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Article

Bromite Ion Catalysis of the Disproportionation of Chlorine Dioxide with Nucleophile Assistance of Electron-Transfer Reactions between ClO_2 and BrO_2 in Basic Solution

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The rate of ClO_2 conversion to ClO_2^- and ClO_3^- is accelerated by BrO_2^-, repressed by ClO_2^-, and greatly assisted by many nucleophiles ($Br^- > PO_4^{3-} > HPO_4^{2-} > CO_3^{2-} > Cl^- \sim OH^- > CH_3COO^- \sim SO_4^{2-} \sim C_5H_5N \gg H_2O$). The kinetics (at $p[H^+] = 9.3–12.9$) show that the first step of the mechanism is an electron transfer between ClO_2 and BrO_2^- ($k_1 = 36$ M^{-1} s^{-1}) to give ClO_2^- and BrO_2. This highly reversible reaction ($k_1/k_{-1} = 1 \times 10^{-6}$) accounts for the observed inhibition by ClO_2^-. The second step is an electron transfer between ClO_2 and BrO_2 to regenerate BrO_2^- and form ClO_3^-. A novel aspect of the second step is the large kinetic contribution from nucleophiles (k^{Nu}) that assist the electron transfer between ClO_2 and BrO_2. The k^{Nu} (M^{-2} s^{-1}) values at 25.0 °C vary from 2.89×10^8 for Br^- to 2.0×10^4 for H_2O.

Introduction

Bromine dioxide (BrO_2) is much more reactive than the corresponding chlorine species (ClO_2) and less is known about its redox chemistry. Pulsed radiolysis of BrO_3^- solutions has been used to generate trace levels of BrO_2 in neutral and basic solutions.[1,2] This BrO_2 undergoes very rapid disproportionation with a rate proportional to $[BrO_2]^2$ and a complex dependence in $[OH^-]$.[1] Micromolar concentrations of BrO_2 have been generated in sulfuric acid solution by Ce(III) reduction[3] of BrO_3^- and by the reaction between $HBrO_2$ and BrO_3^-.[4] For a brief period $NaBrO_2$ was available commercially, but this is no longer the case. We have prepared $NaBrO_2$ in a mixture of nonreactive salts on the basis of the method of Noszticzius et al.[5] with additional steps to remove all NaOBr and most of the NaBr.

This work pertains to the mechanisms of the reaction between ClO_2 and BrO_2^- in basic solutions. We show that BrO_2^- catalyzes the overall disproportionation of ClO_2 via BrO_2 as a steady-state intermediate. Furthermore, electron-transfer reactions between BrO_2 and ClO_2 are catalyzed by many nucleophiles.

Experimental Section

Preparation of $NaBrO_2$. $Ba(BrO_2)_2$ was prepared from the disproportionation of $Ba(OBr)_2$ as described by Noszticzius, Noszticzius, and Schelly[5] but with several modifications. The reaction slurry was maintained at pH 10.0−10.5 (as opposed to pH 11) to increase the rate of formation of $Ba(BrO_2)_2$. This allowed for greater conversion of $Ba(OBr)_2$ to $Ba(BrO_2)_2$ in a 2 h reaction time. Also, the reaction slurry was kept at a lower temperature (−10 to −20 °C) in an ice−methanol bath. The lower temperature permitted increased precipitation and collection of $Ba(BrO_2)_2$. The collected barium salt, dissolved in a minimum amount of water, contained mostly $Ba(BrO_2)_2$, $BaBr_2$, and $Ba(OH)_2$ with small amounts of $Ba(OBr)_2$ and $Ba(BrO_3)_2$. Since OBr^- may compete with BrO_2^- in many redox reactions, it is important that its concentration be minimized. The removal of $Ba(OBr)_2$ was achieved by stepwise addition of Na_2SO_3, which reduces OBr^- to Br^-. Sulfite reacts much more rapidly with OBr^- ($k = 1 \times 10^8$ M^{-1} s^{-1})[6] than with BrO_2^- ($k = 3.7$ M^{-1} s^{-1})[7] and permits preferential removal of OBr^-. The solution was monitored spectrophotometrically and shown to be free of OBr^- ($\epsilon = 332$ M^{-1} cm^{-1} at 329 nm).[6] Bromide ion was removed by ion exchange with solid AgOH (prepared fresh by the addition of NaOH solution to either Ag_2SO_4 or $AgNO_3$). The Ba^{2+} ions were exchanged with Na^+ ions by the addition of Na_2SO_4 to precipitate $BaSO_4$. The resulting solution was lyophilized

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and stored at −10 °C as a dried salt mixture. Ion chromatographic analysis determined that the solid product contained (by weight) 29.9% $NaBrO_2$, 3.2% $NaBrO_3$, 0.3% NaBr, 4.2% $NaNO_3$, and 41.6% Na_2SO_4. The remaining 20.7% is NaOH and waters of crystallization. For our experiments, it was critical to remove all OBr^-. Each of the other salts was tested to determine its effect on the kinetic studies in basic solution.

Reagents. All solutions were made with distilled−deionized water. Chlorine dioxide stock solution was prepared as described previously[8,9] and was protected from light and stored in a refrigerator. This solution was standardized spectrophotometrically based on the molar absorptivity of ClO_2, $\epsilon = 1230\ M^{-1}\ cm^{-1}$ at 359 nm.[8]

Commercially available $NaClO_2$ was treated to remove sodium carbonate and was recrystallized.[8,10] Stock solutions $NaClO_2$ were standardized spectrophotometrically at 260 nm ($\epsilon = 154\ M^{-1}\ cm^{-1}$).[8] Stock solutions of $NaBrO_2$ were prepared daily from the stored solid, and the concentration of BrO_2^- was determined spectrophotometrically at 295 nm ($\epsilon = 115\ M^{-1}\ cm^{-1}$,[11] a value that was confirmed iodometrically).[12] Ionic strength (μ) was controlled with recrystallized $NaClO_4$. All kinetic studies were carried out at 25.0 ± 0.2 °C and $\mu = 1.0$ M.

pH Measurement. An Orion model 720A digital pH meter equipped with a Corning combination electrode was used in all measurements. The electrode was calibrated through titrations of standard $HClO_4$ with standard NaOH to correct the measured pH values to p[H^+] and p[OH^-] (pK_w = 13.60)[13] at 25.0 ± 0.1 °C and $\mu = 1.0$ M ($NaClO_4$).

Products. The reaction products were identified and quantitatively determined via an EPA recommended method[14] by use of a Dionex DX-500 ion chromatograph. Samples were injected via an autosampler (AS40) through a 25 μL injection loop into anion exchange guard (AG9HC) and separation (AS9HC) columns. The analytes were eluted with 9.0 mM Na_2CO_3 at a flow rate of 1.0 mL/min. Suppressed conductivity detection (ED40), with an ASRS-Ultra suppressor in the gas-assisted self-regeneration mode (SRS) and a current of 100 mA, was used to determine the analytes. The product distributions were obtained by mixing ClO_2 and BrO_2^- reactant solutions. The mixtures were capped, and the solutions were reacted for 5 min (essentially to completion) and were quenched by purging any remaining ClO_2 with Ar.

A Perkin-Elmer Lambda-9 UV−vis−NIR spectrophotometer was used to acquire reaction spectra for slower reactions after ClO_2 solutions were T-mixed with BrO_2^- solutions in carbonate buffer p[H^+] 10.30. Spectral scans were taken from 250 to 450 nm at 100 s intervals and after the reaction was complete.

Kinetics. Kinetic studies were performed on an Applied Photo-Physics SX 18 MV stopped-flow spectrophotometer (APPSF, optical path length = 0.962 cm). The progress of the BrO_2^-/ClO_2 reaction was followed by observing the disappearance of ClO_2 at 359 nm in the presence of excess BrO_2^- ($\epsilon_{359} = 45.3\ M^{-1}\ cm^{-1}$) and excess ClO_2^- ($\epsilon_{359} = 1.3\ M^{-1}\ cm^{-1}$). All rate constants were determined from the average of five pushes. SigmaPlot 4.0[15] was used for the regression analysis.

Table 1. Ion Chromatographic Determination of Products for the Reaction between BrO_2^- and ClO_2[a,b]

p[H^+]	[BrO_2^-]$_f$/[BrO_2^-]$_i$[c]	[ClO_2^-]$_f$/[ClO_3^-]$_f$[c]
10.17	1.00 ± 0.04	0.99 ± 0.04
10.43	1.04 ± 0.04	1.00 ± 0.04
11.35	1.04 ± 0.04	1.03 ± 0.04

[a] Reactions and conditions: [BrO_2^-]$_i$ = 0.133 mM; [ClO_2]$_i$ = 0.271 mM; [CO_3^{2-}]$_T$ = 0.10 M; 25.0 °C; 300 s reaction time. [b] IC determinations showed that the concentrations of small amounts of Br^- and BrO_3^- in the reactants (from the $NaBrO_2$ sample) were unchanged in the products. [c] [BrO_2^-]$_f$, [ClO_2^-]$_f$, and [ClO_3^-]$_f$ are the product concentrations.

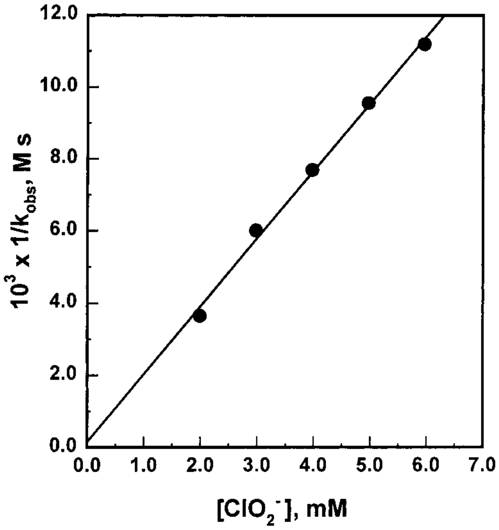

Figure 1. Dependence of the reciprocal of the second-order rate constant (k_{obs}) for the disproportionation of chlorine dioxide on the chlorite concentration. Conditions: 0.280 mM [ClO_2]; 18.90 mM [BrO_2^-]; 0.10 M [CO_3]$_T$; p[H^+] 9.45. Slope = (1.88 ± 0.07) s, and intercept = (1.5 ± 3.0) × 10^{-4} M s.

Results and Discussion

Reaction Stoichiometry. Chlorine dioxide disproportionates slowly in basic solution to form chlorite and chlorate ions.[16] The addition of $NaBrO_2$ to ClO_2 in base greatly accelerates the disproportionation and gives 1:1 stoichiometry that corresponds to eq 1. Ion chromatographic results (Table 1) show (within experimental error) that equal amounts of ClO_2^- and ClO_3^- are formed and no BrO_2^- is consumed. Since our added $NaBrO_2$ has small amounts of $NaBrO_3$ and NaBr present, we also analyzed for BrO_3^- and Br^- before and after the reaction and found no change in their concentrations. Separate tests show that BrO_3^-, NO_3^-, and ClO_4^- have no effect on the rate of ClO_2 disproportionation. Spectrophotometric results from 250 to 450 nm show that, after all the ClO_2 reacts, the remaining spectrum corresponds exactly to the initial spectrum of the added BrO_2^- plus the spectrum of ClO_2^- formed.

$$2ClO_2 + 2OH^- \xrightarrow{BrO_2^-} ClO_2^- + ClO_3^- + H_2O \qquad (1)$$

Kinetics. The rate of ClO_2 loss has a mixed order dependence in ClO_2 for which an integrated rate expression cannot be determined. Although the data can be analyzed by instantaneous rate methods, we found it more convenient

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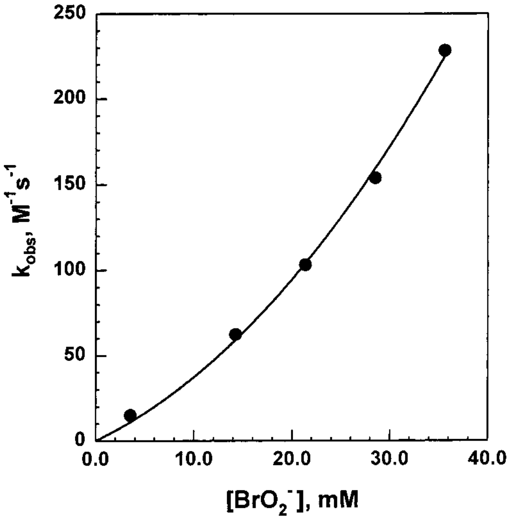

Figure 2. Bromite dependence of k_{obs} for its reactions with ClO_2. Conditions: 0.322 mM $[ClO_2]$; 5.48 mM $[ClO_2^-]$; 0.10 M $[CO_3]_T$; $p[H^+]$ 9.50. Regression fit: $k_{obs} = (2.7 \pm 0.4) \times 10^3[BrO_2^-] + (1.0 \pm 0.1) \times 10^5[BrO_2^-]^2$.

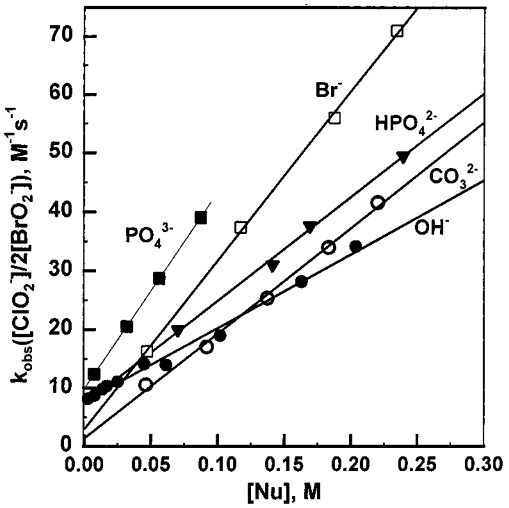

Figure 3. Dependence of k_{obs} on the concentration of nucleophiles where $k_{obs}[ClO_2^-]/2[BrO_2^-] = (k_1/k_{-1})(\sum k^{Nu}[Nu])$. For $[OH^-]$ the intercept is $(k_1/k_{-1})(k^{H_2O} + k^{BrO_2^-}[BrO_2^-] + k^{ClO_2^-}[ClO_2^-] + k^{SO_4^{2-}}[SO_4^{2-}])$. For other nucleophiles the intercept includes contributions $k^{OH^-}[OH^-]$ as well.

to add excess chlorite ion ($[ClO_2^-]_i > 6[ClO_2]_i$) to the BrO_2^- reactant solution to give excellent second-order fits where $-d[ClO_2]/dt$ equals $k_{obs}[ClO_2]^2$.

Chlorite ion suppresses the rate, and Figure 1 shows that reciprocal values of k_{obs} are directly proportional to $[ClO_2^-]$, when ClO_2^- is added in excess. Added BrO_2^- greatly accelerates the rate, and k_{obs} has both a first-order and a second-order contribution in $[BrO_2^-]$ as seen in Figure 2.

Effect of Nucleophiles on the Kinetics. Buffers were present in the kinetic studies to ensure that constant pH was maintained despite the consumption of base (eq 1). The large molar absorptivity of ClO_2 permitted use of low concentrations in the kinetic studies, typically 3×10^{-4} M or less. Hence, buffer concentrations of 0.05 M or less were sufficient for pH control during the reaction. However, buffer concentrations have a large effect on the k_{obs} values as shown in Figure 3. The effect of $[OH^-]$ in the absence of buffers is also shown in Figure 3, where the intercept permits a rate constant for H_2O to be evaluated. Although the sensitivity of k_{obs} to concentrations of OH^-, PO_4^{3-}, CO_3^{2-}, and HPO_4^{2-} is large, there is almost no dependence on the Brønsted base strength of these species. However, this acceleration does not extend to every anion as shown by the lack of effect of ClO_4^-, NO_3^-, or BrO_3^-. A fit of the rate dependence on $p[H^+]$ from 9.5 to 10.53 in carbonate buffer indicates the absence of a HCO_3^- path. Additional studies showed significant acceleration by pyridine and sulfate, as well as acetate, chloride, and bromide ions. This suggests that it is the nucleophilic properties of the species rather than their proton abstraction properties that govern their reactivity.

Mechanism. The mechanism in eqs 2−4 is proposed for the reaction between ClO_2 and BrO_2^-, where BrO_2 is a steady-state intermediate:

$$ClO_2 + BrO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClO_2^- + BrO_2 \qquad (2)$$

$$ClO_2 + BrO_2 + Nu \xrightarrow{k^{Nu}} [NuClO_2^+] + BrO_2^- \qquad (3)$$

$$[NuClO_2^+] + 2OH^- \xrightarrow{\text{fast}} Nu + ClO_3^- + 2H_2O \qquad (4)$$

The net result is that ClO_2 disproportionates in accord with eq 1 and the reaction rate is catalyzed by BrO_2^- and by nucleophiles (Nu). The first step (eq 2) is a thermodynamically uphill electron-transfer reaction to give ClO_2^- and BrO_2. Bromine dioxide is a highly reactive compound that is capable of disproportionating to form BrO_2^- and BrO_3^-.[1−4] However, this does not take place because the concentration of BrO_2 is very low compared to ClO_2 so that the reactions in eqs 3 and 4 generate ClO_3^- and regenerate BrO_2^-. The reaction between BrO_2 and ClO_2 has been proposed as an intermediate step in the reduction of bromate ion by chlorous acid.[17,18] The rate constant for the BrO_2/ClO_2 reaction at 1.0−2.0 M $[H^+]$ has been estimated to be 1.2×10^5 M^{-1} s^{-1}. Thermodynamically, eqs 3 and 4 are very favorable and overcome the unfavorable step in eq 2. Nucleophiles (Nu) assist the electron transfer in eq 3 because the formation of ClO_2^+ is not favorable for this electron transfer. Equation 3 includes more than one step, but it is written to indicate a transition state that consists of $(ClO_2BrO_2Nu)^‡$. The resulting rate expression given in eq 5 corresponds to the observed kinetics:

$$\frac{-d[ClO_2]}{dt} = \frac{2k_1(\sum k^{Nu}[Nu])[BrO_2^-][ClO_2]^2}{k_{-1}[ClO_2^-] + (\sum k^{Nu}[Nu])[ClO_2]} \qquad (5)$$

Typical concentrations of ClO_2 are low and k_{-1} is very large,[19] so that the addition of excess ClO_2^- leads to the inequality $k_{-1}[ClO_2^-] \gg (\sum k^{Nu}[Nu])[ClO_2]$. This gives therate expression in eq 6 that allows use of second-order integrated rate constants where k_{obs} is expressed by eq 7.

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Table 2. Summary of Rate Constants for the Reaction between ClO_2 and BrO_2^- [a]

nucleophiles	pK_a^{HNu}	n[b]	$10^{-2}(k_1/k_{-1})k^{Nu}$, $M^{-2}\,s^{-1}$	k^{Nu}, $M^{-2}\,s^{-1}$ [e]
H_2O	−1.74	0	0.00020(2)[d]	2.0×10^4
Py	5.19	3.6	0.350(1)	3.5×10^7
SO_4^{2-}	1.12	2.5	0.36(2)	3.6×10^7
OAc^-	4.61	2.72	0.41(1)	4.4×10^7
OH^-	15.39	4.2	1.25(4)	1.25×10^8
Cl^-		3.04	1.28(5)	1.28×10^8
CO_3^{2-}	9.46	*c*	1.49(6)	1.49×10^8
HPO_4^{2-}	8.21	3.8	1.64(7)	1.64×10^8
ClO_2^-	1.72	*c*	2.2(6)	2.2×10^8
PO_4^{3-}	11.08	*c*	2.3(3)	2.3×10^8
BrO_2^-	3.43	*c*	2.3(3)	2.3×10^8
Br^-		3.89	2.89(6)	2.89×10^8

[a] Conditions: 25.0 °C; $\mu = 1.0$ M. [b] $n = \log(k^{Nu}/k^{H_2O})$ for CH_3X substitution; the values are obtained from ref 22. [c] The n values are not available. [d] $(k_1/k_{-1})(k^{H_2O}/55.5)$ to give $M^{-2}\,s^{-1}$. [e] The k^{Nu} values were calculated from the k_1 value (36 $M^{-1}\,s^{-1}$) obtained in this work, and the k_{-1} value (3.6×10^7 $M^{-1}\,s^{-1}$) is from ref 19.

$$\frac{-d[ClO_2]}{dt} = \frac{2k_1(\sum k^{Nu}[Nu])[BrO_2^-][ClO_2]^2}{k_{-1}[ClO_2^-]} = k_{obs}[ClO_2]^2 \tag{6}$$

$$k_{obs} = \frac{2k_1(\sum k^{Nu}[Nu])[BrO_2^-]}{k_{-1}[ClO_2^-]} \tag{7}$$

Determination of k_1k^{Nu}/k_{-1} Values. As the concentration of the nucleophiles increase, there is a directly proportional increase in k_{obs} in accord with eq 7. The effects are large; for example, there is a 4-fold increase in k_{obs} with $[CO_3^{2-}]$ (Figure 3). Variation of hydroxide ion concentration in the absence of buffers gives values for $k_{obs}[ClO_2^-]/2[BrO_2^-]$, where the slope equals $(k_1/k_{-1})k^{OH^-}$ and the intercept is $(k_1/k_{-1})(k^{H_2O} + k^{ClO_2^-}[ClO_2^-] + k^{BrO_2^-}[BrO_2^-] + k^{SO_4^{2-}}[SO_4^{2-}])$. (The last term is included because Na_2SO_4 is present in the $NaBrO_2$ preparation). The rate constant for the water path ($k_1k^{H_2O}/k_{-1} = 1.1 \pm 0.1$ $M^{-1}\,s^{-1}$) is determined by subtracting the contributions by ClO_2^-, BrO_2^-, and SO_4^{2-} from the intercept value. Similarly, variation of $[CO_3^{2-}]$ at constant $p[H^+]$ in Figure 3 gives a slope equal to $(k_1/k_{-1})k^{CO_3^{2-}}$ and an intercept equal to $(k_1/k_{-1})(k^{H_2O} + k^{OH^-}[OH^-] + k^{ClO_2^-}[ClO_2^-] + k^{BrO_2^-}[BrO_2^-] + k^{SO_4^{2-}}[SO_4^{2-}])$. In this manner, corresponding values of the $(k_1/k_{-1})k^{Nu}$ rate constants for PO_4^{3-}, HPO_4^{2-}, CH_3COO^-, SO_4^{2-}, and pyridine are determined and given in Table 2. Initially, we expected a correlation between the base strength of OH^-, PO_4^{3-}, CO_3^{2-}, and HPO_4^{2-} and their k^{Nu} values, but these ions have similar rate constants despite large differences in their basicity. The k^{Nu} values decrease somewhat for pyridine and acetate ion, but these species are still effective as nucleophiles that assist the reaction between ClO_2 and BrO_2.

Second Catalytic Role of BrO_2^-. According to the proposed mechanism, the reaction is expected to be first-order in bromite. However, Figure 2 shows that the rate constant also has a squared dependence in $[BrO_2^-]$. This indicates that BrO_2^- may also act as a nucleophile in eq 3. If this is the case, the observed second-order rate constant can be expressed by eq 8, where $a = 2k_1\sum k^{Nu}[Nu]/k_{-1}[ClO_2^-]$ and $b = 2k_1k^{BrO_2^-}/k_{-1}[ClO_2^-]$ and $\sum k^{Nu}[Nu]$ is the sum of the other nucleophilic paths. Equation 8 gives a quadratic dependence on $[BrO_2^-]$ for k_{obs}, which is consistent with our results from the $[BrO_2^-]$ dependence study.

$$k_{obs} = \frac{2k_1(\sum k^{Nu}[Nu] + k^{BrO_2^-}[BrO_2^-])[BrO_2^-]}{k_{-1}[ClO_2^-]} = a[BrO_2^-] + b[BrO_2^-]^2 \tag{8}$$

Nucleophilic Catalysis by ClO_2^-. The ClO_2^- concentrations used in most of our kinetic studies were at least 25-fold smaller than $[buffer]_T$ and 5-fold smaller than $[BrO_2^-]$. Therefore, the effect of ClO_2^- as a nucleophilic catalyst could be overlooked. If ClO_2^- acts as a nucleophile, we would not be able to observe an acceleration of the rate by increasing $[ClO_2^-]$ because $k_{-1}[ClO_2^-]$ would simultaneously suppress the rate. However, catalytic enhancement by ClO_2^- in eq 3 can compensate for the inhibition. Thus, at high $[ClO_2^-]$, the reaction rate would no longer depend on $[ClO_2^-]$. When ClO_2^- has much higher concentrations than all other nucleophiles, the ClO_2^- path becomes dominant in the nucleophilic route and the following inequalities are valid: $k^{ClO_2^-}[ClO_2^-] \gg \sum(k^{Nu}[Nu])$ and $k_{-1}[ClO_2^-] \gg (\sum k^{Nu}[Nu])[ClO_2]^2$. Equation 9 gives the corresponding rate expression where the rate is independent of the concentration of ClO_2^-.

$$-\frac{d[ClO_2]}{dt} = \frac{2k_1(k^{ClO_2^-}[ClO_2^-])[BrO_2^-][ClO_2]^2}{k_{-1}[ClO_2^-]} = \frac{2k_1k^{ClO_2^-}[BrO_2^-][ClO_2]^2}{k_{-1}} \tag{9}$$

To test this proposal, the rates were measured using $[ClO_2^-] = 1.193$ M and $[ClO_2^-] = 1.550$ M on the UV spectrophotometer under the conditions $p[H^+] = 9.34$, $[CO_3]_T = 0.10$ M, $[BrO_2^-] = 0.0259$ M, and $[ClO_2]_i = 2.8 \times 10^{-4}$ M. Excellent second-order reactions in $[ClO_2]$ were observed with $k_{obs} = 11.7 \pm 0.1$ $M^{-1}\,s^{-1}$ for 1.193 M $[ClO_2^-]$ and $k_{obs} = 11.8 \pm 0.2$ $M^{-1}\,s^{-1}$ for 1.550 M $[ClO_2^-]$. These two k_{obs} values agree well, and the result supports a substantial nucleophilic role for the ClO_2^-. The $(k_1/k_{-1})k^{ClO_2^-}$ value is calculated to be $(2.2 \pm 0.6) \times 10^2$ $M^{-2}\,s^{-1}$.

Effect of Higher $[ClO_2]$ on the Reaction Order. The general rate expression in eq 5 predicts that an increase in the initial ClO_2 concentration at lower levels of $[ClO_2^-]$ will reduce the reaction order in $[ClO_2]$. The resulting mixed-order dependence in $[ClO_2]$ is analyzed by an initial rate method with a five-point smoothing derivative program.[20,21] The initial rate in terms of the absorbance (A) change can be expressed by eq 10, where $a = 2l\epsilon k_1[BrO_2^-]$, $b = k_{-1}[ClO_2^-]/(\sum k^{Nu}[Nu])$, l is the cell path length (0.962 cm), and ϵ is the molar absorptivity of ClO_2. Figure 4 shows the fit of eq 11 when $[BrO_2^-] = 16.68$ mM, $[ClO_2^-] = 1.82$ mM, $[CO_3^{2-}]_T = 0.10$ M, and $p[H^+] = 9.44$. This slope gives $k_1 = 36 \pm 2$ $M^{-1}\,s^{-1}$ and $k_{-1}/(\sum k^{Nu}[Nu]) = 2.41$, where $\sum k^{Nu}[Nu] = (k^{CO_3^{2-}}[CO_3^{2-}] + k^{BrO_2^-}[BrO_2^-] + k^{ClO_2^-}[ClO_2^-])$.

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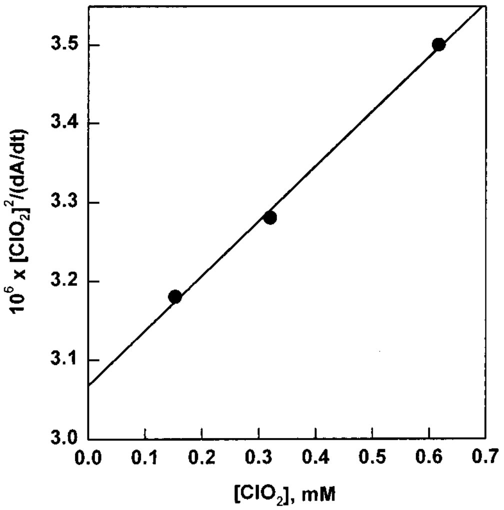

Figure 4. Initial instantaneous rate date (d*A*/d*t*) at higher concentrations of ClO_2 used to resolve values for k_1 which equals $(\text{slope})^{-1}(2l\epsilon[BrO_2^-])^{-1} = 36 \pm 2\ M^{-1}\ s^{-1}$.

Contributions from $k^{OH^-}[OH^-]$ and k^{H_2O} are negligible under the conditions used.

$$-\frac{dA}{dt}=\frac{a[ClO_2]^2}{b+[ClO_2]} \tag{10}$$

$$-\frac{[ClO_2]^2}{dA/dt}=\frac{b}{a}+\frac{[ClO_2]}{a} \tag{11}$$

Resolution of Rate Constants. Huie and Neta[19] generated BrO_2 by pulsed radiolysis and reported a rate constant of $3.6 \times 10^7\ M^{-1}\ s^{-1}$ (at pH 9.2 and an unspecified room temperature) for its reaction with ClO_2^- to give ClO_2 and BrO_2^-. With this k_{-1} value, it is possible to assign k^{Nu} values for each of the nucleophiles (Table 2). These third-order rate constants ($M^{-2}\ s^{-1}$) vary from 2.89×10^8 for Br^- to 2.0×10^4 for H_2O. The relative magnitude of k^{Nu} is the following: $Br^- > BrO_2^- \sim PO_4^{3-} \sim ClO_2^- > HPO_4^{2-} > CO_3^{2-} > Cl^- \sim OH^- > OAc^- > SO_4^{2-} \sim py \gg H_2O$. The values do not correlate with the base strength of these species. For example, hydroxide ion is a stronger Brønsted base than ClO_2^- by a factor of $10^{13.7}$, but ClO_2^- is more reactive as a nucleophile by a factor of 1.6 in assisting electron transfer from ClO_2 to BrO_2.

Nucleophilicity scales (*n*) have been established on the basis of the substitution with CH_3X (X = Br or I) that include some of the species in this study.[22] Figure 5 shows the correlation between nucleophilicities of eight species and their catalysis of ClO_2 oxidation by BrO_2.

Nucleophile Assistance of Electron Transfer. The experimental rate laws indicate a transition state composition of $[ClO_2BrO_2Nu]^{\ddagger}$ for the electron-transfer reaction from ClO_2 to BrO_2. Without the nucleophile the electron-transfer process would require a large reorganizational energy to form ClO_2^+ and BrO_2^- with very unfavorable initial products. It seems reasonable that the role of the nucleophile is to form a $NuClO_2$ species that is a more favorable electron donor. When Nu is OH^-, even a weakly associated $HOClO_2^-$ species could transfer an electron to BrO_2 to give $HOClO_2$ and BrO_2^-. Chloric acid ($HOClO_2$) is a stable molecule and is a very strong acid that would react very rapidly with any of the bases present to give chlorate ion (ClO_3^-) as a final product. With other nucleophiles, intermediate products such as $(O_3POClO_2)^{2-}$, for example, may rapidly hydrolyze to PO_4^{3-} and ClO_3^-. Since this occurs after the rate-determining electron-transfer reaction, these hydrolysis reactions do not appear in the rate expressions, nor do any of the stoichiometry studies show evidence of $NuClO_2^+$ species as products. On the other hand there would be ample time for hydrolysis reactions (eq 4) to occur with any of the nucleophiles.

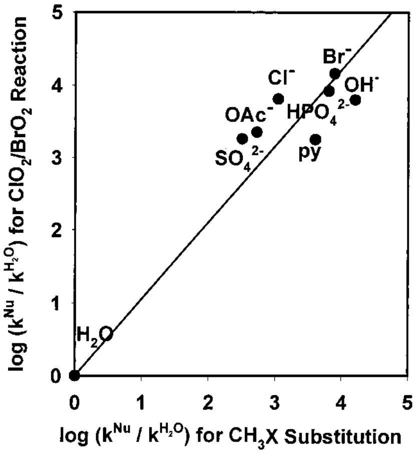

Figure 5. Nucleophilicity correlation.

Another detailed mechanism to consider is the initial formation of an electron pair bond between ClO_2 and BrO_2, which are both free radicals. The disproportionation reaction of BrO_2 is believed to proceed via Br_2O_4.[1,2] In our studies, the BrO_2 concentration is extremely low because its formation in eq 2 is thermodynamically unfavorable. However, the ClO_2 concentration is much greater and reactant intermediates such as $O_2ClOBrO$ or $OClOBrO_2$ may be possible. The role of the nucleophile would then be to associate with these intermediates via electron-pair donation that would permit heteronuclear bond cleavage to give $NuClO_2^+$ and BrO_2^- as initial products.

We have used ab initio calculations[23] to determine structures for proposed adducts between ClO_2 and OH^-, Br^-, and Cl^- to give intermediates $HOClO_2^-$, $BrClO_2^-$, and $ClClO_2^-$ that could transfer an electron to BrO_2 to give BrO_2^-. These structures along with the bond distances and atomic charges are shown in Figure 6. In each case there is a weak interaction between the nucleophile and ClO_2 with bond distances and ΔH_r values of 2.487 Å and -34.2 kcal mol^{-1} for OH^-, 2.988 Å and -16.4 kcal mol^{-1} for Cl^-, and 3.197 Å and -14.9 kcal mol^{-1} for Br^-. The $HOClO_2^-$ adduct prefers an orientation for OH that suggests some H-bonding may contribute to its ΔH value. These anionic adducts should be suitable to transfer an electron to BrO_2.

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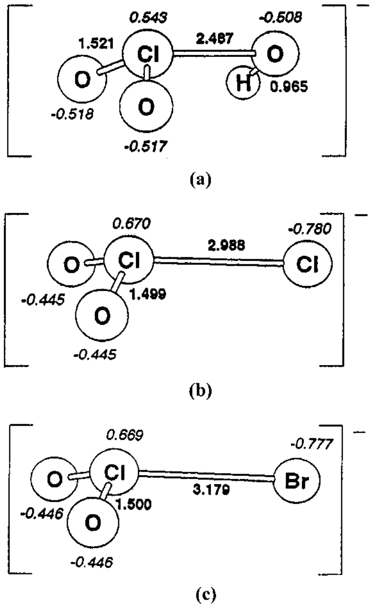
(23) Frisch, M. J.; et al. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, 1998.

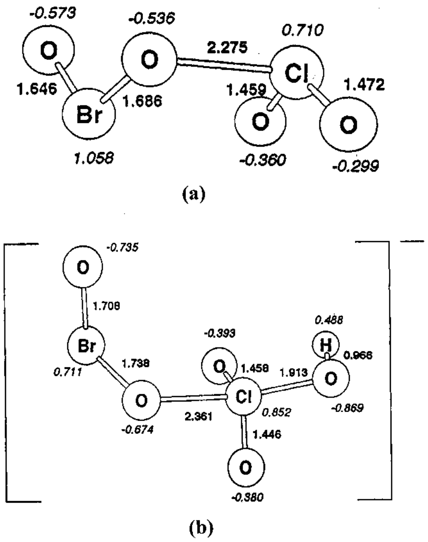


(a)

(b)

(c)

Figure 6. Equilibrium geometries (bond distances in Å) and atomic charges (italics) for possible intermediate adducts of ClO_2 with OH^-, Cl^-, and Br^-: (a) $HOClO_2^-$; (b) $ClClO_2^-$; (c) $BrClO_2^-$.



(a)

(b)

Figure 7. Equilibrium geometries (Å) and atomic charges (italics) for (a) OBrOCl(O)O and (b) its OH^- adduct $[OBrOCl(O)_2OH]^-$.

Figure 7a shows a structure for an alternative mechanism where the two free radicals (ClO_2 and BrO_2) first form a weak electron pair bond to give OBrOCl(O)O, where ΔH_r is -1.43 kcal mol^{-1} and the connecting O−Cl bond is 2.275 Å. An alternate OClOBr(O)O structure has the same energy. Addition of OH^- to either OBrOCl(O)O or OClOBr(O)O can occur at the Cl or Br sites. Optimization of the structures for the OH^- adduct show a consistent preference (ca. 20 kcal mol^{-1}) for binding at the Cl site to give $[OBrOCl(O)_2OH]^-$ (Figure 7b). ΔH_r for its formation is -62.6 kcal mol^{-1}. The calculations indicate that a significant amount of negative charge from OH^- is transferred to the O−Br−O portion of the molecular ion. Heteronuclear cleavage of the elongated O−Cl bond (2.361 Å) in the $[OBrOCl(O)_2OH]^-$ adduct would give BrO_2^- and $HOClO_2$ as the initial products.

The kinetics show that Nu, ClO_2, and BrO_2 must come together in the transition state. The ab initio calculations support $NuClO_2$, ClO_2BrO_2, and $NuClO_2BrO_2$ as possible intermediates. Although solvation of these species is not included, the calculations are helpful in visualizing possible mechanisms. The electron-transfer step between BrO_2 and the adducts in Figure 6 could be “outer sphere”, but if a bonding pathway occurs, then a structure such as Figure 7b is likely.

Electrode Potentials for Bromine Dioxide. Our experimental value for k_1 and the pulsed radiolysis[19] value for k_{-1} give an equilibrium constant $K_1 = k_1/k_{-1} = 1.0 \times 10^{-6}$, which corresponds to an $E°$ value of -0.355 V for eq 2. $E°$ for the ClO_2/ClO_2^- couple is 0.934 V,[24,25] so this gives $E° = 1.289$ V for the BrO_2/BrO_2^- couple. This value falls between $E°$ values of 1.21 V estimated by Stanbury[25] and 1.33 V given by Field et al.[26] for the BrO_2/BrO_2^- couple.

Conclusions

Electron-transfer reactions between ClO_2 and BrO_2 are catalyzed by many nucleophiles. The magnitude of the effect is large and does not depend on the Brønsted base strength of the nucleophiles but rather on the extent of their interaction with ClO_2 (or a ClO_2BrO_2 intermediate). The results suggest that this process might be an overlooked phenomenon in other electron-transfer reactions where one of the reactants needs to expand its coordination in order to permit favorable electron transfer. The kinetic consequence in the present system is that bromite ion and other nucleophiles cause a manyfold increase in the rate of disproportionation of chlorine dioxide.

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Supporting Information Available: Tables and figures with supplemental data. This material is available free of charge via the Internet at http://pub.acs.org.

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