Nitrogen-15 Magnetic Resonance Spectroscopy of Trioxodinitrate: N-Protonation of an Oxoanion[1]

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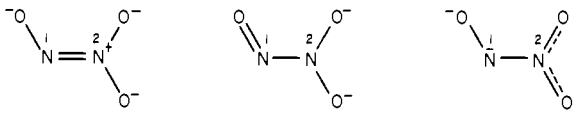
Abstract: ^{15}N NMR spectra have been obtained for anion I. In the deprotonated form $N_2O_3^{2-}$ (pH 13), resonances occur at 355.2 and 339.5 ppm for N(1) and N(2), respectively, referred to $NH_3(l)$. The N(2) resonance position remains unchanged in the monoprotonated form $HN_2O_3^-$ (pH 7.8), while the N(1) resonance undergoes a 24-ppm upfield shift (pH 8), indicating protonation at N(1). This conclusion is corroborated by an observed NOE = −2.1 for N(1) at pH 8. The coupling constant $^1J_{^{15}N-^{15}N}$ = 16.6 Hz for $N_2O_3^{2-}$. Both ^{15}N resonances exhibit broadening with decreasing pH, to an extent that is substantial in the case of N(2), which also shows a small upfield shift between pH 7.8 and pH 6.8. Implications of these results for interpretation of the protonation-induced destabilization of the anion are discussed.

In recent studies of the thermal decomposition of trioxodinitrate in aqueous solution,[3-6] it has been demonstrated that the dibasic anion $N_2O_3^{2-}$ is destabilized upon protonation to the monobasic form $HN_2O_3^-$, which decomposes in a first-order process to form nitrite and the reactive intermediate species nitrosyl hydride (HNO). The latter rapidly dimerizes to form N_2O, unless hydroxylamine is present, in which case a competing, pH-dependent reduction to N_2 is observed.[7] The rate of thermal decomposition is remarkably independent of pH in the range ca. 4–8,[3,4] corresponding to the region of predominance of $HN_2O_3^-$ over $N_2O_3^{2-}$ and $H_2N_2O_3$, in keeping with the reported values pK_1 = 2.51 and pK_2 = 9.72.[8] At low pH an even greater degree of destabilization is introduced by a number of complex interactions with HNO_2,[4,6] but Hughes and Wimbledon have shown that $H_2N_2O_3$ of itself is more stable against thermal decomposition, as opposed to its behavior in the (unavoidable) presence of HNO_2, than $HN_2O_3^-$.[4] *trans*-Hyponitrous acid, $H_2N_2O_2$, and its dibasic anion $N_2O_2^{2-}$ exhibit analogously high stability relative to the monoprotonated anion $HN_2O_2^-$.[9]

From crystallographic data[10] it is clear that the anion $N_2O_3^{2-}$ exists predominantly in resonance form I, with only minor con-



I II III

tributions from forms II and III. Normal electrostatic considerations would lead one to expect protonation to occur at a charge center on oxygen at either side of the anion. However, a lone pair is available at N(1) in I, and that atom could conceivably become the site of first protonation. N-Protonation could also occur at either N(1) or N(2) in II, and at N(1) in III, to the extent that these resonance forms may be significant in solution. It is of interest to know where protonation occurs, to assist interpretation of the observed N–N bond destabilization. In addition, a study of the nitric oxide–hydroxylamine reaction has produced evidence of a nitrosyl hydride intermediate with properties different from those of the species produced by $HN_2O_3^-$ decomposition.[7] Since one of these species may be HNO and the other NOH, with their deprotonated forms NO^- in distinct electronic states, detailed interpretation of $HN_2O_3^-$ decomposition may assist identification of the species produced in that process.

We report here the results of a study of $N_2O_3^{2-}$ and $HN_2O_3^-$ by ^{15}N NMR. Prior NMR measurements on trioxodinitrate have been restricted to the dibasic ion. Logan and Jolly are reported[11] to have observed a single ^{14}N resonance, at 310 ppm downfield from aqueous NH_4Cl, for $Na_2N_2O_3$ in 0.5 M NaOH. Mason et al.[12] report a single broad-line ^{14}N NMR resonance whose shape suggests two unresolved lines, for $Na_2N_2O_3$ in 0.1 M NaOH, at 368 ppm downfield from saturated NH_4^+(aq). Schultheiss and Fluck[13] have reported ^{15}N resonances at 309.5 and 325 ppm downfield from aqueous NH_4Cl (unspecified concentration) for $Na_2N_2O_3$ containing 30% ^{15}N at both N positions and a coupling constant $^1J_{^{15}N-^{15}N}$ of 16.9 Hz. This measurement was carried out in D_2O solution at room temperature, and since no addition of NaOD is reported, we assume that the basicity of the solution was fixed by the (unspecified) concentration of the strong base $N_2O_3^{2-}$, in which case the value of pD would have been very much lower than that of 0.1 M NaOD, but the concentration of $N_2O_3^{2-}$ would still have been overwhelmingly greater than that of $DN_2O_3^-$. Arguing on the basis of the small observed isotope shifts due to $^{15}N-^{14}N$ interaction, Schultheiss and Fluck assigned the lower field resonance (325 ppm) to N(2) and the high field resonance (309.5 ppm) to N(1). As will be seen below, the correct assignment is reversed.

Experimental Section

$Na_2O^{15}NNO_2$ was synthesized as previously described,[3,6] employing $^{15}NH_2OH$·HCl at 95% ^{15}N (Prochem). $Ag^{15}NO_3$ was prepared from $H^{15}NO_3$ (8.8 M, 95% ^{15}N, Weizmann Institute) by ion exchange (Dowex 50W-X8, Ag^+ form) and then treated with C_2H_5I in ethanolic solution to form $C_2H_5O^{15}NO_2$,[14] which was vacuum distilled at room temperature and subsequently treated with NH_2OH to form $Na_2ON^{15}NO_2$ and separately with $^{15}NH_2OH$ to form $Na_2O^{15}N^{15}NO_2$. High yields are not realized in these syntheses, particularly so when NH_2OH cannot be used in stoichiometric excess, a circumstance that imposed severe limitations

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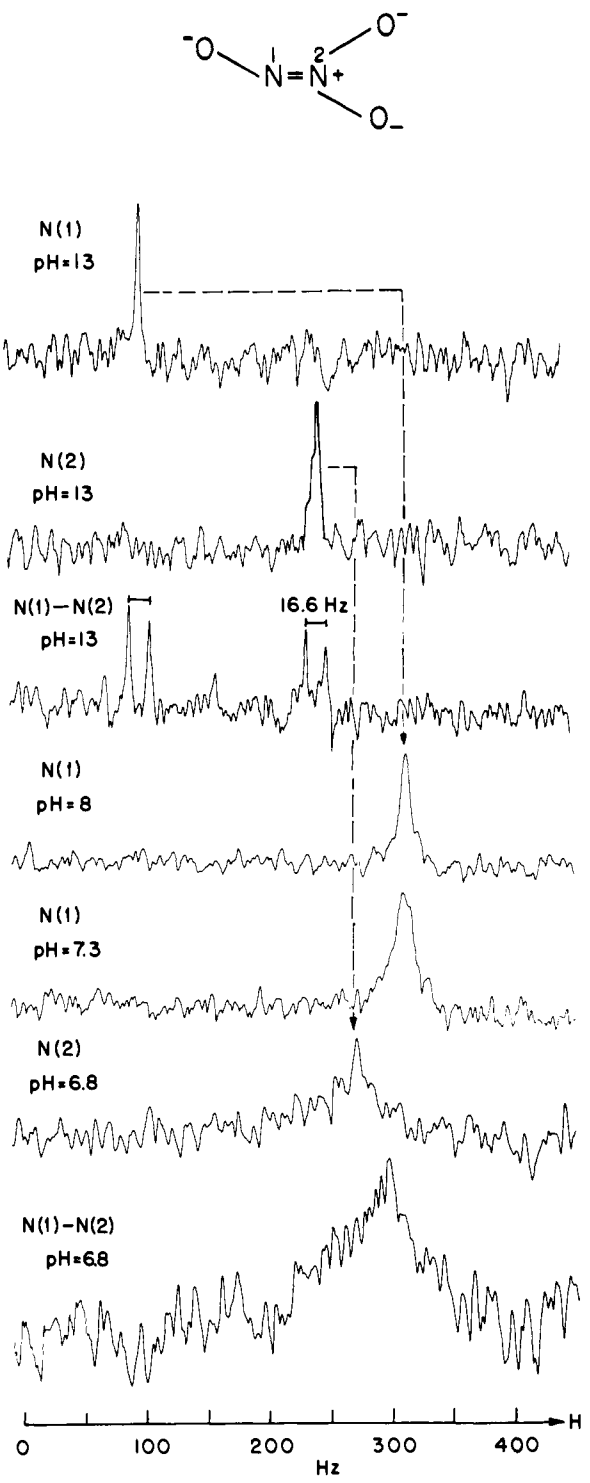


Figure 1. ^{15}N NMR spectra of trioxodinitrates as reported in Table I. (Monoprotonated $ON^{15}NO_2H^-$ at pH 7.8 has been omitted.)

on the quantities of isotopic compounds available for NMR measurements. For each measurement, 1 mL of aqueous solution (containing 20% D_2O) in the trioxodinitrate concentration range ca. 0.2–0.5 M was employed. For the deprotonated form, the $Na_2N_2O_3$ was dissolved in 0.1 M NaOH. For the monoprotonated form, $Na_2N_2O_3$ was first dissolved in the H_2O/D_2O solvent, and solid boric acid was then added to the solution in an amount observed with natural abundance material to bring the pH to 8.5 or below, i.e., using the strong base $N_2O_3^{2-}$ itself to produce the needed conjugate in the borate buffer system. (Total boric acid/borate concentrations were around 1 M.) The pH of each such solution was measured directly. In several instances the pH was remeasured after trioxodinitrate decomposition had gone to completion; no variation in excess of 0.1 unit was observed. NMR measurements were carried out in $HN_2O_3^-$ at two different pH levels, with consequences to be described in the next section.

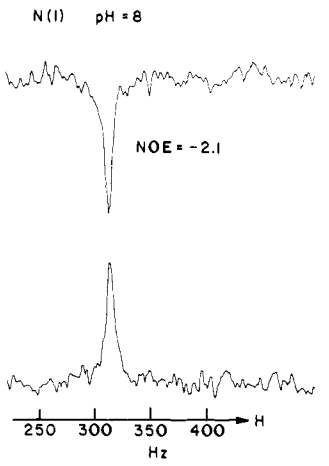


Figure 2. Measurement of NOE in the $^{15}N(1)$ resonance at pH 8.0: upper, fully decoupled; lower, gated decoupled.

Because trioxodinitrate is readily air-oxidized to nitrite, all solution preparations were carried out under N_2, employing N_2-deaerated solvent. Since $HN_2O_3^-$ decomposes at 25 °C with a half-life of 20 min, monoprotonated solutions were prepared at 0 °C, and all NMR measurements were carried out at 5 ± 1 °C. The value of $\Delta H^{\ddagger}$ for the thermal decomposition is 100 kJ mol^{-1} (Hughes and Wimbledon,[4] corroborated by us for purposes of this study) so that the half-life is extended to 6 h at 5 °C. For each experiment, the N_2-filled, 10-mm NMR tube was sealed immediately after solution preparation.

^{15}N NMR measurements were performed at 9.12 MHz on a Bruker WH-90 pulse-FT spectrometer equipped with variable-temperature accessories which maintain temperature to ±1 °C. The spectrometer was locked on internal D_2O. Chemical shifts were measured relative to an external 8.8 M HNO_3 solution (95% ^{15}N). Each spectrum is the Fourier transform of the accumulation of the free induction decays (16 000 data points) of several radiofrequency pulses (200–2000), each of 75° flip angle, with 10–15-s recovery between pulses. These NMR conditions were chosen on the basis of preliminary T_1 measurements. NOE effects were studied by using 3–4-W broad-band proton noise decoupling.

Results and Discussion

The results of our experiments are displayed in Figures 1 and 2 and Table I; their major features may be summarized as follows.

(1) Sharp resonances are observed for N(1) and N(2) in the deprotonated anion, separated by 15.7 ppm, with the N(1) resonance downfield from N(2).

(2) Doubly labeled, deprotonated compound provides two well-resolved doublets; the measured coupling constant $^1J_{^{15}N-^{15}N}$ is 16.6 Hz.

(3) The ^{15}N resonance for N(1) is shifted upfield 23.9 ppm by reduction of the pH from 13 to 8.0, i.e., by formation of the monoprotonated anion. The position of this resonance is not affected by further reduction of pH to 7.3. However, the N(1) resonance at pH 8 is slightly broadened with respect to the deprotonated form and more so at pH 7.3.

(4) The position of the ^{15}N resonance for N(2) is effectively unchanged by protonation: the pH 13 (deprotonated) and pH 7.8 (monoprotonated) values are the same within error. However, an upfield shift of 4.8 ppm occurs between pH 7.8 and 6.8, bringing the N(1) and N(2) resonances to within 3.7 ppm of each other. The N(2) resonance is also broadened substantially by decreasing pH.

(5) At pH 6.8 $\Delta\delta_{^{15}N-^{15}N}$ is small, and one would expect the spectrum for doubly labeled compound to approximate an AB quartet. However, because both resonances are markedly broadened, fine features could not be resolved and no coupling constant was obtained for $HN_2O_3^-$. (Since the first-order rate constant for $HN_2O_3^-$ decomposition is independent of pH in this region, the pH dependence of line width was unanticipated; limitations of material precluded repetition of the measurement at a higher and more favorable pH.)

(6) Proton decoupling showed no substantial effect on either resonance, except for the case of N(1) at pH 8.0, for which an inversion of signal indicated an NOE of about −2.1 (Figure 2).

Table I. ^{15}N Chemical Shifts of Isotopic Trioxodinitrate Species

species	pH	δ_{obsd}[a]	$\delta_{NH_3(l)}$[b]	$\Delta\delta$[c]	$^1J_{^{15}N-^{15}N}$, Hz	NOE[d]
$O^{15}NNO_2^{2-}$	13	−10.7	355.2			−
				+15.7		
$ON^{15}NO_2^{2-}$	13	−26.4	339.5			−
$O^{15}N^{15}NO_2^{2-}$, N(1)	13	−10.5	355.4		16.6	
				+15.9		
$O^{15}N^{15}NO_2^{2-}$, N(2)	13	−26.4	339.5		16.6	
$O^{15}NNO_2H^-$	8.0	−34.6	331.3			+
				−8.3		
$ON^{15}NO_2H^-$	7.8	−26.3	339.6			−
$O^{15}NNO_2H^-$	7.3	−34.6	331.3			−
				−3.5		
$ON^{15}NO_2H^-$	6.8	−31.1	334.8			−
$O^{15}N^{15}NO_2H^-$	6.8			−3.7	*e*	

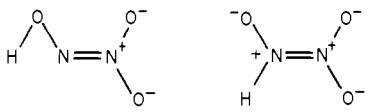
[a] Ppm relative to external 8.8 M HNO_3. [b] Ppm relative to anhydrous NH_3, correction constant = 365.9.[15] [c] $\Delta\delta = \delta_{N(1)} - \delta_{N(2)}$. [d] + indicates signal inversion. [e] Not measured.

Since the concentration of $N_2O_3^{2-}$ does not change with time, this indicates that NOE = 0 for the pH 13 measurements. For N(1) at pH 8.0, however, the magnitude of the NOE reported is a minimum value, since $HN_2O_3^-$ decomposition during FT accumulation introduces an error in signal height comparison; the two resonances shown in Figure 2 include equal numbers of transients obtained sequentially on the same solution sample, the gated decoupled signal having been obtained first and the fully decoupled signal immediately thereafter.

If the $N_2O_3^{2-}$ measurements of Schultheiss and Fluck[13] are assumed to be referred to saturated NH_4Cl and the appropriate correction of 27.3 ppm is applied,[15] their values are 352.3 and 336.8 ppm relative to $NH_3(l)$, in reasonable agreement with ours. However, these authors have incorrectly assigned the downfield resonance to N(2). As they recognized in their argument, ^{15}N resonances at –NO generally occur downfield from those at $-NO_2$; our results show that this relation is preserved in this case. Our measurement of $^1J_{^{15}N-^{15}N}$ (16.6 Hz) is also in agreement with that of ref 13 (16.9 Hz). Both our measurements and those of ref 13 appear to be in disagreement with the single broad-line ^{14}N resonance position reported in ref 12, to an extent beyond the small expected range of isotope shifts.[16] Agreement with the ^{14}N value reported in ref 11 is considerably better. This value is reported for $Na_2N_2O_3$ in 0.5 M NaOH, while both ours and that of ref 12 are given for 0.1 M NaOH; it seems highly unlikely that these chemical shifts could be substantially influenced by OH^- concentration in this pH region, a supposition that is reinforced by the close agreement between our values at 0.1 M NaOH and those of ref 13 under conditions probably equivalent to a pH in the range 11.5–12.0. It is interesting to note that a single ^{14}N resonance has been reported for $N_2F_3^+$, a species that is isoelectronic to $N_2O_3^{2-}$, at 354 ppm[17] (corrected to $NH_3(l)$).

The major question that motivated this work concerns the site of first protonation of $N_2O_3^{2-}$, and the fact that it is the N(1) resonance that exhibits the major effect indicates clearly that this occurs at the –NO side of the anion. We now inquire whether it is the O or the N atom that is implicated. The known effects of N-protonation upon ^{15}N chemical shifts exhibit a wide range, from +25 ppm (downfield) for $NH_3 \rightarrow NH_4^+$, through −4 ppm for aniline → anilinium ion, −102 ppm for pyridine → pyridinium ion, to −150 ppm for *trans*-azobenzene → protonated *trans*-azobenzene.[18] The observed shift at N(1) of −24 ppm lies within this range, and its direction corresponds to that observed in other N=N systems. Considerably less information is available concerning the effects on ^{15}N (or ^{14}N) chemical shifts of protonation at neighboring O atoms. However, ^{14}N resonance measurements have been reported for the most closely analogous case, that of *trans*-hyponitrous acid (HO—N=N—OH) in both deprotonated and diprotonated forms.[19] Effectively no difference of resonance position was detected for the two forms, although the reported uncertainty due to quadrupole broadening permits a possible maximum difference of 10 ppm. In the case of HNO_3, there is less than 1-ppm difference in ^{15}N chemical shift between $NaNO_3$ and HNO_3 at 1 M concentration, but at high concentrations the ^{15}N chemical shift of HNO_3 exhibits a concentration dependence (lacking in alkali metal nitrate salt solutions), that results in a total upfield shift of ca. 27 ppm between 1 and 16 M.[20] We do not believe this shift can be ascribed wholly or simply to O-protonation of NO_3^-; it probably reflects a complex combination of solvent effects, ion pairing, and the presence of nitrogen species other than HNO_3, possibly even including dimers.[21,22] In the case of the congener acid H_3PO_4, sequential, threefold O-protonation is accompanied by a total ^{31}P NMR shift $\Delta\delta$ of only 5 ppm.[21] Finally, while a substantial change in the NMR spectrum of $N_2O_3^{2-}$ could in principle be associated with a change in the ΔE^{-1} contribution to the paramagnetic shielding term, the electronic spectroscopic change upon protonation in this case is known to occur at rather high energy (λ_{max} = 250 nm → 237 nm),[3] and in any event a shift from this cause should affect both N atoms.

We conclude from the above considerations that the observed direction and magnitude of shift of the $^{15}N(1)$ resonance indicate protonation at nitrogen. The conclusion is confirmed by the observation of an NOE of at least −2.1 for N(1) at pH 8.0. The NOE reflects the relative importance of the contribution of the $^1H-^{15}N$ dipolar relaxation and can range between 0 and −4.93. Since NOE = 0 for N(1) in $N_2O_3^{2-}$, the contribution to N(1) relaxation by dipole–dipole interaction with water is negligible. Spin–lattice relaxation of N(1) is therefore dominated by other mechanisms, presumably by spin-rotation as found for other small nitrogen-containing molecules in solution.[24] The observed NOE of −2.1 at pH 8.0 indicates a very substantial contribution from $^1H-^{15}N$ dipolar relaxation to N(1) relaxation in the anion $HN_2O_3^-$ (about half of the total relaxation rate). In principle, this contribution could arise from either of the forms



but since the dipole–dipole interaction depends upon r^{-6}, the O-protonated species would clearly provide much the smaller NOE

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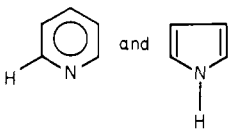
of the two cases. An idea of the distance and connectivity dependence of NOE can be obtained by comparison with the cases of pyridine and pyrrole



for which the NOE's (measured neat) are −0.4 and −4.3, respectively.[25] Since the distances and connectivities H—C—N in pyridine and H—O—N in O-protonated $HN_2O_3^-$ would be very similar and the tumbling rates of the two molecules should also be similar, the analogy is closely relevant. A more quantitative case can be made on the basis of T_1 measurement. For N(1) in $N_2O_3^{2-}$ (pH 13) at 25 °C, our measured value for T_1 was ca. 8 s; T_1 for the protonated species was not measured but would be either the same or shorter due to dipole–dipole interactions. (We can qualitatively report it to be somewhat shorter, on the basis of the smaller number of transients required to develop a given S/N level at fixed operating conditions.) For our measured NOE of −2.1, the relation between observed relaxation T_1^{obsd} and the dipolar contribution T_1^{DD} is $T_1^{obsd} = T_1^{DD}/2.4$.[26] The calculated value for T_1^{DD} in pyridine, for which the H–N distance is similar to that in the postulated O-protonated $HN_2O_3^-$ species, is ca. 1000 s.[25] A similar T_1^{DD} in $HN_2O_3^-$ would imply a T_1^{obsd} of ca. 400 s. For the case of pyrrole, in which the N–H interaction is direct, T_1^{DD} = 46 s,[25] a value that would yield T_1^{obsd} = 20 s if applied to N-protonated $HN_2O_3^-$. There is thus more than 1 order of magnitude of difference between T_1^{obsd} values expected for the O-protonated and N-protonated forms. The small T_1^{obsd} in our case (≤8 s) is similar in magnitude to the value based upon T_1^{DD} in the N-protonated case of pyrrole. While this consideration is semiquantitative, it rules out large contributions to relaxation from O-protonated anions and confirms our conclusion that the large observed NOE is due to N-protonation.

At the lower pH 7.3, signal inversion was not observed upon proton decoupling as in the case of pH 8.0, hence the NOE was altered from −2.1 to a value somewhere in the range 0 to −1. (We cannot specify it more exactly than that, because of uncertainty caused by the combination of lengthened FT accumulation times and continued decline in $HN_2O_3^-$ concentration, the former due to line broadening.) Similar changes in NOE with pH have been previously observed for protonation at nitrogen.[27] For the NOE changes to be more fully understood in this case, a more detailed study of both NOE's and T_1's would be necessary; however, because of the problem of $HN_2O_3^-$ decomposition, this would be most difficult to achieve. The broadening of N(1) observed at the lower pH (see Figure 1) may indicate that H^+-exchange processes contribute to the T_2 relaxation mechanism of N(1); further studies would be needed to define the exchange processes and for the determination of exchange rates. A more substantial broadening with decreasing pH is observed for the N(2) resonance, and in this case there is a concomitant small shift to higher field. These observations may suggest that we are observing effects due to a small extent of second protonation occurring at N(2). Such protonation would affect particularly the N(2) line width, as observed (Figure 1). No NOE was detected for N(2) at any of the three pH levels employed. This is expected since the extent of protonation of this nitrogen (if any) would be necessarily very small at pH 7.8 and 6.8 and relaxation may be affected primarily via an exchange mechanism.

$HN_2O_3^-$ is known to undergo an interaction with carboxylic buffer species at pH 4.9 that causes some scrambling of N atoms,[6] but H_3BO_3 at pH 8.5 gives no evidence of such an interaction.[3] Monobasic trioxodinitrate decomposition is also known to display dynamic reversibility in the presence of excess nitrite[5,6] but again under very different conditions from those employed in this study. Neither of these appears to be a likely cause of the pH-dependent broadening and resonance shift at N(2), and our suggestion concerning appearance of a small proportion of a diprotonated species seems to be a preferable explanation despite the troubling fact that pK_1 has the low value 2.5.[8] The protonation associated with pK_1 could be at oxygen, and N(2)-protonation at higher pH restricted to the very minor proportion corresponding to the structural contribution of resonance form II. In these speculative terms, the unimolecular decay of $HN_2O_3^-$ may be considered a feature of either of the species IV or V. Hughes and Wimbledon

IV V

have pointed out[5] that homolysis of N=N (in, e.g., IV) would produce a nitrite biradical, which is unlikely in view of the observation of reversibility.[5,6] Heterolysis of V, however, accompanied by N(2) to O proton transfer, would form the known molecular species HNO and HNO_2. (Both would become deprotonated in the pH regime employed here, if the HNO is identical with that observed by pulse radiolysis,[28] pK = 4.7.) It is not so clear how the pH independence of the first-order decay constant of $HN_2O_3^-$ can be rationalized within this interpretation or what role the possible O-protonated tautomers of V might have. While our results indicate predominating N-protonation, the presence of other tautomeric forms at equilibrium is not ruled out. In the case of *trans*-$H_2N_2O_2$, which is stable relative to $HN_2O_2^-$,[9] both protons appear to be bound to oxygen.[19] The evidence that $H_2N_2O_3$ is more stable against thermal decomposition than $HN_2O_3^-$[4] suggests a similar possibility in the case of this species.

Much of the interpretation given in the above paragraph is necessarily speculative. With regard to the central question of the site of first protonation of $N_2O_3^{2-}$, however, we believe our conclusion to be quite secure. While we recognize that our study would have benefitted from additional kinds of measurements that were simply precluded by the extreme experimental intractability of this system, the evidence that we have been able to develop makes a very strong case for protonation at N(1). To the best of our knowledge, this instance of N-protonation in preference to available charge centers at oxygen is unique. Finally, we now conclude that the intermediate species produced in $HN_2O_3^-$ decomposition is almost certainly HNO and not NOH.

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(27) Leipert, T. K.; Noggle, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 269. However, the possibility that NOE and broadening effects may have been influenced by trace paramagnetic impurities can not be excluded; see e.g. Irving, C. S.; Lapidot, A. *J. Am. Chem. Soc.* **1975**, *97*, 5945.
(28) Grätzel, M.; Taniguchi, S.; Henglein, A. *Chem. Ber.* **1970**, *74*, 1003.