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Kinetics and Mechanisms of the Reactions of Hypochlorous Acid, Chlorine, and Chlorine Monoxide with Bromite Ion

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The reaction between BrO_2^- and excess HOCl (p[H$^+$] 6–7, 25.0 °C) proceeds through several pathways. The primary path is a multistep oxidation of HOCl by BrO_2^- to form ClO_3^- and HOBr (85% of the initial 0.15 mM BrO_2^-). Another pathway produces ClO_2 and HOBr (8%), and a third pathway produces BrO_3^- and Cl^- (7%). With excess HOCl concentrations, Cl_2O also is a reactive species. In the proposed mechanism, HOCl and Cl_2O react with BrO_2^- to form steady-state species, $HOClOBrO^-$ and $ClOClOBrO^-$. Acid facilitates the conversion of $HOClOBrO^-$ and $ClOClOBrO^-$ to $HOBrOClO^-$. These reactions require a chainlike connectivity of the intermediates with alternating halogen–oxygen bonding (i.e. $HOBrOClO^-$) as opposed to Y-shaped intermediates with a direct halogen–halogen bond (i.e. $HOBrCl(O)O^-$). The $HOBrOClO^-$ species dissociates into HOBr and ClO_2^- or reacts with general acids to form BrOClO. The distribution of products suggests that BrOClO exists as a BrOClO·HOCl adduct in the presence of excess HOCl. The primary products, ClO_3^- and HOBr, are formed from the hydrolysis of BrOClO·HOCl. A minor hydrolysis path for BrOClO·HOCl gives BrO_3^- and Cl^-. An induction period in the formation of ClO_2 is observed due to the buildup of ClO_2^-, which reacts with BrOClO·HOCl to give 2 ClO_2 and Br^-. Second-order rate constants for the reactions of HOCl and Cl_2O with BrO_2^- are $k_1^{HOCl} = 1.6 \times 10^2$ M^{-1} s^{-1} and $k_1^{Cl_2O} = 1.8 \times 10^5$ M^{-1} s^{-1}. When Cl^- is added in large excess, a Cl_2 pathway exists in competition with the HOCl and Cl_2O pathways for the loss of BrO_2^-. The proposed Cl_2 pathway proceeds by Cl^+ transfer to form a steady-state ClOBrO species with a rate constant of $k_1^{Cl_2} = 8.7 \times 10^5$ M^{-1} s^{-1}.

Introduction

The mechanisms of the redox reactions of ClO_2^- have been studied much more than the corresponding BrO_2^- reactions. The reaction of ClO_2^- with several nonmetal oxidizing agents (HOCl, HOBr, Cl_2) proceeds by X^+ transfer (X = Cl or Br) to form a metastable $XClO_2$ intermediate.[1−3] Taube and Dodgen[4] used ^{38}Cl-labeling experiments to show that the connectivity of the Cl_2O_2 intermediate must be either ClCl(O)O (Y-shaped) or ClOClO (chainlike). Although many authors imply the XCl(O)O structure for these intermediates,[5−8] this work indicates a XOClO structure is preferred.

Furman and Margerum[2] have shown that the reaction of HOBr with ClO_2^- forms a steady-state intermediate, $HOBrOClO^-$ (or $HOBrCl(O)O^-$), that reacts with general acids to form BrOClO (or BrCl(O)O). The reaction of BrOClO with ClO_2^- forms 2 ClO_2 and Br^-, which competes with its hydrolysis to form ClO_3^- and Br^-. The complementary reaction between HOCl and BrO_2^- has been proposed to produce BrO_3^- and Cl^-, presumably by a similar mechanism.[9] The products of the HOCl/BrO_2^- reaction were not analytically determined by Lewin and Avrahami[9] but were assumed on the basis of previous knowledge of similar reactions of halites with hypohalous acids. The present work shows that this assumption is not valid. (The formation of BrO_2, analogous to the formation of ClO_2 from the HOBr/ClO_2^- reaction, is not observed from the HOCl/BrO_2^- reaction due to rapid BrO_2 disproportionation.)[10]

In a gas-phase theoretical study of the reaction of HOCl with BrO_2^-, Guha and Francisco[11] found that a chainlike

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$HOClOBrO^-$ adduct is preferred over the Y-shaped HOCl-Br(O)O$^-$ structure. They also state that the interconversion from $HOClOBrO^-$ to $HOBrOClO^-$ is not allowed (in the gas phase), due to a large kinetic barrier. However, the present work examines the $HOCl/BrO_2^-$ reaction in aqueous solution where this interconversion is possible due to the presence of proton donors. The rate constants and mechanisms for the reactions of BrO_2^- with HOCl, Cl_2O, and Cl_2 are determined. The connectivity of $HOClOBrO^-$, $HOBrOClO^-$, and BrOClO intermediates is discussed on the basis of the proposed mechanisms.

Experimental Section

Reagents. Stock solutions of $NaClO_4$ were prepared from the recrystallized salt. The preparation of $NaBrO_2$ was reported previously.[12] The $NaBrO_2$ salt (63.4 wt %) contained H_2O (12.2%), NaOH (14.1%), Na_2SO_4 (1.9%), $NaBrO_3$ (7.0%), and NaBr (1.3%) impurities. Solutions of BrO_2^- were standardized spectrophotometrically at 295 nm ($\epsilon = 115$ M^{-1} cm^{-1}).[13] Stock solutions of OCl^- ($[OCl^-] = [Cl^-]$) were prepared by dispersing Cl_2 gas through 0.3 M NaOH. "Chloride-free" OCl^- solutions were made as reported previously.[1] Solutions of OCl^- were standardized spectrophotometrically at 292 nm ($\epsilon = 362$ M^{-1} cm^{-1}).[2]

Methodology and Instrumentation. All pH measurements were corrected to p[H$^+$] on the basis of electrode calibration ($\mu = 0.50$ M). Kinetic data were obtained with the ionic strength controlled at 0.50 M ($NaClO_4$). The pK_a values for HOCl and $H_2PO_4^-$ at $\mu = 0.50$ M are 7.50[14] and 6.46,[15] respectively. The concentration of $HBrO_2$ (pK_a 3.59(5)[16]) is negligible from p[H$^+$] 6−7. The disproportionation of BrO_2^- is very slow[17] and under the conditions of this study does not compete with the $HOCl/BrO_2^-$ reaction. Spectrophotometric measurements were performed on a Perkin-Elmer Lambda 9 UV−vis−NIR spectrophotometer. Stopped-flow measurements of the loss of BrO_2^- at 250 nm ($\epsilon = 345$ M^{-1} cm^{-1}) or the formation of ClO_2 at 360 nm ($\epsilon = 1220$ M^{-1} cm^{-1}) were performed on an Applied Photophysics stopped-flow spectrometer. Ion chromatographic separations were obtained as described previously.[18]

The products of the reaction were determined by mixing solutions of excess HOCl (also containing $H_2PO_4^-$ and HPO_4^{2-}) with BrO_2^-. Within 10 s, a portion of the $HOCl/BrO_2^-$ mixture was transferred to a cuvette and inserted into a Spectronic 20-D spectrophotometer. The increase in absorbance due to ClO_2 at 359 nm was followed until the absorbance reached a maximum. The maximum absorbance was used to calculate the yield of ClO_2 from the reaction. Aliquots were removed and mixed with a solution of excess NO_2^- to quench the reaction. The NO_2^- rapidly reduces HOCl to Cl^-,[19] HOBr to Br^-,[20] and ClO_2 to ClO_2^- [21] and prevents chromatographic column degradation by these species. An aliquot of the quenched reaction was removed and mixed with a solution containing excess OH^- to prevent further reactions between NO_2^- and ClO_2^-. Samples were then injected on the ion chromatograph to determine BrO_3^- and Br^-. The concentration of BrO_3^- and Br^- was corrected for the initial concentration of these ions in the BrO_2^- stock solution. Due to the NO_2^- quench reaction, the concentration of Br^- determined in the product study was the sum of [HOBr] and [Br^-]. The yield of ClO_3^- was determined by subtracting the yield of ClO_2 from the yield of Br^-. The yield of ClO_3^- was also determined by using the ion chromatograph and gave similar results (±5%).

Results and Discussion

Products of the $HOCl/BrO_2^-$ Reaction. The reaction of 0.15 mM BrO_2^- with excess HOCl produces ClO_3^-, ClO_2, Cl^-, BrO_3^-, and HOBr. Any Br^- produced from the $HOCl/BrO_2^-$ reaction reacts rapidly with HOCl to form HOBr and Cl^-.[22] Variation of $[HOCl]_T$ (6.53−11.4 mM), $[H_2PO_4^-]_T$ (25−75 mM), and p[H$^+$] (6.16−6.98) has little effect on the product distribution (Supporting Information Table S1). The primary path (85 ± 1%, based on the initial concentration of BrO_2^-) is a multistep oxidation of HOCl by BrO_2^- to form ClO_3^-, HOBr, and Cl^- (eq 1). Other pathways produce BrO_3^- and Cl^- (eq 2) or ClO_2, HOBr, and Cl^- (eq 3) in yields of 7 ± 2% and 8 ± 1%, respectively. These yields apply to an initial BrO_2^- concentration of 0.15 mM. Increasing the concentration of BrO_2^- to 0.62 mM increases the yield of ClO_2 to 19 ± 1%.

$$2HOCl + BrO_2^- \rightarrow ClO_3^- + HOBr + Cl^- + H^+ \quad (1)$$

$$HOCl + BrO_2^- \rightarrow BrO_3^- + Cl^- + H^+ \quad (2)$$

$$3HOCl + 2BrO_2^- \rightarrow 2ClO_2 + 2HOBr + Cl^- + OH^- \quad (3)$$

The distribution of products from the reaction of HOCl with BrO_2^- is quite surprising. First, the assumption that HOCl oxidizes BrO_2^- only to BrO_3^- is not correct,[9] since this path (eq 2) represents only 7% of the reaction. In fact, the oxidation of HOCl by BrO_2^- to form ClO_3^- (eq 1) is the major stoichiometric path for this reaction. Another unexpected result is the formation of ClO_2 as a product of the reaction. Previous studies of the $HOBr/ClO_2^-$ reaction[2] showed that the reaction of ClO_2^- with BrOClO is responsible for the formation of ClO_2 in that system. Since there is no added ClO_2^- in the $HOCl/BrO_2^-$ reaction, it was not clear initially how ClO_2 could be formed in the reaction. We will show in the following sections that ClO_2^- plays a vital role as an intermediate in the $HOCl/BrO_2^-$ reaction.

Kinetics of ClO_2 Formation. The increase in absorbance due to ClO_2 at 360 nm from the reaction of excess HOCl with BrO_2^- is typical of an autocatalytic reaction (Figure 1a

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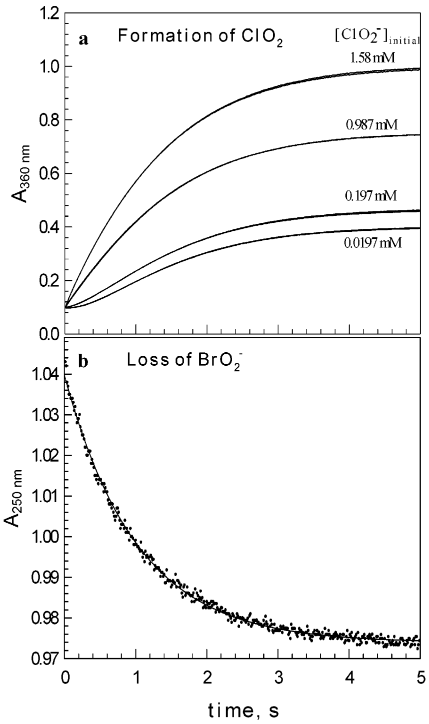

Figure 1. (a) Absorbance at 360 nm versus time following the formation of ClO_2 from the $HOCl/BrO_2^-$ reaction with variable concentrations of ClO_2^-. $[BrO_2^-] = 1.52$ mM, $[HOCl]_T = 16.1$ mM, $[H_2PO_4^-]_T = 0.100$ M, p[H^+] 6.32, $\mu = 0.50$ M, $\lambda = 360$ nm, and $T = 25.0$ °C. For each condition, three replicate traces were obtained and are included in this graph. (b) Absorbance at 250 nm versus time following the loss of BrO_2^- from the $HOCl/BrO_2^-$ reaction. $[BrO_2^-] = 0.185$ mM, $[HOCl]_T = 16.5$ mM, $[H_2PO_4^-]_T = 0.080$ M, p[H^+] 5.99, $\mu = 0.50$ M, $\lambda = 250$ nm, $T = 25.0$ °C, and no added ClO_2^-.

and Supporting Information Figure S1). The formation of ClO_2 is preceded by an induction period of 0.3−10 s that decreases with increasing concentrations of HOCl. After the induction period, the kinetic traces fit a pseudo-first-order formation of ClO_2. Over long time periods, ClO_2 decays according to its disproportionation reaction that is catalyzed by HOCl.[23,24] However, this has less than a 1% effect on the yield of ClO_2 from the relatively rapid $HOCl/BrO_2^-$ reaction.

The addition of initial concentrations of ClO_2^- to the $HOCl/BrO_2^-$ reaction reduces the induction time and gives a marked increase in the yield of ClO_2 (Figure 1a). When $[ClO_2^-]_i = [BrO_2^-]_i$, there is no evidence of an induction period and the kinetic trace follows a first-order formation of ClO_2. The reaction of HOCl with ClO_2^- is much slower than the observed reaction and cannot explain these observations.[1] When the induction period is excluded from the first-order fit, the observed rate constants (k_{obsd}) are identical for each of the kinetic traces in Figure 1a. This shows that the observed rate constant for the formation of ClO_2 is independent of the concentration of ClO_2^-. On the basis of these data, we conclude that ClO_2^- is an intermediate species in the $HOCl/BrO_2^-$ reaction that builds up to an appreciable concentration in the induction period. Earlier work[2] shows that ClO_2^- reacts rapidly with another reactive intermediate (BrOClO) to form ClO_2.

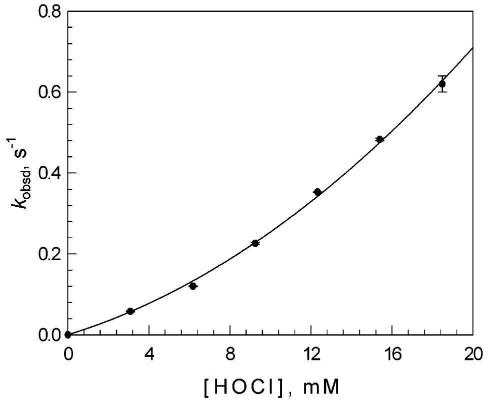

Figure 2. Dependence of the observed rate constant on the concentration of HOCl for the $HOCl/BrO_2^-$ reaction. $[BrO_2^-] = 0.158$ mM, $[H_2PO_4^-]_T = 80$ mM, p[H^+] 6.38, $\mu = 0.50$ M ($NaClO_4$), $\lambda = 250$ nm, and $T = 25.0$ °C. The line is a curve fit of eq 6 to the data. The error bars represent the standard deviation of an average of three runs (each run consists of an average of five kinetic traces).

Kinetics of BrO_2^- Decay. The loss of absorbance due to BrO_2^- at 250 nm (Figure 1b) in the presence of excess HOCl is a first-order decay with no evidence of an induction period (eq 4). The observed rate constants determined for the loss of BrO_2^- are similar to those determined for the formation of ClO_2 after the induction period. Since the kinetic traces at 250 nm are not preceded by an induction period, these data are used to determine the rate parameters for the reaction.

$$-d[BrO_2^-]/dt = k_{obsd}[BrO_2^-] \tag{4}$$

A plot of the observed rate constant versus the concentration of HOCl shows a first- and second-order dependence in [HOCl] (Figure 2). HOCl is in equilibrium with small amounts of chlorine monoxide (Cl_2O) in aqueous solution (eq 5).[25]

$$2HOCl \rightleftharpoons Cl_2O + H_2O \quad K_f^{Cl_2O} = 0.0115\ M^{-1} \tag{5}$$

Chlorine monoxide, despite its relatively small equilibrium concentration, has been shown[25] to compete with HOCl in the oxidation of $Ni^{II}(CN)_4^{2-}$. The reaction of Cl_2O with BrO_2^-, in addition to a direct $HOCl/BrO_2^-$ pathway, accounts for the observed kinetic dependence in [HOCl] (eq 6).

$$k_{obsd} = k_a[HOCl] + k_b[HOCl]^2 \tag{6}$$

The conditional rate constants, k_a and k_b, are dependent upon the concentration of H^+. The values of k_a and k_b were determined at several acidities (Figure 3 and Supporting Information Table S2). These data indicate the presence of acid-catalyzed pathways for the reactions of both HOCl and Cl_2O with BrO_2^- and also show a kinetic saturation effect at large [H^+]. This type of kinetic dependence is consistent with the expressions for k_a and k_b in eqs 7 and 8 (where w, x, y, and z are parameters defined by the mechanism). The

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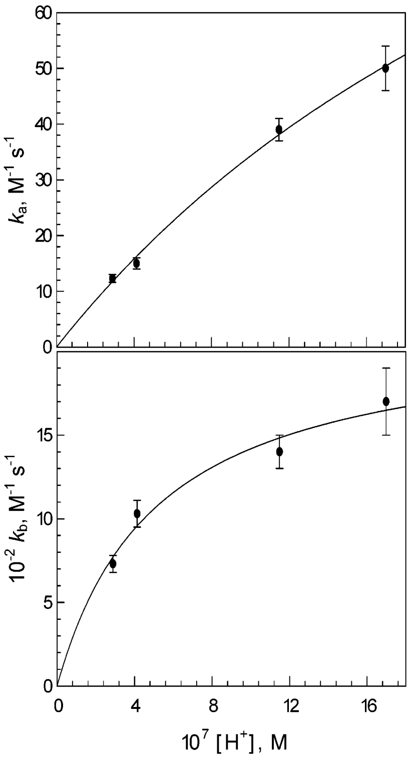

Figure 3. Dependence of k_a and k_b on the concentration of H^+ for the $HOCl/BrO_2^-$ reaction, where k_a represents the HOCl path and k_b represents the Cl_2O path. $[BrO_2^-] = 0.173-0.185$ mM, $[H_2PO_4^-]_T = 80$ mM, $\mu = 0.50$ M ($NaClO_4$), $\lambda = 250$ nm, and $T = 25.0$ °C. The lines are the curve fits of eqs 7 and 8 to the data. The error bars represent the standard error from the fit of eq 6 to k_{obsd} vs [HOCl] data at each [H^+].

values of k_a increase slightly (<10%) with increasing concentrations of phosphate buffer (Supporting Information Figure S2 and Table S3), while the values of k_b increase by a factor of 2. However, this effect is small compared to the effect of increasing [H^+] and the rate parameters for the phosphate-assisted pathway were not resolved.

$$k_a = \frac{w(x[H^+])}{1 + x[H^+]} \tag{7}$$

$$k_b = \frac{y(z[H^+])}{1 + z[H^+]} \tag{8}$$

Mechanisms of the $HOCl/Cl_2O$ Reaction with BrO_2^-. The lack of variation of the product distribution with changing HOCl concentration indicates that HOCl and Cl_2O react with BrO_2^- by similar pathways. We propose that HOCl and Cl_2O bond with BrO_2^- to form steady-state species, $HOClOBrO^-$ and $ClOClOBrO^-$ (eqs 9 and 11). These adducts react with H^+ to form $HOBrOClO^-$ (eqs 10 and 12). Equations 9−12 are the rate-determining steps for the reaction and account for the experimentally determined kinetics when the steady-state approximation is applied to $HOClOBrO^-$ and $ClOClOBrO^-$. The subsequent reactions of $HOBrOClO^-$ are rapid and do not contribute to the observed kinetics of the reaction.

$$HOCl + BrO_2^- \underset{k_{-1}^{HOCl}}{\overset{k_1^{HOCl}}{\rightleftharpoons}} HOClOBrO^- \tag{9}$$

$$HOClOBrO^- + H^+ \xrightarrow{k_2} HOBrOClO^- + H^+ \tag{10}$$

$$Cl_2O + BrO_2^- \underset{k_{-1}^{Cl_2O}}{\overset{k_1^{Cl2O}}{\rightleftharpoons}} ClOClOBr^- \tag{11}$$

$$ClOClOBrO^- + H^+ + H_2O \xrightarrow{k_3} HOBrOClO^- + HOCl + H^+ \tag{12}$$

On the basis of the mechanism in eqs 9−12, the constants in the rate expressions in eqs 7 and 8 are $w = k_1^{HOCl}$, $x = k_2/k_{-1}^{HOCl}$, $y = K_f^{Cl_2O}k_1^{Cl_2O}$, and $z = k_3/k_{-1}^{Cl_2O}$. A nonlinear fit of the data in Figure 3 according to these rate expressions determines $k_1^{HOCl} = 1.6(3) \times 10^2$ M^{-1} s^{-1} and $k_1^{Cl_2O} = 1.8(2) \times 10^5$ M^{-1} s^{-1}. Therefore, Cl_2O is 1100 times more reactive toward BrO_2^- than HOCl. The rate constants and ratios of rate constants are compiled in Table 1.

The $HOBrOClO^-$ and $HOClOBrO^-$ species are structural isomers, and the kinetic evidence shows that the reverse reaction in eq 10 is not appreciable. This indicates that the $HOBrOClO^-$ isomer is preferred over the $HOClOBrO^-$ isomer, in agreement with gas-phase theoretical calculations[11] that show a greater stability (9.2 kcal/mol) of $HOBrOClO^-$ over $HOClOBrO^-$. Further evidence of the lack of reversibility of eq 10 is seen in previous studies on the $HOBr/ClO_2^-$ reaction,[2] where the conversion of $HOBrOClO^-$ to $HOClOBrO^-$ (the reverse reaction in eq 10) is not observed.

The decomposition of $HOBrOClO^-$ does not contribute to the rate of the $HOCl/BrO_2^-$ reaction, but these reactions are crucial in the determination of the final products. The reactions of $HOBrOClO^-$ have been described in a previous study of the $HOBr/ClO_2^-$ reaction, where ClO_2^- was in excess of HOBr.[2] The dissociation of $HOBrOClO^-$ to HOBr and ClO_2^- (eq 13) competes with its general-acid-assisted decomposition to give BrOClO (eq 14). The metastable BrOClO species either hydrolyzes to form ClO_3^- and Br^- (eq 15) or reacts with ClO_2^- to form 2 ClO_2 and Br^- (eq 16).

$$HOBrOClO^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HOBr + ClO_2^- \tag{13}$$

$$HOBrOClO^- + HA \xrightarrow{k_5^{HA}} BrOClO + H_2O + A^- \tag{14}$$

$$BrOClO + H_2O \xrightarrow[rapid]{k_6} ClO_3^- + Br^- + 2H^+ \tag{15}$$

$$BrOClO + ClO_2^- \xrightarrow[rapid]{k_7} 2ClO_2 + Br^- \tag{16}$$

Furman and Margerum[2] determined the ratios $k_5^{H^+}/k_4 = 3.1 \times 10^5$ M^{-1}, $k_5^{H_2PO_4^-}/k_4 = 8.3$ M^{-1}, and $k_6/k_7 = 1.02 \times 10^{-2}$ M for the reaction of HOBr with excess ClO_2^-. However, the distribution of products (i.e. the k_6/k_7 value) is quite different when HOBr is in excess of ClO_2^-. Data obtained previously[27] showed that the reaction of 12.6 mM HOBr with 0.5033 mM ClO_2^- achieved a 21% yield of ClO_2.

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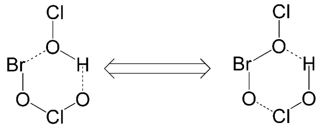
Table 1. Rate Constants for the HOCl, Cl_2O, and Cl_2 Reactions with BrO_2^- [a]

rate const	value
k_1^{HOCl}, M^{-1} s^{-1}	$1.6(3) \times 10^2$
$k_1^{Cl_2O}$, M^{-1} s^{-1}	$1.8(2) \times 10^5$
$k_1^{Cl_2}$, M^{-1} s^{-1}	$8.7(6) \times 10^5$
k_2/k_{-1}^{HOCl}, M^{-1}	$2.8(8) \times 10^5$
$k_3/k_{-1}^{Cl_2O}$, M^{-1}	$1.9(5) \times 10^6$
k_6'/k_7', M	3.5×10^{-4}
k_6'/k_8'	12(3)
$k_{-1}^{Cl_2}/k_6'$, M^{-1}	5(2)
$k_{-1}^{Cl_2}/k_8'$, M^{-1}	$6(1) \times 10^1$

[a] Conditions: 25.0 °C, $\mu = 0.50$ M ($NaClO_4$).

Scheme 1. Structure of the BrOClO·HOCl Adduct



The average concentration of ClO_2^- present in the course of the reaction is approximately 0.25 mM. On the basis of the k_6/k_7 ratio determined in excess ClO_2^-, a yield of less than 5% is predicted. Therefore, the presence of excess HOBr facilitates the formation ClO_2. In this study of the HOCl/BrO_2^- reaction, a similar trend is observed due to the excess HOCl.

Reactions of BrOClO in the Presence of Excess HOCl. Under the conditions of the current study (p[H^+] 6.5, [$H_2PO_4^-$] = 0.04 M), approximately 43% of $HOBrOClO^-$ dissociates into HOBr and ClO_2^- and the other 57% reacts with general acids to form BrOClO. Using the k_6/k_7 ratio determined in the presence of excess ClO_2^-, we calculate that 0.44 mM ClO_2^- is necessary to produce the experimentally determined 8% yield of ClO_2. However, the initial concentration of BrO_2^- is only 0.15 mM and a maximum of 43% of this can be converted to ClO_2^-. Therefore, an alternative explanation must be considered to account for the larger than expected yield of ClO_2 as well as for the formation of 7% BrO_3^- as a minor product. The excess HOCl must react with BrOClO to form an alternate intermediate that reacts differently than BrOClO. We propose that BrOClO associates with HOCl to form a cyclic BrOClO·HOCl adduct. A slight rearrangement of the bonding in BrOClO·HOCl leads to a ClOBrO·HOCl adduct (Scheme 1). These structures are similar to those proposed for the adducts of Cl_2O[26] and BrOCl[18] with OCl^-. The cyclic intermediates in Scheme 1 constitute a species that can react similarly to either BrOClO or ClOBrO. Therefore, nucleophilic attack by H_2O at the internal Cl atom (k_6') leads to the formation of ClO_3^-, HOBr, and Cl^- or attack by H_2O at the Br atom (k_8') forms BrO_3^-, HOCl, and Cl^-. The formation of 2 ClO_2 and Br^- (k_7') takes place by the reaction of ClO_2^- with BrOClO·HOCl. The detailed mechanism of the HOCl reaction with BrO_2^- is shown in Scheme 2. This scheme also includes an alternative pathway (k_9) that is discussed later.

On the basis of the mechanism in Scheme 2, the autocatalytic profile of ClO_2 formation can be rationalized. Before the concentration of ClO_2^- builds up to appreciable levels, the BrOClO·HOCl intermediate hydrolyzes to form predominantly ClO_3^- and Br^-. As [ClO_2^-] becomes larger, the k_7' pathway begins to compete with the k_6' pathway. These competing pathways coupled with the build up of ClO_2^- provide the mechanistic explanation for the delayed formation of small amounts of ClO_2 observed experimentally.

From the relative yields of BrO_3^-, ClO_3^-, and ClO_2, the ratios $k_6'/k_8' = 12(3)$ and $k_6'/k_7'[ClO_2^-] = 11(1)$ are determined. Of the initial BrO_2^- (0.15 mM), only 43% of its loss leads to the formation of ClO_2^- due to the competing k_4 and k_5 steps. This gives a maximum yield of 64.5 μM ClO_2^-. Assuming the average concentration of ClO_2^- over the course of the reaction is half the maximum concentration, the ratio $k_6'/k_7' = 3.5 \times 10^{-4}$ M can be estimated (compared to $k_6/k_7 = 1.02 \times 10^{-2}$ M in the absence of HOCl). Therefore, the formation of ClO_2 from the reaction of ClO_2^- with BrOClO is approximately 30 times more favorable in the presence of excess HOCl. A proposed electron-transfer reaction between ClO_2^- and a BrOClO·HOCl adduct is shown in Scheme 3. The cyclic intermediate helps to promote an electron-transfer reaction with ClO_2^- to give 2 ClO_2, HOBr, and Cl^-.

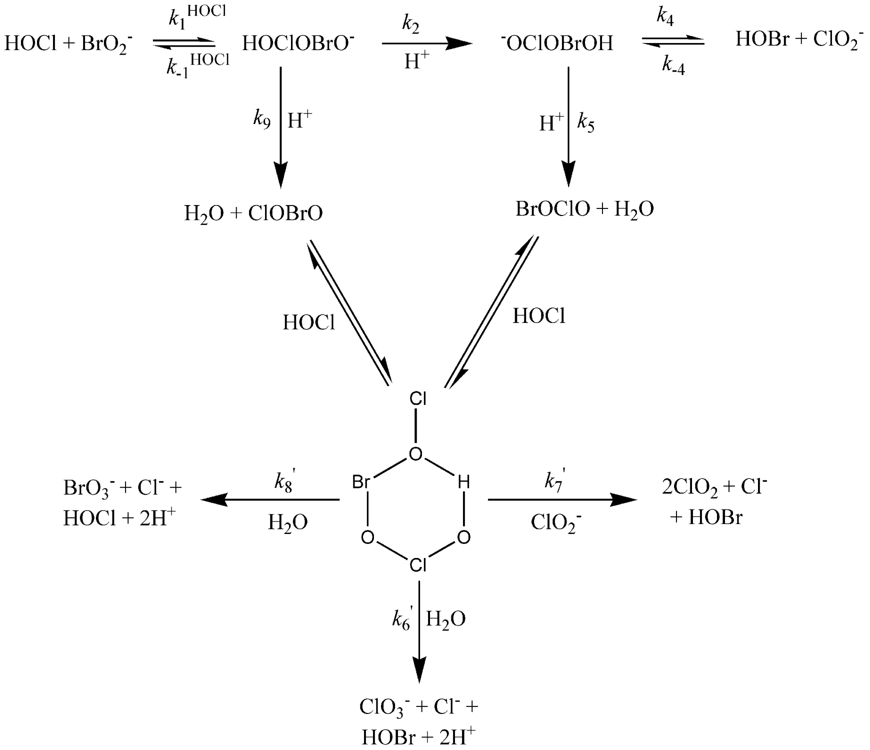
Interconversion of HOCl and BrO_2^- to HOBr and ClO_2^-. The sum of eqs 9, 10, and 13 provides an interconversion pathway for the formation of HOBr and ClO_2^- from HOCl and BrO_2^- (eq 17). On the basis of standard aqueous potentials (Table 2) and the pK_a^{HOCl} value, an equilibrium constant calculated for the reaction in eq 17 at p[H^+] 6.5 is $K = 6.30 \times 10^{-2}$. Accordingly, when [HOCl] = 10 mM, 83.4% of the BrO_2^- would be converted to HOBr and ClO_2^-. However, in the reaction of HOCl with BrO_2^-, this equilibrium is not reached due to the competition between the general-acid-assisted decomposition of $HOBrOClO^-$ to BrOClO (eq 14) and its dissociation to HOBr and ClO_2^- (eq 13).

$$HOCl + BrO_2^- \rightleftharpoons HOBr + ClO_2^- \qquad (17)$$

Guha and Francisco[11] indicate that the $HOClOBrO^-$ to $HOBrOClO^-$ conversion in eq 11 is not allowed due to a kinetic barrier of 30.0 kcal/mol in the gas phase. In aqueous solution, however, water and/or general acids are able to facilitate the interconversion process. On the basis of the kinetic evidence of acid catalysis for this reaction, we propose that water and protons mediate the transfer of H^+ to convert $HOClOBrO^-$ to $HOBrOClO^-$ (Scheme 4).

Another possible pathway exists for the formation of BrO_3^- and ClO_3^- that does not require the interconversion pathway in Scheme 4. A competing pathway to the interconversion of $HOClOBrO^-$ to $HOBrOClO^-$ in eq 11 could be the acid-catalyzed decomposition of $HOClOBrO^-$ to ClOBrO (eq 18). In the presence of excess HOCl, the ClOBrO intermediate could form the cyclic intermediate in Scheme 1 (ClOBrO·HOCl) and hydrolyze to form BrO_3^- or ClO_3^- as represented in Scheme 2. The pathway in eq 18 cannot be distinguished from the formation of BrO_3^- and ClO_3^- through the interconversion pathway. Regardless, the interconversion pathway is necessary to form appreciable

Scheme 2. Proposed Mechanism of the HOCl Reaction with BrO_2^-



Scheme 3. Proposed Mechanism for the Electron Transfer of BrOClO·HOCl with ClO_2^- To Give 2 ClO_2, HOBr, and Cl^-

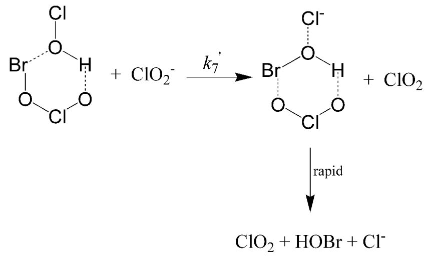
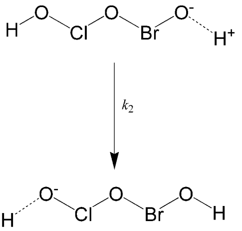


Table 2. Reduction Potentials of Chlorine and Bromine Species in Aqueous Solution

half-reacn	$E°$, V
$ClO_2^- + H_2O + 2e^- \rightarrow OCl^- + OH^-$	0.681[a]
$BrO_2 + e^- \rightarrow BrO_2^-$	1.289[b]
$BrO_3^- + 2H^+ + e^- \rightarrow BrO_2 + H_2O$	1.16[c]
$BrO_3^- + 5H^+ + 4e^- \rightarrow HOBr + 2H_2O$	1.447[a]

[a] Bard, A. J., Parsons, S. R., Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcell Dekker, Inc.: New York, 1985; pp 74−75, 82. [b] Reference 12. [c] Stanbury, D. M. *Advances in Inorganic Chemistry*; Academic Press, Inc.: San Diego, CA, 1989; Vol. 33, p 125.

Scheme 4. Acid-Catalyzed Interconversion of $HOClOBrO^-$ to $HOBrOClO^-$



concentrations of the ClO_2^-, which must build up prior to the formation of ClO_2. Therefore, the value of k_9 must be small compared to k_2 to obtain the products that are observed.

$$\mathrm{HOClOBrO^- + H^+ \xrightarrow{k_9} ClOBrO + H_2O} \qquad (18)$$

Connectivity of $HOClOBrO^-$, $HOBrOClO^-$, and BrOClO Intermediates. The formation of ClO_2 from the reaction of HOCl with BrO_2^- provides excellent evidence for the existence of the interconversion pathway in Scheme 4. One requirement of this process is the formation of a chainlike adduct between HOCl and BrO_2^- with alternating halogen−oxygen bonding, $HOClOBrO^-$. The Y-shaped structure with halogen−halogen bonding, $HOClBr(O)O^-$, does not permit interconversion to $HOBrCl(O)O^-$ without breaking and reforming many bonds. The acid-catalyzed decomposition of $HOClBr(O)O^-$ would form ClBr(O)O. Hydrolysis of ClBr(O)O can only form BrO_3^- and Cl^- as products, which is in disagreement with the experimental data. It follows that $HOBrOClO^-$ and BrOClO also possess a chainlike arrangement because they originate directly from $HOClOBrO^-$.

The formation of the chainlike adduct is logical when nucleophilic/electrophilic interactions are considered. The Cl atom on HOCl is electrophilic and subject to attack by a nucleophile. The O atoms on BrO_2^- are more electronegative than the Br atom and are the most nucleophilic atoms of the ion. Thus, nucleophilic attack of BrO_2^- on HOCl leads to the chainlike adduct. This rationale should extend to other XOXO-type intermediates in aqueous solution (X = Br, Cl). However, our kinetics evidence requires only the $HOClOBrO^-$, $HOBrOClO^-$, and BrOClO species to have the chainlike configuration.

Mechanism and Rate Expression for the Cl_2/BrO_2^- Reaction. Small amounts of Cl_2 are in equilibrium with HOCl when Cl^- is added. The addition of 81.7 mM Cl^- to

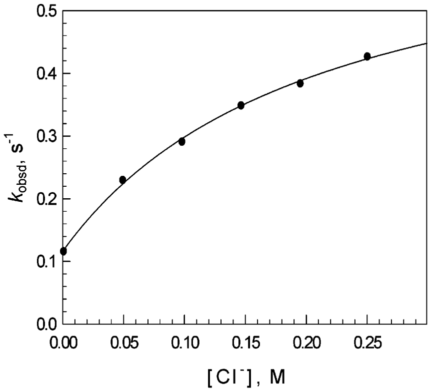


Figure 4. Dependence of the observed rate constant on the concentration of Cl^- for the $HOCl/BrO_2^-$ reaction. $[BrO_2^-] = 0.225$ mM, $[HOCl]_T = 6.53$ mM, p[H$^+$] 6.28, $[H_2PO_4^-]_T = 0.080$ M, $\mu = 0.50$ M (NaClO4), $\lambda = 250$ nm, and $T = 25.0$ °C. The line is a curve fit of eq 21 to the data.

the $HOCl/BrO_2^-$ reaction system (with 0.15 mM BrO_2^-) decreases the yield of ClO_2 from 7.7% to 4.9% and increases the BrO_3^- yield from 6.9% to 9.1% (Supporting Information Table S1). Once again, the major oxidation product is ClO_3^- (∼86%). Stopped-flow studies of the formation of ClO_2 with higher initial concentrations of BrO_2^- (0.21 mM) show an even larger drop in ClO_2 yield with increasing Cl^- concentration. The yield of ClO_2 decreases from 14% to 4% as the concentration of Cl^- increases from 0 to 0.25 M (Supporting Information Table S4). Therefore, Cl^- must provide a catalytic pathway for the formation of ClO_3^- (eq 1) and BrO_3^- (eq 2) but not for the formation of ClO_2 (eq 3).

A plot of the observed rate constant versus the concentration of Cl^- (Figure 4) shows an increase in the rate of the reaction with increasing [Cl^-]. The intercept in Figure 4 corresponds to the competing HOCl and Cl_2O pathways for the loss of BrO_2^-. The saturation of the observed rate constant at high [Cl^-] indicates that there is a reversible path that releases Cl^-. On the basis of the kinetic data and the product distribution with variable [Cl^-], we propose that Cl_2 contributes to the rate of the reaction at large [Cl^-]. Small amounts of Cl_2 are in equilibrium with HOCl in the presence of Cl^- (eq 19, $K_f^{Cl_2} = 960$ M^{-2}).[28] The transfer of Cl^+ from Cl_2 to BrO_2^- forms ClOBrO and releases Cl^- (eq 20).

$$\mathrm{HOCl + Cl^- + H^+ \overset{K_f^{Cl_2}}{\rightleftharpoons} Cl_2 + H_2O} \qquad (19)$$

$$\mathrm{Cl_2 + BrO_2^- + H^+ \underset{k_{-1}^{Cl_2}}{\overset{k_1^{Cl_2}}{\rightleftharpoons}} ClOBrO + Cl^-} \qquad (20)$$

In the presence of excess HOCl, ClOBrO can form a cyclic intermediate, ClOBrO·HOCl (Scheme 1), that reacts as discussed earlier (Scheme 2). Since this mechanism does not contain an interconversion pathway to form ClO_2^-, the yield of ClO_2 decreases as the concentration of Cl^- increases. Allowing eq 20 to be reversible and applying the steady-state approximation to the ClOBrO·HOCl intermediate produces the expression in eq 21 for the Cl_2/BrO_2^- pathway.

$$k_{obsd} = \frac{K_f^{Cl_2} k_1^{Cl_2}[\mathrm{HOCl}][\mathrm{H^+}][\mathrm{Cl^-}]}{1 + \dfrac{k_{-1}^{Cl_2}}{k_6' + k_8'}[\mathrm{Cl^-}]} \qquad (21)$$

A curve fit of eq 21 to the data in Figure 4 is used to obtain $k_1^{Cl_2} = 8.7(6) \times 10^5$ M^{-1} s^{-1} and $k_{-1}^{Cl_2}/(k_6' + k_8') = 4.8(7)$ M^{-1}. The $k_1^{Cl_2}$ value shows that Cl_2 is greater than 5000 times more reactive than HOCl and almost 5 times more reactive than Cl_2O toward BrO_2^-. The values $k_{-1}^{Cl_2}/k_6' = 5(2)$ M^{-1} and $k_{-1}^{Cl_2}/k_6' = 6(2) \times 10^1$ M^{-1} are also determined from the previous k_6'/k_8' ratio.

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Supporting Information Available: Tables and graphs of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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