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Nucleophile Assistance of Electron-Transfer Reactions between Nitrogen Dioxide and Chlorine Dioxide Concurrent with the Nitrogen Dioxide Disproportionation

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The reaction of chlorine dioxide with excess NO_2^- to form ClO_2^- and NO_3^- in the presence of a large concentration of ClO_2^- is followed via stopped-flow spectroscopy. Concentrations are set to establish a preequilibrium among ClO_2, NO_2^-, ClO_2^-, and an intermediate, NO_2. Studies are conducted at pH 12.0 to avoid complications due to the ClO_2^-/NO_2^- reaction. These conditions enable the kinetic study of the ClO_2 reaction with nitrogen dioxide as well as the NO_2 disproportionation reaction. The rate of the NO_2/ClO_2 electron-transfer reaction is accelerated by different nucleophiles ($NO_2^- > Br^- > OH^- > CO_3^{2-} > PO_4^{3-} > ClO_2^- > H_2O$). The third-order rate constants for the nucleophile-assisted reactions between NO_2 and ClO_2 (k^{Nu}, M^{-2} s^{-1}) at 25.0 °C vary from 4.4×10^6 for NO_2^- to 2.0×10^3 when H_2O is the nucleophile. The nucleophile is found to associate with NO_2 and not with ClO_2 in the rate-determining step to give $NuNO_2^+ + ClO_2^-$. The concurrent NO_2 disproportionation reaction exhibits no nucleophilic effect and has a rate constant of 4.8×10^7 M^{-1} s^{-1}. The ClO_2/NO_2/nucleophile reaction is another example of a system that exhibits general nucleophilic acceleration of electron transfer. This system also represents an alternative way to study the rate of NO_2 disproportionation.

Introduction

Recently, it was reported that many different nucleophiles (Nu's) catalyze the electron transfer from ClO_2 to BrO_2 where third-order rate constants increased 4 orders of magnitude from the weakest nucleophile studied (H_2O) to the strongest (Br^-).[1] It was postulated that the nucleophile effect need not be specific to the system studied but may be a more common phenomenon. Since then, the decomposition of ClO_2 in base was found to exhibit a similar nucleophile effect, albeit on a more limited scale of only strong bases acting as nucleophiles.[2] The present study of the reaction between ClO_2 and NO_2 represents a third instance in which nucleophiles accelerate electron transfer between nonmetal dioxide species. This system exhibits effects from a range of nucleophiles comparable to that seen by Wang et al.[1]

The disproportionation of NO_2 to nitrite and nitrate is a concurrent reaction that occurs in solution along with the $NO_2/ClO_2/Nu$ reaction. Two previous studies[3,4] of NO_2 disproportionation, performed by pulse radiolysis methods, showed scattered data and gave different interpretations of the overall reaction mechanism. Yet, many of the results in these two papers are in agreement.[5] The present work represents an alternative way to explore the rate of the NO_2 disproportionation reaction in solution. The NO_2/NO_2 path does not exhibit nucleophile assistance.

Stanbury et al. showed that the reaction of NO_2^- and ClO_2 proceeds via eq 1, and showed that ClO_2^- suppresses the reaction.[6] They observed an increase in ClO_2 reaction order

$$ClO_2 + NO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClO_2^- + NO_2 \qquad (1)$$

when different concentrations of ClO_2^- were added. They determined the forward reaction rate constant ($k_1 = 153$ M^{-1} s^{-1}), and used reduction potentials[7] to establish a value of

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0.016 for the equilibrium constant, $K_1 = k_1/k_{-1}$. We have exploited this equilibrium to study the reactions of NO_2 with ClO_2 as well as NO_2 disproportionation kinetics.

Experimental Section

Chlorine dioxide stock solutions were made as described previously.[8,9] Stock ClO_2 solutions were stored in the dark at 4 °C to slow ClO_2 volatilization and light decomposition. Concentrations of ClO_2 stock solutions were determined via UV/vis spectroscopy ($\epsilon_{359} = 1230$ M^{-1} cm^{-1}).[8] $NaClO_2$ (80% pure, Fluka) was purified to remove Na_2CO_3 via precipitation of $BaCO_3$ upon addition of $BaCl_2$.[8,10,11] To increase yields of recovered $NaClO_2$, water was removed via freeze-drying with a Virtis Freezemobile 12 lyophilizer. The purity of the solid $NaClO_2$ (99.3%) was determined via UV/vis spectroscopy ($\epsilon_{260} = 154$ M^{-1} cm^{-1}).[8] $NaNO_2$ purity (99.5%) was checked via titration of excess OCl^- with previously standardized $Na_2S_2O_3$.[12] Recrystallized and gravimetrically standardized $NaClO_4$ was used for ionic strength (μ) control where μ_T for all solutions was equal to 1.0 M. Carbonate-free NaOH was prepared from Ar-sparged boiled water and saturated NaOH solution. The stock NaOH was stored under Ar to keep atmospheric CO_2 from entering the solution.

For pH measurements a ROSS combination electrode was used. This electrode was calibrated via titration with previously standardized $HClO_4$ and NaOH to allow for determination of pH ($-\log [H^+]$). The pK_w value is 13.60 for the conditions used.[1] UV/vis spectra were taken with a Lambda-9 UV/vis-near-IR spectrophotometer. Kinetic studies were performed on an Applied Photophysics stopped-flow spectrometer (0.962 cm optical path length). All data points shown are an average of at least five replicates. Chromatographic data were collected for the species produced in this reaction by using a Dionex DX-500 HPLC instrument. Samples were injected through a 25 μL injection loop to quaternary amine anion exchange guard and separation columns. Na_2CO_3 (9.0 mM) was used as the eluent at a flow rate of 1 mL/min. Species were quantified via conductivity detection after background suppression with an ASRS-Ultra suppressor which has a self-regenerating current of 100 mA. Conditions for the product study were set to be similar to those used for kinetic determinations ($[ClO_2^-] = 0.06$ M, $[NO_2^-] = 0.020$ M, $[OH^-] = 0.020$ M). After reaction completion, aliquots were added to a 0.1 M $[OH^-]$ solution to minimize the ClO_2^-/NO_2^- reaction.

Conditions for most of the kinetic studies were set so the loss of ClO_2 was second order. Chlorite concentration was kept at 0.060 M, and $[OH^-] = 0.025$ M (pH 12.0). High pH was used to eliminate the need for added buffers and to eliminate interference from the NO_2^-/ClO_2^- reaction, which is catalyzed by Cl^- and H^+.[13]

Results and Discussion

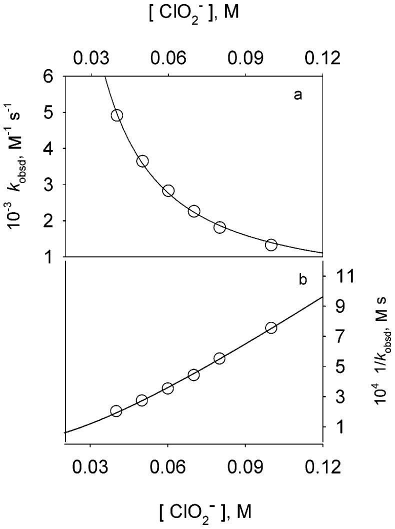

Figure 1. (a) k_{obsd} dependence on chlorite concentration under second-order ClO_2-loss conditions. (b) $1/k_{obsd}$ dependence on chlorite concentration under second-order ClO_2-loss conditions. Conditions for both graphs are 0.02 M NO_2^-, pH 9.80, 5.0 mM $[CO_3]_T$, $\mu = 1.0$ M ($NaClO_4$), and $T = 25.0$ °C. The solid line in (b) shows the curve fit to $a/[ClO_2^-] + b/[ClO_2^-]^2$, where $a = 100(7)$ s^{-1} and $b = 4.0(3)$ M s^{-1}.

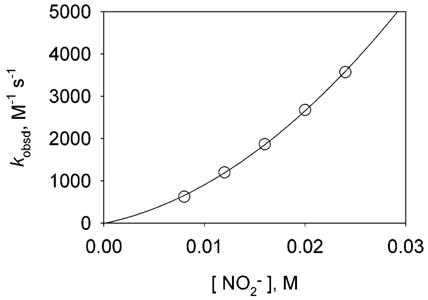

Figure 2. k_{obsd} dependence on nitrite concentration under second-order ClO_2-loss conditions, at 0.06 M ClO_2^-, 0.0512 M Br^-, 0.025 M OH^-, $\mu = 1.0$ M ($NaClO_4$), and $T = 25.0$ °C. The solid line shows the curve fit to $k_{obsd} = k_3'[NO_2^-] + k_4'[NO_2^-]^2$, where $k_3' = 5.0(5) \times 10^4$ M^{-2} s^{-1} and $k_4' = 4.2(2) \times 10^6$ M^{-3} s^{-1}.

A. Kinetics. The reaction between ClO_2 and NO_2^- is first order in both reactants at low $[NO_2^-]$.[6] In the presence of chlorite, the reaction order in ClO_2 changes from first order to second order as the ClO_2^- concentration increases. Stanbury et al. observed this increase in reaction order, but did not mention its significance.[6] When $[ClO_2^-]$ is between 0.040 and 0.10 M at pH 10, the rate of loss of ClO_2 becomes second order. Figure 1a shows the suppression of the rate with increasing ClO_2^- concentration under these conditions. The data in Figure 1b indicate that the chlorite suppression is greater than first order. Conditions with $[ClO_2^-]$ less than 0.040 M were insufficient to maintain preequilibrium conditions (i.e., both a first-order and a second-order dependence in ClO_2 loss is observed, where the first-order dependence comes from the ClO_2/NO_2^- reaction). With ClO_2^- concentration greater than 0.10 M at pH 10 the loss of ClO_2 is no longer second order because of a competing reaction between ClO_2^- and NO_2^-. When the pH is increased to 12.0, a second-order loss of ClO_2 is observed even at higher ClO_2^- concentrations. Thus, at pH 12, the ClO_2^-/NO_2^- reaction is very slow and is not a factor in the kinetics, so most of our studies were conducted at this pH. Figure 2 shows the observed rate constant dependence on $[NO_2^-]$ for second-order ClO_2 loss. Under these conditions the dependence on

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$[NO_2^-]$ is greater than first order, with both first- and second-order contributions.

B. Effect of Nucleophiles. The nucleophiles studied in the present work (Br^-, Cl^-, OH^-, CO_3^{2-}, PO_4^{3-}, NO_2^-, ClO_2^-, and H_2O) were chosen because of their demonstrated effect on the rate of the ClO_2/BrO_2 reaction.[1] For the ClO_2/NO_2^- system, all nucleophiles except Cl^- caused the rate to increase linearly with nucleophile concentration at pH 12.0. Hydroxide is used to control the pH of the solutions, but it also acts as a nucleophile. Studies with high chloride concentrations and much lower hydroxide concentration (pH 10) also failed to show a Cl^- effect.

C. Mechanism. The mechanism in eqs 1−5 is proposed to explain the experimental observations. The rate-determining steps in this mechanism are eqs 3 and 4.

$$ClO_2 + NO_2^- \overset{K_1}{\rightleftharpoons} ClO_2^- + NO_2 \qquad (1)$$

$$NO_2 + NO_2 \overset{K_2}{\rightleftharpoons} N_2O_4 \qquad (2)$$

$$NO_2 + ClO_2 + Nu \xrightarrow{k_3^{Nu}} NuNO_2^+ + ClO_2^- \qquad (3)$$

$$N_2O_4 + H_2O \xrightarrow{k_4} NO_3^- + NO_2^- + 2H^+ \qquad (4)$$

$$NuNO_2^+ + H_2O \xrightarrow{fast} NO_3^- + Nu + 2H^+ \qquad (5)$$

Equation 4 is the hydrolysis of N_2O_4, which when coupled to the equilibrium in eq 2 has been studied previously as the NO_2 disproportionation reaction.[3−5] With added ClO_2^-, eq 1 is under rapid preequilibrium conditions with low levels of NO_2. The equilibrium in eq 2 is also established rapidly.[5] The resulting rate expression, based on the above mechanism, is shown in eq 6. The loss of ClO_2 is second order in the two pathways represented by eqs 3 and 4 when the preequilibria in eqs 1 and 2 are considered. The observed rate constant for this system, eq 7, is composed of two reaction pathways (k_3^{Nu} and K_2k_4). Computer modeling[14] with known parameters for K_1, K_2k_4, and approximate values of k_3^{Nu} shows that the reactions, eq 3 and the product of eqs 2 and 4, proceed at comparable rates. While the NO_2 disproportionation rate constant (K_2k_4) is approximately 100 times larger than the NO_2/ClO_2 reaction rate constant (k_3^{Nu}), the low levels of NO_2 in this system (∼1 × 10^{-6} M) keep the NO_2/NO_2 pathway from dominating the loss of ClO_2. This low level of NO_2 also enables us to set $[NO_2]_T$ (where $[NO_2]_T = [NO_2] + 2[N_2O_4]$) equal to $[NO_2]$ because the overall concentration of N_2O_4 under our conditions is very low. The NO_2 dependence is first order as described in eq 3 and second order as described in eq 4 (after consideration of eq 2). This explains the nitrite dependence shown in Figure 2. The preequilibrium in eq 1 necessitates that the loss of nitrite parallels the loss of NO_2. The fit of the data in Figure 2 follows an $a[NO_2^-] + b[NO_2^-]^2$ equation.[15] The ClO_2^- dependence as shown in Figure 1a (data are fit to an $a/[ClO_2^-] + b/[ClO_2^-]^2$ equation) also is explained by the mechanism. With consideration of the preequilibrium (eq 1), the $NO_2/ClO_2/Nu$ reaction in eq 3 yields an inverse first-order dependence in chlorite while the NO_2 hydrolysis reaction in eq 4 gives an inverse second-order dependence as shown in eq 7. Equation 5 is a rapid reaction where the nucleophile is regenerated to complete the catalytic electron transfer by forming NO_3^-. The reaction between NO_2 and ClO_2 (eq 3) may occur in more than one step, but is written to emphasize the species present in the transition state. To the best of our knowledge, the reaction between ClO_2 and NO_2 in aqueous solution has not been studied, although the reaction has been observed in nonaqueous solvents and in the gas phase.[16−19] However, the reported rate constants in these media are much smaller than we observe in aqueous solution. The $\sum k_3^{Nu}[Nu]$ term in eqs 6 and 7 represents the rate constant for the k_3 pathway when a nucleophile is present at a specific concentration ([Nu]).

$$-\frac{d[ClO_2]}{dt} = \frac{K_1(\sum k_3^{Nu}[Nu])[NO_2^-][ClO_2]^2}{[ClO_2^-]} + \frac{K_1^2K_2k_4[NO_2^-]^2[ClO_2]^2}{[ClO_2^-]^2} \qquad (6)$$

$$k_{obsd} = \frac{K_1(\sum k_3^{Nu}[Nu])[NO_2^-]}{[ClO_2^-]} + \frac{K_1^2K_2k_4[NO_2^-]^2}{[ClO_2^-]^2} \qquad (7)$$

The association of the nucleophile with NO_2 yields ClO_2^- and NO_3^- as products. If the nucleophile were to associate with ClO_2 instead, as was seen previously,[1,2] NO_2^- and ClO_3^- would be the products. Electrode potentials for the two possible reactions shown in eqs 8 and 9

$$NO_2 + ClO_2 + 2OH^- \rightarrow NO_2^- + ClO_3^- + H_2O \; (E_b^\circ = 1.51\ V) \qquad (8)$$

$$NO_2 + ClO_2 + 2OH^- \rightarrow ClO_2^- + NO_3^- + H_2O \; (E_b^\circ = 1.89\ V) \qquad (9)$$

(where the acidic reduction potentials are converted to basic potentials and the solubility equilibrium of NO_2 is employed[7,20,21]) indicate that both pathways are thermodynamically favorable. We indicate in the mechanism that NO_3^- is formed preferentially over ClO_3^-. This is based on a product study for our system, which shows that nitrate is the major product ($\Delta[ClO_2]/\Delta[NO_3^-] = 1.96(4)$). The 2:1 ratio occurs because ClO_2 is lost in eq 1 as well as in eq 3. Small amounts

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of chlorate are detected as products, but the concentrations produced are too low to evaluate and are within the error of zero for the method used. We, therefore, consider the reaction in eq 8 to be a very minor pathway and will focus solely on the reaction in which the nucleophile associates with NO_2.

D. Resolution of Reaction Pathways. The NO_2/NO_2 pathway in the proposed mechanism (eqs 2 and 4) has no nucleophile dependence. Initially, this was not known and necessitated the inclusion of an additional factor in the second term in eq 7 ($\sum k_4^{Nu}[Nu]$) to account for the possibility that the NO_2/NO_2 pathway also depends on nucleophiles. In this case a simple k_{obsd} vs [Nu] study would not lead to separable rate constants. Because of the possibility that eq 4 is assisted by nucleophiles, two different strategies were employed to study the system and to resolve the two rate constants (k_3^{Nu} and $K_2k_4^{Nu}$). A ClO_2^- dependence at varying nucleophile concentrations will separate the k_3^{Nu} path from the k_4^{Nu} path because the k_3^{Nu} path will vary as $1/[ClO_2^-]$ while the k_4^{Nu} path will vary as $1/[ClO_2^-]^2$. Due to the limited range of $[ClO_2^-]$ that will yield pure second-order ClO_2-loss kinetics (i.e., $[ClO_2^-]$ must be large enough to maintain preequilibrium conditions), and because of the rapid drop in rate with increasing $[ClO_2^-]$, a NO_2^- dependence approach was chosen instead. Thus, a NO_2^- dependence at each specific nucleophile concentration is performed. The k_3^{Nu} path has a first-order nitrite concentration dependence, while the k_4^{Nu} path would have a $[Nu][NO_2^-]^2$ dependence. This method has no limitations with respect to $[NO_2^-]$ for second-order ClO_2-loss kinetics as long as NO_2^- remains in excess.

To separate the k_3^{Nu} (ClO_2/NO_2/Nu reaction) rate constant from the k_4^{Nu} (NO_2 disproportionation) rate constant, a set of five separate k_{obsd} vs $[NO_2^-]$ data points are obtained at a specific nucleophile concentration. This procedure is carried out for several different nucleophile concentrations. Each of the plots, representing a nitrite dependence at a set nucleophile concentration, is fit to a combined first-order and second-order rate expression. Figure 2 shows a fit to the data at a $[Br^-]$ of 0.051 M ($k_{obsd} = k_3'[NO_2^-] + k_4'[NO_2^-]^2$). In this case, $k_3' = K_1(\sum k_3^{Nu}[Nu])/[ClO_2^-]$, and if a k_4^{Nu} path exists, $k_4' = K_1^2K_2(\sum k_4^{Nu}[Nu])/[ClO_2^-]^2$. As shown in eq 10,

$$k_3' = \frac{K_1 k_3^{Br^-}[Br^-]}{[ClO_2^-]} + \frac{K_1(\sum k_3^{Nu}[Nu'])}{[ClO_2^-]} \qquad (10)$$

the summation in k_3' can be divided into two terms, one representing the desired nucleophile under study (in this case Br^-), $K_1k_3^{Br^-}[Br^-]/[ClO_2^-]$, and a second term that represents all other nucleophiles, [Nu′], present, $K_1(\sum k_3^{Nu}[Nu'])/[ClO_2^-]$. Figure 3 is a plot of k_3' vs the concentration of bromide. With known values of K_1 and $[ClO_2^-]$, the values of k_3^{Nu} are determined, where k_3^{Nu} represents the k_3 rate constant for the specific nucleophile of interest. All plots of k_3' vs specific nucleophile concentration, except chloride, show a linear increase as expected from the rate expression in eq 10 (see the Supporting Information figures). The intercepts of these plots incorporate the contributions from all other nucleophiles in the system ([Nu′]).

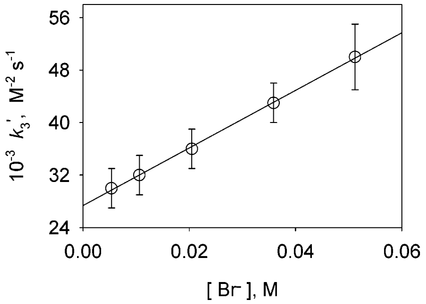

Figure 3. k_3' dependence on bromide concentration, where the slope is $K_1k_3^{Br^-}/[ClO_2^-]$ and the intercept is $K_1(\sum k_3^{Nu}[Nu])/[ClO_2^-]$. Data points represent the coefficients from the first-order nitrite term of several different nitrite dependencies conducted at different bromide concentrations.

1. Lack of Nucleophile Dependence for the NO_2/NO_2 Pathway. Plots of k_4' ($\sum(k_4^{Nu}[Nu])K_1^2K_2/[ClO_2^-]^2$) vs [Nu] show no trend as the nucleophile concentrations increase for all nucleophiles studied (see the Supporting Information figures) except for Br^-, which inhibits the reaction (as discussed later). Because the k_4' term shows no dependence on nucleophile concentration, the summation term is dropped and k_4' becomes $k_4K_1^2K_2/[ClO_2^-]^2$. This leads to the mechanism given in eqs 1−5, and to eq 7. Because the NO_2/NO_2 pathway is now known to be independent of nucleophile concentration, evaluation of the nucleophile dependencies directly from eq 7 is possible. As detailed from eq 7, plots of k_{obsd} vs [Nu] have slopes related to k_3^{Nu}, where [Nu] represents the concentration of the nucleophile with variable concentration. Once values of k_3^{Nu} are known, the K_2k_4 rate constant is determined from the intercept after subtraction of the contributions from all other nucleophiles ($\sum k_3^{Nu}[Nu']$).

This lack of a nucleophile dependence in the K_2k_4 path raises the question as to why nucleophiles have no effect on the rate-determining step of the NO_2/NO_2 pathway. We hypothesize that nucleophiles in the ClO_2/NO_2 reaction assist in the formation of NO_2^+. The $NuNO_2^+$ species, which forms from the NO_2/ClO_2/Nu reaction, stabilizes the NO_2^+ species by association of the nucleophile. On the other hand, in eq 2, two NO_2 molecules can form a relatively stable N_2O_4 molecule. Nucleophiles are not needed to stabilize this species. N_2O_4 is a known species that has a millisecond lifetime in aqueous solution.[4] From the intercept of a plot of k_4' vs [Nu], a value of the NO_2 disproportionation rate constant is obtained. For all nucleophiles studied the average value of K_2k_4 equals $4.8(4) \times 10^7$ M^{-1} s^{-1} ($T = 25.0$ °C, $\mu = 1.0$ M), which is in general agreement with previously obtained values.[5] Our study represents a new method, via use of stopped-flow spectroscopy, for determining the NO_2 disproportionation rate constant. It also reaffirms the pulse radiolysis results,[3−5] where the scatter and uncertainty may lead to speculation as to the validity of the rate constant. Our experiment represents many individual measurements of the NO_2 disproportionation rate constant (during different nucleophile studies), so we are confident in its value.

2. Bromide Inhibition. Unlike all other nucleophiles studied, bromide exhibits a trend in the k_4' vs $[Br^-]$ plot. As $[Br^-]$ increases, the value of k_4' decreases linearly (Figure 4). We hypothesize that bromide can form a strong enough

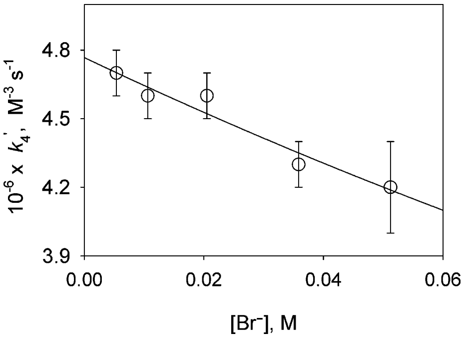

Figure 4. Decrease in rate of the NO_2/NO_2 pathway with increasing [Br^-]. $k_4' = K_1^2K_2(\sum k_4^{Nu}[Nu'])/[ClO_2^-]^2 + K_1^2K_2k_4^{Br^-}[Br^-]/[ClO_2^-]^2$. For all data points, 0.008 M < [NO_2^-] < 0.024 M, [ClO_2^-] = 0.06 M, [OH^-] = 0.025 M, μ = 1.0 M ($NaClO_4$), and T = 25.0 °C. Data are fit to $a/(1 + 2bx + b^2x^2)$, an equation generated by using eq 11 and $[NO_2]_T$, were a equals the intercept and b equals K^{Br^-}.

Table 1. Summary of Rate Constants for the Reaction between ClO_2 and NO_2[a]

nucleophile	n^b	k_3^{Nu}, M^{-2} s^{-1}	nucleophile	n^b	k_3^{Nu}, M^{-2} s^{-1}
H_2O	0	$2.0(5) \times 10^3$ [e]	CO_3^{2-}	d	$1.0(2) \times 10^6$
Cl^-	3.04	*c*	OH^-	4.2	$1.1(4) \times 10^6$
ClO_2^-	d	$0.10(3) \times 10^6$	Br^-	3.89	$1.5(4) \times 10^6$
PO_4^{3-}	d	$0.8(4) \times 10^6$	NO_2^-	4.2[22]	$4.4(6) \times 10^6$

[a] Conditions: 25.0 °C, μ = 1.0 M. [b] n is the nucleophilicity defined as $n = \log(k_3^{Nu}/k^{H_2O})$ for CH_3X substitution, where values were obtained from ref 24. [c] This value is not measurable due to the effects of other nucleophiles present at high pH. [d] Values are not available. [e] k^{H_2O}/55.5 M to give M^{-2} s^{-1}.

complex with NO_2 to sequester NO_2 in a relatively unreactive form (i.e., NO_2Br^-) (eq 11) and hinder NO_2/NO_2 bond

$$Br^- + NO_2 \xrightleftharpoons{K^{Br^-}} NO_2Br^- \qquad (11)$$

formation at the nitrogens. If the sequestered form of NO_2 is NO_2Br^-, the total concentration of NO_2, before NO_2 loss in reaction eqs 3 and 4, equals $[NO_2]_T$, where $[NO_2]_T = [NO_2] + [NO_2Br^-]$. The equilibrium constant (K^{Br^-}) between NO_2 and this unreactive form equals $[NO_2Br^-]/[NO_2][Br^-]$. By solving for NO_2 with these two equations, and by adding this term into the k_4 portion of eq 6, an inverse bromide dependence in the coefficient for the $[NO_2^-]^2$ term results. A fit of the bromide dependence data to such a term yields $K^{Br^-} = 1.3(2)$ M^{-1}. This NO_2Br^- species is further evidence for the nucleophile association with NO_2 rather than with ClO_2 as exhibited by the product study.

E. Determination of k_3^{Nu} Values. The experimental values of k_3' (eq 10) increase linearly with the concentration of the selected nucleophile as shown in Figure 3 for [Br^-]. The relatively large error bars arise because these data points represent the first-order coefficient of the nitrite dependence fit (eq 7). Similar results are obtained for a series of nucleophiles with slopes that permit the evaluation of k_3^{Nu} (Table 1). The intercepts in these plots represent the sum of the rates from all the other nucleophiles present ([Nu′]) in the system. In the case of bromide, the intercept equals $k_3^{H_2O} + k_3^{ClO_2^-}[ClO_2^-] + k_3^{OH^-}[OH^-]$. When hydroxide is the nucleophile of interest, the intercept equals $k_3^{H_2O} + k_3^{ClO_2^-}[ClO_2^-]$. The $k_3^{ClO_2^-}$ rate constant (obtained from a nucleophilic study of ClO_2^-) and the intercept from the hydroxide plot enable the determination of $k_3^{H_2O}$ ($1.0(3) \times 10^5$ M^{-1} s^{-1}). The values of the third-order rate constants increase by a factor of two thousand from the weakest nucleophile (H_2O) to the strongest nucleophile (NO_2^-) as listed in Table 1.

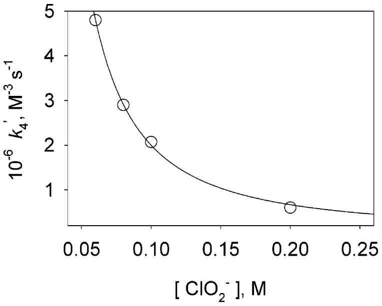

Figure 5. k_4' dependence on chlorite concentration for the nitrite-as-a-nucleophile study. Data points are fit to $k_4' = K_1^2K_2k_4/[ClO_2^-]^2 + K_1k_3^{NO_2^-}/[ClO_2^-]$, where $K_1^2K_2k_4 = 1.33(9) \times 10^4$ M^{-1} s^{-1} and $K_1k_3^{NO_2^-} = 7(1) \times 10^4$ M^{-2} s^{-1}. For all data points, 0.008 M < [NO_2^-] < 0.024 M, [OH^-] = 0.025 M, μ = 1.0 M ($NaClO_4$), and T = 25.0 °C.

F. Nitrite as a Nucleophile. Nitrite is also studied as a possible nucleophile in this system. Because all previous nucleophile studies were conducted as nitrite dependencies, a large nucleophile dependence in nitrite would alter the rate constants obtained. The nucleophilicity (n) of nitrite was previously estimated as 4.2 (i.e., 4 orders of magnitude more reactive than H_2O).[22] Nitrite is a strong nucleophile compared to other nucleophiles studied, and so a large NO_2^- effect is possible. Equation 12 restates eq 7 if nitrite acts as a

$$k_{obsd} = \frac{K_1(\sum k_3^{Nu}[Nu'])[NO_2^-]}{[ClO_2^-]} + \frac{K_1k_3^{NO_2^-}[NO_2^-]^2}{[ClO_2^-]} + \frac{K_1^2K_2k_4[NO_2^-]^2}{[ClO_2^-]^2} \qquad (12)$$

nucleophile. The second term, which represents the nitrite-as-a-nucleophile term, comes from the summation term in eq 7. The $\sum k_3^{Nu}[Nu']$ term in eq 12 represents all nucleophiles present with the exception of NO_2^-. When NO_2^- is a nucleophile, an additional second-order term in nitrite arises, which will not manifest itself in the k_3' constant because k_3' represents only first-order nitrite dependencies. This is also why nitrite is not listed as a contribution to the $\sum k_3^{Nu}[Nu']$ intercept terms for Br^- and OH^- in the previous section.

To study the nitrite effect, NO_2^- dependencies are conducted at several ClO_2^- concentrations. The high pH of the study prevents interference from the ClO_2^-/NO_2^- reaction, so higher ClO_2^- concentrations are used. The first term in eq 12 is first order in NO_2^-, while the second and third terms are second order in nitrite. This enables fits of the k_{obsd} data to a $k_3'[NO_2^-] + k_4'[NO_2^-]^2$ equation for each chlorite concentration. The k_4' coefficients from the above equation are plotted vs [ClO_2^-] (Figure 5), where k_4' is listed in eq 13. A fit of the k_4' values in Figure 5 resolves $k_3^{NO_2^-}$ and K_2k_4. The K_2k_4 value obtained is in agreement with K_2k_4

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(22) Margerum, D. W.; Schurter, L. M.; Hobson, J.; Moore, E. E. *Environ. Sci. Technol.* **1994**, *28*, 331−337.

$$k_4' = \frac{K_1 k_3^{NO_2^-}}{[ClO_2^-]} + \frac{K_1^2 K_2 k_4}{[ClO_2^-]^2} \qquad (13)$$

values obtained from other nucleophile studies. The value of $k_3^{NO_2^-}$ is 4.4(6) × 10^6 M^{-2} s^{-1}. This value is the largest obtained of any nucleophile studied in our system. Therefore, NO_2^-, acting as a nucleophile, does indeed contribute to the rates when other nucleophiles are studied. The lack of a third-order nitrite term, when the k_{obsd} vs $[NO_2^-]$ data are fitted, is further evidence of no nucleophile assistance in the NO_2/NO_2 pathway.

Because the term representing nitrite as a nucleophile is second order with respect to NO_2^- concentration (second term in eq 12), its effect will only manifest itself in the k_4' constant and not the k_3' constant of other nucleophiles studied. Therefore, the value of k_4' needs correction to account for the $K_1k_3^{NO_2^-}/[ClO_2^-]$ term. Because $[ClO_2^-]$ is always kept constant at 0.06 M, this correction is constant and can be subtracted from the overall k_4' term for each nucleophile. The value of 4.8(4) × 10^7 M^{-1} s^{-1} for K_2k_4 given earlier has been corrected to reflect the finding that NO_2^- also acts as a nucleophile.

G. Chlorite as a Nucleophile. Chlorite, present in all previous nucleophile studies at 0.06 M, may also act as a nucleophile. Because the ClO_2^- concentration is constant, its effect on the rate will not vary, which is different from the nitrite case. When eq 7 is rewritten with ClO_2^- as a nucleophile, eq 14 results. The first term represents the

$$k_{obsd} = K_1 k_3^{ClO_2^-}[NO_2^-] + \frac{K_1(\sum k_3^{Nu}[Nu'])[NO_2^-]}{[ClO_2^-]} + \frac{K_1^2 K_2 k_4 [NO_2^-]^2}{[ClO_2^-]^2} \qquad (14)$$

dependence of ClO_2^- as a nucleophile. It derives from the $\sum k_3^{Nu}[Nu]$ term in eq 7, which leaves the $\sum k_3^{Nu}[Nu']$ parameter in eq 14 to represent the sum of all nucleophiles present in the system except ClO_2^-. Rate constants can be determined directly from k_{obsd} vs $[ClO_2^-]$ experiments, Figure 6. These data are fit to an $a/[ClO_2^-]^2 + b/[ClO_2^-] + c$ equation, and that fit is shown in Figure 6, where $a = K_1^2K_2k_4[NO_2^-]^2$, $b = K_1(\sum k_3^{Nu}[Nu'])[NO_2^-]$, and $c = K_1k_3^{ClO_2^-}$ from eq 14. From these parameters, K_2k_4 agrees with the previous results and $k_3^{ClO_2^-}$ is 0.10(3) × 10^6 M^{-2} s^{-1}. Chlorite is not a very strong nucleophile in this system, but its effect may still be notable due to its high concentration. A value of $k_3^{ClO_2^-}$ multiplied by the chlorite concentration (0.06 M) is subtracted from the intercept value for the $k_3'[OH^-]$ study to yield $k_3^{H_2O}$.

H. Nucleophile Assistance for the ClO_2/NO_2 Reaction. The rate expression in eq 6, for the mechanism in eqs 1−5, shows a nucleophile dependence for the k_3 step but not for the K_2k_4 steps. The transition state for the k_3 step is $(ClO_2\text{-}NO_2Nu)^{\ddagger}$, where the presence of the nucleophile in the transition state facilitates electron transfer to give $NuNO_2^+$ and ClO_2^-. For the nucleophiles studied, the charges of the nucleophile-associated metastable intermediates range from a +1 species ($H_2ONO_2^+$) when water is the nucleophile to a doubly negative species ($PO_4NO_2^{2-}$) when PO_4^{3-} is the nucleophile. In the case of OH^-, the intermediate is $HONO_2$, which at this pH rapidly deprotonates to form products. Other nucleophiles behave in a similar manner, where the nucleophile-associated species hydrolyze in a rapid step that does not appear in the rate expression.

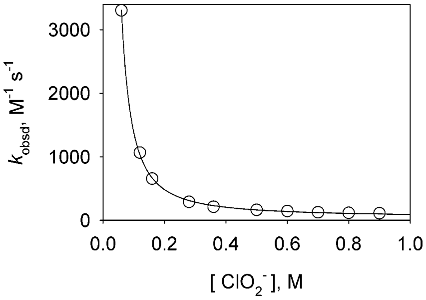

Figure 6. k_{obsd} dependence on chlorite concentration for the chlorite-as-a-nucleophile study. Data points are fit to $k_{obsd} = a/[ClO_2^-]^2 + b/[ClO_2^-] + c$, where $a = 9.2(3)$ M s^{-1}, $b = 43(5)$ s^{-1}, and $c = 40(10)$ M^{-1} s^{-1}. For all data points, $[NO_2^-] = 0.024$ M, $[OH^-] = 0.025$ M, $\mu = 1.0$ M ($NaClO_4$), and $T = 25.0$ °C.

Wang et al. discussed two association mechanisms for nucleophile-assisted electron-transfer reactions.[1] Similar alternative mechanisms may occur for the ClO_2/NO_2/Nu path. In the first possible mechanism ClO_2 associates with NO_2, and in a second step the nucleophile binds to the ClO_2NO_2 species. This association would then facilitate the electron transfer, after which occurs a heteronuclear bond cleavage to form ClO_2^- and $NuNO_2^+$. The second possible mechanism involves NO_2/Nu association initially, followed by reaction with ClO_2. Odeh et al. showed that in the ClO_2/OH^- system both mechanisms occur.[2] They observed a ClO_2Nu species reaction with another ClO_2 while concurrently a strongly basic nucleophile associates to a Cl_2O_4 species, leading to products. In our system, the inhibition of the NO_2/NO_2 pathway with the formation of NO_2Br^- suggests prior nucleophile association with NO_2, but this does not rule out the formation of ClO_2NO_2 first, followed by nucleophile addition.

I. Lack of Nucleophile Assistance for the NO_2/NO_2 Pathway. The NO_2/NO_2 pathway (K_2k_4) exhibits no evidence of a nucleophile effect. This indicates that nucleophiles are not involved in the rate-determining step as in the ClO_2/NO_2 reaction. Because the establishment of an equilibrium between NO_2 and N_2O_4 is rapid,[5] the rate-determining step for the NO_2/NO_2 pathway is a combination of eqs 2 and 4. Because eq 4 is the slow step for this pathway, the lack of any nucleophile dependence indicates that the only "nucleophile" that affects the reaction is water, with a rate constant (K_2k_4) of 4.8(4) × 10^7 M^{-1} s^{-1}. A hydroxide effect would be expected since the nucleophilicity of OH^- is 4 orders of magnitude larger than that of water, but none is seen. Similarly, no other strong bases show an effect in this reaction. Treinin and Hayon reported that the N_2O_4 hydrolysis reaction is independent of pH, which confirms our observation.[3] A similar conclusion was reached when the absorption of gaseous NO_x (where $NO_x = N_2O_4 + N_2O_3$) into an alkali solution was studied.[23] The lack of a nucleophile effect for the NO_2/NO_2 pathway suggests that any nucleophile assistance, if present, must occur in a subsequent rapid step.

Conclusions

Several nucleophiles accelerate the electron transfer from NO_2 to ClO_2 as shown in eq 15. This is the third such example where expansion of the coordination of a nonmetal

$$NO_2 + ClO_2 + Nu \rightarrow (NuNO_2ClO_2)^{\ddagger} \rightarrow NuNO_2^{+} + ClO_2^{-} \tag{15}$$

dioxide facilitates an electron transfer. In the previous two examples, the nucleophile associates with ClO_2. In the present case, the nucleophile associates with NO_2, which indicates the nucleophilic effect is a general phenomenon that is not limited to only Nu/ClO_2 interactions. In all three cases the nucleophile associates with the reducing species, and this assists the transfer of an electron to the oxidizing species. The third-order rate constants for the $ClO_2/NO_2/Nu$ reaction increase by 3 orders of magnitude from the water-assisted reaction to the nitrite-assisted reaction. Only chloride shows no increase in rate with increases in concentration. The effect of chloride on the rate may not be large enough to prevent OH^- from overwhelming it. On the other hand, the NO_2/NO_2 pathway is not assisted by nucleophiles. The disproportionation of NO_2 occurs as a rate-determining step, but no increase in rate is observed with added nucleophiles. This indicates that the N_2O_4 hydrolysis reaction is not assisted by nucleophiles or bases. The current system represents a new way to study the NO_2 disproportionation reaction.

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

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