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Kinetics and Mechanism of Nitrite Oxidation by $HOBr/BrO^-$ in Atmospheric Water and Comparison with Oxidation by $HOCl/ClO^-$

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The rate of the reaction of nitrite with hypobromite/hypobromous acid was studied over a wide range of H^+ concentrations ($6.5 \leq -\log [H^+] \leq 10$). The kinetics were measured as a function of NO_2^-, H^+ and total Br(I) ($[HOBr]_{total} = [HOBr] + [BrO^-] + [BrNO_2]$) concentrations. A mechanism is proposed for nitrite oxidation involving the reversible formation of $BrNO_2$, which is then attacked by NO_2^- to yield N_2O_4 in the rate-determining step. The second-order rate coefficient k_1 for the latter reaction was determined at different ionic strengths in two aqueous media: NaCl and Na_2SO_4. Finally, a quantitative comparison of nitrite oxidation by $HOBr/BrO^-$ and $HOCl/ClO^-$ is presented.

Introduction

Kinetic studies of nitrite reactions are of interest due to their importance in atmospheric chemistry. Nitrite mixing ratios are reported to be in the range of several ppbv in atmospheric water.[1] With the interest in acid deposition and the chemistry leading to the formation of nitric and sulfuric acids during the 1970s and 1980s, a great deal of research was carried out on nitrite reactions at the low concentrations relevant to atmospheric conditions.[2,3] As a result of these studies, it was concluded that uptake of NO and NO_2 into atmospheric water droplets, followed by their oxidation in the liquid phase, do not contribute significantly to the formation of nitrate and acidity in fog and clouds. The major source of HNO_3 in fog, clouds, and particles is thought to be gas-phase oxidation of NO_x to gaseous HNO_3, followed by facile uptake of the latter into the condensed phase.[4] However, oxidation of nitrite ions present in the aqueous phase of the atmosphere must be also taken into account. Among such reactions that produce nitrates, aqueous phase oxidation of NO_2^- by HOX/XO^-, where X = Cl and Br, is important for acidity production and for the NO_3^- budget in continental clouds and fogs. These reactions are shown in eqs 1 and 2. Once formed,

$$NO_2^- + XO^- \rightarrow NO_3^- + X^- \tag{1}$$

$$NO_2^- + HOX \rightarrow NO_3^- + X^- + H^+ \tag{2}$$

nitrates are removed from the atmosphere by gas-phase reactions, dry deposition and wet removal pathways. HNO_3 thus contributes to acid rain.

Aqueous reactions of nitrite with HOX/XO^- are also a source of XNO_2. The formation of $BrNO_2$ and $ClNO_2$, two important halogen reservoirs, may have an important impact on the oxidizing potential of the Earth's troposphere via their reactions with aerosol particles.[5] Marine aerosols present in the troposphere consist of sea-salt particles containing chloride and bromide, which are generated by breaking waves on the ocean's surface, and which contribute most of the total aerosol mass.[6]

To correctly model and predict atmospheric nitrite reactions, it is necessary to perform controlled laboratory experiments. Nitrite oxidation by $HOCl/ClO^-$ and aqueous chlorine, Cl_2, has already been the subject of several reports;[7−12] however, the oxidation of nitrite by bromine species has been much less studied.[13] To accurately reproduce environmental conditions, one must recognize that very high ionic strengths, as high as 20 M, may be present in highly concentrated aerosols.[14] Concentrated Na_2SO_4 solutions may be representative of continental and polluted clouds, whereas NaCl solutions may be representative of marine clouds. Data indicate that the range of acidities found in aerosols and raindrops (pH of ~5 ± 3), are appropriate for studies of most of the controlling processes and rates.[15]

The work described in this paper focuses on the oxidation of nitrite by hypobromite/hypobromous acid solutions, carried out at different ionic strengths and in the presence of different supporting electrolytes. To our knowledge, the present paper is the first to report systematic, laboratory-based, kinetic investigations of this reaction. Pendlebury and Smith[13] studied the oxidation of nitrite by aqueous bromine (Br_2). Some of us have previously shown the effect of ionic medium on the rate constants for oxidation of dissolved SO_2 by H_2O_2 and by O_3.[16−19] The importance of ionic strength for the rate of oxidation of nitrite by $HOCl/ClO^-$ has also been demonstrated.[12,20] Here we describe the mechanism and kinetic parameters for oxidation of nitrite by $HOBr/BrO^-$ over a wide range of acidity (pH from 6.5 to 10), using two supporting electrolytes (NaCl and Na_2SO_4) at various ionic strengths (ranging from 0.1 to 1.0 M).

Experimental Section

Reagents. Sodium hypochlorite solutions were freshly prepared from commercial aqueous solutions with about 3.5% active chlorine (Prolabo, Rectapur). Bromide solutions were prepared from NaBr (Merck, p.a.). Br_2 solutions (Acros, p.a.) were protected from exposure to light as well as from exposure to ambient air. Hypobromite solutions were prepared by two methods:

(1) From Br_2: Brown-red solutions of Br_2 were titrated with $AgNO_3$ solution in an ice bath to the colorless endpoint and

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then filtered. This method was used to prepare $HOBr/BrO^-$ in neutral media in the absence of bromide:

$$Br_2 + AgNO_3 + H_2O \rightarrow AgBr(s) + BrO^- + NO_3^- + 2H^+ \quad (3)$$

(2) From bromide: This method was used to prepare alkaline solutions of BrO^-. Aqueous solutions of sodium hypochlorite and bromide were mixed in equimolar concentrations. After a few minutes, the pH increased to 10 and BrO^- formed. This method is simpler than the previous one, but results in the formation of hypobromite in the presence of bromide ion (and consequently to Br_2 formation in neutral or acidic solutions).

Nitrite solutions were prepared from reagent grade $NaNO_2$ (Carlo Erba, p.a.) and were standardized with MnO_4^-.[21] Sodium hydroxide, hydrochloric acid, and sulfuric acid solutions were prepared by diluting Carlo Erba, Normex standard solutions. Buffer solutions were prepared from CH_3COONa, $Na_2B_4O_7 \cdot 10H_2O$, and Na_2HPO_4 (Merck, p.a.). Reagents were used without any further purification. Distilled water was purified by passing through an ion-exchanger (Millipore). All solutions were freshly prepared to avoid complications due to decomposition of hypobromite or hypobromous acid. Oxygen-free solutions were obtained by bubbling with argon (Air Liquide) prior to analytical and kinetic measurements.

H^+ Concentration and pK_a Measurements. $[H^+]$ measurements were made with a Tacussel Ionoprocesseur II equipped with a Tacussel TB/HA glass electrode and a (Ag/AgCl/0.1 M NaCl) reference electrode. In Na_2SO_4 medium ($I = 0.50$ M, for example), a solution of 0.010 M NaOH + 0.16 M Na_2SO_4 was used as the standard. Using the apparent constant $K_w = [H^+][OH^-]$ and $pK_w = 13.11$,[12,20] we calibrated the electrode using $-\log [H^+] = 11.11$ for this standard at 298 K. Values of pK_w at different ionic strengths (0.05−4.56 M) in both NaCl and Na_2SO_4 media have been reported previously.[12,20] Thus, for a given ionic medium, the logarithm of the proton concentration was measured.

Kinetic Measurements. Nitrite reactions in alkaline solution were followed using a UV−vis spectrophotometer (Shimadzu Model 1601) interfaced to a PC. Data sets were acquired using Biokine commercial software.[22] Faster reactions (i.e., in neutral solution) were followed using a stopped-flow spectrophotometer (Applied Photophysics Model SX 18 MV), with a mixing time of <5 ms. The observation cell had a 2 mm path length. Observed rate constants are reported as the average of at least three replicate experiments.

For kinetic measurements, nitrite solutions (from 2.5×10^{-3} to 4.0×10^{-2} M) in a given electrolyte medium were mixed (1:1 mixing ratio) with a hypobromite solution in the same medium and at the same $[H^+]$. The nitrite ion concentration was large enough to ensure that the reaction kinetics were always pseudo-first-order. Measurements were carried out at 298 ± 1 K. The reactions were followed at 330 nm (BrO^-) in alkaline medium and at 290 nm (HOBr) in more acidic medium, following the loss of [Br(I)] (Figure 1).

Results

Determination of pK_a. Prior to this study, the acid dissociation constant (pK_a) of HOBr had not been measured at different ionic strengths. Therefore hypobromite solutions were titrated by an acidimetric method, in which a calibrated electrode was used to measure the change in $[H^+]$ as HCl or H_2SO_4 was added to an alkaline BrO^- solution. These titrations were performed in NaCl or Na_2SO_4 solutions at constant ionic strength ranging from 0.05 to 2.0 M at 298 K. The variation of K_a as a function of ionic strength is shown in Figure 2. According to the extended Debye−Hückel formula, the acidity constant can be written as a function of ionic strength:

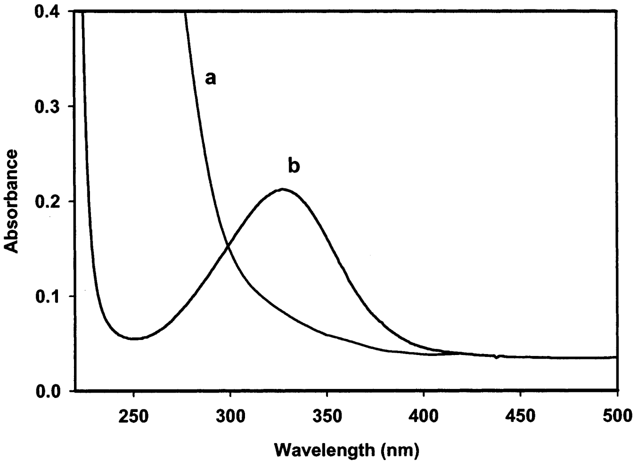

Figure 1. UV−vis spectra of Br(I) in 1.0 M NaCl: (a) pH = 6; (b) pH = 10.

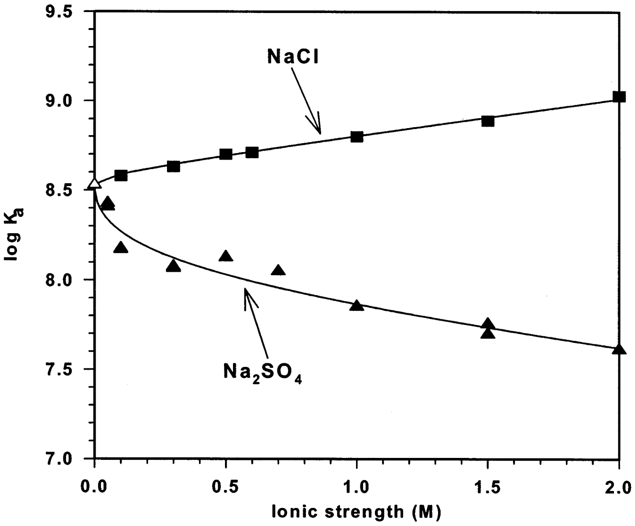

Figure 2. Influence of ionic strength on the acidity constant of HOBr at 298 K.

$$\log K_a = -\frac{A'\sqrt{I}}{1+\sqrt{I}} + B'I + \log K_0 \quad (4)$$

where $K_a = [H^+][BrO^-]/[HOBr]$, A' and B' are adjustable parameters that are a function of the absolute temperature and of the support electrolyte concentration, K_0 represents the acidity constant at infinite dilution, and I is the ionic strength.

The parameters in eq 4 were calculated from nonlinear fits to the data in Figure 2. In each medium, the values of K_a can be expressed as eqs 5 and 6. The value of pK_0 is in good agreement with the literature (pK_0 = 8.69).[23]

$$\log K_a = -\frac{0.155\sqrt{I}}{1+\sqrt{I}} + 0.196I + 8.53 \quad \text{in NaCl at 298 K} \quad (5)$$

$$\log K_a = -\frac{1.01\sqrt{I}}{1+\sqrt{I}} + 0.159I + 8.53 \quad \text{in Na}_2\text{SO}_4 \text{ at 298 K} \quad (6)$$

Br(I) Speciation. The kinetics experiments described below were performed in the pH range from 6.5 to 10.0, where the

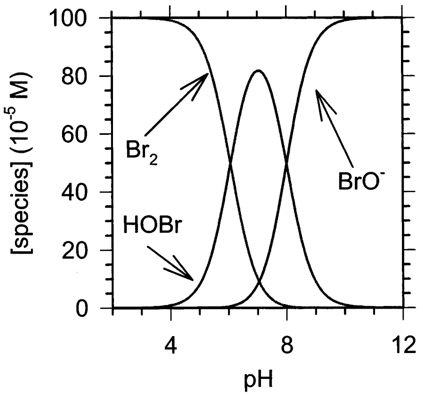

Figure 3. Speciation of Br(I) in 1.0 M NaCl.

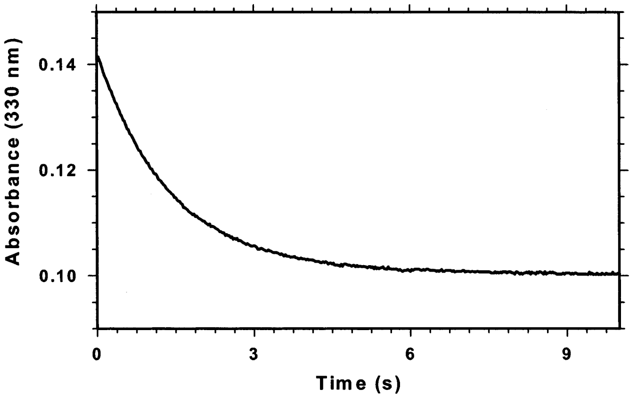

Figure 4. Kinetic profile obtained from stopped-flow spectrophotometer: $[NO_2^-] = 1 \times 10^{-2}$ M; $[HOBr]_{total} = 1 \times 10^{-3}$ M; 1.0 M NaCl; pH = 7.8 at 298 K; [phosphate] = 0.02 M.

predominant N(III) species is NO_2^-. In this range, both HOBr as well as its conjugate base BrO$^-$ must be taken into account. Bromine (Br_2) formation in acidic solution complicates the determination of the rate law at lower pH and thus these conditions were to be avoided. The ionic strength was maintained constant at either 1.0 or 0.10 M with a supporting electrolyte (NaCl or Na_2SO_4). The speciation of Br(I) in these media was calculated using a commercial software package.[24] In 1.0 M NaCl, onset of Br_2 formation occurs at pH < 7.5, Figure 3. However, in Na_2SO_4 with $I = 1.0$ M, bromine forms at pH < 6.5, because of the lower pK_a of HOBr in the latter medium. In this study, therefore, we assumed that there is no formation of either Br_2 or Br_3^-.

Determination of the Rate Law

HOBr/BrO$^-$ Dependence. In the presence of constant [H$^+$] and excess [NO$_2^-$], addition of 1.0 mM Br(I) resulted in plots of absorbance versus time that are exponential functions, Figure 4. The reaction therefore exhibits first-order kinetics with respect to the total Br(I) concentration ($[HOBr]_{total} = [HOBr] + [BrO^-] + [BrNO_2]$), eq 7:

$$-\frac{d[HOBr]_{total}}{dt} = k_{obs}[HOBr]_{total} \qquad (7)$$

NO$_2^-$ Dependence. Figure 5 shows the variation of the pseudo-first-order rate coefficients obtained at constant H$^+$ concentration with [NO$_2^-$] ranging from 2.5×10^{-2} to 4.0×10^{-3} M at different ionic strengths in NaCl and Na_2SO_4 media. The slopes of the log–log plots obtained at all [H$^+$] values indicate that the reaction is second order with respect to [NO$_2^-$].

H$^+$ Dependence. Studies were carried out at different H$^+$ concentrations (− log [H$^+$] between 6.5 and 10.0) with constant nitrite concentration (0.010−0.040 M for different series of experiments) in different media and at different ionic strengths. The pseudo-first-order rate coefficients decrease as [H$^+$] decreases, Figure 6. Furthermore, the reaction order with respect to H$^+$ concentration varies across the [H$^+$] range shown. In more acidic media (− log [H$^+$] < 8), a mixture of phosphate, borate, and acetate (0.010 M each) buffer was used to establish [H$^+$]. There was no evidence that the presence of these buffers affects the reaction rate.

Discussion

Proposed Mechanism. Kinetic and mechanistic studies of nitrite oxidation by Br_2 and Cl_2 as well as HOCl/ClO$^-$ have been reported by a number of authors.[9−11,25,26] These investigators demonstrated that the reaction of NO_2^- with HOCl or X_2 (where X = Cl or Br) proceeds via the initial formation of the corresponding nitryl halide (XNO_2):

$$X_2 + NO_2^- \rightleftharpoons XNO_2 + X^- \qquad (8)$$

$$HOX + NO_2^- \rightleftharpoons XNO_2 + OH^- \qquad (9)$$

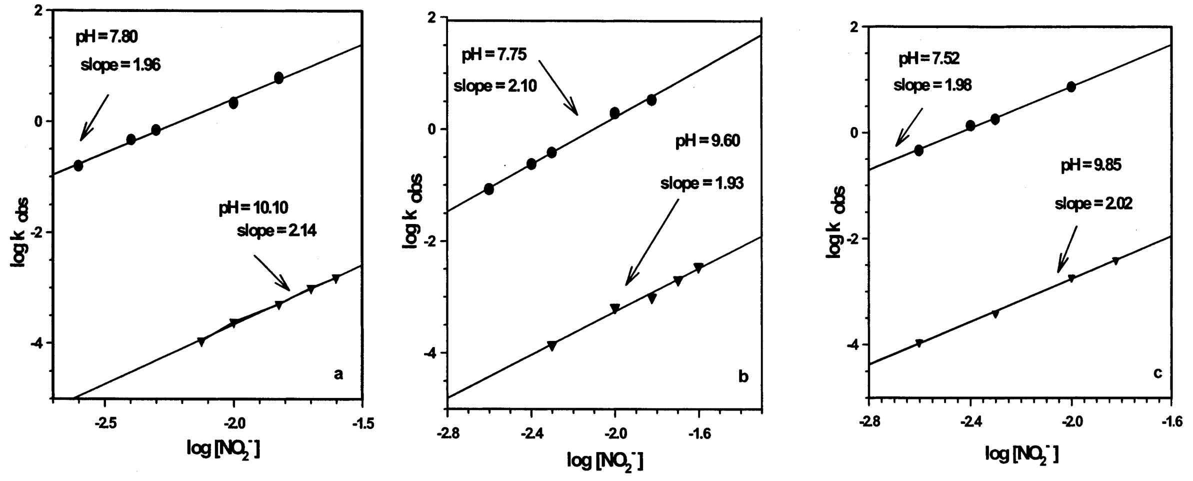

Figure 5. Dependence of k_{obs} on nitrite concentration, in various ionic media: (a) NaCl, $I = 1.0$ M; (b) Na_2SO_4, $I = 1.0$ M; (c) NaCl, $I = 0.10$ M.

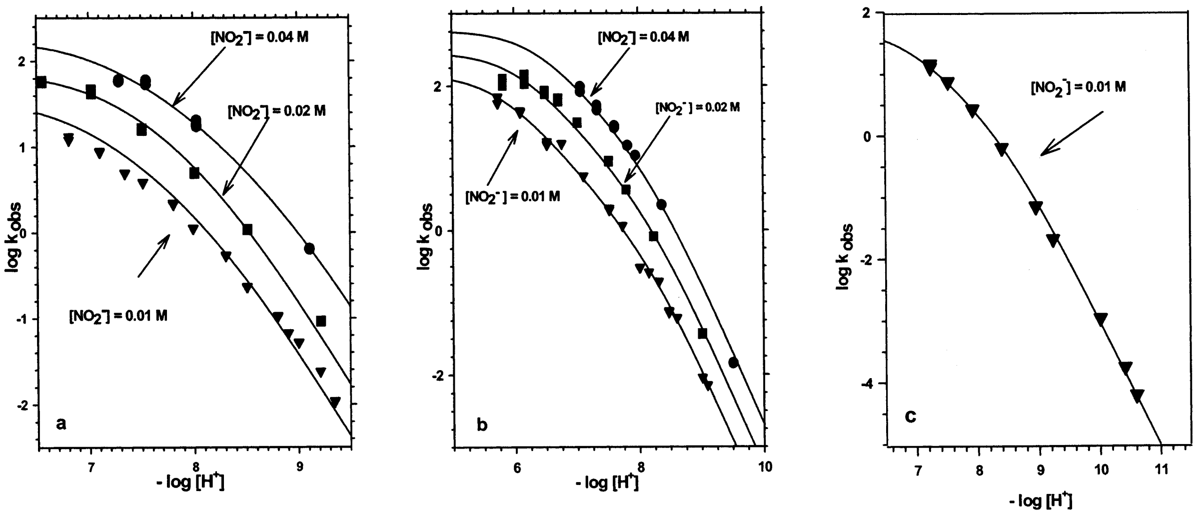

Figure 6. Pseudo-first-order rate constants (k_{obs}) for nitrite oxidation as a function of [H^+] at 298 K in various ionic media: (a) NaCl, $I = 1.0$ M; (b) Na_2SO_4, $I = 1.0$ M; (c) NaCl, $I = 0.10$ M. Solid lines are fits to eq 16 (see text).

To our knowledge, the mechanism of nitrite oxidation by HOBr/BrO^- has not been previously discussed. On the basis of our kinetic results, we propose the following mechanism for this reaction:

very fast $$HOBr \overset{K_a}{\rightleftharpoons} BrO^- + H^+ \qquad (10)$$

fast $$HOBr + NO_2^- \overset{K_1}{\rightleftharpoons} BrNO_2 + OH^- \qquad (11)$$

slow $$BrNO_2 + NO_2^- \xrightarrow{k_1} N_2O_4 + Br^- \qquad (12)$$

In the proposed mechanism, nitrite reacts with HOBr in a fast preequilibrium to produce nitryl bromide ($BrNO_2$), eq 11. The latter reacts with nitrite, eq 12, in the rate-determining step. The fate of N_2O_4 can be either dissociation to $NO_{2(g)}$ or hydrolysis to $NO_3^- + NO_2^-$, eq 13. The latter is more likely at low concentrations, such as those found in the atmosphere.

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad (13)$$

On the basis of a preequilibrium treatment for the intermediate $BrNO_2$, eq 14,

$$[BrNO_2] = \frac{K_1[H^+][HOBr][NO_2^-]}{K_w} \qquad (14)$$

and substituting for [HOBr], eq 15,

$$[HOBr] = \frac{K_aK_w[H^+][HOBr]_{total}}{K_w + K_aK_w[H^+] + K_1K_a[H^+]^2[NO_2^-]} \qquad (15)$$

we obtain the rate law shown in eq 16,

$$-\frac{d[HOBr]_{total}}{dt} = \frac{k_1K_1K_a[NO_2^-]^2[H^+]^2}{K_w + K_aK_w[H^+] + K_aK_1[NO_2^-][H^+]^2}[HOBr]_{total} \qquad (16)$$

The parameters k_1, K_1, K_a, and K_w were evaluated from the data in Figure 6 by a nonlinear least-squares fitting procedure. The results at $T = 298$ K are summarized in Table 1 as a function of medium and ionic strength. The values of K_a and K_w so derived are in good agreement with our values obtained by direct measurement. The mechanism shown in eqs 10−13 is similar to our proposed mechanism for nitrite oxidation by HOCl/ClO^-.[12,20] However, the hydrolysis of XNO_2, which was kinetically significant in the case of nitrite oxidation by HOCl/ClO^-, is slow and can be neglected for X = Br. Instead, reaction with nitrite (eq 12) dominates the loss of $BrNO_2$ in water under our experimental conditions. This finding agrees with results obtained in a previous study,[11] which showed that the hydrolysis of $BrNO_2$ is slow. These investigators,[11] with reference to a mechanism suggested by previous work,[13] estimated a value of 1.3×10^4 M^{-1} s^{-1} for the rate coefficient for reaction of $BrNO_2$ with NO_2^- (eq 12) without specifying the ionic environment or ionic strength. This value is in excellent agreement with our value in Na_2SO_4 medium and 2−3 times higher than our values in NaCl media (see Table 1).

TABLE 1: Kinetic and Thermodynamic Parameters[a] for the Oxidation of Nitrite by BrO^-/HOBr at 298 K

medium	pK_a [b]	10^{-3} k_1 (L mol^{-1} s^{-1})	10^6 K_1	pK_w [c]
Na_2SO_4 ($I = 1.0$ M)	8.25 (7.87)	(14 ± 3)	(5.6 ± 1.1)	12.95 (12.95)
NaCl ($I = 1.0$ M)	8.50 (8.80)	(3.8 ± 0.8)	(14 ± 3)	13.68 (13.69)
NaCl ($I = 0.10$ M)	8.27 (8.58)	(5.5 ± 1.1)	(10 ± 2)	13.75 (13.74)

[a] Derived from the fit to eq 16. Errors represent only the statistical error at the 2σ level. [b] Values in parentheses determined by titration (this work). [c] Values in parentheses from ref 12.

Zetzch and co-workers[25] reported that nitryl chloride hydrolyzes (eqs 17 and 18) via the transient intermediate NO_2^+.

$$ClNO_2 \rightleftharpoons NO_2^+ + Cl^- \; (k'_1/k'_{-1}) \qquad (17)$$

$$NO_2^+ + H_2O \rightarrow NO_3^- + 2H^+ \; (k'_2) \qquad (18)$$

The loss of $ClNO_2$ in chloride solution is much slower than that in water, indicating that the main loss process, k'_1 followed by k'_2, is suppressed by k'_{-1} in the presence of Cl^-. Frenzel and co-workers[11] reported that the hydrolysis of $BrNO_2$ is much slower than that of $ClNO_2$.

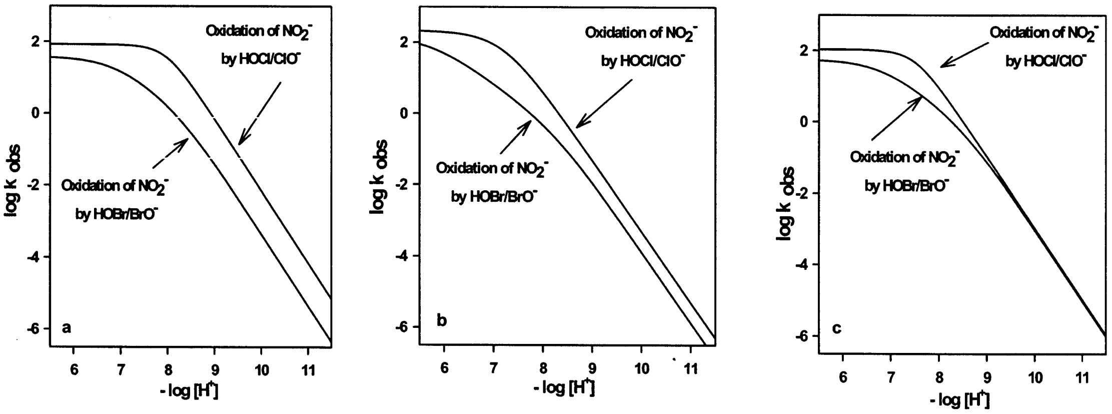

Figure 7. Comparison of rates of oxidation of nitrite by HOCl/ClO$^-$ and by HOBr/BrO$^-$: [NO_2^-] = 0.010 M; (a) NaCl, I = 1.0 M; (b) Na_2SO_4, I = 1.0 M; (c) NaCl, I = 0.10 M.

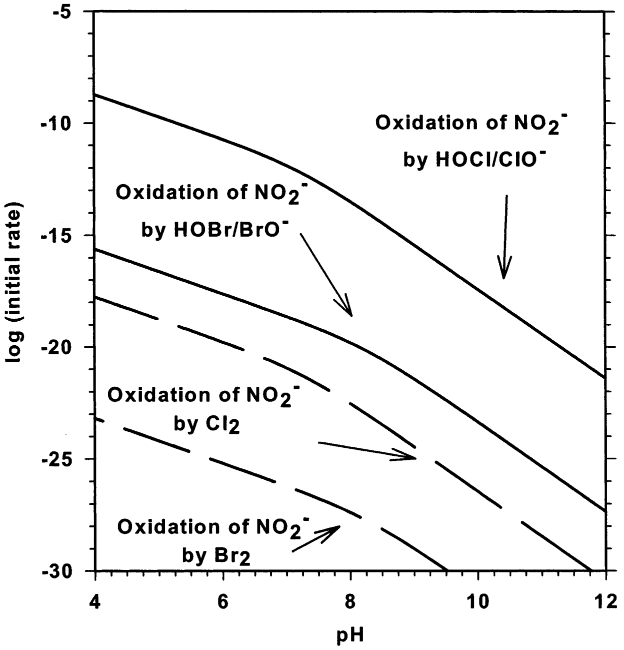

Figure 8. Comparison of the initial rates of nitrite oxidation by X(I) and X(0). Dashed lines are based on rates measured by Pendlebury and Smith.[13,25] The initial concentration of each species is 10^{-8} M. NaCl, I = 1.0 M at 298 K.

Comparison between HOBr and HOCl as Oxidants for Nitrite. In Figure 7, we compare the reaction rate coefficients for oxidation of nitrite by HOCl/ClO$^-$ [12,20] and by HOBr/BrO$^-$ at different ionic strengths and in different media. Under all conditions, nitrite oxidation by HOCl/ClO$^-$ is as fast or faster than that by HOBr/BrO$^-$. This is not too surprising because we would expect the reaction with stronger electrophile $Cl^{\delta+}$ to be faster. The difference is more striking under acid conditions than under neutral conditions. At lower ionic strength (I = 0.10 M), and in alkaline medium, these reactions have almost the same rate coefficient, despite the greater driving force for the Cl(I)/Cl(−I) couple relative to Br(I)/Br(−I). Under some environmentally relevant conditions, it is possible that HOCl/ClO$^-$ reacts preferentially with Br$^-$ rather than NO_2^- so that the less reactive HOBr/BrO$^-$ performs the oxidation of NO_2^-. This will be discussed in a forthcoming publication.[27]

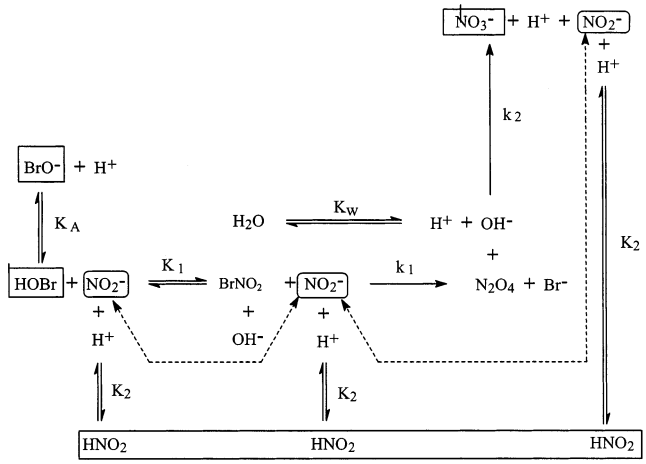

Figure 9. Global diagram of proposed mechanism for nitrite oxidation by HOBr/BrO$^-$.

We also compared the global rates of nitrite oxidation by Cl(I) and Br(I) at concentrations relevant to atmospheric conditions (10^{-8} M), Figure 8. In this scenario, we simulate conditions under which the comproportionation reactions of HOCl and HOBr have enough time to be established, eq 19.

$$XO^- + X^- + 2H^+ \rightleftharpoons X_2 + H_2O \qquad (19)$$

This allows us to combine our results with those for nitrite oxidation by Cl_2 and Br_2 reported in previous work.[13,26] As shown in Figure 8, for kinetic reasons, nitrite oxidation by X(I) is faster than by X(0) under all environmentally relevant acidity conditions.

Conclusions

The rate coefficients for oxidation of nitrite by Br(I) have been determined in three different ionic strengths in two ionic environments. This laboratory study was carried out under ionic conditions approaching those in the continental and marine atmosphere (concentrated droplets). The reaction leading to N_2O_4 formation from a $BrNO_2$ intermediate is the rate-determining step, with $k_1 = (14 \pm 1) \times 10^3$, $(3.8 \pm 0.3) \times 10^3$, and $(5.5 \pm 0.4) \times 10^3$ M^{-1} s^{-1} in Na_2SO_4 (I = 1.0 M) and NaCl (I = 1.0 and 0.10 M) media, respectively. The global mechanism for the reaction of NO_2^- with HOBr/BrO$^-$ is shown in Figure 9.

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