Inorg. Chem. **1982**, *21*, 2461–2468

Contribution from the Chemistry Division,
Oak Ridge National Laboratory,[1] Oak Ridge, Tennessee 37830

Oxidation of Hydroxylamine by Nitrous and Nitric Acids

M. R. BENNETT, GILBERT M. BROWN,* L. MAYA, and F. A. POSEY

Received July 20, 1981

The kinetics of the reaction of hydroxylamine with nitrous acid and with nitric acid were studied in an acidic nitrate medium. The mechanism of the reaction with nitrous acid in an acidic perchlorate medium, proposed by previous workers, is O-nitrosation of the hydroxylammonium ion; our data are consistent with this mechanism at an ionic strength of 2 M. The data at higher ionic strength (3 and 4 M), when compared to an extended treatment of the proposed mechanism, indicate either a deviation from this mechanism at high acid concentration or a change in one of the principal species in solution. Raman and UV spectroscopies were unable to verify a change in the species. In the reaction of hydroxylamine with nitric acid, we identified HNO_2, N_2O, and N_2 as products. This reaction is autocatalytic in HNO_2, and the distribution of products is dependent on the initial concentrations of HNO_2, NH_3OH^+, and HNO_3. The product N_2O derives from the nitrosation of NH_3OH^+. The reaction of the intermediate N_2O_4 with NH_2OH produces HNO_2, and N_2 is postulated to arise from the reaction of HNO_2 with hyponitrous acid, which is an intermediate in the nitrosation of NH_3OH^+. A kinetic model is partially successful in rationalizing the distribution of products.

Introduction

The reaction of hydroxylamine with nitrous acid (eq 1) in

$$HNO_2 + NH_2OH \rightarrow N_2O + 2H_2O \qquad (1)$$

dilute concentrations of mineral acids has been extensively investigated. These studies include detailed kinetic measurements in $HClO_4$ solution[2] and product distributions by ^{15}N and ^{18}O isotopic labeling.[2b,3-5] At low pH and low concentrations of HNO_2, the reaction in perchlorate and sulfate media is postulated to proceed by O-nitrosation of the hydroxylammonium ion. This determination was made on the basis of the rate expression for reactions of the *N*-methyl and *O*-methyl derivatives of hydroxylamine;[2b] the latter reagent reacts considerably slower in acidic solution by the traditional diazotization path. Kinetics and stoichiometric studies of reaction 1 have been extended to nitric acid solutions in this report.

The oxidation of hydroxylamine by nitric acid becomes kinetically important at HNO_3 concentrations greater than ~2 M. A study of the reaction has been published by Pembridge and Stedman.[6] The reported reaction products were HNO_2 and N_2O, and HNO_2 was identified as an essential catalyst.[6] We find a difference in the yields of HNO_2 and N_2O from that observed by these workers, and we also find N_2 as a significant product at low initial concentrations of NH_3OH^+.

Experimental Section

A stock solution of hydroxylammonium nitrate was prepared by the following procedure. Reagent grade $(NH_3OH)_2SO_4$ was dissolved in water, and most of the SO_4^{2-} was precipitated by the addition of a slightly less than stoichiometric amount of $Ba(NO_3)_2$. The solution was filtered and the remaining SO_4^{2-} replaced with NO_3^- by passing the solution through an anion-exchange resin bed (Dowex 2-X8) in the NO_3^- form. The solution was analyzed for NH_3OH^+ content by the BrO_3^- titration method suggested by Vogel.[7] Analysis for SO_4^{2-} by the ORNL Analytical Chemistry Division indicated less than 2×10^{-2} M SO_4^{2-} in a 2 M NH_3OH^+ solution. This $(NH_3OH)NO_3$ solution was extremely stable; its titer changed by less than 5% over a period of 20 months. Solutions of HNO_2 were generated immediately before use by adding a weighed amount of $NaNO_2$ to the desired electrolyte or by adding an aliquot of a solution of $NaNO_2$ to the reaction mixture. Solutions of $NaNO_2$ and HNO_2 were protected from strong room light. Other chemicals (HNO_3 and $LiNO_3$) were of reagent grade and were used without further purification. Solutions of HNO_3 were initially sparged with an inert gas to remove NO_x.

The yields of gaseous products were determined by gas chromatography (Shimadzu GC5A) or by total gas volume with a 0–10 psia pressure transducer. Helium was used as a blanket gas and carrier gas for analysis of products by GC. Blank experiments indicated the procedure was satisfactory to eliminate atmospheric contamination. Samples for analysis were withdrawn with a pressure-lock syringe through rubber serum caps. The yield of HNO_2 produced by the reaction of hydroxylamine with nitric acid was determined spectrophotometrically on a Pye-Unicam Model SP8-100, Cary Model 15, or a Gilford updated Beckman DU spectrophotometer. Sample compartments of the spectrophotometers were maintained at 25 °C with circulating water baths. The majority of HNO_2 determinations were carried out with air-saturated solutions; several experiments with Ar- or He-saturated solutions indicated no change within experimental error. The presence of a gas space over the solutions was not a factor since the HNO_2 yields in the experiments described above and yields in the stopped-flow spectrophotometer were identical. (The latter instrument by its design does not leave a gas space above the solution.) GC experiments indicated NO was not a significant product of the reaction at ambient temperatures although evidence for NO was obtained at temperatures above 65 °C. The experiments were conducted under conditions such that ≥0.01 mol of NO/mol of NH_3OH^+ could be detected. We assume the origin of NO at higher temperatures (>65 °C) was decomposition of HNO_2.

Slower kinetic experiments to determine the rate of appearance or disappearance of HNO_2 ($t_{1/2} > 20$ s) were carried out with one of the spectrophotometers mentioned above at the 372-nm adsorption maximum of HNO_2. Faster reactions were monitored in a kinetic stopped-flow spectrophotometer. This instrument consisted of a thermostated (25 °C) Aminco-Morrow stopped-flow mixing apparatus adapted to fit a Beckman DU monochromator. The tungsten lamp was powered by a Hewlett-Packard Model 6264B dc power supply. Changes in transmitted light were monitored with an RCA Model 6903 photomultiplier tube with standard operational amplifier current-to-voltage conversion circuitry; these changes were recorded on a storage oscilloscope or a conventional recorder. Changes in transmitted light were converted to changes in absorbance by the relationship $A_t - A_\infty = \log (I_\infty/I_t)$, where A is the solution absorbance, I is the intensity of the transmitted light, and the subscripts t and ∞ refer to any time t and time infinity, respectively. (The subscript 0 will be used to refer to time zero.) Although this spectrophotometer is an unreferenced single-beam instrument, the photomultiplier tube and lamp-power supplies are well regulated; signals were stable for more than 1 h after being warmed up.

The Raman spectra of solutions of hydroxylammonium nitrate were obtained with a Ramanor Model HG-27 spectrophotometer. An argon ion laser (Spectra Physics Model 164) operating at the 514.5-nm line was the excitation source.

Results and Discussion

Species Present in Solutions of Nitrous Acid and Hydroxylamine in Nitric Acid. In aqueous solution, NH_3OH^+ has a

---

(1) Operated by Union Carbide Corp. for the Department of Energy.
(2) (a) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 2824–2830. (b) Morgan, T. D. B.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 344–349.
(3) Hussain, M. A.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 597–603.
(4) Bothner-By, A.; Friedman, L. *J. Chem. Phys.* **1952**, *20*, 459–462.
(5) Clusius, K.; Effenberger, E. *Helv. Chim. Acta* **1955**, *38*, 1834–1843.
(6) Pembridge, J. R.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1657–1663.
(7) "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed.; Longmans, Green and Co.: New York, 1978; p 394.

0020-1669/82/1321-2461$01.25/0

pK_a of 5.96.[8] There is no evidence in the literature for further protonation of NH_3OH^+ in strong acid. The species present in dilute HNO_3 solution is therefore the hydroxylammonium ion. As noted in a later section, the results of kinetic studies of the reaction of HNO_2 with NH_3OH^+ suggest another species of NH_3OH^+ may be generated at high HNO_3. Raman spectra of hydroxylammonium nitrate solutions were examined for evidence of association of NH_3OH^+ with NO_3^- or HNO_3. The solutions were 0.1 M in NH_3OH^+ in an electrolyte made of varying proportions of $LiNO_3$ and HNO_3, with a total ionic strength of 4.0 M. The solutions examined contained 0.2, 0.5, 2.0, and 3.0 M HNO_3. In addition, a solution with no added electrolyte was examined, as well as a 1.8 M $(NH_3OH)NO_3$ solution with no background electrolyte. The most prominent bands in all the spectra are those due to the symmetric stretching vibration of NO_3^- at 1047 cm^{-1} [9] and the NH and OH stretching frequencies which appear as a broad band in the 3500-cm^{-1} region.

It was hoped that a band due to a higher order complex such as $HNO_3 \cdot NH_3OH \cdot NO_3$ could be observed. The spectra in all cases showed a single symmetrical band for the $\nu_1(NO_3^-)$ vibration. Apparently if the postulated complex was present, the change in the $\nu_1(NO_3^-)$ vibration was not different enough from the free ion, which was present in a relatively large excess, to be detected. The OH and NH stretching bands are too broad to detect any change among the solutions examined. Higher order complexes such as ion pairs therefore cannot be ruled out. However, evidence for the association of molecular HNO_3 with neutral molecules in nonaqueous media is well-defined.[10]

The species present in dilute aqueous solutions of HNO_2 have been discussed in a recent review.[11] The pK_a of HNO_2 is 3.15,[8] and therefore no appreciable concentration of NO_2^- is present in the acid solutions employed in this study. The equilibria to be considered are given in eq 2–4. The equilibrium constant for reaction 2 is 3×10^{-3} M^{-1}.[12] The absorbance of HNO_2 solutions in perchloric acid is reported to obey Beer's law for concentrations of ≤ 0.05 M.[13] Similar results were found in this study for NO_3^- solutions.

$$2HNO_2 \rightleftarrows N_2O_3 + H_2O \qquad (2)$$

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O \qquad (3)$$

$$HNO_2 + HNO_3 \rightleftarrows N_2O_4 + H_2O \qquad (4)$$

The UV spectrum of HNO_2 in $LiNO_3$–HNO_3 solutions (4.0 M ionic strength) shows the characteristic "four finger" pattern with well-defined maxima at 387, 372, and 359 nm, although the high energy maximum at ~347 nm is distorted in very dilute solutions by the NO_3^- background. At the 372-nm peak, there is no deviation from Beer's law in the HNO_2 concentration range 4×10^{-3}–3.2×10^{-2} M (3.0 M HNO_3) with ϵ_{372} 55.9 ± 0.7 M^{-1} cm^{-1}. Furthermore, a plot of A_{372} vs. A_{387} is linear with a zero intercept. At the concentrations of HNO_2 employed in this study, a negligible fraction of total nitrous acid existed as N_2O_3. In the concentration range in which the absorbance is directly proportional to $[HNO_2]_T$, we find no systematic variation of the extinction coefficient with an increase in $[HNO_3]$ at constant $[NO_3^-]_T$. The average value of ϵ_{372} in 1 M HNO_3 ($[HNO_2] = 1.2 \times 10^{-2}$ M) is 55.9 ± 1.1 M^{-1} cm^{-1}. In agreement with the results of Longstaff and Singer,[14] there is no evidence for any appreciable conversion of HNO_2 to NO^+ or N_2O_4 at $[HNO_3] \leq 4$ M. Therefore, the principal N(III) species present in the nitric acid solutions employed in this study is molecular nitrous acid. However, the species NO^+ and N_2O_4 will be postulated as reactive intermediates.

Table I. Observed First-Order Rate Coefficients for the Disappearance of HNO_2 as a Function of Hydroxylamine and Nitric Acid Concentrations at 25 °C

μ, M	$[H^+]$, M	$[NH_3OH^+]_0$, M	k_{obsd}, s^{-1}	a_{H^+}, M
2.0	0.20	0.10	0.255	
2.0	0.50	0.10	0.56	
2.0	1.50	0.10	1.12	
2.0	1.90	0.10	1.28	
2.0	1.00	0.10	1.06	
2.0	1.00	0.20	1.90	
2.0	1.00	0.25	2.49	
2.0	1.00	0.40	4.39	
2.0	1.00	0.65	5.98	
2.0	1.00	0.75	6.42	
4.0	0.20	0.10	1.65	0.255
4.0	0.30	0.10	2.22	0.381
4.0	0.50	0.10	2.91	0.633
4.0	1.00	0.10	2.80	1.254
4.0	2.00	0.10	1.88	2.469
4.0	2.00	0.20	3.96	2.469
4.0	3.00	0.10	1.01	3.634
4.0	3.90	0.10	0.64 ± 0.08	4.648

Reaction of Hydroxylamine with Nitrous Acid. The stoichiometry of reaction 1 was confirmed at 1 M HNO_3 by measurement of the N_2O produced in the reaction of excess NH_3OH^+ with HNO_2. The kinetics of reaction 1 were readily separated from other reactions at lower concentrations of HNO_3 (<2 M). At higher concentrations of HNO_3, the kinetics of the desired reaction were separable by using relatively high initial concentrations of NH_3OH^+.

The disappearance of HNO_2 was measured in the presence of a tenfold or greater excess of NH_3OH^+. In all cases plots of log $(A_t - A_\infty)$ vs. time were linear for 3.5–4 half-lives. These plots indicate the reaction is first order in $[HNO_2]_T$. Although the initial concentration of HNO_2 was not systematically varied, the observed rate constants are independent of $[HNO_2]_0$ in the range 4×10^{-3}–1.2×10^{-2} M. Rate measurements at a total ionic strength of 2.0 M (maintained by adding $LiNO_3$) and at a constant HNO_3 concentration of 1.0 M were determined as a function of the initial NH_3OH^+ concentration. These determinations indicate the reaction is also first order in $[NH_3OH^+]$. The reaction kinetics were also measured as a function of HNO_3 concentration at ionic strengths of 2.0 and 4.0 M. The observed first-order rate coefficients as a function of $[HNO_3]$, $[NH_3OH^+]$, and ionic strength are summarized in Table I.

A mechanism for reaction 1 in acidic solution has been proposed by Stedman and co-workers.[2] The reaction pathway involves O-nitrosation of the hydroxylammonium ion (eq 5–9).

$$HNO_2 + H^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} NO^+ + H_2O \qquad (5)$$

$$NO^+ + NH_3OH^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \underset{\text{I}}{NH_3ONO^+} + H^+ \qquad (6)$$

$$NH_3ONO^+ \xrightarrow{k_7} ONNH_2OH^+ \qquad (7)$$

$$ONNH_2OH^+ \rightarrow \text{HONNOH (cis and trans)} + H^+ \qquad (8)$$

$$\text{HONNOH (cis)} \xrightarrow{\text{fast}} N_2O + H_2O \qquad (9a)$$

$$\text{HONNOH (trans)} \rightarrow N_2O + H_2O \qquad (9b)$$

---

[8] The quoted values are at 25 °C and extrapolated to zero ionic strength: Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4.

[9] Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 98.

[10] Davis, W. *Nucl. Sci. Eng.* **1962**, *14*, 159.

[11] Stedman, G. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 113–170.

[12] Markovits, G. Y.; Schwartz, S. E.; Newman, L. *Inorg. Chem.* **1981**, *20*, 445–450.

[13] Bunton, C. A.; Stedman, G. *J. Chem. Soc.* **1958**, 2440–2444.

[14] Longstaff, J. V. L.; Singer, K. *J. Chem. Soc.* **1954**, 2610–2617.

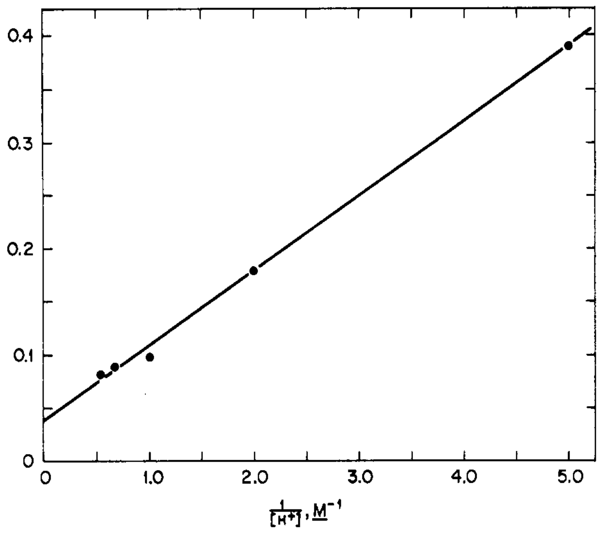

Figure 1. Plot of $1/k'$ vs. $1/[H^+]$ for the reaction of hydroxylammonium ion with nitrous acid at 2.0 M ionic strength (25 °C).

The isomerization of the intermediate (I) was proposed to become the rate-limiting step at high acid concentrations. A steady-state treatment of NO^+ and intermediate (I) leads to the rate equation (10). In deriving this equation, terms in

$$\frac{-d[HNO_2]}{dt} = \frac{d[N_2O]}{dt} = \frac{k_5k_6/k_{-5}[HNO_2][NH_3OH^+][H^+]}{1 + k_{-6}/k_7[H^+]} \qquad (10)$$

the denominator containing $[NH_3OH^+]$ were neglected since the expermental results do not show rate saturation at high $[NH_3OH^+]_0$. The data obtained at 2.0 M ionic strength are in quantitative agreement with a rate expression of the form of eq 10. The observed second-order rate coefficient, k', is obtained by dividing the observed first-order rate coefficient by the concentration of NH_3OH^+. Figure 1 is a linear plot of $1/k'$ vs. $1/[H^+]$ as predicted by eq 10. The second-order rate coefficient was equated to the expression $a[H^+]/(1 + b[H^+])$ where a is k_5k_6/k_{-5} and b is k_{-6}/k_7. The calculated values of a and b are 14.2 ± 0.7 $M^{-2}\,s^{-1}$ and 0.54 ± 0.08 M^{-1}, respectively. The interpretation of the parameter b changes if other approximations are used in deriving the rate expression. This will be discussed in more detail in a later section.

The experimental rate expression for reaction 1 is more complicated at 4.0 M ionic strength. The first-order dependence on $[HNO_2]$ and $[NH_3OH^+]$ is retained; however, the observed second-order rate coefficient, k', reaches a maximum between 0.5 and 1.0 M H^+ and decreases at higher nitric acid concentrations. This kinetic behavior was noted in earlier work for reaction 1 in a perchlorate medium at 3 M ionic strength ($NaClO_4$ and $HClO_4$).[2b] Equation 10 suggests that k' may become independent of $[H^+]$, but it does not predict a maximum. Previous workers[2b] suggested a maximum might be observed if k_7 decreased at higher ionic strength. The proposed mechanism (eq 5–9) involves the preequilibrium formation of NO^+. Therefore, the second-order rate coefficients were fitted to the calculated proton activities. Water and proton activity coefficients in the mixed $LiNO_3$–HNO_3 electrolyte were calculated by the method of Pitzer et al.[15-17] The appropriate equations were obtained from ref 16. The difference parameters θ and ψ were assumed to be 0; on the basis of results with (H^+, Li^+) mixed electrolytes of Cl^- and ClO_4^-, this is a valid approximation.[16] The appropriate constants for the $LiNO_3$ and HNO_3 system were those recommended by Pitzer and Mayorga.[17] The calculated activity of H_2O is virtually constant (1.232–1.235), and the proton activity is nearly directly proportional to concentration for $HNO_3 \leq 2$ M. The calculated proton activities are included in Table I.

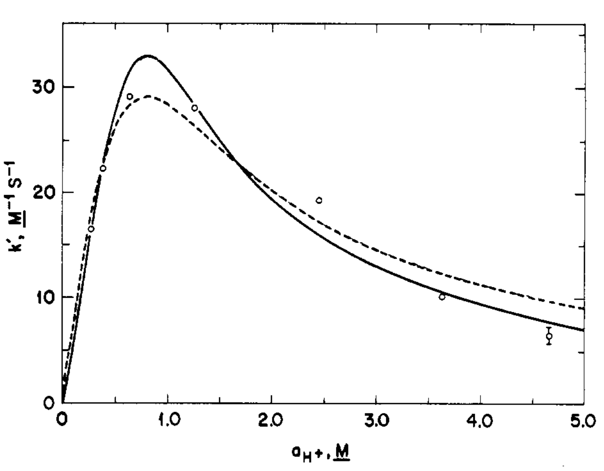

Figure 2. Plot of k' vs. a_{H^+}, the activity of protons, for the reaction of hydroxylammonium ion with nitrous acid at 4.0 M ionic strength (25 °C). Solid line is a nonlinear least-squares fit to eq 13. Dashed line is a fit by the procedure given in the Appendix.

A more exact treatment of the mechanism outlined in eq 5–9 can be used to generate a rate expression which predicts a maximum in k' as a function of proton activity or concentration. The approximations used in deriving the expression are outlined in detail in an appendix. The first-order rate of disappearance of $[HNO_2]$ is given by eq 11. The ratio

$$k_{obsd} \approx k_5k_6k_7[H^+][NH_3OH^+]/[(k_5[H^+] + k_{-5}) \times (k_{-6}[H^+] + k_7) + k_6[NH_3OH^+](k_5[H^+] + k_7)] \qquad (11)$$

$k_{obsd}/[NH_3OH^+]$ is constant at constant $[H^+]$, and terms inverse in $[NH_3OH^+]$ will be neglected. The expression for the second-order rate coefficient, k', can be arranged in the form of eq 12. The important conclusions are that K_5 (=

$$k' \approx \frac{K_5k_6(a_{H^+})}{1 + (K_5 + (k_{-6}/k_7))(a_{H^+}) + K_5(k_{-6}/k_7)(a_{H^+})^2} \qquad (12)$$

k_5/k_{-5}) is a rapidly established equilibrium and k_6 is the overall rate-limiting step. The form of this rate expression is a result of not requiring the species NO^+ and I to be at a steady state.

The second-order rate coefficients are shown as a function of proton activity in Figure 2. The solid line is a fit of the data to expression 13. A nonlinear least-squares fitting

$$k' = \frac{c(a_{H^+})}{1 + d(a_{H^+}) + f(a_{H^+})^2} \qquad (13)$$

routine[18] was used to evaluate the constants c, d, and f which have best fit values of 52.4 ± 10.6 $M^{-2}\,s^{-1}$, −0.88 ± 0.35 M^{-1}, and 1.53 ± 0.21 M^{-2}, respectively. The negative value for the coefficient d indicates the expression in eq 12 is inadequate to describe the complete data set. The parameter d is extremely sensitive around the maximum. The data set is somewhat limited and may indicate the parameter d is near 0. The rate-determining step (eq 6) is expected to be highly dependent on ionic strength. Nitric acid is not completely dissociated at the higher concentrations employed in this study (the degree of dissociation of 4 M HNO_3 is 0.866).[19] The

---

[15] Pitzer, K. S. *Acc. Chem. Res.* **1977**, *10*, 371–377.

[16] Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701–5707.

[17] Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300–2308.

[18] Lietzke, M. H. Report ORNL-3259; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

constant ionic strength approximation will be less valid as the HNO_3 concentration increases. Therefore, the method of fitting the data outlined in the Appendix was used. This method heavily weights the data at low acid concentrations by using the initial slope, the maximum rate constant, and the proton activity at which the maximum occurs. The fitting parameters $c = 75\ M^{-2}\ s^{-1}$, $k_{max} = 29\ M^{-1}\ s^{-1}$, and $(a_{H^+})_{max} = 0.8$ M were employed; the calculated curve is shown as a dashed line in Figure 2.

The rate constants measured in this work can be compared to literature data by examining the initial slopes of plots of k' vs. $[H^+]$ at various ionic strengths and by identifying conditions in which a maximum is observed in plots of k' vs. $[H^+]$. The initial slope provides an estimate of K_5k_6 (eq A17). The second-order rate coefficients (k') measured in this work are in good agreement with values reported in other mineral acids at a similar acidity and ionic strength. Second-order rate coefficients have been reported[2b] as a function of $[H^+]$ at 0 °C in a mixed $HClO_4$–$NaClO_4$ electrolyte at a constant ionic strength of 3 M. These values were corrected to 25 °C with an activation energy of ~65 kJ mol^{-1},[6] the value measured in 4 M $HClO_4$. The corrected values for k' (at $[HClO_4] < [HClO_4]_{max}$) fall between those measured in this work at 2 and 4 M ionic strength. The second-order rate coefficient has also been reported in 1.0 M HNO_3 at variable ionic strength due to changes in $[NH_3OH^+]_0$.[20] Extrapolation to infinite dilution in $[NH_3OH^+]_0$ gives an estimated value for K_5k_6. The appropriate value in 0.1 M $HClO_4$ can be obtained from literature data[2a] after correction to 25 °C with an Arrhenius activation energy of ~61 kJ mol^{-1}. The variation in K_5k_6 with ionic strength is 2.5, 6, 14, 44, and 75 $M^{-2}\ s^{-1}$ for 0.1,[2a] 1,[20] 2, 3,[2b] and 4 M ionic strength, respectively. If we ignore the ionic strength dependence of the activities of the species involved in equilibrium 5, then K_5k_6 should increase with increasing ionic strength because reaction 6 involves two positively charged reactants. This is the observed trend. The maximum rate constant, k'_{max}, in the 3 M perchlorate electrolyte occurs at an acid concentration of approximately 1.3 M.[6] The maximum in 4 M nitrate occurs at a proton activity of 0.8 M. Maxima were not observed at 2 M and lower ionic strengths. The approximate rate expression (eq 12) predicts the maxima should occur at lower proton activities at higher ionic strength due to the ionic strength dependence of k_{-6} (see eq A18). In a qualitative sense, the approximate expression (eq 12) for the second-order rate coefficient is in agreement with the data.

A comparison of the absolute values of the rate constants and the variation of the rate constants with ionic strength argues that the mechanism of this reaction is similar in perchlorate and nitrate media at lower acid concentrations. The trends are in agreement with the mechanism outlined in eq 5–9. Our data, obtained at constant ionic strength and correlated with the proton activity instead of a Hammett acidity function, and the literature data in 3 M perchlorate cannot be interpreted quantitatively within the framework of eq 12. The numerical values evaluated for K_5, k_6, and k_{-6}/k_7 are inconsistent. The value for K_5 is too large, and this results in a greater decrease in k' at higher acid concentration than would reasonably be expected. The basic reaction scheme is probably correct, but some changes appear necessary for quantitative agreement to high acid. Either one of the principal species in solution is changing or the acid dependence of the steps following nitrosation is incorrect. Spectroscopic measurements do not support a change of species. Previous workers[2b] have argued that the decrease in the second-order rate coefficient at higher acid concentrations is due to a decrease in k_7 with increasing ionic strength. The extended treatment of reactions 5–9 (eq 12) does not require this interpretation.

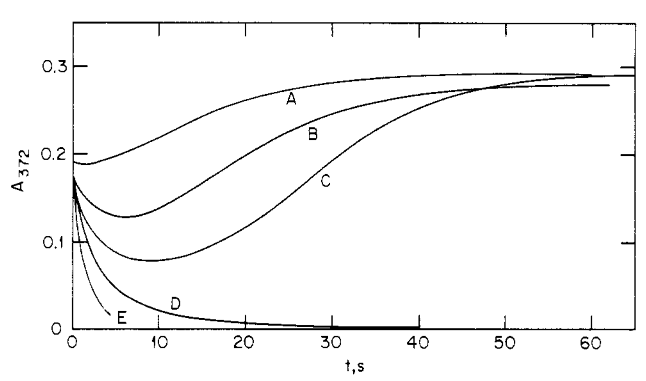

Figure 3. The absorbance of 372 nm vs. time for an initial HNO_2 concentration of ~4 × 10^{-3} M as a function of the initial hydroxylamine concentration (25 °C, 3 M HNO_3, 4 M ionic strength): A, 2 × 10^{-2} M; B, 3 × 10^{-2} M; C, 4 × 10^{-2} M; D, 5 × 10^{-2} M; E, 7 × 10^{-2} M (ϵ_{372} 50 ± 2 $M^{-1}\ cm^{-1}$).

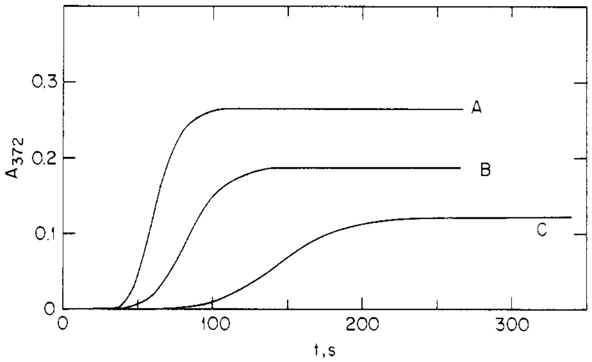

Figure 4. Time dependence of absorbance at 372 nm as a function of the initial hydroxylamine concentration with $[HNO_2]_0 < 4 \times 10^{-5}$ M (25 °C, 3 M HNO_3, 4 M ionic strength). Initial NH_3OH^+ concentration: A, 1.2 × 10^{-2} M; B, 6.0 × 10^{-3} M; C, 3.0 × 10^{-3} M.

Reaction of Hydroxylamine with Nitric Acid. At HNO_3 concentrations greater than 2 M, the reaction of HNO_3 with dilute solutions of hydroxylamine produces HNO_2 as a product. As noted by Pembridge and Stedman,[6] we find this reaction to be autocatalytic. The relative rate of this reaction should be put in perspective with the rate of the reaction of HNO_2 with NH_3OH^+, which was discussed in the previous section. Figure 3 shows the results of a series of experiments at constant acid with approximately the same initial concentration of HNO_2 and various initial concentrations of NH_3OH^+ (3.0 M H^+, μ = 4.0 M). The time dependence of $[HNO_2]$ shown in Figure 3 illustrates the transition from the reaction described in eq 1 to more complex behavior. The decay of HNO_2 at the highest concentration of NH_3OH^+, 7 × 10^{-2} M, is exponential, and the ratio $k_{obsd}/[NH_3OH^+]_0$ is identical with that determined at higher concentration (Table I). At lower initial concentrations of NH_3OH^+, $[HNO_2]$ decreases at short times followed by an increase at longer times, resulting in a net increase in the concentration of HNO_2. At sufficiently low initial $[NH_3OH^+]$ (<2 × 10^{-2} M), the initial decrease in $[HNO_2]$ is not observed.

In the absence of deliberately added HNO_2, the appearance of HNO_2 is autocatalytic as shown in Figure 4 for $[H^+]$ = 3 M. As previously indicated by Pembridge and Stedman,[6] HNO_2 is a necessary catalyst for the reaction of nitric acid with hydroxylamine. The induction period is highly dependent on the initial concentration of NH_3OH^+, and this is illustrated

---

(19) Davis, W.; DeBruin, H. J. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1069–1083.
(20) Davis, W.; Maya, L.; Kelmers, A. D.; Valentine, K. Report ORNL-TM-7264; Oak Ridge National Laboratory: Oak Ridge, TN, 1980.

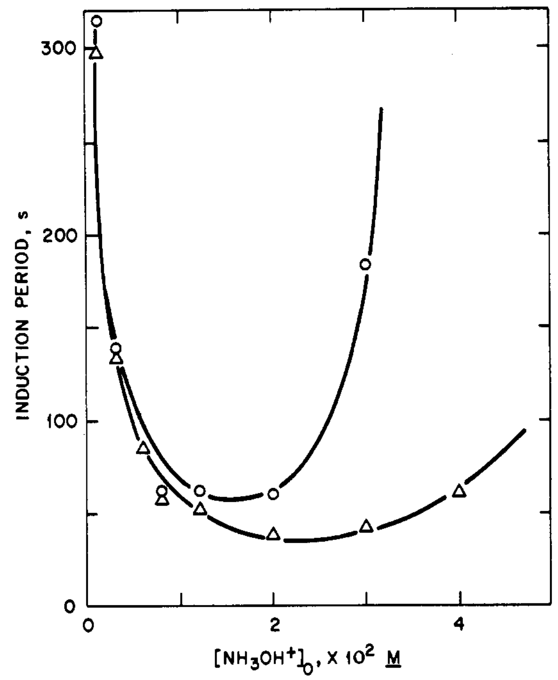

Figure 5. Plot of the induction period vs. the initial hydroxylamine concentration with an initial HNO_2 concentration of $<10^{-4}$ M (25 °C): circles, 3 M HNO_3; triangles, 4 M HNO_3.

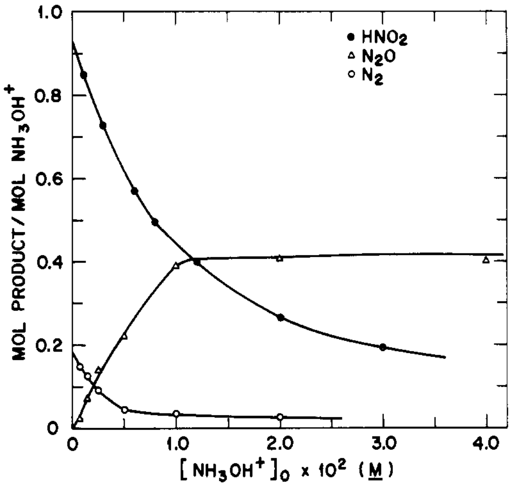

Figure 6. Plot of the yields of the products as a function of the initial concentration of hydroxylamine (25 °C, $[HNO_2]_0 < 10^{-4}$ M, 3 M H^+). Products: filled circles, HNO_2; triangles, N_2O; open circles, N_2.

in Figure 5. The induction period for this purpose is defined as the time when dA_{372}/dt is a maximum. Relatively concentrated solutions of hydroxylamine in nitric acid are stable for long periods of time. This behavior is explained by observations (Figure 5) that the induction period tends to increase at high hydroxylamine concentrations.

The observed products from the reaction of hydroxylamine with nitric acid are HNO_2, N_2O, and N_2. The yields of products are dependent on both the initial NH_3OH^+ and HNO_2 concentrations as well as the HNO_3 concentration. Figure 6 is a plot of the yields of these products as a function of the initial NH_3OH^+ concentration in the absence of deliberately added HNO_2 at a HNO_3 concentration of 3.0 M (μ = 4.0 M). The net yields of HNO_2 and N_2 reach a maximum as the NH_3OH^+ concentration approaches 0. The N_2O yield increases rapidly as the NH_3OH^+ concentration increases. Analogous results were observed at 4.0 M HNO_3. The extrapolated maximum HNO_2 yields are not particularly

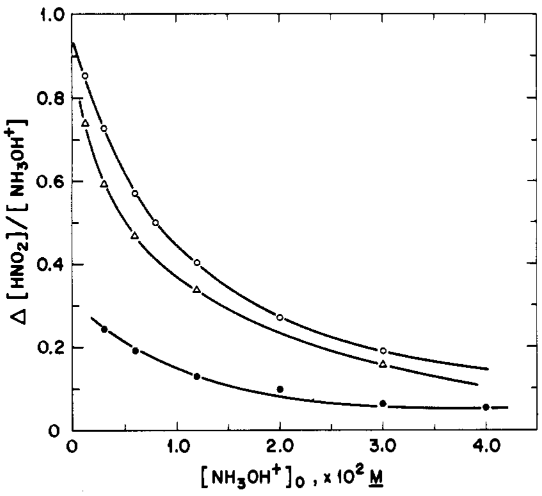

Figure 7. Plot of the net yield of HNO_2 vs. the initial NH_3OH^+ concentration for several initial HNO_2 concentrations (25 °C, 3 M H^+, 4 M ionic strength). $[HNO_2]_0$: open circles, $\leq 4 \times 10^{-5}$ M; triangles, 10^{-3} M; closed circles, 4×10^{-3} M.

Table II. Initial Rate of Net Formation of HNO_2 as a Function of $[HNO_2]_0$ and $[NH_3OH^+]_0$ at 25 °C (3.0 M H^+, 4.0 M Ionic Strength)

$10^3[NH_3OH^+]_0$, M	$10^3[HNO_2]_0$, M	$10^5 v_i$, M s^{-1}
1.20	0.36	0.71
1.20	0.82	1.14
1.20	1.65	1.45
3.00	0.39	2.00
3.00	0.79	3.41

dependent on HNO_3 concentration although the range of $[HNO_3]$ investigated is limited. The dependence of the HNO_2 yield on the initial HNO_2 concentration was investigated in some detail at 3.0 M HNO_3. The results are shown in Figure 7 as a function of the initial NH_3OH^+ concentration. The maximum HNO_2 yield (net production of HNO_2) is obtained at low initial HNO_2 concentration. As previously observed by Pembridge and Stedman,[5] the maximum yield of HNO_2 for a fixed concentration of NH_3OH^+ occurs at an HNO_3 concentration of ~5.3 M. It is obvious from these data that the yields of the various products are controlled by the kinetics of competing reactions. Therefore, it seems inappropriate to ascribe a stoichiometry to this process.

Many of the results obtained in this work are in agreement with those previously reported.[6] However, one observation is in sharp contrast. We observe N_2 as a significant reaction product at low initial $[NH_3OH^+]_0$. This product was apparently missed because gas analyses were made at an initial concentration of NH_3OH^+ where N_2 is not a significant product. Second, we find no evidence for simple first-order dependencies on the concentration of HNO_2 and NH_3OH^+ in kinetic experiments measuring the rate of appearance of HNO_2 with low initial NH_3OH^+. At a constant NH_3OH^+ concentration, an increase in the initial HNO_2 concentration does shorten the induction period. Although the previous approach[6] is valuable as a first approximation, we observe that an initial concentration of HNO_2 approximately equal to the initial NH_3OH^+ concentration is required to completely remove the induction period. Under these latter conditions, a first-order rate of appearance of HNO_2 is not expected. Typical data are shown in Figure 8 for reaction in 3.0 M HNO_3 (μ = 4.0 M). An analogous effect was also observed in 4.0 M HNO_3. The data in Figure 8 and other data at 3.0 M H^+ were treated by the method of initial rates. The experimental results are summarized in Table II. The initial rate divided by the product of the initial HNO_2 and NH_3OH^+

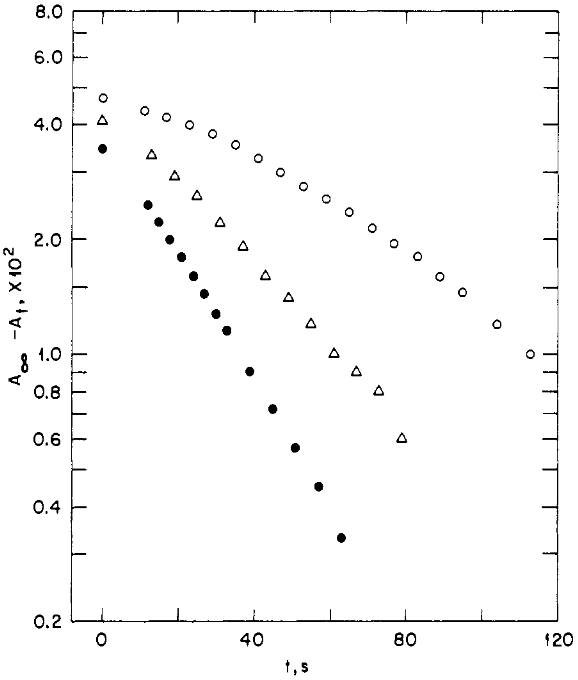

Figure 8. First-order plot for the net appearance of nitrous acid at 372 nm and an initial NH_3OH^+ concentration of 1.2×10^{-3} M (25 °C, 3 M H^+, 4 M ionic strength). Initial HNO_2 concentration: open circles, 3.8×10^{-4} M; triangles, 8.2×10^{-4} M; closed circles, 1.67×10^{-3} M.

concentrations provides a reasonable estimate of the second-order rate coefficient for the net appearance of HNO_2. The average value for the entries in Table II is 13 M^{-1} s^{-1}. Although the data show scatter, this analysis indicates the rate of net appearance of HNO_2 is competitive with the rate of disappearance of HNO_2 expected from reaction 1. The second-order rate coefficient for reaction 1 at 3 M H^+ is 10 M^{-1} s^{-1} (see Table I). The isotopic composition[6] of N_2O from the reaction of ^{15}N-labeled hydroxylamine and isotopically normal nitric acid supports reaction 1 as the origin of N_2O.

Pembridge and Stedman[6] suggested the reaction given by eq 14 is occurring in competition with eq 1 for the reaction

$$2HNO_3 + NH_2OH \rightarrow 3HNO_2 + H_2O \qquad (14)$$

of hydroxylamine. These workers suggested the reaction sequence in eq 15–19 to account for the observed autocatalytic

$$HNO_2 + H^+ + NO_3^- \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} N_2O_4 + H_2O \qquad (15)$$

$$N_2O_4 + NH_2OH \xrightarrow{k_{16}} HNO + N_2O_3 + H_2O \qquad (16)$$

$$N_2O_4 + HNO \rightarrow HNO_2 + N_2O_3 \qquad (17)$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \qquad (18)$$

$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+ \qquad (19)$$

appearance of HNO_2. On the basis of a steady-state treatment of N_2O_4 (the equilibrium described by eq 15 lies far to the left) and reaction 16 as the rate-determining step, the theoretical rate of appearance of HNO_2 by reaction 14 is given by eq 20.

$$\text{rate} = \frac{(k_{15}/k_{-15})k_{16}K_{19}[HNO_2][NH_3OH^+][NO_3^-]}{1 + (k_{16}/k_{-15})K_{19}([NH_3OH^+]/[H^+])} \qquad (20)$$

This mechanism appears reasonable since the inverse dependence on $[NH_3OH^+]$ is consistent with the relative stability of more concentrated solutions of hydroxylamine. At constant acid and nitrate concentrations, the general form of the rate expression is eq 21.

$$\text{rate} = \frac{g[HNO_2][NH_3OH^+]}{1 + h[NH_3OH^+]} \qquad (21)$$

We suggest that an additional reaction is occurring between HNO_2 and hyponitrous acid, $H_2N_2O_2$ (eq 8), to account for the observation of N_2 as a product. Hyponitrous acid is an intermediate in the nitrosation of NH_3OH^+ (eq 1 and eq 5–9). The reaction of HNO_2 with $H_2N_2O_2$ (eq 22) has been studied

$$HNO_2 + H_2N_2O_2 \rightarrow N_2 + HNO_3 + H_2O \qquad (22)$$

in some detail in aqueous perchloric acid by Buchholz and Powell[21] and by Hughes and Stedman.[22] The mechanism suggested by these workers is given by eq 23–26, where eq 24

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad (23)$$

$$NO^+ + H_2N_2O_2 \rightarrow HONNONO + H^+ \qquad (24)$$

$$HONNONO \rightarrow NO_2 + N_2 + \cdot OH \qquad (25)$$

$$NO_2 + \cdot OH \rightarrow HNO_3 \qquad (26)$$

is the rate-determining step. The experimentally observed rate law is eq 27, where h_0 is the Hammett acidity function (h_0 is

$$\frac{-d[HNO_2]}{dt} = \frac{d[N_2]}{dt} = (k + k_a h_0)[H_2N_2O_2][HNO_2] \qquad (27)$$

~25 for 3 M HNO_3). At 25 °C in perchloric acid, the experimentally determined values[21] of k and k_a are 0.4 M^{-1} s^{-1} and 0.08 M^{-2} s^{-1}; thus, the expected second-order rate constant under our conditions is given by eq 28. The importance of

$$k_{22} = (k + k_a h_0) \approx 2.4 \ M^{-1}\ s^{-1} \qquad (28)$$

this reaction depends on the relative stability of $H_2N_2O_2$ in this medium. Literature reports suggest that *cis*-$H_2N_2O_2$ is short-lived in solution whereas *trans*-$H_2N_2O_2$ is relatively stable. Spectroscopic detection of $H_2N_2O_2$ is impossible due to the interference of the electrolyte medium.

The observed product yields can be accounted for, at least in a qualitative sense, by the competition of the four reactions eq 29–32. A quantitative treatment will be attempted for two

$$HNO_2 + NH_3OH^+ \rightarrow H_2N_2O_2 + H_2O + H^+ \qquad (29)$$

$$2HNO_3 + NH_3OH^+ \rightarrow 3HNO_2 + H^+ + H_2O \qquad (30)$$

$$HNO_2 + H_2N_2O_2 \rightarrow HNO_3 + N_2 + H_2O \qquad (31)$$

$$H_2N_2O_2 \rightarrow N_2O + H_2O \qquad (32)$$

limiting cases; in both a constant excess of HNO_3 and a low initial concentration of HNO_2 are present. (1) The yields of HNO_2 and N_2 are maximized and the yield of N_2O approaches 0 as the initial concentration of NH_3OH^+ approaches 0. (2) At higher initial concentration of NH_3OH^+, the yield of N_2O is relatively constant, N_2 is a minor product, and the yield of HNO_2 is approaching an asymptotic limit.

In the first case, the rate of reaction 31 appears to be fast compared to the other reactions. The net reactions to be considered are reactions 30 and 33. Reaction 33 is obtained

$$2HNO_2 + NH_3OH^+ \rightarrow HNO_3 + N_2 + 2H_2O + H^+ \qquad (33)$$

by combining reactions 29 and 31. Extrapolating the yields of HNO_2 and N_2 to an initial NH_3OH^+ concentration of 0 allows the ratio of rate constants to be interpreted at constant HNO_3 concentration. With reference to eq 10 and 21 and the appropriate stoichiometric factors, the rate of net appearance of HNO_2 is given by eq 34. An analogous treatment leads

$$\frac{d[HNO_2]}{dt} = 3g[HNO_2][NH_3OH^+] - 2k'[HNO_2][NH_3OH^+] \qquad (34)$$

---

[21] Buchholz, J. R.; Powell, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 2350–2353.
[22] Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 4230–4234.

to an expression for the disappearance of NH_3OH^+ (eq 35).

$$-\frac{d[NH_3OH^+]}{dt} = g[HNO_2][NH_3OH^+] + k'[HNO_2][NH_3OH^+] \quad (35)$$

The elimination of time from eq 34 and 35 gives eq 36, and

$$-\frac{d[HNO_2]}{d[NH_3OH^+]} = \frac{3g - 2k'}{g + k'} \quad (36)$$

integrations from the limits $[HNO_2]_{t=0}$ to $[HNO_2]_{t=\infty}$ and $[NH_3OH^+]_0$ to $[NH_3OH^+]_\infty$, the latter quantity being 0, give an expression for the yield (eq 37). The data in Figure 6 (3.0

$$\frac{[HNO_2]_\infty - [HNO_2]_0}{[NH_3OH^+]_0} = \frac{3g/k' - 2}{g/k' + 1} \quad (37)$$

M H^+, 4.0 M ionic strength) show the limiting yield of HNO_2 is 0.93; the calculated value of the ratio g/k' is 1.44. A treatment of the rate of appearance of N_2 (eq 38) leads to

$$\frac{d[N_2]}{dt} = k'[HNO_2][NH_3OH^+] \quad (38)$$

expression 39 for the yield.

$$\frac{[N_2]_\infty}{[NH_3OH^+]_0} = \frac{k'}{g + k'} = \frac{1}{g/k' + 1} \quad (39)$$

The ratio g/k' calculated from the yield of N_2 in Figure 6 and eq 39 is 3.5, a value in poor agreement with that calculated above. The initial rate of the net appearance of HNO_2 at low $[NH_3OH^+]$ can be used to estimate the parameter g by using eq 34. The value of k' measured in 3 M H^+ is 10 M^{-1} s^{-1}. Thus the initial rate divided by the product of the initial concentrations of HNO_2 and NH_3OH^+ is $3g - 2k'$. Although there is some scatter in these data, the calculated ratio g/k' is 1.2 in reasonable agreement with the value estimated from the net yield of HNO_2.

In the second limiting region, reactions 29 and 32 are rapid compared to reaction 31. Reaction 31 is ineffective in scavenging the HNO_2 produced by reaction 30. We will, to a first approximation, ignore the small yield of N_2. The reactions to be considered are thus (1) and (30). In reaction 30, the higher concentration of NH_3OH^+ shifts the rate-determining step to the production of the reactive intermediate, N_2O_4 (see eq 15). The equations describing the time dependence of the concentrations of HNO_2, NH_3OH^+, and N_2 at constant $[H^+]$ are eq 40–42. The yields of HNO_2 and N_2 are calculated

$$\frac{d[HNO_2]}{dt} = 3g/h[HNO_2] - k'[HNO_2][NH_3OH^+] \quad (40)$$

$$-\frac{d[NH_3OH^+]}{dt} = g/h[HNO_2] + k'[HNO_2][NH_3OH^+] \quad (41)$$

$$\frac{d[N_2O]}{dt} = k'[HNO_2][NH_3OH^+] \quad (42)$$

by integrating the ratios of eq 40 and 41 and eq 42 and 41, respectively (eq 43 and 44). The ratio g/h is equal to

$$\frac{[HNO_2]_\infty - [HNO_2]_0}{[NH_3OH^+]_0} = \frac{4g}{k'h[NH_3OH^+]_0} \ln\left[1 + \frac{k'h}{g}[NH_3OH^+]_0\right] - 1 \quad (43)$$

$$\frac{[N_2O]_\infty}{[NH_3OH^+]_0} = 1 - \frac{g}{k'h[NH_3OH^+]_0} \ln\left[1 + \frac{k'h}{g}[NH_3OH^+]_0\right] \quad (44)$$

$k_{15}[H^+][NO_3^-]$, the first-order rate coefficient for formation of N_2O_4. The rate constant k_{15} was measured by Abel, Schmid, and co-workers[23] in a series of papers in which the kinetics and equilibrium of HNO_2 formation and decomposition were studied (eq 45). The rate of formation of HNO_2

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O \quad (45)$$

was demonstrated to involve the intermediate formation of N_2O_4 (eq 15). The third-order rate constant, $k^0{}_{15}$, has the value 2.7×10^{-2} M^{-2} s^{-1} at 25 °C and extrapolated to infinite dilution. A numerical rate constant appropriate to the conditions of this study is obtained from the relationship $k_{15} = k^0{}_{15}/(\gamma_{HNO_3})^2$,[24] where γ_{HNO_3} is the activity coefficient of nitric acid (see Table I). The calculated ratio g/h is thus 3.2×10^{-1} s^{-1} at 3 M H^+. This value, combined with the measured value of 10 M^{-1} s^{-1} for k' in this medium, can be used to calculate the yields of HNO_2 and N_2O as a function of the initial NH_3OH^+ concentration (eq 43 and 44). The value of g/h required to approximate the experimentally observed yields of HNO_2 and N_2O in Figure 6 is $\sim 5 \times 10^{-2}$–10^{-1} s^{-1}. These values are about a factor of 3–6 smaller than the value measured by Abel and Schmid.[24] The data of the latter authors were obtained in a dilute ionic medium, and the small amount of data available suggests the rate constant k_{15} decreases with increasing ionic strength. The detailed mechanism for the reaction 15 may be the reaction of the equilibrium concentration of NO^+ with NO_3^-. The rate of the reaction of oppositely charged ions is expected to decrease with increasing ionic strength. An absolute comparison of the experimental and calculated yields in this second limiting region does not appear feasible. A single value of the parameter $g/k'h$ will not simultaneously fit both the HNO_2 and N_2O yields, although the shapes of the curves are in reasonable agreement with eq 43 and 44.

Conclusions

The reaction of nitrous acid with hydroxylamine in acidic nitrate solutions follows the reaction scheme outlined by earlier workers. The second-order rate coefficients in HNO_3 solutions are in good agreement with those reported in $HClO_4$ solutions. A more exact treatment of the rate expression, based on the proposed mechanism, is in better agreement with the experimental data than correlations based on the Hammett acidity function. However, a deviation of the experimental results from those predicted by the model at high acid suggests some modification in the steps following the nitrosation of NH_3OH^+ may be appropriate.

The reaction of hydroxylamine with nitric acid is more ambiguous. Nitrogen is observed as a significant product at low initial concentrations of hydroxylamine. This previously unidentified product may result from the reaction of hyponitrous acid with nitrous acid. It is clear that several reactions are occurring simultaneously. A kinetic model is partially successful in rationalizing the distribution of products as a function of the initial hydroxylammonium ion concentration. The treatment presented in this work is not completely satisfactory, and other reactions may also be occurring. It seems clear that a determination of the rates and equilibrium constants of reactions 2–4 at relatively high nitric acid concentrations is essential for a better understanding of this complex system.

Acknowledgment. We gratefully acknowledge the assistance of T. J. Sworski and H. F. Holmes with some of the calcu-

---

[23] Hughes, M. N. *Q. Rev.* **1968**, *22*, 1–13.

[24] Abel, E.; Schmid, H. *Z. Physik. Chem.* **1928**, *132*, 55–77; **1928**, *134*, 279–300. Abel, E.; Schmid, H.; Babad, S. *Ibid.* **1928**, *136*, 135–145; **1928**, *136*, 419–429. Abel, E.; Schmid, H. *Ibid.* **1928**, *136*, 430–436. Abel, E.; Schmid, H.; Römer, E. *Ibid.* **1928**, *148*, 337–348.

lations. This research was sponsored by the Office of Nuclear Fuel Cycle, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

Appendix

The mechanism for reaction of hydroxylammonium ion with nitrous acid (eq 5–9) can be expressed as the generalized reaction scheme of eq A1–A3 since both protons and hydroxylammonium ion are used in swamping excess.

$$\mathrm{A} \underset{k_{\mathrm{ba}}}{\overset{k_{\mathrm{ab}}}{\rightleftharpoons}} \mathrm{B} \tag{A1}$$

$$\mathrm{B} \underset{k_{\mathrm{cb}}}{\overset{k_{\mathrm{bc}}}{\rightleftharpoons}} \mathrm{C} \tag{A2}$$

$$\mathrm{C} \xrightarrow{k_{\mathrm{cd}}} \mathrm{D} \tag{A3}$$

The differential equations describing the time dependence of the concentrations of species A, B, C, and D are eq A4–A7.

$$\mathrm{d}[\mathrm{A}(t)]/\mathrm{d}t = -k_{\mathrm{ab}}[\mathrm{A}(t)] + k_{\mathrm{ba}}[\mathrm{B}(t)] \tag{A4}$$

$$\mathrm{d}[\mathrm{B}(t)]/\mathrm{d}t = k_{\mathrm{ab}}[\mathrm{A}(t)] - (k_{\mathrm{ba}} + k_{\mathrm{bc}})[\mathrm{B}(t)] + k_{\mathrm{cb}}[\mathrm{C}(t)] \tag{A5}$$

$$\mathrm{d}[\mathrm{C}(t)]/\mathrm{d}t = k_{\mathrm{bc}}[\mathrm{B}(t)] - (k_{\mathrm{cb}} + k_{\mathrm{cd}})[\mathrm{C}(t)] \tag{A6}$$

$$\mathrm{d}[\mathrm{D}(t)]/\mathrm{d}t = k_{\mathrm{cd}}[\mathrm{C}(t)] \tag{A7}$$

At time zero and under the conditions of our experiments, the species A and B are initially present in the equilibrium concentrations $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ ($[\mathrm{B}]_0 = k_{\mathrm{ab}}[\mathrm{A}]_0/k_{\mathrm{ba}} = K_{\mathrm{ab}}[\mathrm{A}]_0$) and the species C and D are initially absent. The Laplace transform is taken of eq A4–A7, resulting in a series of four equations in four unknowns (eq A8–A11), where s is the Laplace variable and dependence of a species on s indicates the concentration of the species in the Laplace plane.

$$(k_{\mathrm{ab}} + s)[\mathrm{A}(s)] - k_{\mathrm{ba}}[\mathrm{B}(s)] = [\mathrm{A}]_0 \tag{A8}$$

$$k_{\mathrm{ab}}[\mathrm{A}(s)] - (s + k_{\mathrm{ba}} + k_{\mathrm{bc}})[\mathrm{B}(s)] + k_{\mathrm{cb}}[\mathrm{C}(s)] = -K_{\mathrm{ab}}[\mathrm{A}]_0 \tag{A9}$$

$$k_{\mathrm{bc}}[\mathrm{B}(s)] - (s + k_{\mathrm{cb}} + k_{\mathrm{cd}})[\mathrm{C}(s)] = 0 \tag{A10}$$

$$k_{\mathrm{cd}}[\mathrm{C}(s)] - s[\mathrm{D}(s)] = 0 \tag{A11}$$

Solution of eq A8–A11 for the variable $[\mathrm{A}(s)]$ yields eq A12.

$$[\mathrm{A}(s)] = [\mathrm{A}]_0\{[s^2 + s(k_{\mathrm{ab}} + k_{\mathrm{ba}} + k_{\mathrm{bc}} + k_{\mathrm{cb}} + k_{\mathrm{cd}}) + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cd}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cd}} + k_{\mathrm{bc}}k_{\mathrm{cd}}]/[s^3 + s^2(k_{\mathrm{ab}} + k_{\mathrm{ba}} + k_{\mathrm{bc}} + k_{\mathrm{cb}} + k_{\mathrm{cd}}) + s(k_{\mathrm{ab}}k_{\mathrm{bc}} + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cd}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cd}} + k_{\mathrm{bc}}k_{\mathrm{cd}}) + k_{\mathrm{ab}}k_{\mathrm{bc}}k_{\mathrm{cd}}]\} \tag{A12}$$

The observed disappearance of $[\mathrm{HNO_2}]_T$ is clearly exponential for greater than 90% of the reaction. Thus we are searching for a solution of the form of eq A13 which implies a Laplace transform of the form of eq A14.

$$[\mathrm{A}(t)] = (\mathrm{constant}) \exp[-k_{\mathrm{obsd}}t] \tag{A13}$$

$$[\mathrm{A}(s)] = (\mathrm{constant})\left[\frac{1}{s + k_{\mathrm{obsd}}}\right] \tag{A14}$$

We recognize that higher powers of s refer to the time dependence of the concentration of species A at very short times. Therefore terms in s^2 and s in the numerator and terms in s^3 and s^2 in the denominator will be dropped. The resulting equation for the concentration of species A in the Laplace plane is then eq A15.

$$[\mathrm{A}(s)] = [\mathrm{A}]_0[(k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cd}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cd}} + k_{\mathrm{bc}}k_{\mathrm{cd}})/(k_{\mathrm{ab}}k_{\mathrm{bc}} + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cd}} + k_{\mathrm{bc}}k_{\mathrm{cd}})]/[s + [k_{\mathrm{ab}}k_{\mathrm{bc}}k_{\mathrm{cd}}/(k_{\mathrm{ab}}k_{\mathrm{bc}} + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cd}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{bc}}k_{\mathrm{cd}}k_{\mathrm{bc}}k_{\mathrm{cd}})]] \tag{A15}$$

Inverse Laplace transformation gives an expression for $[\mathrm{A}(t)]$ which can be differentiated with respect to time (eq A16).

$$-\frac{\mathrm{d}[\mathrm{A}(t)]}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{A}(t)] \tag{A16}$$

$$k_{\mathrm{obsd}} = k_{\mathrm{ab}}k_{\mathrm{bc}}k_{\mathrm{cd}}/(k_{\mathrm{ab}}k_{\mathrm{bc}} + k_{\mathrm{ab}}k_{\mathrm{cb}} + k_{\mathrm{ab}}k_{\mathrm{cd}} + k_{\mathrm{ba}}k_{\mathrm{cb}} + k_{\mathrm{ba}}k_{\mathrm{cd}} + k_{\mathrm{bc}}k_{\mathrm{cd}})$$

We will use the definitions

$$k_{\mathrm{ab}} = k_5[\mathrm{H^+}] \qquad k_{\mathrm{ba}} = k_5[\mathrm{H_2O}] \qquad k_{\mathrm{bc}} = k_6[\mathrm{NH_3OH^+}]$$

$$k_{\mathrm{cb}} = k_{-6}[\mathrm{H^+}] \qquad k_{\mathrm{cd}} = k_7$$

and note the observed first-order rate coefficient divided by the initial $\mathrm{NH_3OH^+}$ concentration is a constant at constant $\mathrm{HNO_3}$ concentration. The resulting expression for the second-order rate coefficient as a function of acid concentration is eq A17. (In deriving this expression, terms inverse in $[\mathrm{NH_3OH^+}]$ were neglected).

$$k' = \frac{K_5k_6[\mathrm{H^+}]}{1 + (K_5 + k_{-6}/k_7)[\mathrm{H^+}] + K_5k_{-6}[\mathrm{H^{2+}}]^2/k_7} \tag{A17}$$

This equation predicts k' as a function of acid should have a maximum. Experimental observation of the initial slope (S_{in}) in a plot of k' vs. $[\mathrm{H^+}]$, the value of $[\mathrm{H^+}]$ at which the maximum occurs, and the maximum rate constant are required to evaluate the parameters K_5, k_6, and k_{-6}/k_7. The value of $[\mathrm{H^+}]$ at which the maximum occurs is obtained by differentiating eq A17 with respect to $[\mathrm{H^+}]$, setting the derivative equal to 0, and solving for $[\mathrm{H^+}]_{\mathrm{max}}$.

$$([\mathrm{H^+}]_{\mathrm{max}})^2 = k_7/K_5k_{-6} \tag{A18}$$

Substitution of eq A18 in eq A17 gives the value of the maximum rate constant, k'_{max}:

$$k'_{\mathrm{max}} = \frac{K_5k_6}{2(K_5k_{-6})^{1/2}/k_7 + K_5 + k_{-6}/k_7}$$

$$k'_{\mathrm{max}} = \frac{S_{\mathrm{in}}[\mathrm{H^+}]_{\mathrm{max}}}{2 + [\mathrm{H^+}]_{\mathrm{max}}(K_5 + k_{-6}/k_7)}$$

Registry No. $\mathrm{NH_2OH}$, 7803-49-8; $\mathrm{HNO_2}$, 7782-77-6; $\mathrm{HNO_3}$, 7697-37-2.