minimum vertical separation occurs at an energy lower than that of the δ_u orbital in the undistorted molecule. Thus, populating δ_u in the bent geometry would require that additional energy be supplied in order for δ_u to be populated in the linear geometry. This additional energy either could be abstracted from the crystal or could originate from vibrational energy of the UO_2^{2+} ion itself if the total energy of the states at the crossover point were greater than that of the $^3\pi_u$ state in the linear molecule. In either case, a consequence of this analysis is that the TL intensity should decrease as the temperature is decreased, contrary to our experimental observations. Thus, the bending IMD is not a likely mechanism.

In contrast, the compression could populate the δ_u orbital. However, the energy of the crossing point is well above the energy of the δ_u orbital in the undistorted molecule. In order to assess the reasonableness of this mechanism, a quantitative estimate of the amount of compression needed to reach the crossing point is required. Using the harmonic oscillator approximation and the U–O force constant of 0.715 mdyn/Å,[22] a compression of 1.1 Å is required to raise the energy of the system to that observed in emission (2.5 eV). Because of the increase in anharmonicity in higher vibrational levels, the above compression is an overestimate. On the other hand, more than 2.5 eV is required to reach the crossing point requiring a larger compression. A compression on the order of 1 Å is probably a reasonable estimate. However, 1 Å represents a 50% shortening of the 2-Å U–O bond. It is difficult to imagine how such compression can occur before relaxation processes such as shear and fracture of the crystal release the pressure. However, although the compression IMD mechanism appears unlikely, it cannot be totally ruled out.

Although the UO_2^{2+} ion is ideal for analysis of the IMD mechanism, it does not lend itself as readily for analysis of the other triboexcitation mechanisms. Tribofluorescent compounds will probably be more suitable because the short-lifetime emission can capture dynamic features of the system under stress before complete mechanical relaxation can occur. The interpretation of the new spectral features will allow the plausibility of the other mechanisms to be assessed. These aspects of triboluminescence are currently under investigation in our laboratories.

Acknowledgment. This work was supported by the Army Research Office, Durham, N. C. Professor J. Enemark is also thanked for helpful comments.

Registry No. $UO_2(NO_3)_2 \cdot 6H_2O$, 13520-83-7.

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Thermal Decomposition of Oxyhyponitrite (Sodium Trioxodinitrate(II)) in Aqueous Solution[1]

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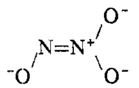
Received October 10, 1974 AIC40701J

The decomposition of $Na_2N_2O_3$ in aqueous solution has been studied over a wide range of pH values by kinetic measurements based upon uv absorption, by uv spectroscopy, and by tracer experiments using the labeled form $Na_2(O^{15}NNO_2)$. The decomposition is first order in $HN_2O_3^-$ and occurs at a rate that is independent of pH in the range <4 to >8 [$k_1 = (4.6 \pm 0.4) \times 10^{-4}$ sec^{-1} at 25°]. The reaction products are exclusively $N_2O + NO_2^-$, and the nitrogen atoms in the N_2O come exclusively from the N atom bound to a single O atom, at pH values 3 and above. The rate of decomposition of $N_2O_3^{2-}$ is low and decreases with increasing pH. The rate of decomposition of $H_2N_2O_3$ to give $N_2O + NO_2^-$ is greater than that of $HN_2O_3^-$. The only NO produced at pH 3 is formed by disproportionation of HNO_2, but at pH 2 a mixture of NO and N_2O is produced without any NO_2^- being detected. The nitrogen atoms in this N_2O product derive from both atoms in the $Na_2N_2O_3$. The reaction product is exclusively NO in strong acid. The value of λ_{max} falls from 250 nm at high pH to 237 ± 0.5 nm for solutions in which $HN_2O_3^-$ predominates; ϵ for $HN_2O_3^-$ has the value 5460 ± 240 M^{-1} cm^{-1} at 237 nm. A second peak is found at 196 nm for $HN_2O_3^-$, with some suggestion of a decline in λ_{max} at pH 3 and below. Angeli's hypothesis of HNO (or NOH) as intermediate in the decomposition and direct precursor of N_2O has been confirmed. It is postulated that N═N bond breakage to produce HNO and NO_2^- is the primary controlling process in acidic as well as in basic solutions. Under this postulate, directly produced NO in acid solution is not formed by a dehydration reaction but by a redox process in which a species related to HNO, possibly H_2NO^+, attacks NO_2^- or HNO_2.

Introduction

The decomposition of Angeli's salt ($Na_2N_2O_3$) to form N_2O and NO_2^- in neutral or alkaline medium is the process that led to the first speculation concerning existence of nitroxyl (HNO) as an intermediate species.[2] This substance, formally sodium trioxodinitrate(II), which we shall call oxyhyponitrite as suggested by Addison, *et al.*,[3] but which has been variously named nitrohydroxylamite and hyponitrate elsewhere in the literature, has been the subject of a number of investigations whose principal objects have been elucidation of structure.[3-8]

On the basis of these, culminating in the crystallographic study of Hope and Sequeira,[8] the structural assignment



appears unambiguous for the doubly charged anion. The placement of the proton on the monobasic anion is not certain, but it appears most plausible that the free acid (which has not been directly observed) would have one of its protons attached to the single oxygen atom bound to the left-hand nitrogen. Sturrock, *et al.*,[4b] reported values of 2.51 and 9.70 for pK_1 and pK_2, respectively. An earlier claim[9] that a peroxy form of oxyhyponitrite is formed by a reaction between dinitrogen tetroxide and hyponitrite has been disproven by Scott[10] and by Vosper.[11]

Pyrolysis of $Na_2N_2O_3$ produces $NaNO_2$, N_2, N_2O, NO, and O_2.[12] In solution, oxyhyponitrite is readily oxidized by atmospheric oxygen to nitrite.[13] In the absence of air, aqueous solutions of oxyhyponitrite have long been known to decompose slowly to the products NO_2^- and N_2O. Naik, *et al.*,[13] reported that this mode of decomposition occurs also in dilute acids and that solutions are substantially stabilized by the addition of strong base. It has also been known since the time of Angeli that upon addition of strong acid to $Na_2N_2O_3$ solutions, NO is produced. Cambi[14] has reported, and Hunt, *et al.*,[4a] confirmed, that the N atoms appear quantitatively as NO in the reaction between $Na_2N_2O_3$ solution and *ca.* 1.0 *M* H_2SO_4. The effect of pH on the distribution of products from the two decomposition reactions has been explored by Veprek-Siska, *et al.*,[15] by measurement of volumes of gases liberated upon complete decomposition of fixed quantities of $Na_2N_2O_3$ under varying conditions. From their results, the fourfold volume increase resulting from the shift from ($N_2O + NO_2^-$) to NO as reaction product appears to occur sharply at pH 5, with only a small suggestion of mixed products occurring in the range pH 5 to pH 3.

Kinetic studies of the decomposition of aqueous oxyhyponitrite have been limited in both number and scope. By comparing gas volumes evolved by samples of equal size in equal time intervals, Veprek-Siska, *et al.*,[15] have shown that decomposition of $Na_2N_2O_3$ in H_2O is quite slow and only modestly influenced by added OH^- at 20° but considerably faster and more pH dependent at 55°, for ca. 0.07 *M* $Na_2N_2O_3$ dissolved in base in the range 0–1.0 *M* OH^-. Spectrophotometric measurements reported by Smith and Hein[16] show an accurately first-order process that is relatively rapid (half-life *ca.* 10 min) and strongly inhibited by addition of OH^-, observations that conflict strongly with those of Veprek-Siska, *et al.* The temperature is not specified by Smith and Hein; also, since measures for the exclusion of air are not mentioned in their paper, it can plausibly be suspected that their observations pertain to oxidation of $Na_2N_2O_3$ and not the decomposition reaction.

Much of the interest in the decomposition of Angeli's salt has focused upon the presumed intermediate species nitroxyl as the precursor of N_2O. While this species has been observed by matrix isolation[17] and its anionic salts are well characterized, its existence is otherwise restricted to the role of kinetic intermediate. In the case of oxyhyponitrite decomposition, this role has not been unambiguously demonstrated, although Hendrickson and Jolly[6] have shown by ^{15}N labeling that nitrite is formed exclusively from the nitrogen that is bound to two oxygen atoms in the reaction between Ag^+ and $N_2O_3^{2-}$ to yield NO_2^-, Ag, and NO, demonstrating the formation of an intermediate NO^- (or AgNO) in that reaction.

In this paper we report the results of kinetic measurements of the thermal decomposition of oxyhyponitrite in aqueous solution and of experiments bearing on the conditions governing the appearance of NO as a decomposition product. In addition, we report the results of tracer studies in which ^{15}N has been incorporated in the nitrogen atom bound to a single oxygen atom in the anion $(O^{15}NNO_2)^{2-}$.

Experimental Section

Synthesis of $Na_2N_2O_3$. Crystalline $Na_2N_2O_3$ was prepared by the modification of Angeli's synthesis described by Hunt, *et al.*,[4a] *i.e.* by reaction between NH_2OH and $C_4H_9ONO_2$ in absolute methanolic solution containing $NaOCH_3$. Reactions were carried out at 0° under N_2, and best yields were obtained with NH_2OH in stoichiometric excess and with very long reaction times. Products were repurified by solution in minimum volume of H_2O and reprecipitation by addition of CH_3OH, with attendant loss such that 30% could be counted a good yield. The precipitate was dried *in vacuo* at 120° and stored under nitrogen in a drybox. Na analyses: calculated for $Na_2N_2O_3$, 37.70%; found (flame photometry), 37.8%; found (gravimetric), 37.6%.[18] Uv spectrum criterion of purity: the uv spectrum of a 2.250×10^{-4} *M* solution of our principal $Na_2N_2O_3$ product in 1 *M* NaOH showed a maximum at 250 nm with measured ϵ_{max} 8147 M^{-1} cm^{-1}, in reasonable agreement with Vosper's value of 8450 at the same wavelength.[11]

Synthesis of $Na_2(O^{15}NNO_2)$. This compound was synthesized by reaction between $^{15}NH_2OH$ (24.0 atom % ^{15}N; Prochem, Ltd.) and $C_4H_9ONO_2$. Small yield was deliberately accepted since a stoichiometric excess of NH_2OH could not be used: a pilot synthesis based upon 1.0 g of isotopically normal NH_2OH–HCl as starting material yielded 0.0230 g of $Na_2N_2O_3$ after careful purification and drying. The measured extinction coefficient of this product at 250 nm in 1 *M* NaOH is 7784 M^{-1} cm^{-1}. A similarly small yield of ^{15}N-labeled compound was prepared by an identical procedure.

Kinetics of Decomposition. The rate of decomposition of oxyhyponitrite was measured by uv spectrophotometry, using a Cary 14 spectrophotometer. Appropriate buffer solutions, generally at the 0.1 *M* concentration level, were prepared and transferred to an adapted reaction cell and reference cell under CO_2- and O_2-free conditions. $NaClO_4$ solution was added as needed for maintenance of particular ionic strength values. In some instances EDTA was added at the 10^{-4} *M* concentration level in an effort to improve reproducibility, but without notable effect on the rate constants obtained. Reaction and reference cells were held at constant temperature in the Cary 14 instrument, where the solution in the reaction cell was stirred and flushed with dry, O_2-free N_2 or Ar 0.5–1 hr before introduction of $Na_2N_2O_3$. Since it was established that $Na_2N_2O_3$ stock solutions could not be maintained even at very high pH without some decomposition, solid sodium oxyhyponitrite was added in an amount (*ca.* 15 mg) calculated to establish an initial concentration of about 10^{-4} *M*. Since initial studies provided a strong impression of a first-order process, it was unimportant that the exact initial concentration was unknown. Mixing, inert gas flushing, and temperature control were continued throughout each kinetic run.

Decomposition was followed by measuring the decrease in $N_2O_3^{2-}$ absorption, rather than increase in NO_2^- absorption, because of the very much greater extinction coefficients of the former. $Na_2N_2O_3$ solution shows a strong peak at λ_{max} 250 nm in strong base,[2] between the major NO_2^- maxima at 355 and 210 nm and hence not subject to interference from this source. With decreasing pH, however, λ_{max} falls as the monobasic anion $HN_2O_3^-$ becomes predominant; careful measurements at pH 8, 7, 6, and 3 yield the value λ_{max} 237 ± 0.5 nm. Optical absorbance measurements were made accordingly at this or a slightly lower wavelength. Single-wavelength absorbance was recorded continuously, and temperature control, flushing, and mixing were maintained, until completion of the decomposition reaction so that the quantity A_∞ could be measured. First-order reaction plots (log $(A_t - A_\infty)$ *vs.* *t*) were then constructed. In a small number of instances, at pH 5 (acetate buffer) and pH 8.5 (borate buffer), the Guggenheim method for first-order kinetics was applied,[19] with results that did not differ significantly from those obtained as described above.

In order to obtain more detailed information, a series of kinetic runs was carried out, over the pH range 1.9–8.0, in which broad sweeps of the uv spectrum were carried out at intervals, rather than continuous recording at a single wavelength. The information of interest was contained in the range 190–250 nm, the portion below 200 nm being included in order to incorporate a previously unreported $HN_2O_3^-$ peak at *ca.* 196 nm. In these instances, generally concordant rate constant

Table I. First-Order Rate Constants for $Na_2N_2O_3$ Decomposition at 25.0 ± 0.2°

pH	Buffer	μ	10^4k_1, sec^{-1}
13.0	KOH	0.10	0.0015[a]
12.0	KOH	0.50	0.012
10.0	H_3BO_3	0.50	0.92
9.0	H_3BO_3	0.50	2.9
7.9	KH_2PO_4	0.13	5.7
7.8	H_3BO_3	0.13	5.0
7.5	KH_2PO_4	0.13	5.1
7.2	KH_2PO_4	0.14	3.7 ± 0.6[b]
7.1	KH_2PO_4	0.12	4.0 ± 0.4[c]
6.0	KH_2PO_4	0.06	4.4
5.7	CH_3COOH	0.12	5.1
5.0	CH_3COOH	0.12	4.3 ± 0.3[d]
4.5	CH_3COOH	0.12	3.9
3.1	$HClO_4$	0.10	9.2
3.1	$HClO_4$	0.001	27
1.9	$HClO_4$	0.10	50

[a] Estimated. [b] Average of 17 measurements. [c] Average of 5 measurements. [d] Average of 4 measurements.

values were obtained by plotting log $(A_t - A_\infty)$ *vs.* t at several different values of λ.

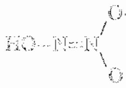
Decomposition of $Na_2(O^{15}NNO_2)$. Milligram-sized samples of ^{15}N-labeled oxyhyponitrite, synthesized as described above, were placed in a vessel with a side-arm compartment containing 10 ml of buffer or other solution at appropriate pH, in isolation from the salt. The solution was outgassed by a series of freeze–pump–thaw cycles and then added to the fully evacuated, $Na_2N_2O_3$-containing vessel, by opening a valve and rotating the side arm. Vigorous, immediate gas evolution was observed in every instance, generally followed by a period of more leisurely emission of gas bubbles from within a clear solution. After sufficient time had been allowed for essential completion of the reaction, the solution was frozen at Dry Ice–acetone temperature; the entire gas product was then passed through a helical trap at Dry Ice temperature and condensed into a sample bulb at liquid N_2 temperature. Mass spectra of these samples and of commercial N_2O at natural abundance for reference were obtained in a Consolidated-Nier mass spectrometer (Brookhaven National Laboratory).

Decomposition times were as follows: at pH 8.5 (borate buffer, $\mu = 0.13$, two runs), 22 hr; at pH 5.0 (acetate buffer, $\mu = 0.11$), 26 hr; at pH 3.0 ($HClO_4$–$NaClO_4$, $\mu = 0.11$), 120 min; at pH 2.0 ($HClO_4$–$NaClO_4$, $\mu = 0.13$), 60 min; in 1 *M* $HClO_4$, 1 *M* HCl, and 0.5 *M* H_2SO_4, 15 min. Temperature of the reaction vessel was controlled at 24.5°.

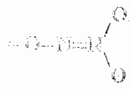
Results and Discussion

Kinetic Studies. First-order rate constants measured over a broad pH range are given in Table I, with information concerning the buffers or other solutions employed and corresponding ionic strengths. The value at pH 13 is an estimate based upon experience with a stock solution at that concentration, over several weeks' time. Uncertainties of measurement must be counted as substantial in all instances, as is indicated by deviations from mean values in instances of multiple repetition. Despite extreme care and attention to standardization of procedures, the measurements proved to be relatively poorly reproducible for reasons that we did not succeed in identifying. The extreme values in the case of the 17 runs at pH 7.2, for example, were 2.9×10^{-4} and 5.5×10^{-4}. In addition to the problem of reproducibility, the first-order kinetic plots showed other erratic aspects. While many of them were absolutely straight lines over 4 or 5 half-lives, others would exhibit slight curvature after 1–3 half-lives, corresponding to small decreases in rate. In a few instances curvature was observed in the initial portion, followed by satisfactorily linear regions; the cause in these cases was probably initial inhomogeneity of the solution. The majority of values shown are based upon regions of linearity extending over at least 2 half-lives, and the extent of observed curvature was small in every case. No obvious order other than first order was found applicable in analyzing the data. We are confident that the primary process in this reaction is kinetically first order in oxyhyponitrite, although it is clear that there are secondary perturbations on the process that we are not in a position to interpret.

The data show that the rate of decomposition is essentially independent of pH in the region pH 4.5–8 and that it is markedly and increasingly retarded above pH 9 and increases at pH 3 and below. A species distribution curve based upon the values of Sturrock, *et al.*,[4b] for pK_1 and pK_2 (2.51 and 9.70, respectively) shows that $HN_2O_3^-$ should be the overwhelmingly predominant species in the range of observed rate constancy (96% at pH 4, 93% at pH 8.5). These rates therefore correspond to the decomposition of that species, *via* a mechanism most plausibly involving the rupture of bonds between nitrogen atoms in either



or



consistent with the Angeli hypothesis

$$HN_2O_3^- = NO_2^- + HNO \text{ (or NOH)}$$

If the anion is protonated on the single-oxygen end, the intermediate would more plausibly be NOH, but if the proton is bound to the two-oxygen nitrogen, it could itself play a role in an intramolecular rearrangement leading to N=N bond rupture and formation of HNO as intermediate, the form that has been identified by matrix isolation.[17]

At high pH the species $N_2O_3^{2-}$ predominates, and it is clearly more stable against thermal decomposition than $HN_2O_3^-$. The possibility that decomposition proceeds entirely through the protonated anion, which would constitute *ca.* 0.05% of the total at pH 13, is not ruled out by our observations. At the lower pH range the rate of decomposition increases, presumably because of an increasing proportion of undissociated dibasic acid $H_2N_2O_3$ (24% at pH 3, 76% at pH 2), whose stability against thermal decomposition would thus appear to be less than that of $HN_2O_3^-$. This is a question requiring more detailed information, however, since it is known that NO appears as a product under acid conditions.

The only rate data previously reported in the literature refer to measurements obtained in strongly alkaline solution. Veprek-Siska, *et al.*,[15] reported a measurement based on the volume of N_2O evolved by $Na_2N_2O_3$ added to H_2O in fixed time. From the concentration given we calculate that the initial pH would have been about 9.6, and the decomposition rate at 20° appears to be considerably slower than our observation at pH 10. Smith and Hein[16] reported data for decomposition of $Na_2N_2O_3$ added to H_2O, at an unspecified temperature, from which we calculate the value $k_1 = 1.0 \times 10^{-3}$ sec^{-1}. Since the pH was high in this instance (but cannot be calculated from the information given), this is clearly very much faster than our observed rates. However, Veprek-Siska, *et al.*, have also reported a measurement of the rate of O_2 uptake by $Na_2N_2O_3$ solution, at initial pH 9.6 and 20°, from which we compute a rate constant $k_1 = 7 \times 10^{-2}$ sec^{-1} (assuming a process first order in $N_2O_3^{2-}$). While this is greater than the rate reported by Smith and Hein, it was presumably carried out in the presence of pure O_2 and tends to confirm our suspicion that the results of Smith and Hein pertain to a predominantly oxidative process due to incompletely excluded atmospheric O_2.

Spectral Studies. Decomposition was carried to completion

Table II. $Na_2(O^{15}NNO_2)$ Decomposition Experiments

Row no.		N_2O	pH 8.5 (1)	pH 8.5 (2)	pH 5.0	pH 3.0	pH 2.0	$HClO_4$ (1 *M*)	HCl (1 *M*)	H_2SO_4 (0.5 *M*)
1	46	0.0021	0.0876	0.0873	0.0474	0.095	0.032	0.0066	0.0066	0.0058
2	45	0.0078	0.582	0.570	0.413	0.600	0.349	0.0386	0.0420	0.0306
3	44	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
4	31	0.0020	0.206	0.186	0.135	0.215	0.434	2.24	2.36	1.79
5	30	0.491	0.718	0.661	0.625	0.734	3.01	16.0	16.87	12.8
6	$46/\Sigma N_2O$	0.0021	0.0525	0.0526	0.0325	0.0559	0.023	0.0063	0.0063	0.0056
7	$45/\Sigma N_2O$	0.0077	0.349	0.343	0.283	0.353	0.253	0.037	0.0400	0.0299
8	$44/\Sigma N_2O$	0.990	0.599	0.602	0.685	0.588	0.724	0.957	0.953	0.964
9	$31/\Sigma NO$	0.0041	0.222	0.220	0.178	0.227	0.126	0.123	0.123	0.124
10	$\Sigma N_2O/(\Sigma N_2O + \Sigma NO)$	0.675	0.644	0.661	0.661	0.642	0.286	0.0545	0.0516	0.0665
11	$[2(46) + 45]/2\Sigma N_2O$		0.226	0.224	0.204	0.232	0.149	0.025	0.026	0.020

at pH 8 in borate buffer, with sweeps of the wavelength range 190–250 nm carried out at periodic intervals. Oxyhyponitrite peaks were observed at 237 and 196 nm; in successive spectra the absorbance at these wavelengths decreased, and a peak at 210 nm, characteristic of NO_2^-, appeared and grew. The succession of spectra produced two isosbestic points, at 220 and 199 nm. Similar spectral patterns were observed in phosphate buffer at pH 8, 7.5, 7.0, and 5.7. Plots of absorbance *vs.* wavelength were used to obtain the value 237 ± 0.5 nm for λ_{max} in $HN_2O_3^-$, and ϵ was determined to be 5460 ± 240 M^{-1} cm^{-1} at that wavelength.

In similar experiments carried out in acetate buffer at pH 5.7, 5.0, and 4.5, successive spectra established a clean intersection at 220 nm, showing the simultaneous growth of NO_2^- and decay of $HN_2O_3^-$, but absorbance declined steeply below this wavelength in all spectra so that the second isosbestic point was obscured. We have identified no specific interaction as the cause of this change of spectroscopic properties.

Experiments were carried out at pH 3.1, using $HClO_4$–$NaClO_4$ solution. (Since these solutions are not buffered, some change of pH was expected; measured pH values upon completion of the two experiments were 3.3 and 3.6.) Isosbestic points were observed at 217 and 202 nm in these experiments. Absorbance at 210 nm at this pH was observed to rise through a maximum and then gently decline after approximately 1 hr. It is clear that NO_2^- is a principal product of the decomposition at this pH, and the decline in its concentration is clearly ascribable to disproportionation of HNO_2 to NO and NO_3^-.

An experiment carried out with HCl at pH 3 also showed clear and unmistakable growth in the 210-nm peak. However, a second experiment carried out with HCl at pH 2.5 showed the expected decay of $HN_2O_3^-$ peaks, but only a suggestion of absorption at 210 nm. Finally, in an experiment using $HClO_4$ + $NaClO_4$ at pH 1.9 only oxyhyponitrite decay was observed; no NO_2^- peak at 210 nm appeared. While disproportionation of HNO_2, if any were formed, would be faster in these last two cases than at pH 3, the well-known kinetics of that reaction are such that a 210-nm peak would have appeared and risen through a maximum, as at pH 3 but over a shorter period of time. Furthermore, since NO_3^- is a product of the disproportionation and NO_3^- also absorbs in the region around 210 nm, we would eventually have seen some growth at that wavelength if NO_2^- had formed in the decomposition.

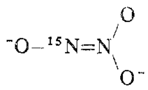
We conclude that the decomposition proceeds by N=N bond breakage, leading to NO_2^- formation, at pH values as low as 3.0. This is at variance with the report of Veprek-Siska, *et al.*,[15] that a break in decomposition products occurs at pH 5 and also with that of Sturrock, *et al.*,[4b] who reported that decomposition directly to NO occurs at pH values 4.6 and below. Our results indicate that the first NO to appear, at pH 3, is a product of HNO_2 disproportionation and not $H_2N_2O_3$ decomposition, a conclusion that is reinforced by evidence reported in the following section of this paper. Since disproportionation is a relatively slow reaction, and very highly pH dependent, the amount of NO product will depend upon the total reaction time at any given pH. Veprek-Siska, *et al.*, based their conclusions upon total gas volume evolved for "complete decomposition" of $Na_2N_2O_3$ in unspecified time. Their total gas volumes could include substantial proportions of NO from disproportionation; for complete decomposition to N_2O + NO_2^-, followed by complete disproportionation of HNO_2, 1 mol of $HN_2O_3^-$ would give rise to $^1/_2$ mol of N_2O + $^1/_3$ mol of NO, for a total of $^5/_6$ mol. The NO detected by Sturrock, *et al.*, below pH 4.6 was also probably produced by disproportionation. Inadvertently incomplete exclusion of O_2 could also lead to erroneous impressions about NO as product, since 1 mol of $N_2O_3^{2-}$ produces 2 mol of NO_2^- under oxidative conditions, which upon complete disproportionation would produce $^2/_3$ mol of NO gas (itself subject to oxidation, however).

To confirm our conclusion that the observed decline in absorbance at 210 nm at pH 3.0 was associated with HNO_2 disproportionation, a solution of $NaNO_2$ in $HClO_4$–$NaClO_4$ at pH 3.0 was placed in the reaction cell with the usual rigorous exclusion of air. Gradual decline in the 210-nm peak was observed. In an experiment carried out under identical conditions but without exclusion of air, a gradual increase at 210 nm was observed. In the absence of O_2, 1 mol of HNO_2 gives rise to $^1/_3$ mol of NO_3^- upon disproportionation, but in the presence of O_2 the product NO is oxidized to NO_2, which undergoes disproportionative hydrolysis, with ultimately complete conversion to NO_3^-. The observed rise in absorbance at 210 nm results from the fact that $\epsilon_{NO_3^-} > \epsilon_{NO_2^-}$ at this wavelength.

The existence of a sharp break in decomposition products below pH 3 appears to be established by our uv absorption measurements and confirmed by the results reported in the next section. The experiment conducted at pH 2.5 in HCl shows only a suggestion of a transient peak at 210 nm, and the experiment at pH 1.9 in $HClO_4$–$NaClO_4$ solution shows none whatever. The decay of absorbance at 237 nm ($HN_2O_3^-$) at this pH is accurately first order over about 6 half-lives. A spectrum of the reaction solution covering the range 200–390 nm after 14 min of reaction time shows none of the spectral features characteristic of HNO_2, although disproportionation of any NO_2^- product would be far from complete under these conditions.[20] The maxima in the two oxyhyponitrite absorptions are found at 237.0 and 193.5 nm in this spectrum and at pH 3.0; the shift of λ_{max} in the second of these peaks (down from 196 nm at higher pH) may be an indication of the presence of $H_2N_2O_3$, although the precision in this region, in which wide slit opening is required, is such that we cannot be certain about this point.

Decomposition of $Na_2(O^{15}NNO_2)$. Mass spectra for tank N_2O at natural abundance and for product gas obtained by decomposition of ^{15}N-labeled oxyhyponitrite in borate buffer at pH 8.5 (two runs), at pH 5.0 in acetate buffer, at pH 3.0 and 2.0 in $HClO_4$–$NaClO_4$ solution, in 1 *M* $HClO_4$, in 1 *M* HCl, and in 0.5 *M* H_2SO_4 are given in Table II. All peak heights, appropriately corrected for background, are reported relative to mass 44. Neglecting the contributions of naturally abundant ^{17}O and ^{18}O and assuming negligible contribution of the species $^{15}N^{15}N$, the peaks at masses 46, 45, 44, 31, and 30 are taken to correspond to the species $^{15}N^{15}NO$, ($^{15}N^{14}NO$ + $^{14}N^{15}NO$), $^{14}N^{14}NO$, ^{15}NO, and ^{14}NO, respectively. The quantities $\sum N_2O$ and $\sum NO$ represent the peak height sums (46 + 45 + 44) and (31 + 30). The parent N_2O molecule undergoes rupture to form NO on electron impact to a considerable extent, as shown by the presence of a sizable mass 30 peak in tank N_2O. In row 10 of Table II it is seen that the proportion of parent N_2O^+ peaks to all $N_2O^+ + NO^+$ peaks is essentially the same in gas produced by $Na_2N_2O_3$ decomposition at pH 8.5, 5.0, and 3.0 as in tank N_2O; the product is thus nearly entirely N_2O at those pH values.

From the results of Hendrickson and Jolly[6] we anticipated that ^{15}N incorporated through hydroxylamine in the synthesis of $Na_2N_2O_3$ should find its way exclusively to the position shown



$$^{-}O-^{15}N{=}N(O)O^{-}$$

Upon N=N rupture the unlabeled N atom should thus remain in solution as NO_2^- and ^{15}N would appear exclusively in N_2O under conditions leading to these two products alone. This expectation is borne out in row 11 of Table II, where the quantity shown corresponds to the fraction of ^{15}N atoms present in all forms of N_2O. The hydroxylamine used in synthesis contained 24% ^{15}N; the values at pH 8.5 and 3.0 are sufficiently close to that value, and the value at pH 5.0 is nearly so, that we can assert the nitrogen of hydroxylamine has been quantitatively converted to N_2O, *via* $Na_2(O^{15}NNO_2)$.

If the product N_2O is formed from a symmetric precursor intermediate, such as would be the case if HNO (or NOH) resulting from N=N bond cleavage were to dimerize to form hyponitrous acid HO—N=N—OH (Angeli's hypothesis), ^{15}N atoms should be randomly distributed among the various isotopic varieties of N_2O. For this case, we predict 5.8% of N_2O at mass 46, 36% at mass 45, and 58% at mass 44. In rows 6–8 of Table II it can be seen that these predictions are adequately corroborated for N_2O produced at pH 8.5 and 3.0. Additional corroboration of randomness at these pH values is found in row 9: the NO produced by electron impact bond breakage has the same ^{15}N content as total N_2O (row 11), showing that $^{15}N^{14}NO$ and $^{14}N^{15}NO$ are present in equal amounts. (Randomization by rearrangement following electron impact is ruled out since it has been shown that such rearrangement occurs only to the extent of a few per cent.[21])

The results of our experiment at pH 3.0 are remarkably similar to those at high pH, corroborating our conclusion that the products are nearly exclusively N_2O and NO_2^- at these extremes and that the reaction pathways are thus identical. (The duration of the pH 3 experiment was not long enough to permit significant formation of NO by disproportionation.) If the value $pK_1 = 2.5$ is correct,[4b] the compound should be 24% $H_2N_2O_3$ at pH 3. To the extent that undissociated acid may be present at this pH, its effect is limited to an increase in rate of decomposition (see Table I), since there is absolutely no effect on the distribution of products.

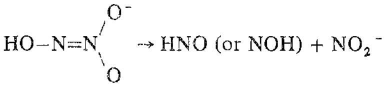
The experiment at pH 5, carried out in an acetate buffer medium, indicates that some modification of pathway may result from the presence of acetate: the proportions of $^{15}N^{15}NO$ and ($^{15}N^{14}NO$ + $^{14}N^{15}NO$) are distinctly smaller, and the total ^{15}N present in both N_2O and NO peaks is somewhat smaller than the proportion introduced *via* hydroxylamine, although the value in row 10 indicates that the product gas is entirely N_2O. As reported in the preceding section, the uv spectroscopy of reaction mixtures based on acetate buffer showed distinct differences from the other systems. However, we cannot be certain that a difference in pathway exists on the basis of the single experiment reported here, and we note that the rate of decomposition in acetate buffers appears to be no different from other buffer systems (see Table I).

The experiment carried out at pH 2.0 shows a product gas that is a mixture of N_2O and NO (row 10), containing perhaps 40–50% of N_2O, showing direct production of NO for the first time. The NO observed mass spectrometrically, a mixture of reaction product NO and NO produced by electron impact on N_2O, contains 12.6% ^{15}N, *i.e.*, a nearly twofold isotopic dilution, implying that both N atoms in $Na_2N_2O_3$ have come into play. That there has been isotopic dilution of the nitrogen in N_2O is shown by the value in row 11, 14.9% ^{15}N; it is substantial, but less than twofold. It seems probable that the directly produced NO, seen here for the first time, incorporates N atoms at random from both halves of the oxyhyponitrite and that the N_2O is produced in part by a new route which involves both N atoms and in part by the same route which predominates at pH 3.

The three experiments in concentrated acid show essentially identical results. The product gas is nearly entirely NO, of just the isotopic composition which would be expected for a quantitative reaction in which both atoms in $Na_2(O^{15}NNO_2)$ are incorporated in NO. Although we took extraordinary precautions to exclude carbonate, it seems possible that most of the small mass 44 peak may be ascribable to CO_2 rather than N_2O, since the mass 45 and 46 peaks would otherwise be somewhat greater than observed.

Summary and Conclusions

Thermal decomposition of oxyhyponitrite is first order in $[HN_2O_3^-]$, and its rate is independent of pH in the range of pH about 4 to somewhat greater than 8. The decomposition of $N_2O_3^{2-}$ is very much slower than that of $HN_2O_3^-$, and the products of decomposition are exclusively N_2O and NO_2^- at pH 3 and above. The nitrogen atoms in N_2O produced at both ends of this range derive exclusively from the single-oxygen atom in $HN_2O_3^-$ and are randomly distributed, in apparent confirmation of Angeli's hypothesis of nitroxyl as intermediate



$$HO-N{=}N(O^{-})O \rightarrow HNO\ (or\ NOH) + NO_2^{-}$$

$$2HNO\ (or\ NOH) \rightarrow HO-N{=}N-OH$$

$$HO-N{=}N-OH \rightarrow N_2O + H_2O$$

(It is possible, but not proven, that some modification of this pathway may occur in the presence of acetate.) It should be noted that the actual formation of hyponitrous acid, while assumed in most existing literature, is not a requirement for interpretation of the evidence. It is known that N_2O exchanges oxygen with H_2O only extremely slowly if at all,[22] and it seems reasonable to discount the dehydration mechanism in favor of direct production of N_2O by interaction between HNO molecules

$$HNO + HNO \rightarrow N_2O + H_2O$$

i.e., to consider $H_2N_2O_2$ a transition state rather than an intermediate.

The appearance of NO as product first occurs at pH <3 in what seems to be an abrupt appearance of a new process, for which NO_2^- is not a product, and which is accompanied by a striking increase in the rate of overall oxyhyponitrite decomposition. The production of NO has been universally treated in the literature as a dehydration reaction

$$H_2N_2O_3 \rightarrow 2NO + H_2O$$

If this is the predominant mode of $H_2N_2O_3$ decomposition, however, NO should surely be produced in increasing proportion as pH is decreased and the fraction of $H_2N_2O_3$ increases. Instead, however, NO is not observed as product at pH 3 although this fraction should be 24% if $pK_1 = 2.51$. (This value may be open to some question, since it is based upon potentiometric titrations which were not extended below pH 4.6.[4b]) Also, although a mixture of N_2O and NO is found at pH 2 and the NO contains N atoms from both sides of the $H_2N_2O_3$ molecule, the N_2O appears to include some atoms from both sides also, in contrast to the observations at higher pH. This does not appear to be consistent with a simple competition between N=N breakage-controlled and dehydration-controlled processes. It is known that NO does not exchange oxygen atoms with H_2O under a broad range of conditions,[23] and again it seems reasonable to discount the dehydration mechanism. (It is also known that no oxygen atoms from solvent H_2O appear in the N_2O product of $HN_2O_3^-$ decomposition.[22])

We postulate that cleavage of the N=N bond in oxyhyponitrite to form asymmetric products remains the primary process in its decomposition in strongly acidic as well as basic solutions. That the rate of this cleavage is faster for the doubly protonated form than for $HN_2O_3^-$ is illustrated by the observed increase in rate at pH 3, an increase that is not accompanied by production of NO. Thus, we believe that the decomposition rate is controlled by the production of HNO (or NOH) and NO_2^- at all conditions. Over the vast pH range ~3–8, N_2O is produced in a rapid-follow process involving only nitroxyl. Below pH 3, we postulate the inception of a competing rapid-follow process, which quickly becomes dominant, in which a species derived from HNO attacks NO_2^- (or HNO_2), producing NO in a redox reaction. In view of the sharp pH dependence, we speculate that this species could be H_2NO^+, for example, in which case the final NO producing reaction would be the process

$$H_2NO^+ + NO_2^- \rightarrow 2NO + H_2O$$

or

$$H_2NO^+ + HNO_2 \rightarrow 2NO + H_3O^+$$

That it cannot be the increasing concentration of HNO_2 with decreasing pH that is the critical factor in NO production is demonstrated by the fact that there is no direct NO product at pH 3, although a large proportion of nitrite produced at that pH would be rapidly protonated. This factor may well play an important role in the rapid rise in decomposition rate at low pH values, however. Finally, in order to account for the apparent scrambling of nitrogen atoms in the N_2O that constitutes a portion of the product gas at pH 2, we speculate that the transition-state species ($H_2N_2O_3$ or $H_3N_2O_3^+$) must have some tendency to re-form HNO, a tendency that rapidly gives way to direct NO production with decreasing pH.

Registry No. $Na_2N_2O_3$, 13826-64-7; $Na_2(O^{15}NNO_2)$, 53716-33-9.

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Self-Consistent Field Calculation of Nitrosyl Hydride and Nitrogen Hydroxide

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Received July 26, 1974 AIC40508P

SCF calculations of nearly double-ζ quality have been done on the nitrosyl hydride molecule and its isomer, HON. The system is found to have a low-lying triplet state, which is expected to aid in the dimerization to $H_2O_2N_2$, hyponitrous acid.

Some interest has been centered upon nitrosyl hydride, HNO, as a system which is produced in an excited state by the reaction of H and NO. There is subsequent chemiluminescence, presumably from the transition $^1A''$ to $^1A'$. Thrush and his coworkers have studied this reaction extensively.[1] The spectrum of HNO has been obtained both in the gas phase[2] and in the solid.[3] In the gas phase HNO is known to undergo further reaction, the first step of which is apparently dimerization to $H_2N_2O_2$.[4]

On the theoretical side Peslak, Klett, and David[5] and Ditchfield, Del Bene, and Pople[6] have given SCF calculations of the geometry of HNO, and Salotto and Burnelle[7] have given calculations using the unrestricted Hartree–Fock method. Peslak, Klett, and David have also examined the geometry of the isomer HON, nitrogen hydroxide. Krauss[8] has examined this system to test mechanisms for the H–NO afterglow.

The various properties of HNO which lead to these observations have been attributed to the effect of the perturbation of the hydrogen atom on the diatomic molecule orbitals of NO by Orgel.[9] Heretofore, such considerations have apparently been qualitative only, and it is of considerable interest to examine the perturbation of these orbitals with *ab initio* techniques. Therefore, a series of calculations was undertaken to examine both the orbital energies and the total energy as