .

Experimental Section

Reagents. Doubly deionized, distilled water was used for all solution preparation. Stock solutions of NaClO_4 were recrystallized in water before use. ClO_2 solutions,¹⁴ NaOCl solutions,¹⁴ and “Br⁻-free” NaCl solutions¹⁸ were prepared as previously reported. The hypochlorite solutions were standardized spectrophotometrically at 292 nm ($\epsilon_{\text{OCl}^-} = 362 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁴ Commercial sodium chlorite was purified as previously reported.¹⁴ The ClO_2^- solutions were standardized spectrophotometrically at 260 nm ($\epsilon_{\text{ClO}_2^-} = 154 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁴ Perchloric acid, prepared from 70% HClO_4 , was used to acidify NaOCl solutions in the preparation of Cl_2 solutions.

Methodology and Instrumentation. The measured pH was converted to $\text{p}[\text{H}^+]$ on the basis of electrode calibration at $\mu = 1.0 \text{ M}$. NaClO_4 or NaCl was used to control ionic strength. A T-mixer was used to mix solution A (containing Cl^- and H^+) and solution B (containing Cl^- and OCl^-) to confine the resulting Cl_2 solution within a syringe. The total chlorine concentration is defined as $[\text{Cl}_2]_{\text{T}} = [\text{Cl}_2] + [\text{Cl}_3^-] + [\text{HOCl}]$. On the 0–50 ms time scale, HOCl is unreactive,¹⁵ and its contribution to total chlorine is neglected. The reaction was initiated by mixing the A + B solution with solution C (containing Cl^- , ClO_2^- , and HOAc/OAc^-) and followed at 359 nm for ClO_2 formation ($\epsilon_{359} = 1230 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁴ The concentration of HClO_2 ($\text{p}K_{\text{a}} = 1.61$)¹⁹ is negligible under the conditions of this study ($\text{p}[\text{H}^+] = 3.6\text{--}6.0$). When only chlorine hydrolysis pathways were studied, the reaction was followed at 240 nm for the loss of Cl_3^- ($\epsilon_{240} = 7000 \text{ M}^{-1} \text{ cm}^{-1}$).²⁰ Kinetic data were obtained by using

an Applied PhotoPhysics stopped flow spectrophotometer (APPSF) model SX-18MV with an optical path length of 0.962 cm. The APPSF was calibrated to determine the mixing efficiency of the instrument using well-characterized chemical reactions such as $\text{IrCl}_6^{2-}/\text{Fe}(\text{CN})_6^{4-}$, $\text{NH}_2\text{Cl}/\text{I}^-$, and the Dushman reaction.^{21–23} The observed rate constants were corrected for the mixing efficiency of the APPSF on the basis of eq 7

$$k_{\text{r}} = \left(\frac{1}{k_{\text{obsd}}} - \frac{1}{k_{\text{mix}}} \right)^{-1} \quad (7)$$

and the dead time of the instrument (t_{d}) was determined from eq 8.

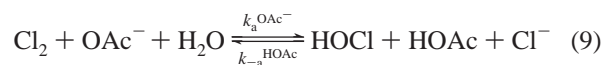
$$t_{\text{d}} = - \frac{\ln\left(\frac{\Delta A_{\text{obsd}}}{\Delta A_{\text{pred}}}\right)}{k_{\text{obsd}}} \quad (8)$$

At a drive pressure of 120 psi, the value of k_{mix} is $4620 \pm 120 \text{ s}^{-1}$ and t_{d} is $2.0 \pm 0.1 \text{ ms}$. However, visual inspection showed that t_{d} varied between 2 and 3 ms over the course of this study, so each stopped-flow trace was examined individually to determine the starting point of the first-order fit.

Results and Discussion

Competition between Cl_2 Hydrolysis and the $\text{Cl}_2/\text{ClO}_2^-$ Reaction. Prior to mixing with the ClO_2^- solution, the chlorine solution is typically kept at pH 2 and 1.0 M Cl^- . Under these conditions, the solution consists of 78% Cl_2 , 14% Cl_3^- , and 8% HOCl. The ClO_2^- solution is buffered at pH 3.6–6.0 with HOAc/OAc^- in order to avoid reactions of HClO_2 . Upon mixing the chlorine solution with the buffered ClO_2^- solution, the chlorine solution experiences a rapid increase in pH. The rapid increase in pH causes a shift in the Cl_2/HOCl equilibrium toward formation of HOCl. However, this equilibrium is not established instantaneously compared to the $\text{Cl}_2/\text{ClO}_2^-$ reaction. The loss of Cl_2 through hydrolysis competes with the $\text{Cl}_2/\text{ClO}_2^-$ reaction, and the kinetic analysis must account for this. The reverse reaction of HOCl, Cl^- , and H^+ to form Cl_2 is much slower than the $\text{Cl}_2/\text{ClO}_2^-$ reaction. Therefore, the concentration of HOCl in the chlorine solution will not affect the rate of the reaction.

Lifshitz and Perlmutter-Hayman²⁴ and Wang and Margerum²⁵ showed that Cl_2 hydrolysis in acetic acid/acetate buffer proceeds through two parallel pathways: an acetate-assisted hydrolysis pathway²⁴ (eq 9)



and a conventional hydrolysis pathway²⁵ (eq 10).



(17) Toth, Z.; Fabian, I. *Inorg. Chem.* **2000**, *39*, 4608–4614.
 (18) Jia, Z.; Margerum, D. W. *Inorg. Chem.* **1999**, *38*, 5374–5378.
 (19) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4, p 134.
 (20) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 5872–5878.

(21) Baron, C. D.; Margerum, D. W. Unpublished results.
 (22) Dickson, P. N.; Margerum, D. W. *Anal. Chem.* **1986**, *58*, 3153–3158.
 (23) Xie, Y.; McDonald, M. R.; Margerum, D. W. *Inorg. Chem.* **1999**, *38*, 3938–3940.
 (24) Lifshitz, A.; Perlmutter-Hayman, B. *J. Phys. Chem.* **1961**, *65*, 753–757.
 (25) Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 1050–1055.

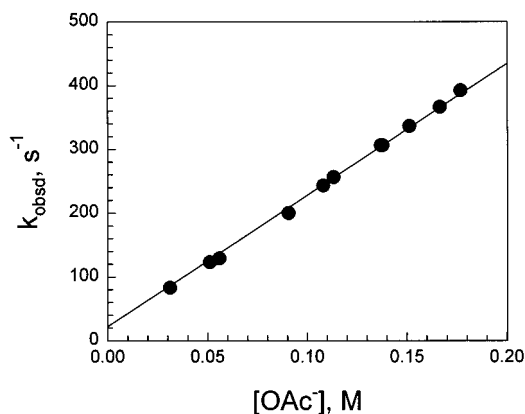
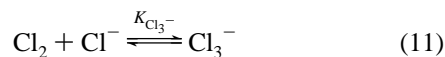


Figure 1. Dependence of the first-order rate constant of Cl_2 hydrolysis on acetate concentration. $[\text{Cl}_2]_{\text{T}} = 0.43 \text{ mM}$, $[\text{Cl}^-] = 0.78\text{--}0.96 \text{ M}$, $\text{p}[\text{H}^+] = 4.42(3)$, $\mu = 1.0 \text{ M}$ (NaCl), $25.0 \text{ }^\circ\text{C}$, $\lambda = 240 \text{ nm}$.

The values of $k_{\text{a}}^{\text{H}_2\text{O}}$ and $k_{-\text{a}}^{\text{H}^+}$ obtained by Wang and Margerum,²⁵ 22.3 s^{-1} and $21\,400 \text{ M}^{-2} \text{ s}^{-1}$, respectively, were determined at $25.0 \text{ }^\circ\text{C}$ with an ionic strength of 0.50 M . The $k_{\text{a}}^{\text{H}_2\text{O}}$ value is also valid at $\mu = 1.0 \text{ M}$, since both species are uncharged. However, the value of $k_{-\text{a}}^{\text{H}^+}$ will change with ionic strength and can be extrapolated using the Debye–Hückel–Brønsted–Davies relationship.²⁵ The value of $k_{-\text{a}}^{\text{H}^+}$ at $m = 1.0 \text{ M}$ is $22\,900 \text{ M}^{-2} \text{ s}^{-1}$.

Since Lifshitz and Perlmutter-Hayman²⁴ studied the reaction in eq 9 at $9.5 \text{ }^\circ\text{C}$ with no ionic strength control, the rate constants for the acetate-assisted pathway under the conditions of this study ($25.0 \text{ }^\circ\text{C}$, $m = 1.0 \text{ M}$) were measured. The acetate concentration is determined using $\text{p}K_{\text{a}}^{\text{HOAc}} = 4.61$.²⁶ A plot of k_{obsd} vs $[\text{OAc}^-]$ has a slope of $k_{\text{a}}^{\text{OAc}^-} = (2.06 \pm 0.03) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and an intercept of $k_{\text{a}}^{\text{H}_2\text{O}} = 22 \pm 4 \text{ s}^{-1}$ (Figure 1). The $k_{\text{a}}^{\text{H}_2\text{O}}$ value agrees with that obtained by Wang and Margerum.²⁵ The value of $k_{-\text{a}}^{\text{HOAc}}$ under these conditions can be calculated from $k_{-\text{a}}^{\text{HOAc}} = (k_{\text{a}}^{\text{OAc}^-} k_{-\text{a}}^{\text{H}^+} / K^{\text{HOAc}} k_{\text{a}}^{\text{H}_2\text{O}}) = 52 \text{ M}^{-2} \text{ s}^{-1}$. All observed rate constants for the reaction of Cl_2 with ClO_2^- are corrected for hydrolysis of Cl_2 .

Trichloride Suppression. At $\text{p}[\text{H}^+] = 4.5$, large concentrations of Cl^- are required to shift the equilibrium in eq 10 toward formation of Cl_2 . In this study, the concentration of Cl^- is $0.5\text{--}1.0 \text{ M}$. Under these conditions, an appreciable amount of Cl_3^- is in rapid equilibrium with Cl_2 , according to eq 11 ($K_{\text{Cl}_3^-} = 0.18 \text{ M}^{-1}$).²⁰ Since NaCl is also used to control ionic strength, the concentration of Cl^- varies from one reaction to another.



Therefore, k_{obsd} is corrected for the fraction of total chlorine ($[\text{Cl}_2]_{\text{T}} = [\text{Cl}_2] + [\text{Cl}_3^-]$) present as Cl_2 . Combining the correction for Cl_3^- , hydrolysis, and mixing efficiency, a corrected pseudo-first-order rate constant for the $\text{Cl}_2/\text{ClO}_2^-$ reaction is defined in eq 12.

$$k_{\text{corr}} = k_{\text{r}}(1 + K_{\text{Cl}_3^-}[\text{Cl}^-]) - k_{\text{a}}^{\text{OAc}^-}[\text{OAc}^-] - k_{\text{a}}^{\text{H}_2\text{O}} \quad (12)$$

(26) Portanova, R. et al. *Inorg. Chim. Acta* **1974**, *8*, 233–240.

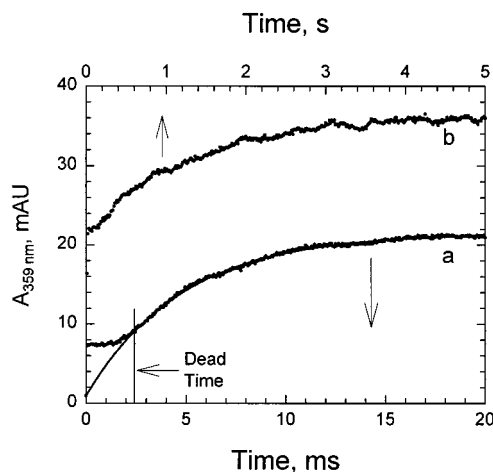


Figure 2. (a) Absorbance versus time for the $\text{Cl}_2/\text{ClO}_2^-$ reaction, where 35% of the reaction has occurred in the dead time (2.5 ms). The solid line (only visible when $t < 2.5 \text{ ms}$) is the exponential fit to the data. (b) Absorbance versus time for the subsequent HOCl reaction. $[\text{Cl}_2]_{\text{T}} = 20 \text{ } \mu\text{M}$, $[\text{ClO}_2^-] = 0.300 \text{ mM}$, $[\text{OAc}^-]_{\text{T}} = 58 \text{ mM}$, $[\text{Cl}^-] = 0.50 \text{ M}$, $\text{p}[\text{H}^+] = 4.44$, $\mu = 1.0 \text{ M}$ (NaClO_4), $25.0 \text{ }^\circ\text{C}$, $\lambda = 359 \text{ nm}$.

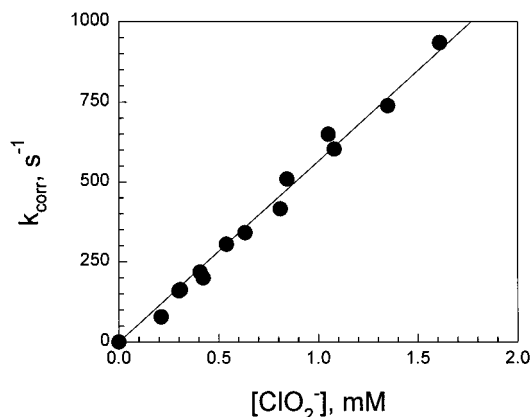
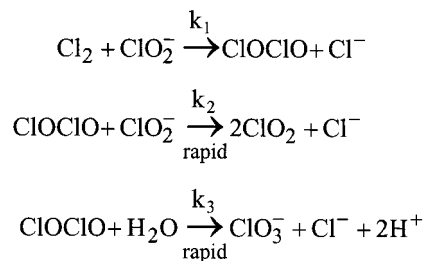


Figure 3. Dependence of the first-order rate constant for the $\text{Cl}_2/\text{ClO}_2^-$ reaction on chlorite concentration. $[\text{Cl}_2]_{\text{T}} = 15\text{--}85 \text{ } \mu\text{M}$, $[\text{OAc}^-]_{\text{T}} = 0.05\text{--}0.43 \text{ M}$, $[\text{Cl}^-] = 0.50\text{--}1.0 \text{ M}$, $\text{p}[\text{H}^+] = 4.20\text{--}6.04$, $\mu = 1.0 \text{ M}$ (NaCl), $25.0 \text{ }^\circ\text{C}$, $\lambda = 359 \text{ nm}$.

Kinetics and Mechanism. Under typical conditions, the reaction between Cl_2 and ClO_2^- goes to completion within $10\text{--}20 \text{ ms}$. The dead time on the APPSF instrument is $2\text{--}3 \text{ ms}$, so the first $25\text{--}50\%$ of the reaction cannot be followed. Upon mixing under pseudo-first-order conditions (ClO_2^- in at least 10-fold excess of Cl_2), the reaction shows a first-order increase in absorbance due to the formation of ClO_2 , indicating a first-order dependence on $[\text{Cl}_2]$ (Figure 2a). After correction of k_{obsd} for mixing, Cl_3^- , and hydrolysis pathways, k_{corr} values are independent of $\text{p}[\text{H}^+]$, $[\text{OAc}^-]_{\text{T}}$, and $[\text{Cl}^-]$. This indicates that acids, bases, and chloride ion do not contribute to the reaction during the rate-determining step. As the concentration of ClO_2^- increases, k_{corr} increases with a first-order dependence on $[\text{ClO}_2^-]$ (Figure 3). The least-squares slope of the data gives a rate constant of $k_1 = (5.7 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at $25.0 \text{ }^\circ\text{C}$ for the reaction of Cl_2 with ClO_2^- . This rate constant is 35 times larger than the previously estimated value by Aieta and Roberts.¹²

Using the known behavior of the system with respect to $[\text{ClO}_2^-]$, $[\text{OAc}^-]$, $[\text{Cl}^-]$, and $[\text{H}^+]$, a detailed mechanism is

Scheme 1. Proposed Mechanism for the Reaction of Chlorine and Chlorite Ion



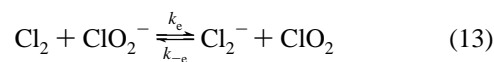
proposed in Scheme 1. Cl_2 reacts with ClO_2^- in the rate-determining step by transfer of Cl^+ to form ClOClO and Cl^- . Since there is no inhibition of the rate by Cl^- (other than from formation of unreactive Cl_3^- , for which the observed rate constant has already been corrected) and a first-order dependence in $[\text{ClO}_2^-]$ is observed, the ClOClO intermediate must react rapidly with ClO_2^- to produce ClO_2 or rapidly hydrolyze to produce ClO_3^- . The yield of ClO_2 (determined from ΔA , $\epsilon_{359} = 1230 \text{ M}^{-1} \text{ cm}^{-1}$) is typically 20–60%, according to the stoichiometry in eq 1, but is uncertain due to Cl_2 volatility and the small absorbance changes ($\Delta A = 6\text{--}100 \text{ mAU}$). In a competing reaction, Cl_2 hydrolyzes to form HOCl . At 0.3 mM ClO_2^- and 0.05 M OAc^- , this hydrolysis accounts for the loss of 30% of the initial Cl_2 . However, if the Cl_2 lost to hydrolysis is taken into consideration, the yield of ClO_2 is never greater than 80%. Therefore, a significant amount of ClO_3^- must be formed from the oxidation of ClO_2^- by Cl_2 under these conditions. Details about the formation of ClO_3^- and ClO_2 from the ClOClO intermediate under similar conditions have been discussed by Jia et al.¹⁵

Rate constants for the reaction of ClOClO (or Cl_2O_2) with ClO_2^- have been postulated in several studies^{9,11,16} of complex chlorite reactions for the purpose of making accurate simulations of their behavior. Values ($\text{M}^{-1} \text{ s}^{-1}$) of 1×10^4 (Rabai and Beck),⁹ 5×10^8 (Fabian and Gordon),¹⁶ and 2×10^5 (Rabai and Orban)¹¹ have been suggested. Our kinetic study of the $\text{Cl}_2/\text{ClO}_2^-$ system shows that the rate constant for the reaction between ClOClO and ClO_2^- must be $\gg 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. This inequality is necessary to have a first-order dependence in $[\text{ClO}_2^-]$. Thus, in Scheme 1, the k_1 step is the rate-determining step and the reactions of ClOClO (k_2 and k_3) are rapid. Therefore, the rate constant used by Fabian and Gordon is plausible.

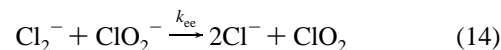
Atom Transfer vs Electron-Transfer Mechanism. The proposed mechanism (Scheme 1) indicates a nucleophilic attack on Cl_2 by an oxygen atom on ClO_2^- , followed by the transfer of Cl^+ and elimination of Cl^- to give ClOClO . The rapid reactivity of Cl_2 in this case is attributed to its ability to behave as an electrophile.

The reaction between Br_2 and ClO_2^- , as reported by Toth and Fabian,¹⁷ proceeds through two successive electron-transfer steps. The first step involves the transfer of an electron from ClO_2^- to Br_2 to form ClO_2 and Br_2^- . In the second step, Br_2^- reacts with another ClO_2^- to form ClO_2 and 2Br^- . Evidence of ClO_2 suppression in their reaction rate supports the electron-transfer mechanism.

Chlorine is also a strong oxidizing agent, and the possibility exists for an electron to transfer from ClO_2^- to Cl_2 to form ClO_2 and a reactive Cl_2^- species (eq 13).



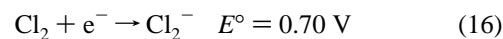
A second electron transfer would yield 2Cl^- and another ClO_2 (eq 14).



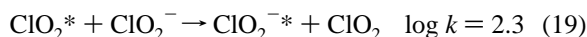
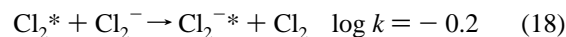
The steady-state rate expression for this mechanism would have a complex order in $[\text{ClO}_2^-]$ and a $[\text{ClO}_2]$ term in the denominator (eq 15).

$$\frac{-d[\text{Cl}_2]}{dt} = \frac{k_e k_{ee} [\text{ClO}_2^-]^2 [\text{Cl}_2]}{k_{-e} [\text{ClO}_2] + k_{ee} [\text{ClO}_2^-]} \quad (15)$$

Since the experimental data show a first-order dependence in $[\text{ClO}_2^-]$, the reaction between Cl_2 and ClO_2^- (k_e) must be the rate-determining step if a pathway such as this contributes to k_{obsd} . Using reduction potentials²⁷ (eqs 16 and 17)



and self-exchange rate constants²⁸ (eqs 18 and 19),



Marcus theory predicts the rate constant for electron transfer between Cl_2 and ClO_2^- to be $\sim 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$. This is more than 6 orders of magnitude smaller than the rate constant calculated from experimental data.

The simplified Marcus equation used to determine the rate constant assumes that the work required to bring the two molecules together is negligible, which is a safe assumption for a reaction between a neutral and a -1 species in a high ionic strength medium. Another assumption requires that the reaction is an outer-sphere electron-transfer process. While this is appropriate for many reactions between metal complexes, nonmetal redox reactions are more difficult to predict due to the ease of interaction between the two reactants. Any orbital overlap during electron-transfer results in a larger rate constant than simplified Marcus theory predicts.^{29–31} However, the large discrepancy between the

(27) Stanbury, D. M. *Advances in Inorganic Chemistry*; Academic: New York, 1989; Vol. 33, pp 69–138.

(28) Stanbury, D. M. *Advances in Chemistry Series: Electron-Transfer Reactions*; American Chemical Society: Washington, DC, 1997; pp 165–182.

(29) Stanbury, D. M.; de Maine, M. M.; Goodloe, G. *J. Am. Chem. Soc.* **1989**, *111*, 5496–5498.

(30) Stanbury, D. M.; Martinez, R.; Tseng, E.; Miller, C. E. *Inorg. Chem.* **1988**, *27*, 4277–4280.

(31) Bennett, L. E.; Warlop, P. *Inorg. Chem.* **1990**, *29*, 1975–1981.

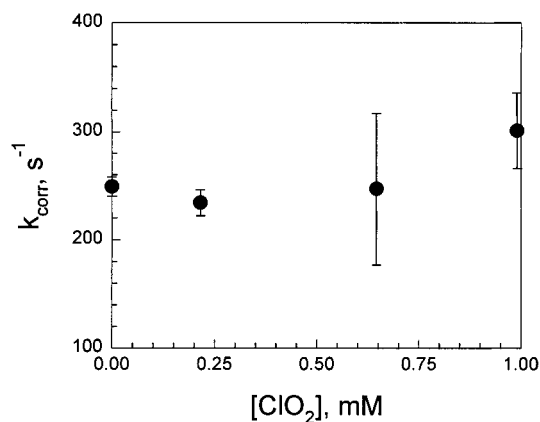


Figure 4. Lack of dependence of the first-order rate constant of the $\text{Cl}_2/\text{ClO}_2^-$ reaction on ClO_2 concentration. $[\text{Cl}_2]_{\text{T}} = 26 \mu\text{M}$, $[\text{ClO}_2^-] = 0.572 \text{ mM}$, $[\text{OAc}^-]_{\text{T}} = 0.102 \text{ M}$, $[\text{Cl}^-] = 0.95 \text{ M}$, $\text{p}[\text{H}^+] = 4.27$, $\mu = 1.0 \text{ M}$ (NaCl), $25.0 \text{ }^\circ\text{C}$, $\lambda = 359 \text{ nm}$. Error bars represent one standard deviation.

estimated Marcus value and the experimentally determined rate constant suggests that electron-transfer is an unlikely pathway.

Experimentally, the electron-transfer mechanism is tested by varying the concentration of ClO_2 . The following argument is based on the expected behavior if the reaction proceeds through an electron-transfer mechanism, as in eqs 13 and 14. The experimental value for the forward path is $k_e = 5.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and the equilibrium constant for the electron-transfer calculated from the reduction potentials is $K_e = 10^{-3.96}$. The reverse path would then have $k_{-e} = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, close to the diffusion limit. The steady-state expression requires $k_{-e}[\text{ClO}_2] \ll k_{ee}[\text{ClO}_2^-]$ to observe a first-order dependence in $[\text{ClO}_2^-]$ and not observe suppression due to $[\text{ClO}_2]$. The rate constant k_{ee} can be no larger than $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the diffusion limit for a reaction between two -1 species. With $k_{-e} \cong k_{ee}$, this simplifies the condition to $[\text{ClO}_2] \ll [\text{ClO}_2^-]$. Data have been taken with an initial added $[\text{ClO}_2]$ in excess of $[\text{ClO}_2^-]$, and no suppression is observed (Figure 4). According to the previous argument, when $[\text{ClO}_2] = [\text{ClO}_2^-]$, at least a 50% decrease in the observed rate constant is expected, if the reaction proceeds by electron transfer. Hence, the kinetic data indicate that the dominant pathway for the $\text{Cl}_2/\text{ClO}_2^-$ reaction must be through Cl^+ transfer. The lack of ClO_2 suppression in the $\text{Cl}_2/\text{ClO}_2^-$ reaction is contrary to the behavior of the $\text{Br}_2/\text{ClO}_2^-$ reaction, where Toth and Fabian¹⁷ found that the initial rate of the reaction decreased by a factor of 50 when $[\text{ClO}_2]$ was increased from 0 to 1 mM.

For both Cl_2 and Br_2 reactions with ClO_2^- , adduct formation to give BrBrOClO^- and ClClOClO^- are reasonable pathways. Experimental evidence suggests that in one case Br_2^- and ClO_2 are formed, while in the other Cl^- and ClOClO are formed. This is followed by more rapid reactions of the respective intermediates, Br_2^- or ClOClO . The greater electrophilicity of Cl_2 compared to Br_2 and the preference for Cl^- versus Br^- elimination appear to favor the Cl^+ -transfer mechanism in the $\text{Cl}_2/\text{ClO}_2^-$ system as opposed to the electron-transfer mechanism in the $\text{Br}_2/\text{ClO}_2^-$ system.

HOCl Reaction with ClO_2^- in the Presence of H^+ and Cl^- . After the rapid Cl_2 reaction with ClO_2^- , a slower

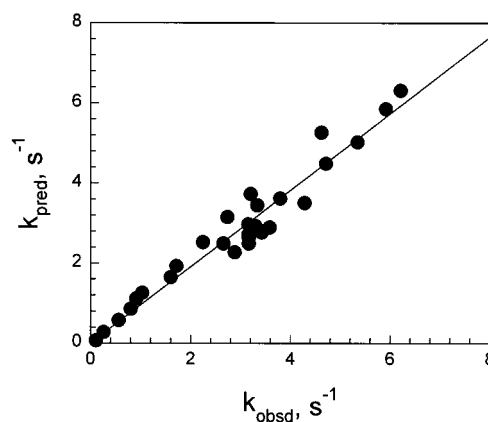


Figure 5. Observed versus predicted rate constants (eq 20) for the HOCl reaction with ClO_2^- via Cl_2 formation. $[\text{Cl}_2]_{\text{T}} = 20\text{--}80 \mu\text{M}$, $[\text{OAc}^-]_{\text{T}} = 0.05\text{--}0.10 \text{ M}$, $[\text{Cl}^-] = 0.79\text{--}0.99 \text{ M}$, $\text{p}[\text{H}^+] = 3.65\text{--}6.04$, $\mu = 1.0 \text{ M}$ (NaCl), $25.0 \text{ }^\circ\text{C}$, $\lambda = 359 \text{ nm}$.

increase in absorbance occurs with $k_{\text{obsd}} = 0.1\text{--}6 \text{ s}^{-1}$ (Figure 2b). Small amounts of HOCl are present initially in the Cl_2 solution (typically 8% of the total chlorine) and HOCl is also produced from the hydrolysis of Cl_2 . The direct reaction of HOCl with ClO_2^- is much too slow to account for the observed reaction rate.¹⁵ Due to the rapid initial reaction with ClO_2^- , the concentration of Cl_2 is depleted in 10–50 ms. As this reaction reaches completion, the Cl_2/HOCl equilibrium will adjust to form more Cl_2 (the reverse reaction in eqs 9 and 10). The formation of Cl_2 from HOCl is much slower than the initial reaction, and this maintains a steady-state amount of Cl_2 that can react rapidly with ClO_2^- to form additional ClO_2 . The mechanism for HOCl reacting through general-acid-assisted pathways to form a steady-state Cl_2 species has a rate expression as shown in eq 20.

$$k_{\text{pred}} = \frac{k_1[\text{ClO}_2^-][\text{Cl}^-](k_{-a}^{\text{HOAc}}[\text{HOAc}] + k_{-a}^{\text{H}^+}[\text{H}^+])}{k_1[\text{ClO}_2^-] + k_a^{\text{OAc}^-}[\text{OAc}^-] + k_a^{\text{H}_2\text{O}}} \frac{1}{1 + K_{\text{Cl}_3}[\text{Cl}^-]} \quad (20)$$

Using the k_1 , $k_a^{\text{OAc}^-}$, and k_{-a}^{HOAc} values determined from this work and the K_{Cl_3} , $k_a^{\text{H}_2\text{O}}$, and $k_{-a}^{\text{H}^+}$ (extrapolated to $\mu = 1.0 \text{ M}$) from Wang and Margerum,²⁵ the value of k_{obsd} for this slower reaction can be predicted and compared to the experimental observed rate constant. The data for k_{pred} vs k_{obsd} with various concentrations of ClO_2^- , HOAc/OAc⁻, and H^+ fall on a straight line with a slope of 0.95 ± 0.04 (Figure 5), which indicates that the proposed rate expression and previously determined rate constants²⁵ accurately predict the observed reaction. This also clearly shows that HOCl is not in rapid preequilibrium with Cl_2 and does not affect the kinetics of the initial $\text{Cl}_2/\text{ClO}_2^-$ reaction. The data show that, in the presence of Cl^- and H^+ , HOCl reacts through a Cl_2 intermediate much faster than through direct reaction with ClO_2^- .

Comparison of the Reactivity and Mechanism of Cl_2 vs HOCl and HOBr. The reaction mechanisms for HOCl¹⁵ and HOBr¹⁴ with ClO_2^- are similar. HOX ($X = \text{Cl}, \text{Br}$) forms an adduct with ClO_2^- that undergoes a general-acid-assisted decomposition to XOCIO (eqs 3 and 4). The XOCIO

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intermediate then reacts in rapid steps to produce ClO_2 and ClO_3^- . The reaction of Cl_2 with ClO_2^- differs from HOCl and HOBr because of the absence of acid assistance. The $\text{Cl}_2/\text{ClO}_2^-$ interaction can be considered to proceed by adduct formation (eq 21)



followed by a loss of Cl^- (eq 22).



Thus, k_1 is a combination of the reactions in eqs 21 and 22. To make a comparison between the reactivity of HOCl ,

HOBr , and Cl_2 , the rate constants for adduct formation with ClO_2^- can be used. For HOCl and HOBr , the rate constants are 1.6 and 97 $\text{M}^{-1} \text{s}^{-1}$, respectively. For Cl_2 , the formation of the adduct must have a rate constant $\geq 5.7 \times 10^5 \text{M}^{-1} \text{s}^{-1}$. Therefore, when reacting with ClO_2^- , the relative electrophilicity (defined as $\log[k_1^x/k_1^{\text{HOCl}}]$, where x is HOCl , HOBr , or Cl_2) for $\text{HOCl}:\text{HOBr}:\text{Cl}_2$ is 0:1.8: ≥ 5.6 .

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Supporting Information Available: Tables of kinetic data and graphs of k_{corr} vs $\text{p}[\text{H}^+]$, $[\text{OAc}^-]$, and $[\text{Cl}^-]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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