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Contribution from the Department of Chemistry,
 State University of New York at Stony Brook, Stony Brook, New York 11794

Properties of Nitroxyl as Intermediate in the Nitric Oxide-Hydroxylamine Reaction and in Trioxodinitrate Decomposition¹

FRANCIS T. BONNER,* LAILA S. DZELZKALNS, and JOHN A. BONUCCI

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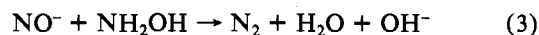
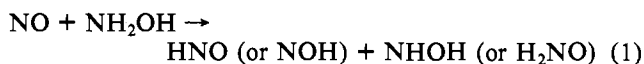
The rate of decomposition of trioxodinitrate monobasic anion (HN_2O_3^-) in aqueous solution is unaffected by the presence of hydroxylamine, but the primary product nitroxyl (HNO) experiences a competition between dimerization to N_2O and reduction to N_2 . The proportion of N_2 increases with pH and with NH_2OH concentration; at pH 8, with NH_2OH in 10-fold excess over HN_2O_3^- , the reaction product is more than 97% N_2 . The reaction between NO and NH_2OH produces equimolar amounts of N_2 and N_2O at pH > 13, but the ratio $\text{N}_2/\text{N}_2\text{O}$ decreases with pH; at pH 8 the product is almost entirely N_2O . The rate of reaction declines sharply with decreasing pH. Observations of reaction product ratios are complicated by simultaneous contributions of NH_2OH disproportionation, which produces N_2 and N_2O in pH-dependent proportions. Tracer experiments employing $^{15}\text{N}^{18}\text{O}$ reactant confirm a previously proposed mechanistic interpretation of the $\text{NO-NH}_2\text{OH}$ reaction in detail: an N-bound H atom is abstracted by NO to form HNO and the radical NHOH . The radical combines with a second NO molecule to form nitrosohydroxylamine, which in turn produces two kinds of N_2O : I, predominantly $^{14}\text{N}^{15}\text{N}^{18}\text{O}$, and II, predominantly $^{15}\text{N}^{14}\text{N}^{16}\text{O}$. The asymmetry of the intermediate is reflected in a higher proportion of I than II in the product at high pH, but these proportions become equalized at pH 8, probably because of tautomerism in the intermediate. Nitroxyl is entirely reduced by NH_2OH to N_2 at high pH but undergoes dimerization to produce a third kind of N_2O , predominantly $^{15}\text{N}^{15}\text{N}^{18}\text{O}$, to an extent that increases with decreasing pH. The tracer experiments also provide support for the hypothesis that nitroxyl is a primary product of hydroxylamine disproportionation. Since the nitroxyl produced in HN_2O_3^- decomposition is preferentially reduced to N_2 at pH 8 in the presence of NH_2OH , while the nitroxyl produced in the $\text{NO-NH}_2\text{OH}$ reaction is almost entirely consumed by self-reaction at the same pH, different intermediate species are produced in these two reactions. Possible explanations for this difference are discussed.

Introduction

In a previous communication from this laboratory² it has been demonstrated that sodium trioxodinitrate(II) ($\text{Na}_2\text{N}_2\text{O}_3$) decomposes in aqueous solution by cleavage of the $\text{N}=\text{N}$ bond to produce the products nitrite and nitroxyl (HNO or NOH), the latter as precursor to N_2O . This conclusion, applying to the monobasic anion HN_2O_3^- as predominating species in the pH range ~4-8, has been subsequently verified by Hughes and Wimbledon.³ The existence of nitroxyl as an intermediate was first proposed by Angeli,⁴ and its participation in the reactions of nitrogen has often been postulated. It has been directly observed by matrix isolation,⁵ and its properties as a gas-phase species have been examined by spectroscopy⁶ and by mass spectrometry.⁷ The gas-phase species described in the literature is invariably HNO , and NOH has not been detected, to the best of our knowledge. It has therefore become customary to designate solution species nitroxyl as HNO , although there appears to be no clear evidence distinguishing between the two possible tautomers in any particular case. The unresolved question of location of the proton in HN_2O_3^- may have a strong bearing on this distinction in the case of the trioxodinitrate decomposition reaction. Nitroxyl in solution has been reported in the literature of radiation chemistry; in particular, pulse radiolysis experiments involving hydrated electrons and hydrogen atoms impacting dissolved NO molecules give rise to a species that has been identified as

HNO .⁸ While these experiments make a convincing case for nitroxyl and even provide a pK value of 4.7 for this species, there does not appear to be any basis in the experiments themselves to distinguish between tautomeric possibilities.

An interesting reaction for which nitroxyl intermediate has been proposed is the reduction of NO by hydroxylamine. This reaction has been studied in 0.5 M NaOH solutions by Cooper, Chilton, and Powell,⁹ who report equimolar quantities of N_2 and N_2O as products and a tracer experiment indicating the appearance of one N atom of NO origin in each of the two product molecules. These authors have postulated the participation of a nitroxyl intermediate, in an interpretation of these facts, in the mechanism



We have given further experimental attention to this reaction, in the conviction that if a nitroxyl intermediate does participate, there should be conditions in which it undergoes the dimerization reaction characteristic of the nitroxyl intermediate observed in trioxodinitrate decomposition. In this paper we report the results of studies which confirm the role of nitroxyl in the $\text{NO-NH}_2\text{OH}$ reaction, but from which we infer that

it is not identical with the nitroxyl intermediate in HN_2O_3^- decomposition.

Experimental Section

Rate of HN_2O_3^- Decomposition. The kinetics of decomposition of $\text{Na}_2\text{N}_2\text{O}_3$, synthesized as described in ref 2, were followed by the UV spectrophotometric method described in the same reference, in the absence and presence of hydroxylamine, at pH 7.0 (phosphate buffer) and 25.0 ± 0.1 °C. The hydroxylamine added to these solutions was NH_2OH , synthesized from $\text{NH}_2\text{OH}\cdot\text{HCl}$ by the procedure of Hurd,¹⁰ and its concentration was determined by the titration method of Milligan.¹¹

Effect of NH_2OH on HN_2O_3^- Decomposition Products. Experiments were conducted at pH 6, 7, and 8 (phosphate buffers, $I = 1.1, 1.3, 1.5$), in which $\text{Na}_2\text{N}_2\text{O}_3$ decomposition took place in the absence and presence of NH_2OH and the product gas was sampled and analyzed at intervals. At each pH, ca. 8.5×10^{-5} mol of $\text{Na}_2\text{N}_2\text{O}_3$ was dissolved in 10 mL of buffer, with NH_2OH present in amounts such that $[\text{NH}_2\text{OH}]_0/[\text{Na}_2\text{N}_2\text{O}_3]_0$ was 0, ca. 1.5, and ca. 10. A fourth experiment was carried out at each pH, in which ca. 1.2×10^{-4} mol of NaNO_2 was substituted for the $\text{Na}_2\text{N}_2\text{O}_3$, and NH_2OH was added at about 10-fold stoichiometric excess. The latter experiments were carried out to determine the maximum contribution to total N_2O via the well-known reaction between nitrous acid and hydroxylamine¹² under conditions of interest in this study.

Each of the experiments described above was carried out in the following way. A weighed quantity of $\text{Na}_2\text{N}_2\text{O}_3$ (or NaNO_2) was placed in a 100-mL reaction vessel which was then evacuated and filled with He to ~ 20 Torr above atmospheric pressure. Just prior to initiation of the experiment the salt was dissolved in a portion of previously deaerated buffer solution, introduced by syringe through a septum. The remainder of the buffer solution needed to bring total solution volume to 10 mL, separately deaerated and containing dissolved NH_2OH in an appropriate amount, was then injected. The gas was then sampled at intervals by withdrawing 0.5 mL in a locking syringe, discarding it, and withdrawing a second slightly larger than 0.5-mL aliquot; this sample was then compressed to 0.5 mL and released to atmospheric pressure immediately prior to injection into the gas chromatograph. Sample size uniformity was maintained, and background N_2 was minimized but not eliminated by these procedures. The experiments were carried out without temperature control but at an ambient temperature of 25 ± 3 °C.

At a later date, two experiments were carried out by employing $\text{NH}_2\text{OH}\cdot\text{HCl}$ as reducing agent, at pH 8 and ionic strengths 1.5 and 0.15, and entirely by the vacuum-line techniques described in the next section.

Gas analyses were performed on an Aerograph 920 gas chromatograph equipped with a 12-ft, $1/4$ -in. Porapak Q column (Applied Science Laboratories, Inc.), employing helium carrier and thermal conductivity detection. Peak areas were estimated by multiplication of height by half-width. In the product ratios reported, N_2 peaks have been corrected for background, and appropriate corrections for detection sensitivity differences and for the solubility of N_2O in water have been applied.

Thermal decomposition of $\text{Na}_2\text{N}_2\text{O}_3$ was also carried out in NaOH solutions at pH 11.7 and 12.6, with and without NH_2OH at 10:1 molar ratio. Since the reaction is very slow under these conditions,² decomposition times of 32 days at pH 11.7, and 57 days at pH 12.6, were allowed. The experiments were carried out in Y-shaped vessels on the vacuum line, degassed by several freeze-pump-thaw cycles, with reaction initiated after degassing by pouring 10 mL of NaOH solution over weighed quantities of solid $\text{Na}_2\text{N}_2\text{O}_3$. The product gases were collected quantitatively by use of a Toepler pump, accessed to the reaction vessel with the solution frozen at 194 K. These product gases were analyzed on an AEI MS-30 mass spectrometer.

The NO- NH_2OH Reaction. Product Distribution Studies. These studies were carried out in the reaction vessel shown schematically in Figure 1. Solutions were prepared by mixing separately deaerated quantities of 0.5 M NaOH solution, 0.5096 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution, and water in amounts designed to provide the desired levels of concentration and pH. An aliquot of each such solution was held for pH measurement, and 10.0 mL was introduced to the reaction vessel through its side port P. The port was then capped, the solution immediately frozen at 194 K with the stirring bar M held on top by an external magnet, and the vessel evacuated. In a normal degassing procedure the vessel was pumped three times at 194 K and once at

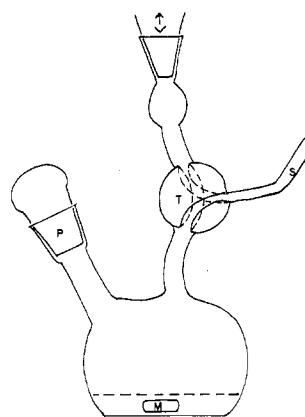


Figure 1. Reaction vessel.

77 K. Reaction was initiated by introduction of purified NO at measured pressure from vacuum system V and then activating the magnetic stirrer. The stirrer was operated at highest feasible speed with the bar held as close to the center of the vessel as possible. Given the focus upon stoichiometry in these experiments, we did not attempt to eliminate the rate limitation of phase mixing but did try to achieve comparability from run to run by maintaining closely similar mixing conditions throughout the series. At measured time intervals the gas phase was sampled by momentarily interrupting the stirring and opening three-way stopcock T to sample volume S. The total volume of the reaction vessel employed in most of these measurements was 148.5 mL and the sample volume was 2.45 mL, so that each sample withdrawn constituted less than 2% of the total gas phase. Each gas sample was transferred quantitatively to a small storage bulb for subsequent gas analysis, by use of a Toepler pump. To avoid introducing water vapor to the gas chromatograph, a spiral trap at dry ice temperature was inserted in the vacuum line between the reaction vessel and the Toepler pump.

The commercial nitric oxide employed in these experiments was purified by repeated trap-to-trap distillation over silica gel at 150 K (1-chlorobutane). Impurities in the NO were below mass spectrometric detection limits. A stock solution of reagent grade hydroxylammonium chloride was stored under a continuous flow of oxygen-free N_2 . The titer of this solution (0.5096 M) was checked regularly over a period of 2 months and was invariably found in agreement with the initial value to within less than 1%. This shows that our storage conditions provided excellent protection against atmospheric oxidation and also that the hydroxylamine disproportionation reaction (to be discussed later) is a negligible source of loss at the pH of this solution (3.1).

These studies were carried out without buffering, and pH measurements were made at the beginning and end of each run. The pH values reported are final values, which generally did not differ from initial values by more than 0.1 unit, with the exception of the pH region of about 2 units centered about pH 9.5, where generally higher levels of change and uncertainty were experienced. This is comprehensible in terms of the equivalence point for hydroxylammonium ion titration at the concentration level employed in most of these experiments, i.e., pH 9.5, based upon $K_a = 1.58 \times 10^{-6}$.¹³ Temperature control was not employed, but the runs were carried out at an ambient temperature generally held at 25.0 ± 3 °C.

Gas analyses for this series were carried out in the Aerograph 920 gas chromatograph with Porapak Q column as previously described but employing a vacuum-line-interfaced sample introduction system rather than hypodermic injection.¹⁴ Gas samples are transferred to the interface region by a Toepler pump, pressurized with He, and then entrained in He carrier gas for delivery to the column by momentary opening of an appropriately arranged four-way capillary stopcock. This greatly improved system removes all uncertainty of background for gas mixtures containing N_2 . Dimensions and geometry are such that high precision and accuracy can be achieved for gas samples at the micromolar level, although only relative concentrations are determinable without an inert reference gas since sample injection is not quantitative. The 12-ft Porapak Q column provides excellent separation of the three components N_2 , NO, and N_2O , provided it is appropriately conditioned for NO by preinjection. Integration of peaks in all of these experiments was carried out on a Hewlett-Packard Model 3373B digital integrator. The molar ratios reported have been

corrected for detection sensitivity and for solubility differences among the three components.

Disproportionation of NH_2OH . At each of the pH levels employed in NO- NH_2OH product distribution measurements, a 10-mL aliquot of degassed NH_2OH solution was allowed to stand for a measured time interval, usually 48 h. The solution was then frozen at 194 K and gaseous products were collected in their entirety and transferred to the GC interface for analysis. Relative quantities of gas produced at different pH levels were roughly indicated by the total pressure of gas as measured in the interface sample loop (~ 3 mL) prior to carrier gas entrainment. In one experiment at high pH the gas phase was sampled and analyzed at intervals over a period of 72 h.

The NO- NH_2OH Reaction. $^{15}\text{N}^{18}\text{O}$ Tracer Studies. Tracer studies were carried out at three pH values, employing $^{15}\text{N}^{18}\text{O}$ gas at high enrichment, obtained from Los Alamos Scientific Laboratory.¹⁵ Reaction systems were prepared and reaction was initiated in the manner described in the preceding section. Samples were withdrawn for GC analyses at reaction times 4.3 h (pH 13.3), 15 h (pH 11.9), 40 h, and 98 h (pH 7.8). In all three cases the reaction was interrupted and samples were withdrawn for isotopic analysis at partial completion (1 h at pH 13.3, 7 h at pH 11.9, 42 h at pH 7.8) and again at times which corresponded to $\sim 100\%$ completion at pH 13.3 and 11.9 (4 h and 48 h, respectively) and $\sim 70\%$ completion at pH 7.8 (100 h). Each gas sample was separated into its three components by the following procedure. First the reaction mixture was frozen at 77 K and N_2 gas was collected by a Toepler pump. The gas mixture was then thawed and refrozen at 194 K, and the remaining gases were transferred to a small bulb by distillation to liquid N_2 temperature. N_2O was then separated from NO by ten bulb-to-bulb distillations through a spiral trap maintained at 113 K (2-methylbutane). Isotopic analyses were carried out on a Consolidated-Nier mass spectrometer.¹⁶

For isotopic characterization of the doubly labeled reactant NO, the relative intensities at masses 29–33 were measured in the same mass spectrometer. Thermal dissociation of NO in the mass spectrometer is expected to contribute some $^{15}\text{N}_2$, and the peak at mass 29 ($^{15}\text{N}^{14}\text{N}$) was therefore used as a basis for apportioning the mass 30 peak between this species and $^{14}\text{N}^{16}\text{O}$. With this correction, and assuming masses 31–33 to consist entirely of $^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}^{18}\text{O}$, and $^{15}\text{N}^{18}\text{O}$, respectively, we calculate that the NO contains 95.1% ^{15}N and 94.5% ^{18}O . These values are approximate, however, since the peaks at masses 31 and 32 undoubtedly include some ^{17}O , to an extent that is unknown to us. This is not important to our purposes, since the intensity at each of the mass numbers 30–33, as a percentage of total reactant NO, provided an entirely sufficient information base for almost all of our calculations.

Results and Discussion

Effect of NH_2OH on $\text{Na}_2\text{N}_2\text{O}_3$ Decomposition Rate and Products. The measured first-order rate constant for decomposition of $\text{Na}_2\text{N}_2\text{O}_3$ at pH 7.00 and 25.0 ± 0.1 °C and initial concentrations $(1.5\text{--}2.7) \times 10^{-4}$ M was $(6.42 \pm 0.11) \times 10^{-4}$ s $^{-1}$ in the absence of hydroxylamine (three measurements). The same quantity measured in the presence of NH_2OH in stoichiometric ratio ranging up to 5.5:1 was $(6.50 \pm 0.20) \times 10^{-4}$ s $^{-1}$ (three measurements).¹⁷ It is clear that hydroxylamine has no effect on this rate, even when present in substantial excess. Although only one pH was employed, it is reasonable to extend this conclusion to a broad pH range, since it has been shown that the rate is independent of pH over the interval in which HN_2O_3^- is the predominant-trioxodinitrate species.^{2,3}

The rate-determining step in HN_2O_3^- decomposition is the cleavage of the N=N bond to produce nitrite and nitroxyl. Since NH_2OH does not alter this rate, we assume that it does not alter the process and that any change in the products of reaction must reflect new processes occurring subsequent to N=N bond cleavage. Over the pH range $\sim 4\text{--}8$, and in the absence of NH_2OH , nitroxyl undergoes an essentially exclusive dimerization process to produce N_2O ,²⁷ and nitrite remains in solution except for HNO_2 disproportionation, which will cause substantial change only at the lower edge of the pH range. Table I shows the effect of NH_2OH on product ratios at three pH values and two different levels of initial

Table I. Gas Products of HN_2O_3^- Decomposition in the Presence of NH_2OH^a

pH	$\text{N}_2/\text{N}_2\text{O}$ (max) $R \approx 1.5$	$\text{N}_2/\text{N}_2\text{O}$ (max) $R \approx 10$	$\text{N}_2\text{O}(\text{NaNO}_2)/$ $\text{N}_2\text{O}(\text{Na}_2\text{N}_2\text{O}_3)$ $t = 100$ min
6.1	1.6	12	0.22
7.2	5.8	29	0.093
8.2	10	32	0.036

^a $R = [\text{NH}_2\text{OH}]_0/[\text{Na}_2\text{N}_2\text{O}_3]_0$. Column 4: ratios of N_2O produced by reaction 6 and by HN_2O_3^- decomposition in 100 min (see text for conditions).

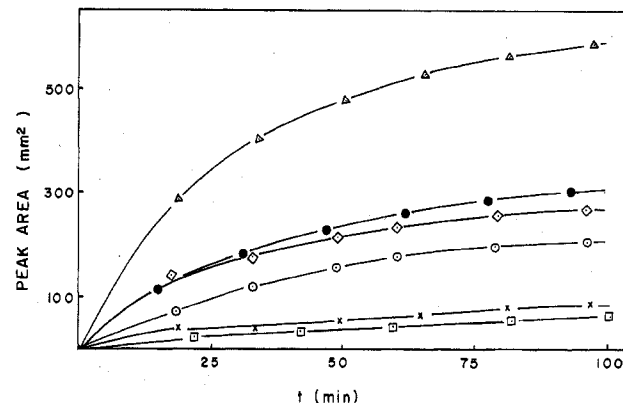
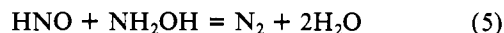
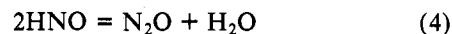


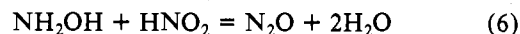
Figure 2. N_2O and N_2 production from 10 mL of phosphate buffer at pH 6.1 and 25.0 °C: ●, N_2O from 0.085 mmol of $\text{Na}_2\text{N}_2\text{O}_3$; □, N_2O from 0.13 mmol of NaNO_2 + 1.3 mmol of NH_2OH (reaction 6); ◇, N_2 from 0.084 mmol of $\text{Na}_2\text{N}_2\text{O}_3$ + 0.13 mmol of NH_2OH ; ○, N_2O from 0.084 mmol of $\text{Na}_2\text{N}_2\text{O}_3$ + 0.13 mmol of NH_2OH ; △, N_2 from 0.082 mmol of $\text{Na}_2\text{N}_2\text{O}_3$ + 0.82 mmol of NH_2OH ; ×, N_2O from 0.082 mmol of $\text{Na}_2\text{N}_2\text{O}_3$ + 0.82 mmol of NH_2OH .

$\text{NH}_2\text{OH}/\text{Na}_2\text{N}_2\text{O}_3$ ratio R . It is seen that N_2 is a prominent product under all of the conditions explored, indicating that in the presence of NH_2OH a competition is established between the dimerization and reduction reactions:



The proportion of N_2 product is large at pH 6.1 and increases with both pH and increasing mole ratio R .

Column 4 in Table I shows the results of experiments designed to set an upper limit to the proportion of N_2O that may be produced in the reaction



under conditions similar to those applicable to columns 2 and 3, where the source of nitrite would be self-decomposition of $\text{Na}_2\text{N}_2\text{O}_3$. Here NaNO_2 in an amount 50% greater than the corresponding quantities of $\text{Na}_2\text{N}_2\text{O}_3$ has been allowed to react with a 10-fold excess of NH_2OH ; ratios of the quantities of N_2O produced in 100 min in this way to that produced by $\text{Na}_2\text{N}_2\text{O}_3$ in excess NH_2OH are reported. It is seen that N_2O is produced by reaction 6 even at pH 8.2 but that N_2O produced in this way constitutes only a small part of total N_2O at pH 6.1 and is negligible at the higher pH values.

Measurements were made at several times at all three pH's, as illustrated in Figure 2 for the case of pH 6.1. This figure shows the growth of N_2O from $\text{Na}_2\text{N}_2\text{O}_3$ alone and from reaction 6 and the growth of N_2 and N_2O from $\text{Na}_2\text{N}_2\text{O}_3$ decomposition at the two NH_2OH concentration levels. The ratios $\text{N}_2/\text{N}_2\text{O}$ in each case exhibit slight curvature, starting gently downward generally before 100 min, and the values of this ratio reported in Table I are maximum values observed within 20–100 min of reaction time.

Table II. NO + NH₂OH Reaction at pH 13.5^a

<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O	<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O
0.50	1.068	2.06	2.0	1.057	0.102
1.0	1.061	0.642	3.0	1.061	0.0157
1.5	1.059	0.252	4.0	1.063	

^a [NH₂OH]₀ = 0.153; P_{NO}^o = 92 Torr; (ⁿNH₂OH/ⁿNO)₀ = 2.23.

Table III. NO + NH₂OH Reaction at pH 12.1^a

<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O	<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O
0.50	0.951	19.4	9.0	0.860	0.553
3.0	0.851	2.42	18.0	0.862	0.144

^a [NH₂OH]₀ = 0.153; P_{NO}^o = 121 Torr; (ⁿNH₂OH/ⁿNO)₀ = 1.70.

The outcome of the competition between dimerization and reduction of nitroxyl could be affected by two pH-dependent factors. First, Coulomb barrier considerations lead one to expect inhibition of the dimerization reaction with increasing deprotonation of HNO. If the nitroxyl found here is identical with the species found in pulse radiolysis by Grätzel et al.,⁸ the reported *K*_a of 2.0 × 10⁻⁵ indicates that little protonated nitroxyl would be present at the lowest pH employed ([NO⁻]/[HNO] = 20 at pH 6). Second, the reactivity of hydroxylamine is altered by deprotonation of NH₃OH⁺, which enhances availability of the nitrogen lone pair. Using the value 1.6 × 10⁻⁶ for *K*_a, we see that substantial change in the [NH₂OH]/[NH₃OH⁺] ratio occurs over the pH range 6–8. Thus it is possible, but by no means certain, that the observed increase in the proportion of product N₂ with pH is more strongly determined by the properties of hydroxylamine than of nitroxyl. In any event it can certainly be said that for nitroxyl of trioxodinitrate origin in the presence of hydroxylamine at pH 8, the process of reduction is overwhelmingly favored over dimerization.

Since the results in Table I are based upon NH₂OH solutions whereas NH₂OH·HCl solutions were employed in later work, two additional experiments were carried out using NH₂OH·HCl solution at pH 8, with an initial NH₂OH/Na₂N₂O₃ ratio of 10, and at ionic strengths 1.5 and 0.15. The maximum N₂/N₂O product ratios observed were 36 at ionic strength 1.5 and 21 at 0.15. The higher value is essentially identical with the result obtained with NH₂OH at comparable ionic strength, i.e., N₂ = ~97% of product gas. The lower value of 21 implies only a small effect of ionic strength: a 10-fold decrease reduced the N₂ content of product by less than 2%. We conclude that neither the presence of Cl⁻ nor ionic strength has a significant effect on the outcome of competition between reactions 4 and 5 at pH 8.

From the trend observed in Table I it is reasonable to expect virtual exclusion of the dimerization reaction in strongly alkaline solutions, as the mechanism proposed by Cooper et al.⁹ for the NO–NH₂OH reaction would require of the NO⁻ intermediate postulated for that case. Experiments on Na₂N₂O₃ decomposition were carried out at pH 11.7 and 12.6, with and without NH₂OH in 10-fold excess. Small quantities of pure N₂O were produced in both cases without NH₂OH, and N₂–N₂O mixtures containing 44 and 61% N₂, respectively, with NH₂OH present. While these results might appear contrary to the trend shown in Table I, the situation is different because of the long reaction periods employed (32 and 57 days, respectively). The N₂/N₂O ratios found appear similar to those subsequently observed in the gas product of hydroxylamine disproportionation in this pH region during much shorter time intervals, and it appears probable that the gas we examined came predominantly from this reaction source.

NH₂OH Reduction of NO. Effect of pH on Reaction Products. The molar ratios N₂/N₂O and NO/N₂O as

Table IV. NO + NH₂OH Reaction at pH 8.1^a

<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O	<i>t</i> , h	N ₂ /N ₂ O	NO/N ₂ O
0.50	1.49	462	24.0	0.0219	2.56
3.0	0.135	37.9	36.0	0.0183	1.42
12.0	0.0361	6.27	53.0	0.0131	0.853

^a [NH₂OH]₀ = 0.153; P_{NO}^o = 117 Torr; (ⁿNH₂OH/ⁿNO)₀ = 1.75.

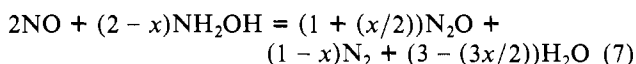
Table V. NO + NH₂OH Reaction Product Distribution as a Function of pH

pH	[NH ₂ OH] ₀	P _{NO} ^o , Torr	(ⁿ NH ₂ OH/ ⁿ NO) ₀	(N ₂ /N ₂ O) _{min}	<i>t</i> * _{1/2} , ^a h
13.1	0.0516	28	2.48	1.045	2.9
13.5	0.153	92	2.23	1.057	0.47
12.1	0.153	121	1.70	0.85	4.5
11.7	0.153	129	1.47	0.76	18.7
11.3	0.153	110	1.87	0.66	12.7
10.0	0.153	115	1.79	0.16	147
8.1	0.153	117	1.75	0.013	39.1
7.2	0.153	112	1.83	0.048	127
6.0	0.153	126	1.63	0.35	1100

^a *t**_{1/2} is the *apparent* half-life for the pseudo-first-order process.

measured in the gas phases of reaction systems at various times are shown for pH values 13.5, 12.1, and 8.1 in Tables II–IV. These three tables exemplify the detailed information at the basis of the more comprehensive Table V, which summarizes our observations over the pH range 6–13.5. The ratio N₂/N₂O in Table V is the minimum observed value in each case. At nearly every pH studied this ratio was high in its first measurement relative to subsequent measurements. In some instances the minimum value was attained and maintained after withdrawal of a small number of samples (pH 11.7, 11.3), in others this occurred toward the end of the series (pH 10.0, 7.2), and on occasion a small increase was observed after attainment of the minimum value (pH 13.5, 12.1). The case of pH 8.2 (Table IV) is unique in that the ratio is very small and displayed a continuing downward trend up to termination of the run. Continuing decline was also observed at pH 6.0.

We postulate that the product ratio N₂/N₂O is less than unity at pH 12 and below because nitroxyl is an intermediate as proposed in the reaction sequence 1–3 and that reduction reaction 3 is not quantitative in less strongly alkaline and in weakly acidic solutions because of competition from dimerization reaction 4. Designating *x* as the fraction of HNO molecules produced in 1 that is diverted to N₂O by dimerization, the overall stoichiometry of the reaction can be expressed as



where the extremes *x* = 0 and *x* = 1 are observed at pH >13 and ~8, respectively. The quantity *x* has been calculated employing observed minimum values of the N₂/N₂O ratio, and P_{NO} at each time *t* has then been calculated using the derived relation

$$(P_{\text{NO}})_t = \frac{(\text{NO}/\text{N}_2\text{O})_t(2 + x)P_{\text{NO}}^o}{(2 + x)(\text{NO}/\text{N}_2\text{O})_t + 4} \quad (8)$$

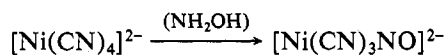
Values of (P_{NO})_{*t*} obtained in this way have been used to construct logarithmic plots, whose initial slopes are the source of the *apparent* half-lives *t**_{1/2} reported in Table V. These plots were in each case linear over the initial period in which NH₂OH was in excess. As previously remarked, phase-mixing limitations were not removed and therefore we do not claim these values to represent true chemical rates. We did attempt to maintain comparable mixing conditions over the entire

Table VI. Gas Product Ratios at Various pH Values for the Hydroxylamine Disproportionation Reaction

pH	t, h	rel press.	N ₂ /N ₂ O
13.5	49	1.0	6.19
12.2	48	0.20	1.60
11.8	73	0.20	1.08
10.9	48	0.15	0.559
7.7	51	0.10	1.56
6.0	48	0.05	1.65

series, and the values $t^{*}_{1/2}$ are reported to provide an idea of the relative reaction rates at the various pH levels employed. They indicate an extremely strong dependence of rate upon pH and also exhibit some irregularities of sequence. The first value is higher than the second because of the more dilute NH₂OH solution employed, but all others are at the same concentration, 0.153 M. The fluctuation at pH 11.7 may have been caused by a slight change in cell geometry in this instance, but we have no explanation for the substantial apparent rate fluctuation at pH 10.

To interpret why the product ratios of N₂/N₂O are greater than 1 at pH 13.5, start out higher than the minimum value and decline at lower pH's, and in some instances increase slightly after reaching a minimum, we turn to the hydroxylamine disproportionation reaction. Although this reaction has been known since 1865,¹⁸ it does not appear to have been extensively investigated. While it is given an occasional line in texts and treatises, it cannot be called a prominent feature of recorded hydroxylamine chemistry. The products of disproportionation are NH₃, N₂, and N₂O. Hieber et al.¹⁹ reported the use of alkaline NH₂OH disproportionation as a means of introducing NO⁻ units into certain coordination complexes, e.g.



On the basis of this evidence, Nast and Föppel²⁰ proposed that the primary disproportionative process is the reaction



and that the distribution of final gaseous products is dependent upon pH, i.e., that reduction of HNO to N₂ predominates in alkaline solution but dimerization to N₂O predominates at acidic pH. Kinetic measurements have been carried out in strong base by Holzapfel,²¹ who claimed an approximately first-order reaction in NH₂OH but observed a shift in stoichiometry occurring with increasing depletion of NH₂OH.

Since none of the available literature on NH₂OH disproportionation was directly applicable to the conditions of our experiments, we conducted additional experiments with the results reported in Table VI. Each corresponds closely to the conditions of an experiment listed in Table V, but without NO added. Table VI shows that the quantity of gas produced in similar time periods declines steadily with pH. As remarked previously, no disproportionative loss was detectable in a 0.5 M stock solution at pH 3 over a 2-month period. The total quantity of gas produced in 10 mL of 0.153 M NH₂OH at pH 13.5 in 49 h was 2–3 μmol, a rate of loss that would lead to a concentration reduction in the range of 12–18% in a 60-day period (assuming N₂ as product). Moews and Audrieth²² showed that hydroxylamine solutions at pH 9 are stable under a nitrogen atmosphere, relative to their behavior under oxidative conditions. Their finding of 0% decomposition in 21 h does not prove stability against disproportionation, however; loss in that period at the rate cited above would not be detectable by titration. Similarly, Cooper et al.⁹ reported no detectable decomposition of alkaline hydroxylamine upon storage for 1 week, but disproportionative loss during 1 week

Table VII. Mass Spectra for the Separated N₂O Product of the ¹⁵N¹⁸O + NH₂OH Reaction at Three pH Values^a

mass	pH 13.3		pH 11.9		pH 7.8	
	1 h (77% com- plete)	4 h (100% com- plete)	7 h (62% com- plete)	48 h (100% com- plete)	42 h (40% com- plete)	100 h (70% com- plete)
48	0.013	0.324	0.237	0.701	0.622	
47	1.042	1.031	1.053	0.964	0.940	0.855
46	0.052	0.056	0.091	0.055	0.120	0.151
45	1.000	1.000	1.000	1.000	1.000	1.000
44	0.034	0.066	0.062	0.043	0.061	0.110
33	(0.421)	0.204	0.269	0.316	0.343	0.309
32	0.052	0.025	0.033	0.102	0.034	0.036
31	0.062	0.028	0.029	0.039	0.055	0.067
30	0.213	0.209	0.261	0.298	0.300	0.287

^a Intensities relative to mass 45.

at our observed pH 13.5 rate could easily be obscured within the error of titration.

The results in Table VI show a sharp decline in N₂/N₂O product ratio with decreasing pH, with this quantity passing through a minimum near pH 11 and then slowly rising; we have no explanation for this minimum and cannot claim certainty about its existence without further study. One disproportionation experiment was carried out at high pH in which the composition of the product gas was determined at several times within a 72-h period; N₂/N₂O ratios slowly increased from 5.5 at 0.5 h to 7.5 at 33 h and then declined to 6.5 at 72 h.

The influence of disproportionation on the products of NO reduction by NH₂OH, as observed in Tables II–V, is readily discerned in broad outline. At high pH, where the actual N₂/N₂O product ratio is presumably 1:1, the disproportionation product is very N₂ rich and is produced rapidly enough to bring a ratio greater than unity to the overall mixture. (We note that the N₂/N₂O ratios are greater than unity in three of the four 20 °C, high-pH measurements reported by Cooper et al.⁹ and that the mean of these four values is 1.14. This was reasonably taken by them to infer 1:1 stoichiometry at the substantially higher level of uncertainty of their measurements.) With decreasing pH the rate of disproportionation is slower but affects reaction product ratios nevertheless, since the NO reduction reaction is also slow. Although the reaction was nearly always initiated as soon as possible after final pumping and thawing of the NH₂OH solution, the first gas sample withdrawn was always N₂ rich relative to subsequent samples. We infer that some degree of initial disproportionation occurred in every instance, under vacuum and prior to introduction of NO. The true product ratio was then approached in subsequent gas samples as reaction product gas developed and diluted this initial gas of disproportionation origin. We believe that the apparent passage of the ratio (N₂/N₂O)_{min} through a minimum value near pH 8 (see Table V) is not real but reflects the very slow rate of reaction; during the long time intervals involved, the disproportionation product becomes an appreciable part of the observed total gas product even at the very slow rate of its own production.

Tracer Experiments with ¹⁵N¹⁸O. The test of our explanation of the decline in product N₂/N₂O ratios with decreasing pH lies in the results of the tracer experiments reported in Tables VII–IX. Intensities of peaks observed at masses 30–48 in the separated product N₂O sampled at two different times in each of three experiments are expressed relative to mass 45 in Table VII. Intensities at masses 28–30 in the corresponding N₂ samples are shown as percentages of total N₂ in Table VIII. In Table IX, the data on the N₂O parent peaks 40–48 are recast to a percentage of total N₂O basis and compared with

Table VIII. Mass Spectra for the Separated N₂ Product of the ¹⁵N¹⁸O + NH₂OH Reaction at Three pH Values^a

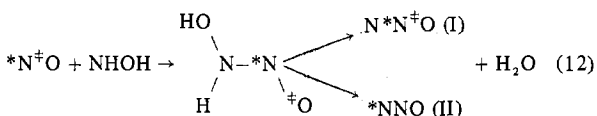
mass	pH 13.3, 1 h	pH 13.3, 4 h	pH 11.9, 7 h	pH 11.9, 48 h	pH 7.8, 42 h	pH 7.8, 100 h	calcd for 95.1% ¹⁵ N in NO
30	0.36	0.36	0.68	0.67	1.11	0.10	0.35
29	91.2	93.3	86.2	88.9	5.15	0.56	94.8
28	8.4	6.3	13.2	10.5	93.75	99.34	4.9

^a Intensities expressed as percentage of total N₂.**Table IX.** Mass Spectra of N₂O at Each of Masses 44–48 as Percent of Total N₂O Product of ¹⁵N¹⁸O + NH₂OH Reaction^a

mass	pH 13.3, 1 h	pH 13.3, 4 h	pH 11.9, 7 h	pH 11.9, 48 h	pH 7.8, 42 h	pH 7.8, 100 h	calcd	
							I + II	I + II + III
48		0.6	12.8	10.3	24.8	22.7	0.2	28.7
47	49.0	47.6	41.6	41.9	33.3	31.2	45.0	32.9
46	2.4	2.6	3.6	2.4	4.3	5.5	2.3	3.2
45	47.0	46.2	39.5	43.5	35.4	36.5	49.8	33.4
44	1.6	3.1	2.5	1.9	2.2	4.0	2.7	1.8

^a Columns 2–7: observed values. Columns 8 and 9: calculated values (see text).
calculated values that will be explained later.

If we assume the mechanism of eq 1–3, then using *N and *O to represent the isotopic labels in the ¹⁵N¹⁸O reactant gas



If the two kinds of N₂O are produced without cleavage of the N–N bond in the intermediate, then I and II should consist predominantly of the species ¹⁴N¹⁵N¹⁸O (mass 47) and ¹⁵N¹⁴N¹⁶O (mass 45), respectively. Reaction 11 should yield N₂ bearing one N atom from each source, but with decreasing pH we postulate that this reaction becomes a pathway of declining importance as the nitroxyl dimerization reaction competes:



Thus N₂O of kind III, predominantly ¹⁵N¹⁵N¹⁸O (mass 48), is expected to appear, while kinds I and II should continue to be produced, and whatever N₂ is produced should continue to include one N atom from NO and one from NH₂OH.

These expectations are generally borne out by the experimental results. First, in Table VII we see that masses 47 and 45 are the principal N₂O species formed at high pH, that they continue to form at the two lower pH's, but that N₂O of mass 48, which is virtually absent at pH 13.3, becomes a prominent product at pH 11.9 and is even more so at pH 7.8. To examine the isomeric content of the N₂O at masses 47 and 45, we turn to the electron-impact-produced NO peaks at masses 30–33. Using the values in column 3 (since the high mass 33 content of column 2 may indicate incomplete NO–N₂O separation) it can be seen that approximately equal amounts of masses 33 and 30 are formed, whereas masses 31 and 32 have very small relative abundances. This is what we would expect of an approximately equimolar mixture of I and II consisting largely of ¹⁵N¹⁴N¹⁶O and ¹⁴N¹⁵N¹⁸O, with little content of the alternative isomers ¹⁴N¹⁵N¹⁶O and ¹⁵N¹⁴N¹⁸O. We conclude that the precursor to these N₂O species is bound between nitrogen atoms, as required by the postulated mechanism. Similar considerations applied to the N₂O at masses 47 and 45 formed at lower pH, columns 4–7, lead to the same conclusion. In these cases, however, the increase in mass 33:mass 30 ratio, anticipated because of the presence of ¹⁵N¹⁵N¹⁸O in substantial amounts, is not observed. We believe

the reason for this is that the doubly N-labeled N₂O at mass 48 gives rise to ¹⁵N₂ on electron impact, so that the mass 30 peak is larger than it would be if it were all ¹⁴N¹⁶O. Calculations based on the mass 29 content of N₂O formed at pH 7.8 show that the effect of ¹⁵N₂ from this source on mass 30 is indeed substantial.

More quantitatively, we have calculated the detailed isotopic content to be expected for N₂O of kinds I and II. This was done by using the measured percentage abundances at masses 30–33 in the ¹⁵N¹⁸O reactant (with mass 30 corrected for ¹⁵N₂), in combination with natural-abundance values for the NHOH radical, to compute the abundances of each of the species ¹⁵N¹⁵N¹⁸O, ¹⁴N¹⁵N¹⁸O, ¹⁵N¹⁴N¹⁸O, ¹⁴N¹⁴N¹⁸O, ¹⁵N¹⁵N¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, and ¹⁴N¹⁴N¹⁶O produced in each of the two possible N₂O-producing modes of reaction 12. The resultant calculated percent abundances at masses 44–48 in an equimolar mixture of I and II are shown in column 8 of Table IX. A similar calculation has been carried out for type III N₂O (reaction 13), and the corresponding calculated values for an assumed equimolar mixture of I, II, and III are shown in column 9 of Table IX. If N₂O products I and II are equally probable and no dimerization reaction occurs, the predicted N₂O composition is that given in column 8. We have used the detailed calculated isomeric content of this mixture to calculate the following predicted mass spectrum in the mass range 30–33: 33, 45.1%; 32, 2.2%; 31, 2.7%; 30, 50.0%. Observed values for product N₂O at reaction completion, pH 13.3 (Table VII, column 3), are as follows: 33, 43.8%; 32, 5.4%; 31, 6.0%; 30, 44.9%. The values at masses 30 and 33 are consistent with a postulate of asymmetric production of I and II, to be discussed later. The values at masses 31 and 32 are larger than the predicted values, but still small. There may be some rearrangement leading to the isomers ¹⁵N¹⁴N¹⁸O and ¹⁴N¹⁵N¹⁶O, but no more than a few percent: calculation shows that the abundances at masses 30–33 would be approximately 1:1:1:1 if the isomeric species were present in equal proportions at each of the masses 45 and 47.

If no N₂ is formed, as is essentially the case at pH 7.8, the mechanism predicts an equimolar mixture of N₂O of kinds I, II, and III, if I and II are produced at equal probability. A calculation for this mixture, similar to the one described above, predicts the following: 33, 60.1%; 32, 2.9%; 31, 3.4%; 30, 33.5%. The data of Table VII, column 6, for pH 7.8 at 42 hours, give the following observed values: 33, 46.9%; 32, 4.6%; 31, 7.5%; 30, 41.0%. The observed values at masses 31 and 32 are again somewhat higher than calculated but show that ¹⁵N¹⁴N¹⁶O and ¹⁴N¹⁵N¹⁸O are indeed the predominant species at masses 45 and 47. As previously remarked, the abundance at mass 30 is in this case distorted by the presence of substantial ¹⁵N₂, so that the apparent discrepancies at

masses 30 and 33 are not meaningful.

In Table VIII the observed mass spectra for N_2 in each of the six gas product mixtures are shown, along with calculated values based upon the assumption that one N atom arises from nitroxyl containing ^{15}N at 95.1% abundance, and the other arises from hydroxylamine at natural abundance. The results at pH 13.3 are consistent with a gas of the predicted composition containing a small proportion of $^{14}N_2$ produced by disproportionation (see Table II). The results at pH 11.9 are consistent with a similar mixture containing a somewhat higher proportion of $^{14}N_2$. The small amount of N_2 obtained at pH 7.8, on the other hand, is almost entirely $^{14}N_2$, showing that reaction 11 is virtually absent under these conditions. (The apparent ^{15}N content, and its extreme variability from one sample to the next, may be largely attributable to incomplete separation of N_2O , which is at a trace level in these very small gas samples.)

The composition of N_2 produced at high pH upon reaction completion (Table VIII, column 3) can be closely simulated by assuming a gas of the composition in column 8, with 1.5% $^{14}N_2$ added: 30, 0.34%; 29, 93.4%; 28, 6.3%. This result may appear to be at variance with the observations of Cooper et al.⁹ However, it is readily shown that, at the lower level of ^{15}N abundance employed by them, inclusion of 1.5% $^{14}N_2$ would have been obscured within the error of their measurements. (Calculated for their gas plus 1.5% $^{14}N_2$: 29, 10.15%; 28, 89.85%. Observed: 10.1% and 89.9%; duplicate observed: 10.4% and 89.6%.)

Finally, we consider the observed distributions of N_2O molecules at parent masses 44–48 in comparison with values calculated for our two idealized mixtures, all as shown in Table IX. At the highest pH 13.3, essentially no III is formed, so the N_2O should be an equimolar mixture of I and II if the latter are equally probable. On comparing the observed values with those of column 8, we see that the percent abundances at 44 and 46 are in good agreement but that mass 47:mass 45 is >1 in the observed mixture although predicted to be <1 in an equimolar mixture. The magnitude of this difference is too large to be accounted as isotope effect, and we postulate that I is produced with higher probability than II under these conditions. This is in turn consistent with the identification of the asymmetric species nitrosohydroxylamine as intermediate, rather than a symmetric species, e.g., *cis*-hyponitrite. It also seems to us to confirm the postulate that it is a nitrogen-bound rather than oxygen-bound hydrogen atom that is abstracted from NH_2OH in step 1 of the mechanism, an event that provides a radical species that is reactive at its nitrogen atom without rearrangement.

Cooper et al.⁹ reported mass 31:mass 30 ratios indicating equal production of the two species at mass 45, implying that the precursor of N_2O either is symmetric or is capable of rapid tautomerization. Here again we believe that the relatively low ^{15}N abundance level employed by them has obscured the asymmetric property of the intermediate. (Calculated for Cooper et al. conditions without asymmetry: $31/30 = 0.055$; with 10% asymmetry = 0.060; observed by Cooper et al.: 0.057.) In our data the presence of ^{18}O contributes to the resolution of this point, in addition to the high ^{15}N content. We are in agreement with the intuition of these investigators that nitrosohydroxylamine is the intermediate but not that its assumed tautomerization occurs rapidly enough at high pH to yield N_2O product symmetrically.

Calculations providing a reasonable fit to the data in column 2 of Table IX have been found for assumed probabilities 0.55 and 0.45 for production of I and II, respectively: 48, 0.2%; 47, 49.1%; 46, 2.5%; 45, 45.7%; 44, 2.5%. The apparent decline in mass 47:mass 45 ratio between 77 and 100% of reaction completion is small but beyond experimental error.

If the hypothesis of Nast²⁰ is correct, hydroxylamine disproportionation may be a source of additional nitroxyl (reaction 9), at natural isotopic abundance. Reaction of the two kinds of nitroxyl could alter the relative proportions of N_2O at masses 47 and 45 since the mixed-precursor intermediate would presumably be symmetric.

The results at pH 11.9 (column 4) are consistent with a mixture that is substantially richer in I than II, plus a small portion of III. In attempting to match the composition of the sample in column 4 by calculation, we find it necessary to assume a somewhat larger proportion of III than corresponds to the value of x (see eq 7) based on GC analysis, a circumstance that we cannot explain. At this pH, the product gas at completion (column 5) is richer in mass 45 than in 47, turned around from the ratio observed at 62% of completion. We believe this may well be accounted for, along with the observed relative decline at mass 48, in terms of the participation of a natural-abundance nitroxyl species as postulated in the previous paragraph.

At pH 7.8 virtually no N_2 forms, and there is presumably no fate available to nitroxyl other than dimerization. In the absence of processes other than reactions 10, 12, and 13 the product N_2O should consist entirely of kinds I, II, and III, with the latter one-third of the total. Comparing the observed composition at 42 hours (column 6) with the values calculated for an equimolar mixture (column 9), we see that this expectation is very nearly realized. We attribute the fact that the proportion at mass 48 is less than the calculated value to interaction of labeled nitroxyl with disproportionation-generated nitroxyl. A reasonably close match to the proportions observed in column 6 is obtained by assuming a 1:1:0.8 mixture of I, II, and III: 48, 24.6%; 47, 34.6%; 46, 3.1%; 45, 35.8%; 44, 2.0%. We note at once that the observed mass 47:mass 45 ratio in this case corresponds closely to that predicted for a 1:1 mixture of I and II. N_2O formed from nitroxyl of mixed origins should indeed contribute equimolar amounts, but since the N_2O at masses 47 and 45 comes predominantly from reaction 12, the result strongly implies that I and II are produced at equal probability at this pH. This appears to be consistent with the conjecture of Cooper et al.⁹ that the nitrosohydroxylamine intermediate undergoes nitrogen-to-nitrogen tautomerization, if we assume that it does so at a rate that is slower than its rate of loss of OH^- (or H_2O) at high pH but becomes comparable to and exceeds the latter rate as pH is decreased.

Our postulate that nitroxyl from disproportionation is a participant in N_2O formation seems reasonable in view of the long reaction time involved and is strengthened by the observation of further decline in the proportion of III at 100 h (column 7). This is seen to be accompanied by a decrease in mass 47:mass 45 ratio, which calculations show to be consistent with symmetric production of I and II, although the observed ratio is somewhat smaller than the predicted value.

Summary and Conclusions

The results described in this paper have developed a detailed and we believe unambiguously clear picture of the $NH_2O-H-NO$ reaction, a picture that both includes and goes beyond verification of the mechanism represented in eq 1–3. In particular, the role of nitroxyl as an intermediate has been proven: $^{15}N^{15}N^{18}O$ is abundantly produced below pH 13, and since all three atoms in this molecule can come only from reactant NO, its precursor must be a species in which nitrogen is bound to oxygen but not to nitrogen. Proof of nitroxyl participation decisively eliminates the alternative mechanism via *N*-(hydroxylamino)nitrosohydroxylamine suggested in ref 9. The N_2O that is not formed by dimerization has been shown to arise from an intermediate in which nitrogens are bound to one another. The evidence that this intermediate is

asymmetric at high pH develops a strong case that it is nitrosohydroxylamine, and the apparent loss of this asymmetry at lower pH suggests that it is capable of tautomeric rearrangement. Asymmetry of the intermediate is also persuasive of the hypothesis that an N-bound H atom is abstracted by NO in the initial formation of nitroxyl. In addition, we believe our results provide strong supporting evidence for the hypothesis that nitroxyl is a primary product of the disproportionation of hydroxylamine.

In addition to all of the above, the results of this study have created a significant new question that we have not yet been able to answer: the nitroxyl intermediate encountered in trioxodinitrate decomposition, which we shall call nitroxyl A, appears to have properties that are significantly different from those of the intermediate of the NO-NH₂OH reaction (nitroxyl B). Whereas nitroxyl A is very much more reactive toward NH₂OH than toward itself at pH 8, nitroxyl B is consumed almost exclusively by self-reaction at the same pH. This comparison is based upon nitroxyl generation at comparable levels of NH₂OH concentration and ionic strength for the two cases, and while a mechanistic interpretation may be possible, none is obvious. E.g., preferential interaction between NH₂OH and nitroxyl A for mechanistic reasons would seem to require some form of interaction between NH₂OH and HN₂O₃⁻. This seems wholly unlikely since the rate of HN₂O₃⁻ decomposition is indifferent to the presence of NH₂OH. In addition, it would be difficult to explain the dependence of product N₂/N₂O ratio on the concentration of NH₂OH in stoichiometric excess on the basis of a specific interaction hypothesis.

Seeking a difference in terms of unlike nitroxyl molecules, therefore, we consider the possibility that they are the two tautomers HNO and NOH. To the extent that the proportion of intermediate in deprotonated form may be crucial in determining the outcome of a competition between dimerization and NH₂OH reduction, we note that form A behaves as though it is fully deprotonated at pH 8, and form B at the higher pH 13. The behavior of form A is consistent with the pK reported for radiolytically produced nitroxyl.⁸ The difference cannot be simply a matter of proton location but must be preserved in the deprotonated forms; i.e., the difference is an electronic difference.

An SCF calculation by Gallup²³ indicates a singlet ground state for HNO and a triplet ground state for NOH, equilibrium angles 109 and 122°, respectively, an energy separation of the two ground states of no more than a few kilojoules but with HNO predicted to be the slightly more stable form, and a barrier of substantial height between the two tautomers. Both the small ground-state energy separation and the substantial barrier seem surprising in view of the fact that NOH does not appear to have been detected in the gas phase. Configuration interaction calculations have recently been carried out by Buenker and Marian,²⁴ similar to the previously reported CI calculations of Wu, Peyerimhoff, and Buenker for HNO.²⁵ These calculations reinforce the presumption that the HNO and NOH ground states have different multiplicities but show an energy separation of ca. 105 kJ mol⁻¹ at equilibrium ground-state configurations (108 and ~115°, respectively), with HNO as the more stable form. A substantial barrier would be required for interpretation of our nitroxyl B as NOH, if this energy separation is correct.

An alternative possibility is that nitroxyl B consists of HNO in an excited triplet state. Wu et al.²⁵ have predicted such a state for HNO at 68 kJ above ground state, and Ishiwata et al.²⁶ have observed such a low-lying state in a chemiluminescence study. This prediction is more quantitative than

that of Gallup,²³ who also identified a low-lying triplet excited state. While 68 kJ is too large a value to account for the observations we have made at thermal energies, further CI exploration by Buenker and Marian²⁴ indicate that the equilibrium form of triplet HNO may have a significantly larger bond angle (~130–140°) than the singlet (108°), in which case the *effective* relative stability of the two states may be much larger than indicated by the vertical energy difference of 68 kJ.

Thus if nitroxyl A is singlet HNO (which is not certain), then nitroxyl B may be singlet (excited) or triplet (ground-state) NOH (although Gallup's calculation²³ predicts a large energy separation in this case) or triplet (excited) HNO. No clear rationale seems accessible to distinguish among these possibilities on mechanistic grounds: abstraction of an N-bound hydrogen atom from NH₂OH could plausibly occur at either the nitrogen or oxygen ends of the NO radical. We continue our efforts to resolve this interesting and significant question.

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Registry No. HN₂O₃⁻, 67180-31-8; NO, 10102-43-9; NH₂OH, 7803-49-8; HNO, 14332-28-6.

References and Notes

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- The numerical values reported in Table I are somewhat higher than the rate constants reported in ref 2 and are in agreement with the values of Hughes and Wimbeldon.³ Reproducibility was generally better than in our earlier study, and we conclude that we may have encountered the atypical synthetic-batch phenomenon reported by Hughes and Wimbeldon.
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- A referee has pointed out the possibility that some of the HNO may be sidetracked to the formation of *trans*-HN₂O₂⁻, whose rate of decomposition to N₂O would not be rapid relative to the HN₂O₃⁻ decomposition. We agree that this possibility exists and that our measurements do not indicate the extent to which it occurs, if at all. It would appear to be a minor pathway at best, however, and we do not think its presence would affect our main argument concerning the competition between N₂O production and reduction to N₂ in the presence of NH₂OH.