5144 *Inorg. Chem.* **1994,** *33,* 5144–5150

Kinetics and Mechanism of the Oxidation of Hydroxylamine by Aqueous Bromine

Richard C. Beckwith, John N. Cooper,[†] and Dale W. Margerum*

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

Received May 4, 1994[®]

The kinetics, stoichiometry, and mechanism of the reaction between hydroxylamine and bromine are determined from pH 0 to 6. Acid suppresses the rate of reaction because NH_3OH^+ is not reactive with Br_2. At low pH, nitrous acid is the first observable product and the stoichiometry of the initial reaction is 2:1 $[Br_2]_T$:$[NH_2OH]_T$ (where $[Br_2]_T = [Br_2] + [Br_3^-]$ and $[NH_2OH]_T = [NH_3OH^+] + [NH_2OH]$). A slower subsequent reaction of NH_3OH^+ with HONO to produce N_2O makes the overall stoichiometry 2:2. The proposed reaction sequence corresponds to the following changes in nitrogen oxidation states: N(−I) → N(I) → N(III) → N(I). At pH 0–2 the reaction between $[Br_2]_T$ and excess $[NH_2OH]_T$ is measured by stopped-flow spectrophotometry; the rate constant for Br_2 and NH_2OH is 1.8×10^9 M^{-1} s^{-1} at 25.0 °C, $\mu = 0.50$ M. The activation parameters at 25.0 °C are $\Delta H^{\ddagger} = 15$ kJ mol^{-1} and $\Delta S^{\ddagger} = -15$ J mol^{-1} K^{-1}, but these values are temperature dependent because $\Delta C_p^{\ddagger} = -440$ J mol^{-1} K^{-1}. A parallel Br_3^- path has a rate constant of 2.4×10^8 M^{-1} s^{-1} at 25.0 °C. The first mechanistic step is postulated to be Br^+ transfer to form an intermediate, BrNHOH. This intermediate reacts rapidly with a second equivalent of Br_2 to form Br_2NOH. Rapid stepwise loss of Br^- first gives BrNO and then HONO. At pH 5–6 the $[NH_2OH]_T$ reaction with $[Br_2]_T$ is much faster and is measured by the pulsed-accelerated-flow method. The initial step appears to consume all the Br_2, but BrNHOH disproportionates to form NH_2OH and Br_2NOH; further stepwise hydrolysis gives NO_2^- and Br^-.

Introduction

Recent work in this laboratory[1] has shown that chlorine rapidly oxidizes hydroxylamine in acid solutions. Even with excess NH_3OH^+, three chlorines react in rapid succession to convert the N(−I) oxidation state of hydroxylamine to a N(V) intermediate that is proposed to be Cl_3NO. This reaction is followed by stepwise reduction of the N(V) species with excess hydroxylamine, first to give nitrous acid, N(III), and then to give nitrous oxide, N(I).

By contrast, bromine oxidation of hydroxylamine was reported by Kudesia[2] in 1976 to have a rate constant of only 1.6 M^{-1} s^{-1}, which is 9 orders of magnitude slower than the chlorine rate constant.[1] In 1984, Jonnalagadda[3] reported a rate constant of only 0.143 M^{-1} s^{-1} for the reaction between NH_2OH and HOBr. The magnitude of these rate constants appears to be unreasonably small, because the Br_2 and HOBr rate constants with NH_2Cl (which is a much weaker base and poorer nucleophile than NH_2OH) are 4.18×10^8 M^{-1} s^{-1} and 2.86×10^5 M^{-1} s^{-1}, respectively.[4] Our present work shows that bromine oxidation of hydroxylamine is actually very rapid; the rate constant is more than 10^9 times larger than previously reported.[2] With excess hydroxylamine the bromine oxidation does not go to N(V), but rather to N(III), and the first observable product is nitrous acid. This is followed by the reduction of nitrous acid by hydroxylamine to give nitrous oxide.[5,6]

We determine the reaction stoichiometry as a function of time and find no evidence under our conditions for the formation of HNO_3 (proposed by Jonnalagadda[3]). Although nitric acid has been reported[7] as a product when bromine oxidizes hydroxylamine, Kurtenacker and Neusser[8] pointed out that this occurs only when large ratios (40 to 60-fold) of $[Br_2]_T/[NH_2OH]_T$ are used. Even a 19-fold excess of $[Br_2]_T$ gives only N_2O. The conditions in our current study have total hydroxylamine ($[NH_2OH]_T = [NH_3OH^+] + [NH_2OH]$) in large excess over total bromine ($[Br_2]_T = [Br_2] + [Br_3^-]$).

The protonation constant (K_H) for hydroxylamine (eq 1) is 1.01×10^6 M^{-1} at 25 °C and an ionic strength (μ) of 0.50 M.[9] Aqueous bromine in the presence of bromide ion is in rapid

$$NH_2OH + H^+ \overset{K_H}{\rightleftharpoons} NH_3OH^+ \qquad (1)$$

equilibrium with the tribromide ion (eq 2), where $K_{Br} = 16.8$

$$Br_2 + Br^- \overset{K_{Br}}{\rightleftharpoons} Br_3^- \qquad (2)$$

M^{-1} at 25 °C and $\mu = 0.50$ M.[10] The value for K_{Br} was measured by Scaife and Tyrrell[10] in molality units, and we converted it to molarity. In the present work, the kinetics of bromine loss are studied as a function of the concentrations of Br^- and $[NH_2OH]_T$ from pH 0 to 6. Stopped-flow spectrophotometry is used for the higher acidities, and the pulsed-accelerated-flow method[11–13] is used for the more rapid reactions from pH 2 to 6. The proposed NH_2OH and Br_2 mechanisms involve Br^+-transfer reactions followed by Br^- elimination to

---

[†] On sabbatical leave from Bucknell University, Lewisburg, PA 17837.

[®] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) Cooper, J. N.; Margerum, D. W. *Inorg. Chem.* **1993**, *32*, 5905–5910.
(2) Kudesia, V. P. *Acta Cienc. Indica* **1976**, *2*, 237–238.
(3) Jonnalagadda, S. B. *Int. J. Chem. Kinet.* **1984**, *16*, 1287–1299.
(4) Gazda, M.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 118–123.
(5) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 2824–2830.
(6) Morgan, T. D. B.; Hughes, M. N.; Stedman, G. *J. Chem. Soc. B* **1968**, 344–349.
(7) Rupp, E; Mader, H. *Arch. Pharm.* **1913**, *251*, 295.
(8) Kurtenacker, A.; Neusser, R. *Z. Anorg. Allg. Chem.* **1923**, *131*, 27–47.
(9) Lumme, P.; Lahermo, P.; Tummavuori, J. *Acta Chem. Scand.* **1965**, *19*, 2175–2188.
(10) Scaife, D. B.; Tyrrell, H. J. V. *J. Chem. Soc.* **1958**, 386–392.
(11) Jacobs, S. A.; Nemeth, M. T.; Kramer, G. W.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* **1984**, *56*, 1058–1065.
(12) Nemeth, M. T.; Fogelman, K. D.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* **1987**, *59*, 283–291.
(13) Fogelman, K. D.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1989**, *28*, 986–993.

0020-1669/94/1333-5144$04.50/0

Table 1. Spectral Characteristics of Relevant Species

species	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
NO_2^-	355	23.3	20
HONO	371	54	1
NO_3^-	302	7.24	20
Br_2	390	175	21
Br_3^-	266	40,900	*a*
HOBr	260	100	21

[a] Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. *Inorg. Chem.* Submitted for publication.

Table 2. Equilibrium Constants at 25.0 °C, μ = 0.50 M

reaction	equilibr const	ref
$Br_2 + Br^- \rightleftharpoons Br_3^-$	16.8 M^{-1}	10
$Br_2 + H_2O \rightleftharpoons HOBr + Br^- + H^+$	2.2 × 10^{-9} M^2	19
$OBr^- + H^+ \rightleftharpoons HOBr$	6.3 × 10^8 M^{-1}	18
$H^+ + NH_2OH \rightleftharpoons NH_3OH^+$	1.01 × 10^6 M^{-1}	9
$HONO \rightleftharpoons H^+ + NO_2^-$	1.1 × 10^{-3} M	22

give nitrous acid (HONO). Similar halogen cation transfer mechanisms have been found with other nucleophiles.[4,13-19]

Experimental Section

Reagents. Distilled, deionized water was used for all solutions. Ionic strength was adjusted to μ = 0.5 M with recrystallized $NaClO_4$. Solutions of $NaClO_4$ and NaBr were prepared from the solid reagents and were standardized gravimetrically. Acidity was adjusted with $HClO_4$ solutions. An Orion Model SA 720 Research digital pH meter and a Corning combination pH electrode were used to measure pH values above 1.5. These pH values were corrected to p[H^+] values at 25.0 °C and μ = 0.50 M based on electrode calibration by titration of standardized $HClO_4$ and NaOH. All chemicals were reagent grade. The concentrations given for kinetic reactions are post-mixing values. Table 1 gives spectrophotometric parameters for species of interest,[20,21] and Table 2 gives related equilibrium constants.[18,19,22]

Solutions of $[Br_2]_T$ were prepared by adding liquid bromine to acidified water and were standardized spectrophotometrically at 390 nm. Sodium bromide was added after standardization to give the desired levels of Br_3^-.

Solutions of NH_2OH were prepared from $NH_2OH{\cdot}HCl$ (Sigma) and were standardized by oxidation with Fe(III) in 1 M H_2SO_4 (eq 3).[23] After the solution was allowed to boil for at least 5 min, it was cooled,

$$2NH_2OH + 2Fe_2(SO_4)_3 \rightarrow N_2O + 4FeSO_4 + 2H_2SO_4 + H_2O \quad (3)$$

and the Fe(II) formed was titrated with standard $(NH_4)_2Ce(NO_3)_6$. This method is superior to the bromate–thiosulfate titration procedure,[24] which we found was not a satisfactory procedure to standardize hydroxylamine due to poor accuracy and precision.

Kinetic and Spectrophotometric Methods. Spectral measurements for the stoichiometry of intermediates and data for slower reactions were obtained with a Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer interfaced to a Zenith 386/20 PC. Faster kinetic determinations used either a Durrum stopped-flow spectrophotometer (Model D-110 with an optical pathlength of 1.88 cm) or a Hi-Tech stopped-flow spectrophotometer (Model SF-3L equipped with a ball-type mixing-observation cell with a 1.60 cm path[25]). Both were interfaced to a Zenith 151 PC with a Metrabyte DASH-16 A/D interface card. Pseudo-first-order rate constants were obtained from plots of ln($A - A_\infty$) versus time, where A is the absorbance of $[Br_2]_T$ for the initial reaction or of HONO for the slower subsequent reaction. Stopped-flow rate constants (k_{raw}) larger than 30 s^{-1} were corrected for mixing limitations of the instruments by using eq 4, where k_{mix} = 1700 s^{-1} for the Durrum[26] stopped-flow and 2900 s^{-1} for the Hi-Tech.[27]

$$k_{obsd} = \frac{k_{raw}}{1 - \dfrac{k_{raw}}{k_{mix}}} \quad (4)$$

Very fast reactions were monitored with a pulsed-accelerated-flow (PAF) spectrophotometer,[11-13] Model IV.[13,28] The PAF method employs integrating observation during continuous flow mixing of short duration (a 0.4 s pulse). The twin-path mixing/observation cell made of PVC has an optical path length of 2.05 cm. Solutions for all PAF experiments were filtered and degassed. Flow was decelerated during the pulse to give a linear velocity ramp with a velocity range of 12.0–3.0 m/s, during which 250 measurements of transmittance data were taken. Under pseudo-first-order conditions, the first-order rate constant k_{obsd} can be determined by using eq 5, where A_v is the absorbance at a

$$M_{exptl} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk_{obsd}} \quad (5)$$

given instantaneous velocity, A_∞ is the final absorbance, A_0 is the absorbance at time zero, b is the reaction path length (0.010 25 m), v is the solution velocity, and k_m is a proportionality constant from the mixing rate constant (k_{mix}), where $k_m = k_{mix}/v$. Linear plots of M_{exptl} vs v have slopes of $1/(bk_{obsd})$. During pulsed-accelerated flow measurements, the solutions, drive syringes, and the mixing cell were thermostated at 25.0 ± 0.1 °C. Each reported rate constant measured by stopped-flow or PAF instruments represents an average of 3–8 trials.

Results and Discussion

Nitrous Acid Formation and Decay. Under acidic conditions the first observable product for the reaction of bromine with excess hydroxylamine is nitrous acid. The distinctive, five-peak absorption spectrum[29] of nitrous acid in the 330–390 nm range allows this product assignment to be made with confidence. The formation of HONO indicates that NH_2OH is oxidized by two equivalents of Br_2 to convert N(−I) to N(III). Yields of nitrous acid were measured spectrophotometrically at pH 1 by use of either the Perkin-Elmer Lambda-9 or the Durrum stopped-flow instruments. Table 3 gives the conditions and results, which show that 1 mol of HONO is produced for every 2 mol of $[Br_2]_T$ reactant. The first six entries in Table 3 show the percent yield of HONO at pH 1–2 as 103 ± 9% based on this stoichiometry. Nitrous acid is the main product even with a twofold excess of $[Br_2]$ over $[NH_2OH]_T$ (first entry in Table 3). No NO_3^- was detectable at 302 nm for this reaction. This rules out a three-Br_2 oxidation of NH_2OH to NO_3^-.

The nitrous acid product decays within minutes due to its reaction with excess hydroxylammonium ion. Figure 1 shows two decay curves measured at 371 nm for the reaction of 1.6 ×

---

(14) Yiin, B. S.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1987**, *26*, 3435–3441.

(15) Nagy, J. C.; Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1988**, *27*, 2773–2780.

(16) Gerritsen, C. M.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2757–2762.

(17) Johnson, D. W.; Margerum, D. W. *Inorg. Chem.* **1991**, *30*, 4845–4851.

(18) Troy, R. C.; Margerum, D. W. *Inorg. Chem.* **1991**, *30*, 3538–3543.

(19) Beckwith, R. C.; Wang, T. X.; Margerum, D. W. To be submitted for publication.

(20) Wetters, J. H.; Uglum, K. L. *Anal. Chem.* **1970**, *42*, 335–340.

(21) Soulard, M.; Block, F.; Hatterer, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2300–2310.

(22) Tummavuori, J.; Lumme, P. *Acta Chem. Scand.* **1968**, *22*, 2003–2011.

(23) Bray, W. C.; Simpson, M. E.; MacKenzie, A. A. *J. Am. Chem. Soc.* **1919**, *41*, 1363–1378.

(24) *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman Scientific and Technical: New York, 1989; p 408.

(25) Wang, Y. L. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1989.

(26) Dickson, P. N.; Margerum, D. W. *Anal. Chem.* **1986**, *58*, 3153–3158.

(27) Gazda, M; McDonald, M. R.; Margerum, D. W. Unpublished work.

(28) Bowers, C. P.; Fogelman, K. D.; Nagy, J. C.; Ridley, T. Y.; Wang, Y. L.; Evetts, S. W.; Margerum, D. W. To be submitted for publication.

(29) Markovits, G. Y.; Schwartz, S. E.; Newman, L. *Inorg. Chem.* **1981**, 20, 445–450.

Table 3. Summary of Data for Nitrous Acid/Nitrite Product^{a}

				$[HONO]_T$ formed		
$p[H^+]_o$	$[NH_2OH]_T$, mM	$[Br_2]_T$, mM	$[Br^-]_i$, M	mM	% yield^{b}	HONO loss *k*, s^{-1}
1.0	1.06	2.12	0	1.01^{d}	95	*c*
1.0	17.6	1.6	0	0.87	109	0.0072
1.0	20.2	1.6	0.20	0.82^{e}	102	0.0502^{e}
1.0	25.0	2.25	0	1.3	118	0.0100
1.0	25.0	2.25	0	1.1	97	0.0096
1.9	47.5	4.89	0	2.3^{f}	96	0.0094^{f}
5.5	1.5	0.16	0.36	0.076^{d}	91	*c*
5.6	37.8	0.16	0.36	0.078^{d}	98	*c*
5.7	1.5	0.16	0	0.064^{d}	80	*c*
5.7	37.8	0.16	0	0.071^{d}	89	*c*
5.9	3.5	0.67	0.15	0.30	89	0.0097^{g}
5.9	5.0	0.67	0.15	0.33	99	0.0097^{g}
5.9	7.56	0.67	0.15	0.33	99	0.0162^{g}
5.9	10.1	0.67	0.15	0.33	99	0.0243^{g}

^{a} Monitored at 371 nm at 25.0 (±0.3) °C; ionic strength variable from 0 to 0.50 M. ^{b} Mole percent $[HONO]_T$ per 0.5 $[Br_2]_T$. ^{c} Not determined. ^{d} Measured with 10-cm cells. ^{e} Determined with Durrum stopped-flow at 26.0 °C. ^{f} Determined at 357 nm by Durrum stopped-flow at 26.0 °C. ^{g} Decay of HONO after acidifying product to pH ~ 1.

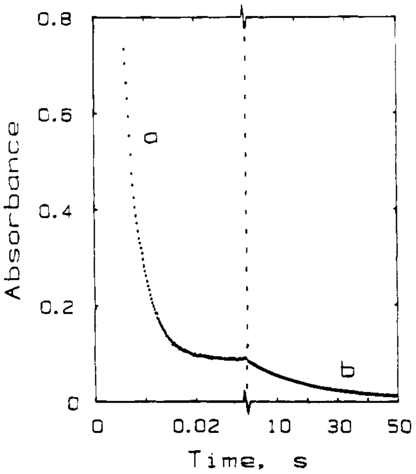

Figure 1. Durrum stopped-flow data at 371 nm for the reaction of $[NH_2OH]_T = 2.02 \times 10^{-2}$ M, $[Br_2]_T = 1.6 \times 10^{-3}$ M, $[Br^-] = 0.2$ M, and $[H^+] = 0.10$ M: (a) loss of $[Br_2]_T$ to form HONO within 30 ms; (b) loss of HONO shown over 50 s.

10^{-3} M $[Br_2]_T$ with 2.02×10^{-2} M $[NH_2OH]_T$ at pH 1. The fast decay is due to loss of the $[Br_2]_T$ signal. The subsequent decay is due to loss of HONO. Stedman and co-workers[5,6] studied the hydroxylamine-nitrous acid reaction and gave the rate expression in eq 6. Their values for k_3 and k_4 were based

$$-\frac{d[HONO]}{dt} = (k_3[H^+] + k_4[Br^-])[NH_3OH^+][HONO] \tag{6}$$

on experimental results at 0 °C, $\mu \approx 0.15$ M. We used their activation energy values of 14.7 kcal/mol for k_3 and 11.7 kcal/mol for k_4 to calculate $k_3 = 2.5$ M^{-2} s^{-1} and $k_4 = 4.1$ M^{-2} s^{-1} at 25 °C.[5,6] Authentic mixtures of $[NH_2OH]_T$ and HONO at $[H^+] = 0.117$ M (25.0 °C, $\mu = 0.52$ M) in our laboratory gave a second-order rate constant of 0.43 M^{-1} s^{-1}, as opposed to their calculated value of $k_3[H^+] = 0.29$ M^{-1} s^{-1}. Our value is consistent with the rate constants in Table 3 when the bromide-catalyzed path is not significant. The discrepancy in these values may originate from a complex temperature dependence due to terms in the rate law dependent on acid concentrations. The exact conditions used to measure their activation energies were not given.[5,6]

Table 4. Stopped-Flow Data^{a}

$[NH_2OH]_T$, mM	$[Br_2]_T$, mM	$[H^+]$, M	$[Br^-]_i$, mM	k_{obsd},^{b} s^{-1}	k_{calcd},^{c} s^{-1}
0.212	0.020	0.10	15	6.29 (0.09)	6.28
1.16	0.020	0.10	15	33.3 (1.0)	34.2
2.12	0.020	0.10	15	63.6 (2.6)	62.7
0.212	0.020	0.10	45	4.88 (0.02)	4.76
0.212	0.020	0.10	75	3.96 (0.05)	3.92
0.212	0.020	0.0095	15	66.0 (5.9)	66.1
0.212	0.020	0.0283	15	22.7 (0.4)	22.2
0.212	0.020	0.051	15	11.9 (0.3)	12.3
0.212	0.020	0.065	15	9.59 (0.30)	9.66
0.212	0.020	0.21	15	3.45 (0.04)	2.99
0.212	0.020	0.051	45	9.37 (0.26)	9.34
0.212	0.020	0.065	45	7.72 (0.19)	7.33
0.212	0.020	0.15	45	3.37 (0.05)	3.18
0.212	0.020	0.21	45	2.40 (0.01)	2.27
0.125	0.012	0.10	200	1.65 (0.01)	1.48
0.125	0.012	0.10	150	1.90 (0.01)	1.70
0.125	0.012	0.10	100	2.27 (0.01)	2.04
0.125	0.012	0.10	45	3.11 (0.05)	2.81
0.125	0.012	0.10	15	4.25 (0.23)	3.70
0.125	0.012	0.10	5	4.78 (0.26)	4.19
0.125	0.012	0.20	15	2.15 (0.06)	1.85
0.125	0.012	0.30	15	1.48 (0.03)	1.23
0.756	0.075	0.5	5	5.91 (0.04)	5.06
15.2	1.4	1.0	0	52.5 (0.9)	54.4

^{a} $\mu = 0.50$ M ($NaClO_4$), 25.0 ± 0.3 °C, Durrum stopped-flow instrument, 266 nm. ^{b} Numbers in parentheses are the first standard deviation. ^{c} Calculated from eq 11 with $k_o = 1.8 \times 10^9$ M^{-1} s^{-1} and $k_1 = 2.4 \times 10^8$ M^{-1} s^{-1}.

Product Determination at pH 5.5–5.9. The reactions corresponding to the last eight entries in Table 3 were studied at a higher pH range where the initial values, $p[H^+]_o$, were 5.5–5.9. Nitrous acid (pK_a 2.96)[22] is the product at pH 1, whereas at pH 5–6 nitrite ion is the product. Nitrite is characterized by a broad absorption band with a peak at 355 nm.[20] Unlike HONO, NO_2^- is inert in the presence of hydroxylamine. The results in Table 3 show that this pH range has yields of $[HONO]_T$ (where $[HONO]_T = [HONO] + [NO_2^-]$) equal to 93 ± 7% relative to a 2:1 $[Br_2]_T$:$[HONO]_T$ stoichiometry, which agrees with the results at pH 1.

Lack of Observable Spectroscopic Intermediates Prior to HONO Formation. Stopped-flow reactions, where $[H^+]$ ranged from 0.01 to 1.0 M, were examined at several wavelengths but failed to detect any intermediates (such as BrNO, Br_2NOH, or BrNHOH) prior to HONO formation. For the reaction between Br_2 and NH_2OH at 357 or 371 nm, two successive first-order decays are observed; loss of $[Br_2]_T$ followed by a slower loss of HONO. At 266 nm, where HONO does not absorb appreciably, only the loss of Br_3^- is seen. If the reaction between bromine and hydroxylamine is fast relative to the stopped-flow time scale, HONO is fully formed within the dead time of the instrument. A slow HONO decay is found, but unlike the chlorine/NH_3OH^+ system,[1] an absorbance increase signaling the formation of HONO is not seen. The conclusion is that intermediate species (between NH_2OH and HONO) are too reactive to be observed under these conditions.

Overall Stoichiometry at pH 1. A series of seven reactions with hydroxylamine in 4–21-fold excess of the bromine concentration were performed at room temperature to determine the stoichiometry. After reacting bromine and hydroxylamine, a sufficient time interval (at least 30 min) was allowed so that subsequent reactions between HONO and NH_3OH^+ were complete before measuring excess hydroxylamine by the iron-cerium method. The overall stoichiometry of $[Br_2]_T$:$[NH_2OH]_T$ was (1.01 ± 0.05):1. This value includes the $[NH_2OH]_T$ that has reacted with nitrous acid. Therefore, the stoichiometry of $[Br_2]_T$ and $[NH_2OH]_T$ is 2:1 on a time scale of seconds, but on

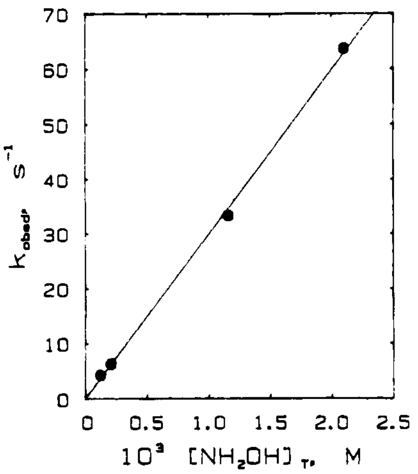

Figure 2. Plot of k_{obsd} vs $[NH_2OH]_T$ as studied by stopped-flow methods with $[Br_2]_T = 2.0 \times 10^{-5}$ M, $[Br^-] = 0.015$ M, and $[H^+] = 0.10$ M.

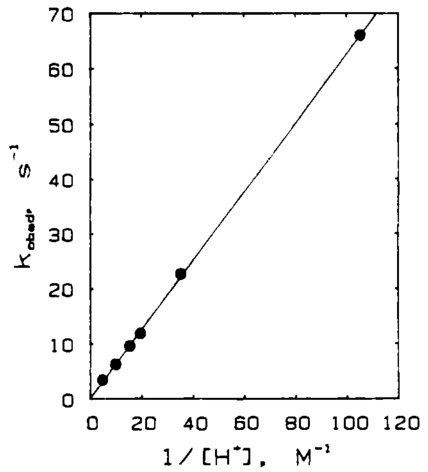

Figure 3. Plot of k_{obsd} vs $1/[H^+]$ as studied by stopped-flow methods with $[NH_2OH]_T = 2.1 \times 10^{-4}$ M, $[Br_2]_T = 2.0 \times 10^{-5}$ M, and $[Br^-] = 0.015$ M.

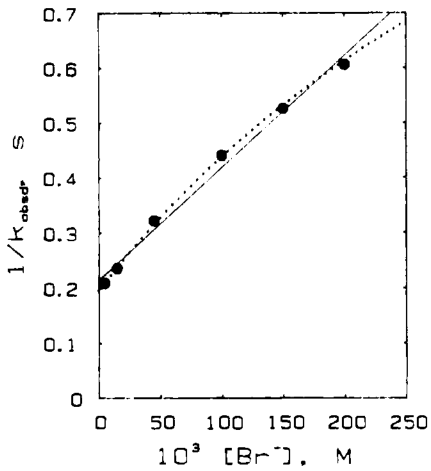

Figure 4. Plot of $1/k_{obsd}$ vs $[Br^-]$ where $[NH_2OH]_T = 1.25 \times 10^{-4}$ M, $[Br_2]_T = 1.2 \times 10^{-5}$ M, and $[H^+] = 0.1$ M. The solid line is the straight-line fit based on eq 10. The dotted line is the nonlinear fit based on eq 11.

a time scale of minutes to hours, the stoichiometry becomes 2:2 in accord with eq 7.

$$2Br_2 + 2NH_2OH \rightarrow 4Br^- + 4H^+ + N_2O + H_2O \qquad (7)$$

Overall Stoichiometry at pH 5.9. The stoichiometry was checked at p[H$^+$] 5.9 with hydroxylamine in 5 to 15-fold excess. All bromine solutions had $[Br^-] = 0.15$ M so that the concentration of HOBr was negligible. The initial pH was 5.9, but the pH decreased during the reaction due to production of $[H^+]$ (eq 7). The pH drop, which ranged from 0.4 to 2.7 pH units, was more pronounced at the lower hydroxylamine concentrations where less self-buffering occurred. The stoichiometry in terms of $[Br_2]_T$:$[NH_2OH]_T$ is (1.1 ± 0.1):1, consistent with the results at higher acidity. However, in order to quantitate the excess hydroxylamine by the iron–cerium method, the reaction products must first be acidified. This results in conversion of nitrite to nitrous acid, which reacts 1:1 with the excess hydroxylamine. There was sufficient time for the nitrous acid to decay before quantitation of the excess hydroxylamine. The above experimental stoichiometric ratio includes the hydroxylamine that was lost after acidification.

Rate Expression in Acid. Results from 24 stopped-flow experiments were used to establish a rate expression for the reaction of bromine with hydroxylamine under acidic conditions. Total hydroxylamine was in at least 10-fold excess for all reactions (Table 4), and HOBr has a negligible concentration under these conditions. The loss of Br_3^- was monitored at 266 nm. Hydroxylammonium ion is transparent at this wavelength. Using eqs 1, 2, and 8, and the definitions of $[NH_2OH]_T$ and

$$\frac{-d[Br_2]}{dt} = 2k[Br_2][NH_2OH] = k_{obsd}[Br_2]_T \qquad (8)$$

$[Br_2]_T$ leads to eq 9 as the expression for k_{obsd}. The factor of 2

$$k_{obsd} = \frac{2k[NH_2OH]_T}{(1 + K_H[H^+])(1 + K_{Br}[Br^-])} \qquad (9)$$

takes into account the 2:1 $[Br_2]_T$:$[NH_2OH]_T$ stoichiometry observed on the stopped-flow time scale. A typical first-order decay is shown in Figure 1a. Linear dependencies in $[NH_2OH]_T$ and $1/[H^+]$ (since $K_H[H^+] \gg 1$) were established and are shown in Figures 2 and 3, respectively. However, a plot to show the bromide ion dependence at constant $[NH_2OH]_T$ (0.125 mM) and constant $[H^+]$ (0.100 M) based on eq 10 (derived from eq 9) revealed two inconsistencies with this model. First,

$$\frac{1}{k_{obsd}} = \frac{K_H[H^+]}{2k[NH_2OH]_T} + \frac{K_H K_{Br}[H^+]}{2k[NH_2OH]_T}[Br^-] \qquad (10)$$

although the plot of $1/k_{obsd}$ vs $[Br^-]$ in Figure 4 is almost linear, the points show some curvature. Second, the slope divided by the intercept should give the value of K_{Br}, the tribromide formation constant. However, this gives a K_{Br} value of 10 M^{-1}, which does not agree well with the literature value of 16.8 M^{-1}.[10] The addition of a term for a tribromide reaction path is included to account for these deviations. Equation 11 shows

$$k_{obsd}\,(s^{-1}) = \frac{2[NH_2OH]_T(k_o + k_1 K_{Br}[Br^-])}{(1 + K_H[H^+])(1 + K_{Br}[Br^-])} \qquad (11)$$

this expression, where k_o is the rate constant for the bromine path, and k_1 represents the tribromide path. From the data in Figure 4, the values for k_o and k_1 are determined by iteration (Marquardt algorithm) to be $k_0 = (2.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1} and $k_1 = (2.4 \pm 0.4) \times 10^8$ M^{-1} s^{-1} at 25.0 °C. The dotted curve in Figure 4 shows the fit of these rate constants to the experimental data. We believe that this is the best set of data to evaluate k_1 because of the large variation in Br^- concentration at constant $[H^+]$ and $[NH_2OH]_T$ values. However, all 24 sets of data in Table 4, where the concentrations of H^+, NH_2OH, and Br^- are varied, are used to evaluate k_o. The k_{obsd} values are weighted based on their precision and are used with the above k_1 value and the expression in eq 11 to give $k_o = 1.8$ (± 0.1) × 10^9 M^{-1} s^{-1}. This result is almost insensitive to the choice of k_1. The last column in Table 4 gives the k_{calcd} values for $k_o = 1.8 \times 10^9$ M^{-1} s^{-1} and $k_1 = 2.4 \times 10^8$ M^{-1} s^{-1} in order to show their agreement with k_{obsd}.

The suggested mechanism I in acid conditions is shown by eqs 12–16, where BrNHOH and Br_2NOH are proposed intermediate species. Equations 12 and 13 are the rate determining steps and all subsequent reactions are fast. The stoichiometric equation for the reaction of bromine and hydroxylamine is given in eq 17, which shows a 2:1 $[Br_2]_T$:$[NH_2OH]_T$ ratio to produce HONO. The overall 1:1 stoichiometry (eq 7) is achieved because a second equivalent of hydroxylammonium ion reacts with HONO (eq 18). The proposed *N*-bromo intermediates are reasonable, but neither BrNHOH nor Br_2NOH have been isolated. However, BrNO (nitrosyl bromide) is a known compound.[30] Studies of diazotization mechanisms[31–34] have given BrNO hydrolysis equilibrium and rate constants in water (eq 19). Schmid[31] reported the hydrolysis equilibrium constant to be 44.6 at 0 °C and 19.6 at 25 °C, and he reported values of 8 × 10^6 for k_f and 1.8 × 10^5 for k_b at 0 °C. Although Schmid did not give any units, he measured time periods in minutes, and other aspects of this paper indicate these rate constants must be in terms of min^{-1} and M^{-2} min^{-1}, respectively. (We point this out because the *Gmelin Handbook* for bromine compounds[30] erroneously reports Schmid's k_f value to be 8 × 10^6 s^{-1}, whereas Ridd's review[32] correctly divides Schmid's values for other rate constants by 60 to give units of s^{-1}.) Ingold[34] reported that the bromide-catalyzed decomposition of HONO had a larger rate constant than the nitrite-catalyzed path by a factor of 8/7, and Schmid[31] used this ratio to compute his k_b value (3.0 × 10^3 M^{-2} s^{-1}) at 0 °C. His corresponding k_f value would be 1.3 × 10^5 s^{-1}.

mechanism I

$$Br_2 + NH_2OH \xrightarrow{k_o} BrNHOH + Br^- + H^+ \tag{12}$$

$$Br_3^- + NH_2OH \xrightarrow{k_1} BrNHOH + 2Br^- + H^+ \tag{13}$$

$$Br_2 + BrNHOH \xrightarrow{k_2} Br_2NOH + Br^- + H^+ \text{ (fast)} \tag{14}$$

$$Br_2NOH \rightarrow BrNO + H^+ + Br^- \text{ (fast)} \tag{15}$$

$$BrNO + H_2O \rightarrow Br^- + HONO + H^+ \text{ (fast)} \tag{16}$$

$$2Br_2 + NH_2OH + H_2O \rightarrow 4Br^- + HONO + 4H^+ \tag{17}$$

$$HONO + NH_3OH^+ \rightarrow N_2O + 2H_2O + H^+ \tag{18}$$

$$BrNO + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HONO + H^+ + Br^- \tag{19}$$

Hughes and Ridd[33] used a colorimetric diazotization reaction to obtain a k_b value of 1.17 × 10^3 M^{-2} s^{-1} at 0 °C. This leads to a value of $k_f = 5.2 \times 10^4$ s^{-1} at 0 °C based on Schmid's equilibrium constant. The activation energy for BrNO hydrolysis has not been reported, but Schmid estimated k_f to be between 10^7 and 10^8 min^{-1} at 25 °C. Thus, we will consider k_f to be greater than 2 × 10^5 s^{-1} at 25 °C.

Table 5. Temperature Dependence Study for the Reaction of Br_2 and NH_2OH[a]

temp, °C	k_{obsd}, s^{-1}	K_{Br}, M^{-1}	log K_H	10^{-9} k_o, M^{-1} s^{-1}	$\Delta H^‡$, kJ/mol
15.00	2.13 (0.03)	18.1	6.243	1.56	19.8
20.05	3.32 (0.08)	17.3	6.121	1.82	17.5
24.95	4.91 (0.14)	16.8	6.006	2.05	15.3
30.00	7.25 (0.19)	15.9	5.895	2.32	13.1
35.00	10.2 (0.5)	15.2	5.787	2.52	10.9

[a] $[NH_2OH]_T = 1.52 \times 10^{-4}$ M, $[Br_2]_T = 1.5 \times 10^{-5}$ M, $[Br^-] = 15$ mM, $[H^+] = 0.10$ M, and $\mu = 0.50$ M.

There are several reasons why we are concerned with the hydrolysis of BrNO. First, the equilibrium constant for eq 19 indicates that under all our conditions the [HONO]/[BrNO] ratios are very large and the hydrolysis reactions to form HONO will be essentially complete. Second, the first-order hydrolysis rate constant is larger than any of our observed rate constants, even at pH 2–6, so that there is no buildup of BrNO concentration. Third, the reaction between BrNO and NH_2OH, which is reported[6] to have a rate constant of 3.7 × 10^7 M^{-1} s^{-1} at 0 °C, should not be competitive with the hydrolysis reaction in eq 16 at any concentrations of NH_2OH used in this work. A direct reaction between BrNO and NH_2OH would give N_2O without the intermediate formation of HONO, whereas we observe nearly quantitative yields of $[HONO]_T$.

Temperature Dependence. The reaction between bromine and hydroxylamine was carried out from 15 to 35 °C to determine the kinetic parameters $\Delta H^‡$ and $\Delta S^‡$. The reaction conditions were $[NH_2OH]_T = 1.52 \times 10^{-4}$ M, $[Br_2]_T = 1.5 \times 10^{-5}$ mM, $[Br^-] = 0.015$ M, $[H^+] = 0.10$ M, and $\mu = 0.50$ M. Measured first-order rate constants were converted to second-order rate constants in accord with eq 11, except that the slower tribromide path could be neglected because only 5% of $[Br_2]_T$ is present as the less reactive tribromide species. Since K_{Br} and K_H values are a function of temperature, literature values from 15 to 35 °C were used for conversion to the second-order rate constant.[9,10] Table 5 shows k_{obsd} values, the equilibrium constants used for K_{Br} and K_H, and the resulting k_o values at each temperature. (Individual values for K_{Br} and K_H that were not directly reported within the reference were interpolated using the appropriate data.)

From Figure 5 at 25 °C, $\Delta H^‡ = 15 \pm 1$ kJ mol^{-1} and $\Delta S^‡ = -15 \pm 1$ J mol^{-1} K^{-1}. However, the experimental points in Figure 5 show curvature, which indicates that the activation enthalpy is not constant with temperature and that an activation heat capacity $\Delta C_p^‡$ must be taken into account. The curvature of the data was found to be statistically significant.[35] A second-order polynomial fit (see dotted line in Figure 5) can be used to extract $\Delta H^‡$ and $\Delta C_p^‡$ as a function of temperature. From 15 to 35 °C, $\Delta H^‡$ (see Table 5) ranges from 20.1 to 10.6 kJ mol^{-1} and $\Delta C_p^‡ = -440$ J mol^{-1} K^{-1}. It is likely that the large value of $\Delta C_p^‡$ results from the breakup or partial breakup of a hydrated structure of Br_2, as shown in eq 20. It is noteworthy that the equilibrium hydrolysis of bromine (to form HOBr, Br^-, and H^+) also has a large negative change in heat capacity.[19]

$$Br_2(H_2O) \rightleftharpoons Br_2 + H_2O \tag{20}$$

---

(30) *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th ed.; Merlet, P., Ed., Springer-Verlag: New York, 1992; Bromine Supplement, Vol. B2, pp 236–254.

(31) (a) Schmid, H. *Monatsh. Chem.* **1954**, *85*, 424–440. (b) Schmid, H.; Fouad, M. G. *Monatsh. Chem.* **1957**, *88*, 631–638.

(32) Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1–49.

(33) Hughes, E. D.; Ridd, J. H. *J. Chem. Soc.* **1958**, 82–88.

(34) Ingold, C. K. *Bull. Soc. Chim. Fr.* **1952**, 667–671.

(35) Kohnstam, G. *Adv. Phys. Org. Chem.* **1967**, *5*, 121–172.

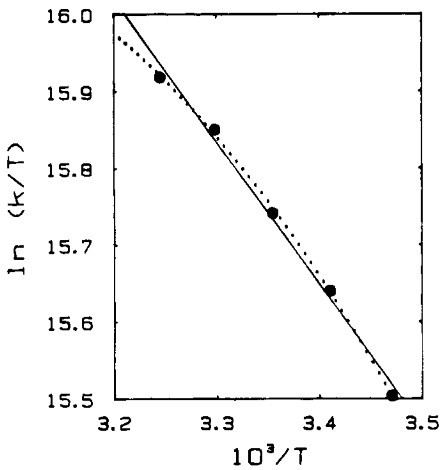

Figure 5. Eyring plot for the reaction between bromine and hydroxylamine from 15.0 to 35.0 °C with $[NH_2OH]_T = 1.52 \times 10^{-4}$ M, $[Br_2]_T = 1.5 \times 10^{-5}$ M, $[Br^-] = 0.015$ M, and $[H^+] = 0.10$ M. The dotted line is the polynomial fit.

Table 6. PAF Data for the Reaction of $Br_2 + NH_2OH$[a]

$[NH_2OH]_T$, mM	$[Br_2]_T$, mM	$[Br^-]_i$, M	$p[\bar{H}^+]$[b]	$10^{-3}\ k_{calcd}$,[c] s^{-1}	$10^{-3}\ k_{obsd}$, s^{-1}	k_{obsd}/k_{calcd}
25.3	0.17	0.0050	2.01	8.5	8.2 (0.1)	0.97
15.2	0.18	0.0049	2.36	11.1	10.2 (0.4)	0.92
12.1	0.074	0.0050	2.42	10.4	11.6 (0.2)	1.12
12.1	0.066	0.0050	2.54	13.7	13.7 (0.5)	1.00
6.05	0.0042	0.297	2.98	5.7	3.9 (0.1)	0.68
0.202	0.0083	0.146	5.31 (5.47)	63.3	21.9 (0.7)	0.35
0.191	0.0091	0.147	5.47 (5.60)	74.6	39 (2)	0.53
0.191	0.0087	0.147	5.56 (5.71)	89.4	37 (4)	0.42
0.191	0.0092	0.147	5.85 (5.86)	110	60 (11)	0.55
0.191	0.0093	0.147	5.92 (5.99)	130	59 (3)	0.45

[a] 25.0 ± 0.1 °C, $\mu = 0.50$ M, 266 nm. [b] Mean $[H^+]_{exptl}$ expressed as $p[\bar{H}^+]$; the values in parentheses are mean $[H^+]_{calcd}$ based on one H^+ released per Br_2, expressed as $p[\bar{H}^+]_{calcd}$. [c] Calculated from eq 11; based on $p[\bar{H}^+]_{calcd}$ values for data above pH 5.3.

A value of $7 \times 10^9\ M^{-1}\ s^{-1}$ can be expected for a diffusion-controlled rate constant, k_D, in the reaction between neutral species in aqueous solution at 25 °C. This is based on $k_D = 8RT/3000\eta$, where η is the viscosity of the solvent.[36] The same expression leads to a $\Delta H_D^\ddagger$ value of 17.4 kJ mol^{-1} for the activation enthalpy of a diffusion-controlled reaction in water, based on the temperature dependence of the viscosity. Our experimental value of k_o for the reaction between Br_2 and NH_2OH is a factor of 4 less than the diffusion-controlled value. Nevertheless, the experimental $\Delta H^\ddagger$ value is 2.0 kJ mol^{-1} less than the $\Delta H_D^\ddagger$ value rather than being larger. This indicates that some preequilibrium steps with small negative ΔH° values occur prior to the rate-limiting step. We would expect the desolvation of $Br_2(H_2O)$ to have a positive rather than a negative ΔH° value. On the other hand, a weak association complex to form Br_2NH_2OH could account for the results where the k_o value is the mathematical product of this association constant and the first-order rate constant for its breakup to give $BrNHOH + Br^- + H^+$.

Kinetics at pH 2−6. Above pH 2 the rate of the bromine-hydroxylamine reaction becomes too fast to follow by stopped-flow methods, so the PAF method is used. (Table 6 gives the conditions.) At $p[H^+]$ values of 2.0 to 2.5, measured k_{obsd} values of 8200 to 13 700 s^{-1} were in excellent agreement with values calculated (k_{calcd}) from eq 11. At pH 3, a low concentration of $[Br_2]_T$ (0.0042 mM) and a high ratio of $[NH_2OH]_T/[Br_2]_T$ (1.4×10^3) was used to prevent pH change during the reaction. Excellent PAF plots were obtained, but the k_{obsd} value was only 68% of the k_{calcd} value. It was not possible to obtain reliable results from pH 4 to 5, because the pH change during the reaction was too large without the addition of other buffers. Suitable buffers such as acetic acid react with bromine.

When the initial $p[H^+]_o$ of both reactants was 5.6−6.1 and the $[NH_2OH]_T/[Br_2]_T$ ratio was 20−24, the buffer capacity of $[NH_2OH]_T$ was sufficient to prevent a large pH change during the reaction, and excellent PAF plots were obtained with k_{obsd} values as large as 60,000 s^{-1}. The pH measured within a few minutes after these reactions was 0.14 to 0.40 pH units less than that of the reactants. This change corresponds to 5/2 H^+ released per Br_2 (eq 21) after correction for buffering. Table 6

$$2Br_2 + NH_2OH + H_2O \rightarrow 4Br^- + NO_2^- + 5H^+ \quad (21)$$

gives the average H^+ concentration during each reaction, expressed as $p[\bar{H}^+]$, based on these experimental measurements. However, there are reasons to believe that the actual pH change during the very rapid observed reaction is much less than this. This is because at pH 5−6 the rate of Br_2 loss may be much faster than the rate of NO_2^- formation. We need to consider the mechanism under these conditions to understand this possibility.

Mechanism at pH 5−6. The ΔpH values, $2(p[H^+]_o - p[\bar{H}^+])$, are smallest for the results in Table 6 when the experimental $p[\bar{H}^+]$ values are 5.85 and 5.92. The PAF plots for these runs were excellent, but the k_{obsd} values are only 50 ± 5% of the expected values (i.e. $k_{obsd}/k_{calcd} \approx 0.5$). We propose a shift in the reaction mechanism to explain this. At pH 5.9 the free NH_2OH concentration is much greater than the concentration of the first product, BrNHOH, and NH_2OH is a much stronger nucleophile than BrNHOH. Hence we propose that all the Br_2 is consumed by NH_2OH, unlike the situation below pH 2 where BrNHOH also reacts with Br_2. However, we must account for the fact that the NO_2^- yield is the same as the HONO yield at low pH. Mechanism II is proposed to account for these facts. The initial reactions of Br_2 and Br_3^-

mechanism II

$$Br_2 + NH_2OH \xrightarrow{k_o} BrNHOH + Br^- + H^+ \quad (12)$$

$$Br_3^- + NH_2OH \xrightarrow{k_1} BrNHOH + 2Br^- + H^+ \quad (13)$$

$$2BrNHOH \rightarrow Br_2NOH + NH_2OH \quad (22)$$

$$Br_2NOH \rightarrow BrNO + H^+ + Br^- \quad (15)$$

$$BrNO + H_2O \rightarrow HONO + Br^- + H^+ \quad (16)$$

$$HONO \rightleftharpoons NO_2^- + H^+ \quad (23)$$

(eqs 12 and 13) are the same as in mechanism I, but there is no contribution from eq 14. Instead, BrNHOH undergoes disproportionation (eq 22) to form Br_2NOH, which then decays by eq 15 and 16 as in mechanism I. Finally, HONO rapidly loses a proton to give NO_2^- (eq 23). The proposed disproportionation of BrNHOH parallels known reactions of bromamine,[37] where the equilibrium constant for eq 24 is $5 \times 10^9\ M^{-1}$.

Mechanism II gives an expression for rate constant, k'_{obsd} in eq 25, where there is no longer a stoichiometric factor of 2 for the rate of loss of $[Br_2]_T$. This explains why k'_{obsd} is half of

---

(36) Caldin, E. F. *Fast Reactions in Solution*; Wiley: London, 1964; p 12.

(37) Inman, G. W., Jr.; Johnson, J. D. *Environ. Sci. Technol.* **1984**, *18*, 219−224.

$$H^+ + BrNH_2 + BrNH_2 \overset{K}{\rightleftharpoons} Br_2NH + NH_4^+ \qquad (24)$$

$$k'_{obsd} = \frac{(k_o + k_1K_{Br}[Br^-])[NH_2OH]_T}{(1 + K_H[H^+])(1 + K_{Br}[Br^-])} \qquad (25)$$

the k_{calcd} value based on eq 11. Mechanism II requires the loss of Br_2 and Br_3^- prior to the slower disproportionation of BrNHOH. Hence, the BrNHOH concentration will build up before it decays via eqs 22, 15, 16, and 23. These reactions were studied at 266 nm where the overwhelming absorbance contribution of Br_3^- masks any absorbance changes caused by the buildup and decay of BrNHOH.

The results at $p[\bar{H}^+] = 5.31$ to 5.56 (Table 6) are consistent with the same explanation,and there is reason to believe that the disproportionation reaction might be slow relative to the rate of loss of Br_2. Thus, the rate constant for bromamine disproportionation (eq 24) is reported[37] to be 2.4×10^8 M^{-2} s^{-1} at 25 °C, so that at pH 6 and 10^{-5} M NH_2Br the first half-life for this reaction is 400 s. Even if the BrNHOH disproportionation rate were 10^5 times faster than this, it would still be slow compared to the loss of Br_2. Therefore, only one H^+ per Br_2 (eq 12) would be released during the Br_2 loss instead of $^5/_2H^+$ per Br_2. The $p[\bar{H}^+]$ values given in parentheses in Table 5 are calculated for 1:1 release of H^+ and correspond to a much smaller change of pH during the reactions from $p[\bar{H}^+]_{calcd}$ 5.47 to 5.99. In the worst case, $\Delta pH = 0.24$ during the reaction.

Finally, it should be mentioned that for eq 26 the relaxation rate constant (eq 27)[38] will be on the same order of magnitude as the first-order rate constants for Br_2 loss at pH 5−6. If the

$$NH_2OH + H^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} NH_3OH^+ \qquad (26)$$

$$\tau^{-1} = k_{12}[\bar{H}^+] + k_{21} \qquad (27)$$

value of k_{12} is 10^{10} M^{-1} s^{-1} (typical of H^+ reactions),[38] then k_{21} is 10^4 s^{-1}. Thus at $p[\bar{H}^+] = 5$, $\tau^{-1} = 1.1 \times 10^5$ s^{-1}, while at $p[\bar{H}^+] = 6$, $\tau^{-1} = 2 \times 10^4$ s^{-1}. This effect will also tend to reduce the loss of NH_2OH due to H^+ released during reactions with Br_2.

Unsatisfactory Alternative Mechanisms. If rapid hydrolysis of BrNHOH occurs to form nitrosyl hydride (eq 28), then it would be difficult to form NO_2^- as a reaction product. This is

$$BrNHOH \rightarrow Br^- + HNO + H^+ \qquad (28)$$

because the dehydrative dimerization rate constant of HNO (eq 29) has been estimated[39] to be very large, (1.8−7.2) × 10^9 M^{-1}

$$HNO + HNO \rightarrow N_2O + H_2O \qquad (29)$$

s^{-1}, so N_2O should form as the immediate product. A pK_a value of 4.7 was measured for HNO from pulse radiolysis studies.[40] Although the presence of NO^- might reduce the dehydrative dimerization rate, N_2O formation would still be very rapid. An alternative pathway that could lead to NO_2^- would involve a rapid bromine exchange between BrNHOH and HNO (eq 30) to give BrNO, which then hydrolyzes (eqs 16 and 23).

$$BrNHOH + HNO \rightarrow BrNO + NH_2OH \qquad (30)$$

While this mechanism is stoichiometrically consistent, some criticisms can be made. If the HNO reaction with itself is as fast as reported, it is difficult to explain the observed high yields of nitrite if any HNO forms. Furthermore, the reverse reaction of eq 30 seems more favorable than the forward reaction. Since NH_3OH^+ has a pK_a of 6.01 and HNO a pK_a of 4.7, hydroxylamine has a higher proton affinity than NO^- by a factor of 20. Therefore, hydroxylamine is likely to have a higher affinity for Br^+ than does HNO.

Comparison to the Reaction of Hydroxylamine and Chlorine. It is useful to compare the reactions of hydroxylamine with both bromine and chlorine. On a time scale of milliseconds, Cl_2 reacts with NH_2OH in 1 M $[H^+]$ with a 3:1 stoichiometry, oxidizing N(−I) in NH_2OH to N(V) (the suggested intermediate is Cl_3NO).[1] In contrast, Br_2 reacts with a 2:1 stoichiometry, oxidizing N(−I) to N(III) (the suggested intermediate is Br_2NOH). This comparison reflects the stronger oxidizing strength of chlorine. Kinetically, hydroxylamine reactions with both Cl_2 and Br_2 have similar second-order rate constants for the first step (1.6×10^9 M^{-1} s^{-1} for Cl_2[1] compared to 1.8×10^9 M^{-1} s^{-1} for Br_2). The association of X_2 with NH_2OH in an encounter complex is expected to be more favorable for Br_2 because of its easier octet expansion. The weaker Br−Br bond is easier to break than the Cl−Cl bond. However, the reaction with Cl_2 leads to formation of the stronger N−Cl bond. These factors appear to offset one another to give similar rate constants for the formation of XNHOH.

Conclusion

A second-order rate constant of 1.8×10^9 M^{-1} s^{-1} has been determined for the reaction between Br_2 and NH_2OH at 25.0 °C. In acid (pH 0−3), two bromines react in rapid succession to give Br_2NOH as a proposed intermediate that decays rapidly to give HONO. Nitrous acid then reacts more slowly with NH_3OH^+ to give N_2O. At pH 5−6 with excess NH_2OH, a different kinetic stoichiometry is observed, and we propose that all the Br_2 is consumed in the first step to give BrNHOH. The fact that NO_2^- is the product is best explained by the subsequent disproportionation of BrNHOH. The ability to study these fast reactions over a wide pH range by use of stopped-flow and pulsed-accelerated flow methods gives insights into the reaction mechanisms. The initial step proposed in all cases is a Br^+ transfer to form BrNHOH. Subsequent reactions via different pathways are proposed to give Br_2NOH and BrNO. The reaction stoichiometry for $[Br_2]_T$:$[NH_2OH]_T$ changes with time and with acidity, but the first observable product is N(III) (HONO or NO_2^-).

Acknowledgment. This work was supported by the National Science Foundation Grant CHE-9024291. R.C.B. is grateful for the National Needs Fellowship cosponsored by Purdue University, the U.S. Department of Education, and DuPont. J.N.C. is grateful to the NSF for a Research Opportunity Award and to Bucknell University for a sabbatical leave grant.

Registry Numbers (supplied by author): Br_2, 7726-95-6; Br_3^-, 14522-80-6; BrNO, 13444-87-6; $BrNH_2$, 14519-10-9; NH_2OH, 7803-49-8; NH_2OH·HCl, 5470-11-1; HONO, 7782-77-6; NO_2^-, 14797-65-0; N_2O, 10024-97-2; HNO, 14332-28-6.

---

(38) Eigen, M.; DeMaeyer, L. In *Technique of Organic Chemistry*, 2nd ed.; Friess, S. L., Lewis, E. S., Weissbergen, A., Eds.; Wiley-Interscience: New York, 1963; Vol. VIII, Rates and Mechanisms of Reaction, Part II, pp 903, 1036.

(39) Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285−4288.

(40) Grätzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003−1010.