Inorg. Chem. **1993,** *32,* 5905–5910 **5905**

Kinetics and Mechanism of the Oxidation of Hydroxylamine by Aqueous Chlorine

John N. Cooper[†] and Dale W. Margerum[*]

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

Received July 28, 1993[•]

The kinetics and mechanism of the reaction between hydroxylamine and chlorine in 0.1–1 M hydrochloric acid have been determined. In 10-fold or greater excess of NH_3OH^+, on the stopped-flow time scale, three distinct steps are observed: the initial rapid formation of an intermediate, which reacts with further hydroxylamine to form nitrous acid, HONO, followed by a slower reduction of HONO with excess NH_3OH^+ to form nitrous oxide. In the presence of a large excess of NH_3OH^+, the stoichiometry several minutes after mixing is $\Delta(NH_3OH^+)/\Delta(Cl_2) = 1.1 \pm 0.2$, which corresponds to a nearly quantitative formation of N_2O. When the reactants are mixed in equimolar ratios, the principal nitrogenous product is nitrate. On the basis of the kinetics and stoichiometry, and by analogy with the well-established F_3NO, the intermediate proposed is Cl_3NO. This intermediate will hydrolyze rapidly to give NO_3^-, but in the presence of excess NH_2OH it is reduced even more rapidly to give HONO. The proposed reaction sequence in a large excess of NH_3OH^+ corresponds to the following oxidation state changes: $N(-I) \rightarrow N(V) \rightarrow N(III) \rightarrow N(I)$. The initial oxidation by 3 equiv of Cl_2 is consistent with a series of Cl^+-transfer steps, where high acidity suppresses the rate of the first reaction with NH_2OH but does not suppress the reactivity of the less basic transients, ClNHOH and Cl_2NOH.

Introduction

Chlorine is widely used as a disinfectant in water treatment.[1,2] In aqueous solutions chlorine hydrolysis occurs (eq 1), but the

$$Cl_2(aq) + H_2O \rightleftarrows HOCl + H^+ + Cl^- \tag{1}$$

formation of HOCl is suppressed by high concentrations of HCl. The equilibrium constant for chlorine hydrolysis has been determined at a variety of temperatures and ionic strengths.[3–7] The value at $\mu = 0.50$, 25.0 °C, is 1.04×10^{-3} M^2.[7]

Hydroxylamine (NH_2OH) is used as an O_2 scavenger[8] in industrial boiler water to inhibit corrosion. It also has been proposed as a Cl_2 scavenger in the purification of HCl[9] and in the preparation of $GeCl_4$.[10] Although the reduction of aqueous chlorine by hydroxylamine has been known for over a century,[11] the stoichiometry and the products are not well established; both nitrate[11] and NCl_3[12] have been reported to form in the reaction of NH_2OH with excess Cl_2. The kinetics of the reactions between Cl_2 and NH_2OH have not been determined previously. The investigation of the interaction of hydroxylamine with halogen oxidants extends our studies of the mechanisms of non-metal redox reactions[13–17] and is part of our continuing examination of chemical reactions that occur in wastewater treatment.

Experimental Section

Reagents. Stock solutions of hydroxylamine were prepared from $NH_2OH{\cdot}HCl$ (Mallinckrodt) and standardized by ferrometry[18] (eq 2). An

$$4Fe^{3+} + 2NH_3OH^+ \rightarrow N_2O + 4Fe^{2+} + 6H^+ + H_2O \tag{2}$$

aliquot of NH_3OH^+ was added to an excess of Fe(III) in 1 M H_2SO_4, the mixture was heated to boiling for at least 5 min and then cooled, and the Fe(II) was determined with Ce(IV) prepared from ceric ammonium nitrate.

Stock solutions of NaOCl were prepared by bubbling Matheson high-purity Cl_2 gas, prewashed in H_2SO_4, into ~0.2 M "carbonate-free" NaOH and then diluted with an additional volume of NaOH. The hypochlorite solutions were assayed at 292 nm, ϵ_{OCl^-} 350 M^{-1} cm^{-1},[17,19] and stored at ~5 °C in Nalgene bottles that had been aged by previous exposure to hypochlorite. No significant loss of absorbance at 292 nm was observed over a period of weeks.

For stoichiometric studies, freshly standardized stock OCl^- in NaOH was T-mixed with excess HCl into a receiver syringe to minimize the head space. In this technique, to ensure uniform mixing conditions, equal volumes of reagents in separate syringes are pushed either mechanically or manually through a two-input mixing chamber of local design by the piston of a Harvard Instruments compact infusion pump. This aqueous chlorine was then either injected directly into, or T-mixed with, $NH_3OH^+Cl^-$ solutions through Kel-F tubing. Loss by volatility was negligible with these methods. Hydrochloric acid was prepared by dilution of Mallinckrodt concentrated HCl, which had previously been established to be Br^--free.[20] Bromine dichloride, $BrCl_2^-$, has a strong UV absorption at 232 nm that would intefere with Cl_3^- determination.[20] Sodium chloride solutions for maintaining ionic strength were prepared by neutralization of HCl with carbonate-free, saturated NaOH.

Spectral and Kinetic Measurements. UV spectra were recorded in quartz cells on a Perkin-Elmer Lambda-9 spectrophotometer interfaced to a Zenith 386/20 microcomputer. Kinetic data were obtained under

---

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

[•] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) White, C. G. *Handbook of Chlorination*; Van Nostrand-Reinhold: New York, 1972.

(2) Rosenblatt, D. H. In *Disinfection: Water and Wastewater*; Johnson, J. D., Ed.; Ann Arbor Science: Ann Arbor, MI, 1975; pp 249–76.

(3) Frank, H. S.; Evan, M. W. *J. Chem. Phys.* **1945,** *13,* 507–32.

(4) Connick, R. E.; Chia, Y. *J. Am. Chem. Soc.* **1958,** *81,* 1280–3.

(5) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962,** *84,* 1355–61.

(6) Margerum, D. W.; Gray, E. T., Jr.; Huffman, R. P. *ACS Symp. Ser.* **1978,** *82,* 278–91.

(7) Wang, T. X.; Margerum, D. W. To be submitted for publication.

(8) Cuisia, D. G.; Hwa, C. M.; Jacob, J. T.; Salutsky, M. L. U. S. Patent 4 067 690; *Chem. Abstr.* **1978,** *88,* 141457h.

(9) (a) Takatomi, H.; Yamauchi, S.; Ogawa, K. Japanese Patent 02 233 503; *Chem. Abstr.* **1991,** *114,* 65261c. (b) Wilson, W. L. Br. Patent 739 144 *Chem. Abstr.* **1956,** *50,* 10354a.

(10) Belaka, E.; Palek, J. Czech Patent 137 349; *Chem. Abstr.* **1971,** *75,* 65754s.

(11) de Bruijn, C. A. L. *Recl. Trav. Chim. Pays-Bas* **1892,** *11,* 18–50.

(12) Dowell, C. T. *J. Am. Chem. Soc.* **1919,** *41,* 124–5.

(13) Yiin, B. S.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1987,** *26,* 3435–41.

(14) Nagy, J. C.; Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1988,** *27,* 2773–80.

(15) Fogelman, K. D.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1989,** *28,* 986–93.

(16) Gerritsen, C. M.; Margerum, D. W. *Inorg. Chem.* **1990,** *29,* 2757–62.

(17) Johnson, D. W.; Margerum, D. W. *Inorg. Chem.* **1991,** *30,* 4845–51.

(18) Bray, W.; Simpson, M.; MacKenzie, A. *J. Am. Chem. Soc.* **1919,** *41,* 1363–78.

(19) Gray, E. T., Jr. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1977.

(20) Kelley, M.; Wang, T. X.; Cooper, J. N.; Margerum, D. W. To be submitted for publication.

0020-1669/93/1332-5905$04.00/0

Table I. Spectral Characteristics at Wavelengths Used for Kinetic Studies

	molar absorptivities, ϵ, M^{-1} cm^{-1}				
λ, nm	Cl_2[a]	Cl_3^-[a]	NO_3^-[b]	HONO[b]	Cl_3NO[c]
220	57.0	10400	3570	893	2300
240	~0.0	6730	61	147	700
260	1.3	1880	1.5	11	470
275	9.0	498	2.7	2.4	134
288	24.3	175	5.2	1.6	79
300	43.9	140	7.1	2.4	52
320	69.0	181	3.2	8.8	17
325	69.7	182	1.8	12.9	5
358	33.5	81.0	~0.0	51.9	*d*
371	18.5	48.8	~0.0	54.0	8
386	9.2	26.0	~0.0	31.6	*d*

[a] Reference 20. [b] This work. [c] Proposed intermediate. [d] Not determined.

Table II. Stoichiometry

Consumption Ratio

$[NH_3OH^+]_i$, M	$[Cl_2]_i$, M	$[NH_3OH^+]_i/[Cl_2]_i$	$[H^+]$, M	$\Delta[NH_3OH^+]/\Delta[Cl_2]$
0.515	0.0147	35.0	0.0040	1.15(0.07)
0.515	0.0147	35.0	0.460	0.91(0.07)
0.515	0.0147	35.0	0.460	1.28(0.22)
				av 1.11(0.18)[a]

Product Distribution

$[NH_3OH^+]_i$, M	$[Cl_2]_i$, M	$[NH_3OH^+]_i/[Cl_2]_i$	$[H^+]$, M	% HONO[b]	% NO_3^-[c]
0.00943	0.0188	0.5	6.8×10^{-4}	3.2	28
0.0158	0.0158	1.0	5.7×10^{-4}	8	18
0.0402	0.0166	2.4	6.4×10^{-4}	4.8	10
0.335	0.0212	15.8	5.3×10^{-3}	0.57	3.3
0.335[d]	0.0204	16.4	5.3×10^{-3}	2.3	2.0
0.503	0.0147	34.2	4.1×10^{-3}	*e*	5.4
0.515	0.0147	35.0	4.1×10^{-3}	*e*	1.4
0.00064	0.00191	0.33	0.100	*e*	32
0.013	0.019	0.61	0.571	2.2	22
0.012	0.0145	0.82	0.582	1.2	26
0.025	0.019	1.32	0.571	*e*	14
0.103	0.019	5.4	0.571	*e*	6
0.308	0.019	16	0.571	*e*	2
0.513	0.019	27	0.571	*e*	1
0.515	0.0147	35.0	0.460	*e*	3.7

[a] Hydroxylamine consumed per chlorine after several minutes. [b] Mole percent HONO per Cl_2 after several minutes. [c] Mole percent NO_3^- per Cl_2. [d] 0.1% EtOH. [e] Below detectable limits.

conditions pseudo-first-order in $[NH_3OH^+]$ and $[H^+]$ at 26.0 °C in 1.0 M Cl^- medium with the Lambda-9 spectrophotometer or with a Durrum stopped-flow spectrophotometer interfaced to a Zenith 151 microcomputer with a MetraByte DASH-16 A/D interface card. For stopped-flow measurements, 250 absorbance–time data pairs were collected in 6–15 replicate runs for each set of initial concentrations. Absorbance was followed at wavelengths from 220 to 389 nm. Observed rate constants, k_i, were corrected for mixing within the flow chamber of the stopped-flow apparatus[21] by eq 3, k_{mix} 1700 s^{-1}.

$$k_{i,\mathrm{cor}} = \left(\frac{1}{k_i} - \frac{1}{k_{\mathrm{mix}}}\right)^{-1} \qquad (3)$$

In high Cl^- concentrations, appreciable amounts of Cl_3^- are present (eq 4);[20] this species has a large molar absorptivity with λ_{max} at 220 nm

$$Cl_2(aq) + Cl^- \rightleftarrows Cl_3^- \qquad K_3 = 0.18\ M^{-1} \qquad (4)$$

(Table I) which enables the loss of Cl_2 to be followed. Hydrochloric acid is essentially transparent at $\lambda > 210$ nm. Hydroxylamine in aqueous acid, pK_a $(NH_3OH^+) = 6.06$[22] at 25 °C, $\mu = 1$ M, has no UV-vis absorbance but its oxidation products (HONO and NO_3^-) can be observed in the UV region (Table I). Nitrous acid ($pK_a = 2.96$, 25.0 °C, $\mu = 0.47$ M)[23] has a highly characteristic spectrum with five peaks between 337 and 386 nm.[24]

Results

Stoichiometry. The products of the chlorine and hydroxylamine reaction depend on the ratio of initial reactant concentrations, the acidity, and the reaction time. The stoichiometries in Table II were assayed within minutes after T-mixing the reactants. The initial and final concentrations of NH_3OH^+ were determined by ceric ferrometry, with which Cl^- does not interfere. With 35-fold excess of $[NH_3OH^+]_i$ to $[Cl_2]_i$, the overall stoichiometry of NH_3OH^+ consumed to Cl_2 consumed is 1.1 ± 0.2 where the large relative uncertainty results from the determination of the small loss in the large excess of NH_3OH^+. The amount of nitrate ion produced under these conditions was only 1–4 mole % of the initial chlorine. Once NO_3^- is formed, it does not react with NH_3OH^+ under these conditions and it can be determined by its UV absorption band at 302 nm (ϵ 7.24 M^{-1} cm^{-1}).[25] Nitrous acid was identified spectrophotometrically as an intermediate product with $\Delta[HONO]/\Delta[Cl_2]$ equal to 0.45 ± 0.05, in accord with eq 5. Nitrous acid continues to react with any excess NH_3OH^+ to

$$2Cl_2 + NH_2OH + H_2O \rightarrow HONO + 4Cl^- + 4H^+ \qquad (5)$$

give N_2O (eq 6). The stoichiometry in eq 6 to give nitrous oxide

$$HONO + NH_3OH^+ \rightarrow N_2O + 2H_2O + H^+ \qquad (6)$$

is well established.[26,27] At high ratios of $[NH_3OH^+]_i/[Cl_2]_i$, HONO disappears after several minutes, whereas it is readily observed at shorter times. The 1/1 stoichiometry for the overall reaction corresponds to eq 7.

$$2Cl_2 + 2NH_2OH \rightarrow N_2O + 4Cl^- + 4H^+ + H_2O \qquad (7)$$

With 0.0057–0.582 M HCl present, the stoichiometries in Table II were assayed over a 0.33–35.0 ratio of $[NH_3OH^+]_i/[Cl_2]_i$. At low ratios over the entire acidity range, NO_3^- is the predominant product with yields, $\Delta(NO_3^-)/\Delta(Cl_2)$, as high as 0.32 for initial mixing ratios, $[NH_3OH^+]_i/[Cl_2]_i = 0.33$. As the excess NH_3OH^+ increases, the yield of NO_3^- decreases to 1–4%. At low acidities and lower excesses of NH_3OH^+, 0.6–8 mole % HONO is detected. Because the reaction in eq 6 is acid assisted,[27] low $[H^+]$ helps to permit the spectrophotometric detection of HONO minutes after mixing; however, in all cases with excess hydroxylamine, HONO production is observed on the stopped-flow time scale.

Kinetics. In general, at each wavelength, complete analysis of the kinetic data requires a minimum of three distinct rate constants, designated hereinafter as k_1, k_2, and k_3 in order of decreasing magnitude (eq 8) without prejudice regarding the mechanistic sequence. Figure 1A shows an absorbance decrease

$$A_{obs} = A_\infty + \sum_i \Delta A_i \exp(-k_i t) \qquad i = 1\text{–}3 \qquad (8)$$

at 371 nm where the Cl_2/Cl_3^- loss, which occurs within 10 ms, is followed by an absorbance increase due to HONO formation. The minimum absorbance at 9 ms indicates an intermediate with

---

(21) Dickson, P. N.; Margerum, D. W. *Anal. Chem.* **1986**, *58*, 3153–8.
(22) Lumme, P.; Lahermo, P.; Tummavouri, J. *Acta Chem. Scand.* **1965**, *19*, 2175–88.
(23) Tummavouri, J.; Lumme, P. *Acta Chem. Scand.* **1968**, *22*, 2003–11.
(24) Bunton, C. A.; Stedman, G. *J. Chem. Soc.* **1958**, 2440–4.
(25) Wetters, J. H.; Uglum, K. L. *Anal. Chem.* **1970**, *42*, 335–40.
(26) Bothner-By, A.; Friedman, L. *J. Chem. Phys.* **1952**, *20*, 459–62.
(27) (a) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 2824–30. (b) Morgan, T. D. B.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 344–9. (c) Hussain, M. A.; Hughes, M. N.; Stedman, G. *J. Chem. Soc. B* **1968**, 597–603.

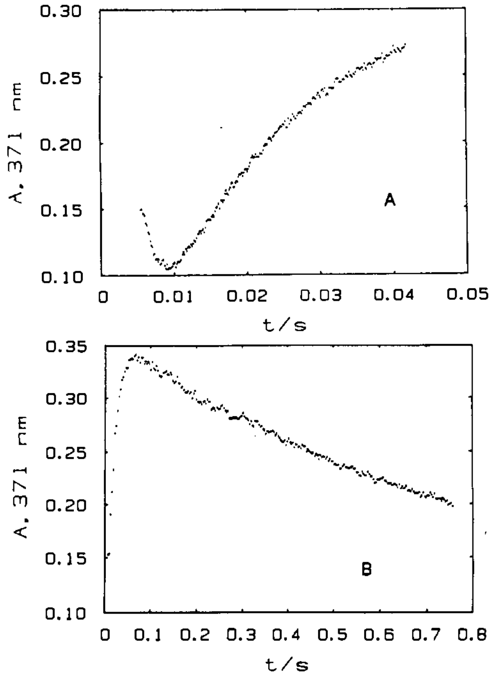

Figure 1. Absorbance changes at 371 nm versus time for the reaction of $[Cl_2]_i$ = 0.006 75 M with $[NH_3OH^+]_i$ = 0.198 M in 1.00 M HCl: (A) loss of Cl_2/Cl_3^- (5–10 ms) and increase of HONO (10–40 ms); (B) increase of HONO (to 50 ms) and its decay (to 750 ms).

low absorptivity at this wavelength. Figure 1B shows the absorbance increase at 371 nm due to HONO formation, which reaches a maximum in 65 ms and is followed by the slower loss of HONO. However, in only a few instances were all three parameters obtained from one run. In general, the data are most easily fit, and the k_i most reliably extracted, if (a) wavelengths are chosen such that the successive ΔA_i values are of comparable magnitude and opposite sign, (b) one of ΔA_i terms vanishes, or (c) times over which data are collected are limited to at most two of the three k's: either to a small fraction of the half-life of the slowest step, k_3, or to after several half-lives of the fastest step, k_1.

Data sets were fit to eq 8 by standard nonlinear-least-squares methods, with initial estimates of the parameters made visually and refined to a convergence criterion of 10^{-6} in the residual sum of squares. Overall, each of the three derived rate constants is linear in $[NH_3OH^+]$ with negligible or small intercepts; k_1 and k_2 are also inverse order in $[H^+]$. Table III provides a complete set of the resolved rate constants. The values obtained for k_2 at low $[NH_3OH^+]/[H^+]$ ratios and shorter wavelengths, 220–260 nm, suffer from the condition that all three ΔA_i are of the same sign and $\Delta A_1 > \Delta A_2$, with the result that these estimates of k_2 are deemed somewhat less reliable than those measured between 389 and 358 nm, where the ΔA_1 and ΔA_2 values are of opposite sign.

Table III. Resolved Rate Constants for Three Sequential First-Order Reactions Observed on Mixing Chlorine and Hydroxylamine[a]

λ, nm	$10^4[Cl_2]$, M	$10^2[NH_3OH^+]$, M	$[H^+]$, M	k_1, s^{-1}	k_2, s^{-1}	k_3, s^{-1}
220	1.37	0.97	1.000	33.7	3.51	*b*
220	1.37	0.97	1.000	*b*	*b*	0.048
220	1.37	0.97	1.000	*b*	*b*	0.048
220	1.35	2.06	1.000	78.5	6.12	*b*
220	1.35	4.12	1.000	114	10.4	*b*
220	1.35	0.97	1.000	39.0	3.79	*b*
220	1.35	2.06	1.000	76.5	6.12	*b*
220	1.35	4.12	1.000	157	11.3	*b*
220	1.35	25.6	1.000	*b*	68.7	2.40
220	1.35	12.2	1.000	324	46.2	1.00
220	1.35	4.58	1.000	157	12.1	*b*
220	1.35	7.63	1.000	227	18.8	*b*
220	1.35	12.2	1.000	293	39.9	*b*
240	2.90	2.29	1.000	87.3	13.6	*b*
260	21.0	2.29	1.000	92.8	13.5	*b*
260	5.97	0.58	1.000	30.5	7.63	*b*
260	7.80	0.98	1.000	39.9	9.65	*b*
260	7.80	1.52	1.000	54.7	12.9	*b*
260	7.80	4.09	1.000	111	25.4	*b*
260	7.80	8.17	1.000	259	43.1	*b*
260	7.20	0.97	1.000	38.9	9.76	*b*
260	7.20	2.04	1.000	67.6	15.1	*b*
260	7.20	3.05	1.000	90.6	18.2	*b*
260	7.20	4.09	1.000	135	26.4	*b*
260	7.20	6.10	1.000	150	24.3	*b*
260	7.20	0.818	1.000	35.7	8.95	*b*
260	7.20	0.818	0.369	87.3	14.1	*b*
260	7.20	0.818	0.122	159	22.3	*b*
260	7.20	6.13	1.000	131	33.7	*b*
275	21.0	2.29	1.000	*b*	14.4	*b*
288	21.0	2.29	1.000	102	13.7	*b*
300	21.0	2.29	1.000	103	13.2	*b*
320	17.6	2.29	1.000	107	*b*	*b*
325	67.0	7.63	1.000	396	35.7	0.39
358	21.5	4.09	1.000	210	25.2	*b*
358	21.5	4.09	0.488	391	37.8	*b*
358	21.5	4.09	0.241	766	55.8	*b*
358	21.5	4.09	0.118	*b*	89.5	*b*
371	67.5	12.20	1.000	618	53.1	*b*
371	67.0	7.63	1.000	275	29.2	*b*
371	67.5	19.80	1.000	849	73.0	1.42
371	67.0	7.63	1.000	253	25.3	0.64
386	71.6	12.25	1.000	*b*	45.7	*b*
386	71.6	12.25	0.352	*b*	94.0	*b*
386	71.6	12.25	0.167	*b*	167	*b*
386	71.6	12.25	0.105	*b*	236	*b*
389	36.0	6.13	1.000	166	32.6	*b*
389	36.0	6.13	0.176	*b*	93.9	*b*
389	36.0	6.13	0.114	*b*	131	*b*

[a] Conditions: 26.0 °C, 1.0 M Cl^- (HCl and NaCl), k's corrected for mixing. [b] Not determined.

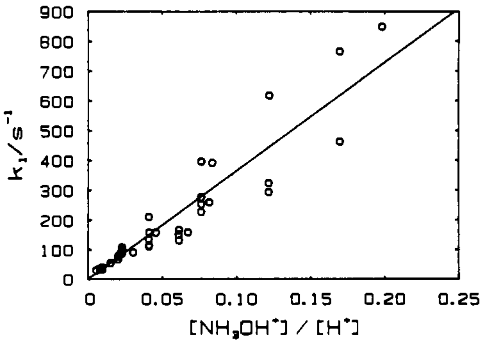

Figure 2. Resolved k_1 rate constants for the loss of Cl_2/Cl_3^- as a function of $[NH_3OH^+]/[H^+]$.

Corrected for mixing, values included in the final fit for k_1 and k_2 are indicated in Table III and are plotted against $[NH_3OH^+]/[H^+]$ in Figures 2 and 3, respectively. The scatter seen for the k_1 values in Figure 2 is a consequence of poorer precision for rate constants measured at wavelengths for which ΔA_1 is relatively small or ΔA_1 and ΔA_2 are of the same sign. A least-squares fit gives an intercept for k_1 of (−8 ± 17), which can be considered to be zero. Forced to zero intercept, the slope for k_1 is given in eq 9. The inverse order in $[H^+]$ corresponds to a bimolecular

$$k_1\,(s^{-1}) = (3.6 \pm 0.2) \times 10^3[NH_3OH^+]/[H^+] \qquad (9)$$

reaction with free NH_2OH. Figure 3 shows that k_2 also is highly dependent on the $[NH_3OH^+]/[H^+]$ values, but the dependence does not appear to be strictly linear. This will be discussed later. The k_3 values are linear in $[NH_3OH^+]$, as shown in Figure 4 for 1.00 M HCl with an intercept that is statistically equal to zero.

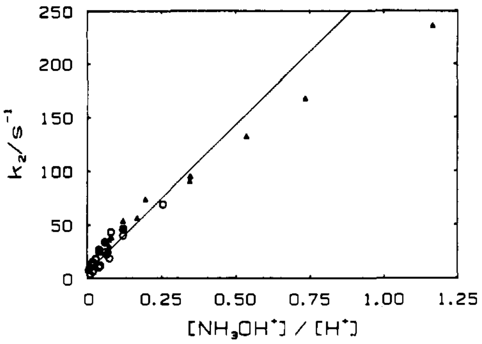

Figure 3. Resolved k_2 rate constants for the loss of the first intermediate (Cl_3NO) (○) and for the increase of the second intermediate (HONO) (▲) as a function of $[NH_3OH^+]/[H^+]$.

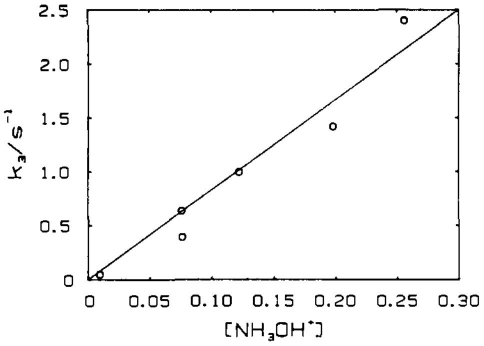

Figure 4. Resolved k_3 rate constants for the loss of HONO in 1.00 M HCl as a function of $[NH_3OH^+]$.

Forced to zero intercept, the slope is given by eq 10.

$$k_3\ (\mathrm{s}^{-1}) = (8.3 \pm 0.5)[\mathrm{NH_3OH^+}] \qquad (10)$$

The k_2 step results in the production of HONO, immediately recognizable by its characteristic spectrum in the near UV region.[24] The production of nitrous acid is consistent with its formation, on the stopped-flow time scale, as an intermediate that is relatively slowly reduced by excess NH_3OH^+ to N_2O. The k_3 step was therefore identified as the reduction of HONO by NH_3OH^+ (eq 6), a reaction that Hughes, Stedman, and co-workers[27] elaborated at 0 °C. Our value for the second-order rate constant, k_3', for the reaction between HONO and NH_3OH^+ is 8.3 $M^{-1}\,s^{-1}$, at 26.0 °C in 1.0 M HCl. This is in good agreement with a calculated value of 7.4 $M^{-1}\,s^{-1}$ obtained from their rate constant of 0.7 $M^{-1}\,s^{-1}$ in 1.0 M $HClO_4$ at 0 °C and an activation energy of 14.7 kcal/mol for the principal term in their rate law. Since authentic mixtures of NH_3OH^+ and HONO at 26 °C in 1.0 M HCl give rates identical to ours, we are confident that the slight disagreement lies in the extrapolation of their data from 0 °C.

The nitrous acid produced in the k_2 step was estimated from the absorbance increase accompanying that step and the known absorptivities of HONO. Estimated with the assumption that at 389–358 nm HONO is the only appreciably absorbing species, the nitrous acid produced per chlorine consumed, $\Delta(\mathrm{HONO})/\Delta(\mathrm{Cl_2})$, averaged 0.45 ± 0.05.

Discussion

The overall 1/1 stoichiometry in the presence of excess hydroxylamine corresponds to the oxidation of N(–I) in NH_2OH by one Cl_2 to give N(I) in $^1/_2N_2O$. However, at low ratios of $[NH_3OH^+]/[Cl_2]$, the stoichiometry changes to $3Cl_2$ per NH_2OH to give N(V) as NO_3^-. With excess NH_3OH^+, the experimental yield of HONO as the second intermediate in the reaction corresponds closely to a stoichiometry of $2Cl_2$ per NH_2OH as N(–I) is converted to N(III). It is clear that the observed first step with a first-order dependence in $[Cl_2]$ must be followed by two more rapid steps that consume more Cl_2 prior to the observed second reaction.

An unusual feature of the observed kinetics is that each of the three sequential steps has a first-order dependence in hydroxylamine concentration. This dependence is expected for the initial oxidation of NH_2OH by Cl_2. Once HONO is identified as the second intermediate, the $[NH_3OH^+]$ dependence for step 3 is consistent with earlier studies[27] in which N(III) is reduced by N(–I) to give N(I) (eq 6). The unexpected behavior was the formation of the first intermediate X, the product of the k_1 step, which then reacts with NH_2OH to form HONO in the k_2 step.

What is the nature of X? Since X appears to be reduced by NH_2OH, it must be a N(V) species that can hydrolyze to give NO_3^-; but X cannot be NO_3^- because once NO_3^- forms, it is not readily reduced by NH_2OH. Nitryl chloride ($ClNO_2$) is a known N(V) species, but it hydrolyzes rapidly in water to give HOCl and NO_2^- [28] and it hydrolyzes rapidly in HCl to give Cl_2 and HONO.[29] Nitryl chloride is a proposed steady-state intermediate[29] in the reaction between Cl_2 and HONO to give NO_3^-, but under our conditions Cl_2 loss is complete before HONO forms. Nitryl chloride does not satisfy our requirements that X be present in appreciable concentrations and that it react with NH_2OH to generate HONO.

We propose that X is trichloramine oxide, Cl_3NO, a N(V) species analogous to the known compound F_3NO.[30] To the best of our knowledge, Cl_3NO has not been isolated. Theoretical calculations indicate that it is a high-energy species[31] and that it is much less stable than the corresponding compounds Cl_3PO and Cl_3AsO.[32] However, these calculations indicate that Cl_3NO should be energetically accessible from the reaction of Cl_2 with NH_3OH^+. With measured values of ΔA_1 and ΔA_2, the effective absorptivities of the reactant Cl_2/Cl_3^- and the second intermediate, HONO, estimates of ϵ_{Cl_3NO}, the absorptivity of the first-formed intermediate can be obtained.[33] Resulting values (Table I) indicate that this species absorbs strongly below 300 nm and absorbs weakly above 325 nm.

Proposed Mechanism. (a) k_1 Dependence. The inverse $[H^+]$ dependence indicates that unprotonated hydroxylamine (eq 11)

$$\mathrm{NH_3OH^+} \rightleftarrows \mathrm{NH_2OH} + \mathrm{H^+} \quad K_a \qquad (11)$$

is the reactive species in the reaction with chlorine. We propose that $3Cl_2$ per NH_2OH are consumed in a series of Cl^+-transfer reactions that constitute the first observed step (eqs 12–14).

$$\mathrm{Cl_2} + \mathrm{NH_2OH} \xrightarrow{k_{1a}} \mathrm{Cl^-} + \mathrm{ClNHOH} + \mathrm{H^+} \qquad (12)$$

$$\mathrm{Cl_2} + \mathrm{ClNHOH} \xrightarrow{k_{1b}} \mathrm{Cl^-} + \mathrm{Cl_2NOH} + \mathrm{H^+} \qquad (13)$$

$$\mathrm{Cl_2} + \mathrm{Cl_2NOH} \xrightarrow{k_{1c}} \mathrm{Cl^-} + \mathrm{Cl_3NO} + \mathrm{H^+} \qquad (14)$$

Equation 12 is rate-limiting in high $[H^+]$, because the free NH_2OH concentration is greatly suppressed. By analogy with $NHCl_2$ and NCl_3,[34] the less basic ClNHOH and Cl_2NOH species are not expected to be protonated. Therefore, the rate expression for the loss of Cl_2 is given by eq 15. The value of the k_{1a} rate constant

---

(28) Collis, M. J.; Gintz, F. P.; Goddard, D. R.; Hebdon, E. A.; Minkoff, G. J. *J. Chem. Soc.* **1958**, 438–45.

(29) Pendlebury, J. N.; Smith, R. H. *Aust. J. Chem.* **1973**, *26*, 1859–61.

(30) MacKenzie, J. S.; Vanderkooi, N.; Sukornick, B.; Wanser, C. A.; Eibeck, R. E.; Stewart, B. B. *J. Am. Chem. Soc.* **1966**, *88*, 2604–5.

(31) Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1983**, *4*, 158–69.

(32) Chang, R.; Goddard, W. A., III. *Surf. Sci.* **1985**, *149*, 341–8.

(33) Espenson, J. H. *Chemical Kinetics and Mechanisms*; McGraw-Hill: New York, 1981; p 67.

(34) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.* **1986**, *25*, 4344–50.

$$\frac{-d[Cl_2]}{dt} = 3k_{1a}[Cl_2][NH_2OH] \qquad (15)$$

is calculated in eq 16, where a small correction is made for Cl_3^-

$$k_{1a} = \frac{k_1(1 + K_3[Cl^-])}{3K_a} = 1.6 \times 10^9\ M^{-1}\ s^{-1} \qquad (16)$$

on the basis that it will be less reactive than Cl_2. Chlorine is so powerful a chlorinating agent that, in the k_1 step, it quickly oxidizes nitrogen all the way to N(V). In the k_2 and k_3 steps, in the presence of excess hydroxylamine, the N(V) intermediate is reduced to N(III) and ultimately to N(I).

(b) k_2 Dependence. We propose that Cl_3NO can be reduced by excess NH_2OH to give intermediates that hydrolyze to form nitrous acid (eqs 17–19). We also propose that Cl_3NO can hydrolyze to give NO_3^- (eq 20) by loss of Cl^-. By analogy with the chemistry of halosulfates, Cl_3NO is expected to hydrolyze far more rapidly than the relatively inert F_3NO; for example, the chlorosulfate anion, $ClSO_3^-$, hydrolyzes 1.3×10^9 times faster[35] than FSO_3^-. In 0.10 M HCl, a 3/1 ratio of $[Cl_2]/[NH_3OH^+]$ gave a NO_3^- yield of 95 ± 8% of the initial hydroxylamine and the k_d rate constant measured at 230 nm is 7.5 ± 1.4 s^{-1}. The overall stoichiometry and rate expression for the formation of nitrous acid from Cl_3NO are given by eqs 21 and 22.

$$Cl_3NO + NH_2OH \xrightarrow{k_{2a}} Cl_2NOH + ClNHOH \qquad (17)$$

$$Cl_3NO + ClNHOH \rightarrow 2Cl_2NOH \qquad (18)$$

$$Cl_2NOH + H_2O \rightarrow 2Cl^- + HONO + 2H^+ \qquad (19)$$

$$Cl_3NO + 2H_2O \xrightarrow{k_d} 3Cl^- + NO_3^- + 4H^+ \qquad (20)$$

$$2Cl_3NO + NH_2OH + 3H_2O \rightarrow 6Cl^- + 3HONO + 6H^+ \qquad (21)$$

$$\frac{-d[Cl_3NO]}{dt} = (k_d + 2k_{2a}[NH_2OH])[Cl_3NO] \qquad (22)$$

From eq 22, the resolved k_2 rate constants can be expressed by eq 23. The line shown in Figure 3 for a least-squares fit of the k_2 values measured from 220 to 300 nm for the loss of Cl_3NO gives $k_d = 6.8 \pm 1.4\ s^{-1}$ and $2k_{2a}K_a = 267 \pm 21\ s^{-1}$. The k_d value is in excellent agreement with the decay constant of 7.5 s^{-1} for Cl_3NO determined from the $3Cl_2/NH_3OH^+$ data. The k_{2a} value equals $(1.53 \pm 0.12) \times 10^8\ M^{-1}\ s^{-1}$, which is only an order of magnitude smaller than the value for k_{1a}.

$$k_2 = k_d + 2k_{2a}K_a\frac{[NH_3OH^+]}{[H^+]} \qquad (23)$$

Most of the larger k_2 values, from 50 to 240 s^{-1}, were based on measurements from 325 to 389 nm that depend on the appearance of HONO. Nevertheless, the measured k_2 values ought to correspond to eq 23, regardless of which species is monitored.[36] It is not clear why the k_2 values greater than 100 s^{-1} deviate from this fit; one possibility is that the rate of either reaction eq 18 or 19 begins to limit the rate of appearance of HONO.

(c) k_3 Dependence. The k_3 step is the reduction of N(III) by NH_3OH^+ to N(I) (eq 6), where the rate expression is given by eq 24,[27] and $k_{3a} = 8.3\ M^{-2}\ s^{-1}$.

$$\frac{-d[HONO]}{dt} = k_{3a}[H^+][NH_3OH^+][HONO] \qquad (24)$$

Alternatives. A different mechanism to explain the NH_2OH dependence in the k_2 step was considered. If the product of the first stage was Cl_2NOH rather than Cl_3NO, then perhaps step 2 is the base-assisted decomposition of this species (eqs 25 and 26). Hydroxylamine is a reasonable Brønsted base that could assist the breakup of Cl_2NOH, but the concentration of free NH_2OH is very low in 1 M HCl. Since there is a 1/1 stoichiometry between Cl_2NOH and HONO, the value of k_B for NH_2OH would be equal to $k_2/K_a \cong 2.2 \times 10^8\ M^{-1}\ s^{-1}$. However, water must also be considered as a Brønsted base for eq 25 and the minimum value of $k_B^{H_2O}$ would be for a Brønsted β value ($\Delta \log k_B/\Delta pK_a$) of unity. Since $pK_a(NH_3OH^+)$ is 6.06 and $pK_a(H_3O^+)$ is –1.74, $\Delta pK_a = 7.80$, so that the $k_B^{H_2O}$ value must be greater than 3.5 $M^{-1}\ s^{-1}$ or for 55.5 M H_2O the minimum first-order rate constant for the hydrolysis would be 200 s^{-1}. This value is much larger than the intercept in Figure 3 and exceeds all but the largest observed first-order k_2 values with NH_2OH present. We conclude that the role of NH_2OH as a base in the k_2 step is inconsistent with the magnitude of the observed rate constants. We know that NO_3^- is formed at lower ratios of $[NH_3OH^+]/[Cl_2]$, and this is also inconsistent with the formation of Cl_2NOH as the final product of the k_1 step.

$$Cl_2NOH + B \xrightarrow{k_B} Cl^- + ClNO + HB^+ \qquad (25)$$

$$ClNO + H_2O \xrightarrow{rapid} Cl^- + HONO + H^+ \qquad (26)$$

Fates for the proposed transient intermediates, ClNHOH and Cl_2NOH, other than reaction with Cl_2 (eqs 13 and 14) include their dissociation reactions (eqs 27 and 28). Nitrosyl hydride (HNO) is reported[37] to dimerize very rapidly to give nitrous oxide (eq 29). The equilibrium formation of nitrosyl chloride (ClNO) has been reported[38] in high concentrations of hydrochloric acid. We prepared ClNO in 7.9 M HCl and on mixing the solutions with water observed that hydrolysis (eq 30) was complete within the time of mixing (~5 ms). However the rates of eqs 27 and 28 under our conditions must be much less than those of eqs 13 and 14, in order for Cl_3NO to form before HONO and in order to have nearly a stoichiometric yield of HONO in step 2.

$$ClNHOH \xrightarrow{k_{1d}} Cl^- + HNO + H^+ \qquad (27)$$

$$Cl_2NOH \xrightarrow{k_{2d}} Cl^- + ClNO + H^+ \qquad (28)$$

$$2HNO \rightarrow N_2O + H_2O \qquad (29)$$

$$ClNO + H_2O \rightarrow Cl^- + HONO + H^+ \qquad (30)$$

In 1919, Dowell[12] suggested NCl_3 as a stable product, on the basis of nonspecific qualitative tests. Nitrogen trichloride has a very characteristic UV spectrum,[39] and we found no evidence

---

(35) (a) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1988**, *27*, 1670–2. (b) Troy, R. C.; Margerum, D. W. *Inorg. Chem.* **1991**, *30*, 3538–43.

(36) Espenson, J. H. *Chemical Kinetics and Mechanisms*; McGraw-Hill: New York, 1981; p 56.

(37) Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285–8.

(38) Schmid, H.; Maschka, A. *Z. Phys. Chem.* **1941**, *49B*, 171–86.

(39) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1942–8.

spectrophotometrically for NCl_3 in any of our experiments. We also tested the products of 3/1 ratios of $[Cl_2]/[NH_3OH^+]$ in 0.1 M HCl by membrane introduction mass spectrometry (MIMS)[40] and found no NCl_3 although it is known to be able to pass easily through the silicone membrane. This experiment also failed to detect Cl_3NO, but we know that Cl_3NO is short-lived under these conditions ($t_{1/2}$ = 100 ms) and theoretical calculations[31,41] indicate that it has a high dipole moment so that it will not readily transport through the hydrophobic silicone membrane.

Conclusions

The reaction of Cl_2 with excess hydroxylamine is novel because of rapid oxidation of N(–I) to N(V), followed by the stepwise reduction of N(V) to N(III) and to N(I). The proposed reaction sequence is given in Scheme I, in which Cl_3NO forms rapidly from three successive reactions of Cl_2 with hydroxylamine that proceed via transient intermediates ClNHOH and Cl_2NOH. None of these intermediates have been isolated, and all three *N*-chloro species must be very reactive with relatively short lifetimes in water. Nevertheless, the existence of Cl_3NO is inferred because a N(V) species is needed that can either hydrolyze to NO_3^- or react rapidly with NH_2OH to form HONO. We also suggest Cl_2NOH and ClNHOH as intermediate species in the reactions of Cl_3NO with NH_2OH.

Therefore, all of the reactions of Cl_2 and of the successive *N*-chloro species can be accounted for in terms of rapid Cl^+-transfer steps (Table IV). It is not necessary to postulate one-electron-transfer steps via high-energy free-radical intermediates to explain the observed products or the kinetics. Higher oxidation state nitrogen–oxygen species (NO_3^- and HONO) are attained by Cl^+ transfer followed by Cl^- elimination.

Scheme I. Proposed Reaction Steps for Chlorine Reaction with Excess Hydroxylamine

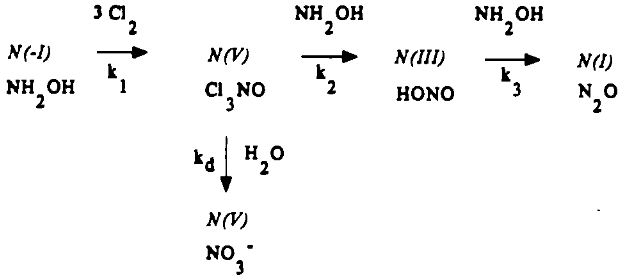

Table IV. Summary of Resolved Rate Constants[a,b]

reaction	rate constant
$Cl_2 + NH_2OH$	$k_{1a} = 1.6 \times 10^9\ M^{-1}\ s^{-1}$
$Cl_3NO + H_2O$	$k_d = 6.8\ s^{-1}$
$Cl_3NO + NH_2OH$	$k_{2a} = 1.53 \times 10^8\ M^{-1}\ s^{-1}$
$HONO + NH_3OH^+ + H^+$	$k_{3a} = 8.3\ M^{-2}\ s^{-1}$

[a] Conditions: 26.0 °C, μ = 1.0 M. [b] Cl_3NO is the proposed formula for an observed intermediate; HONO is an identified intermediate.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-9024291. J.N.C. is grateful to the NSF for a Research Opportunity Award and to Bucknell University for a sabbatical leave grant.

---

(40) Kotiaho, T.; Lister, A. K.; Hayward, M. J.; Cooks, R. G. *Talanta* **1991**, *38*, 195–200.

(41) Rozen, A. M.; Klimenko, N. M.; Krupnov, B. V.; Nikforov, A. S. *Dokl. Phys. Chem.* (*Engl. Transl*) *S.S.S.R.* **1986**, *287*, 915–9.