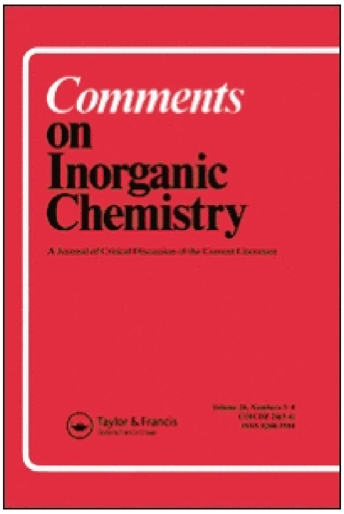

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The Aqueous Solution Chemistry of Nitrogen in Low Positive Oxidation States

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The Aqueous Solution Chemistry of Nitrogen in Low Positive Oxidation States

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Recent developments in the aqueous solution chemistry of nitrogen are described, with particular attention to the low positive oxidation states +1 and +2. The compounds discussed include hyponitrous acid and hyponitrites, nitrosyl hydride (HNO, "nitroxyl"), trioxodinitrate, nitric oxide, and nitroamine. The numerous redox pathways in which these and other nitrogen compounds are participants illustrate the versatility of that element, and bear important relation to current problems in nitrogen cycle research that focus upon the identity and reactivity of nitrogen species in intermediate oxidation states.

Key Words: *hyponitrite, nitric oxide, nitroamine, nitroxyl, trioxodinitrate*

1. INTRODUCTION

The versatility of nitrogen resides in its capacity to occupy all oxidation states between and including −3 and +5, and the existence of numerous varied and facile redox pathways within that unusually broad range. The details of nitrogen chemistry bear vi-

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tally upon fundamental understanding of important biological and environmental processes. Despite the impression held by many chemists that the whole of inorganic nitrogen chemistry has long since been consigned to the textbooks, much rich chemistry of that element remains incompletely explored. While the behavior of low-valent nitrogen plays a particularly important part in oxidation state cycling, it remains among the least widely known aspects of nitrogen chemistry. In this Comment, we undertake to provide a brief perspective and prospective account of recent developments in this field, giving particular attention to oxidation states +1 and +2.

One fundamental feature of the chemistry to be discussed here is that the nitrogen compounds of interest are almost without exception thermodynamically unstable under ordinary conditions. Their reactions are therefore for the most part kinetically rather than energetically driven, placing great importance on the details of stoichiometry in any determination of mechanism. Any study of the reactions of nitrogen compounds should thus include full attention to reaction stoichiometry over as wide a range of conditions as possible, including nitrogen atom balance information, but unfortunately this condition is not always found.

2. HYPONITROUS ACID, $H_2N_2O_2$, AND HYPONITRITES

The study of hyponitrite chemistry suffers from a lack of convenient and clean methods for the synthesis of $Na_2N_2O_2$. The most commonly used method involves the reduction of sodium nitrite with sodium amalgam. The product of this method and others is often heavily contaminated with sodium carbonate, due to contact with atmospheric CO_2 during its preparation and work-up. In many publications, impure hyponitrite has been used withot recognition of this fact. The frequently quoted extinction coefficient[1] for $Na_2N_2O_2$ at 248 nm (λ_{max}) in alkali is 3980 $M^{-1}cm^{-1}$. This was redetermined in 1968 as 6550 ± 200 $M^{-1}cm^{-1}$ by Polydoropoulos and Voliotis,[2] but little attention has been paid to this result. A more recent determination[3] has led to a value of 6900 ± 140 $M^{-1}cm^{-1}$. Work with impure hyponitrite has not affected values of rate constants as the kinetics have usually been first order in hyponitrite, but naturally will have led to errors in stoichiometries.

The self-decomposition of sodium *trans*-hyponitrite in solution was investigated extensively in the 1960's.[4-7] The monoanion $HN_2O_2^-$ is unstable, and decomposes with release of N_2O (Eq. (1)).

$$HN_2O_2^- \longrightarrow N_2O + OH^- \qquad (1)$$

The dianion, $N_2O_2^{2-}$, is stable in solution, and the free acid relatively so at moderate acidity. An acid-catalyzed decomposition occurs in strong acid to give N_2 and NO in addition to N_2O.[8,9] The first order rate constant for $HN_2O_2^-$ decomposition, measured at the midpoint of the pH range between the two pK_a values 7.2 and 11.5, is $7.2 \times 10^{-4}\,s^{-1}$ at 25°C.[4] Nitrogen-15 NMR measurements[10] show a small upfield shift consistent with protonation at oxygen in $HN_2O_2^-$, and isotope tracer experiments have confirmed the proposal of Latimer *et al.*[11] that heterolysis at an N–O bond releases N_2O in which the existing N=N bond is preserved.[10]

In contrast to the slow process of N_2O formation by decomposition of hyponitrite monoanion (Eq. (1)), dehydrative dimerisation of the hyponitrous acid monomer HNO (Eq. (2))

$$HNO + HNO \longrightarrow N_2O + H_2O \qquad (2)$$

occurs extremely rapidly in solution, with an estimated second order rate constant in the range 2 to $8 \times 10^9\,M^{-1}s^{-1}$.[12] It has long been assumed that this process occurs via the formation of the *cis*-isomer of hyponitrous acid as an intermediate, although this species has not been directly observed. The formation of compounds of formula MNO upon absorption of NO gas by solutions of alkali metals in liquid ammonia[13-15] was at one time considered an example of monomeric NO^- formation, but infrared spectroscopy[16] and magnetic susceptibility[17] measurements have shown that the compound contains dimeric units, $N_2O_2^{2-}$. It has in turn been plausibly asserted that this species is *cis*-hyponitrite,[18] consistent with the observation that effervescent release of N_2O occurs when "NaNO" is added to water, although no positive identification appears to have been made. Endeavors to obtain a spectrum of *cis*-hyponitrite in solution by rapid scanning of a solution of "NaNO" in 6 M alkali were unsuccessful, as effervescent release of N_2O also occurs under these conditions.[19]

Significant illumination of the process of *trans*-hyponitrite decomposition has been achieved in a recent study of its catalysis by carbonyl groups and carbon dioxide.[20] The formation of an N-bound carbonyl or CO_2 adduct is proposed, followed by rate-determining isomerisation to give *cis*-hyponitrite, which then rapidly releases N_2O upon departure of the catalyst group. It is suggested[20] that the uncatalyzed process (Eq. (1)) may proceed via protonation at nitrogen (i.e., tautomerization) preceding a rate-controlling isomerisation step. The assumption of tautomerisation is consistent with an observed loss of ^{15}N NMR signal in the monoprotonation pH range,[10] which could have resulted from a combination of decomposition and proton exchange line broadening.

Under acidic conditions hyponitrous acid may undergo rapid decomposition due to the onset of a free radical chain reaction.[5,8,9] This has been attributed to the disproportionation or hyponitrous acid to give nitrous acid, which subsequently reacts with hyponitrous acid.[5] The hyponitrous acid–nitrous acid reaction has proved to be remarkably complex,[21–23] and despite extensive stoichiometric, kinetic and isotopic labelling studies over the acidity range 0.02–8.5 M $HClO_4$, the reaction has not been completely elucidated. At least four pathways have been identified. First of these is direct, uncatalyzed self-decomposition of $H_2N_2O_2$ to yield N_2O. Second is the well-known, reversible disproportionation of HNO_2 to yield NO and nitrate (Eq. (3)).

$$3HNO_2 \rightleftharpoons 2NO + H^+ + NO_3^- + H_2O \qquad (3)$$

The major reactions are the production of N_2 and nitrate (Eq. (4)),

$$H_2N_2O_2 + HNO_2 \longrightarrow N_2 + NO_3^- + H^+ + H_2O \qquad (4)$$

and an apparently nitrous acid-catalyzed $H_2N_2O_2$ decomposition pathway, yielding N_2O (Eq. (5)).[21,22]

$$H_2N_2O_2 \xrightarrow{\text{"nitrous acid"}} N_2O + H_2O \qquad (5)$$

The latter reaction appears to involve the NO product of HNO_2 decomposition (Eq. (3)), since the use of ^{15}NO results in production of N_2O of mixed isotopic composition, and ^{14}NO. Thus, NO is able to catalyze decomposition of hyponitrous acid. As described further on, the existence of a direct reaction between NO and $H_2N_2O_2$ has been verified.[75]

The values of the pseudo-first order rate constant k_{obs} for the HNO_2–$H_2N_2O_2$ reaction increase dramatically with acidity from about 4 M $HClO_4$, reach a maximum value just below 7 M, and decrease precipitously as $[HClO_4]$ is increased beyond 7 M.[23] The rate law was found to be: Rate = $(k_2' + k_3^{**} h_0 a_w)[HNO_2][H_2N_2O_2]$, where $k_2' = 4.62 \times 10^{-4}\ M^{-1}s^{-1}$ and $k_3^{**} = 5.41 \times 10^{-3}\ M^{-2}s^{-1}$ at 0°C. These represent the overall rate constants for the combination of the (N_2 + NO_3^-)-producing reaction (Eq. (4)) and the NO-catalyzed $H_2N_2O_2$ decomposition (Eq. (5)), which is also acid catalyzed. The decrease in rate at high acidity reflects the effect of high $[H^+]$ on the latter reaction through the conversion of HNO_2 to NO^+. This suggests that molecular HNO_2 is itself a kinetically active species, and confirms that the reaction is not a conventional nitrosation. This has been further confirmed by the observation that addition of bromide leads to decreased rates, i.e., that NOBr is unreactive rather than catalytic in this system. It appears unlikely that the acidity function H_0 describes the protonation of $H_2N_2O_2$, but probable that the term $h_0 a_w$ approximates another function that does so. It is surprising that a process thus postulated to occur between $H_3N_2O_2^+$ and the NO from HNO_2 decomposition should show the observed, excellent first order $[HNO_2]$ dependence, since the disproportionation reaction is not usually thought to provide a steady concentration of dissolved NO, and if equilibrium (Eq. (3)) were established the concentration of NO should depend upon $[HNO_2]^{1.5}/[NO_3^-]$. Thus it appears that a direct role for HNO_2 may still be involved, such as that suggested in Eq. (6),

$$H_3N_2O_2^+ + HNO_2 \longrightarrow 2NO + HNO + H_3O^+ \qquad (6)$$

where the HNO product would be expected to undergo dimerization to form N_2O (Eq. (2)).[23]

3. NITROSYL HYDRIDE, HNO ("NITROXYL")

The monomer of hyponitrous acid, HNO, is a highly reactive molecule. It bears the traditional common name "nitroxyl," but is designated as nitrosyl hydride by *Chemical Abstracts* despite the fact that its hydrogen is not hydridic. HNO was first directly observed spectroscopically in 1958 as a matrix isolation[24] and gas phase[25] product of photolysis of H_2/NO mixtures and other systems. Its predominant fate in the gas phase is rapid N_2O formation (Eq. (2)).[26] Direct observation of HNO in aqueous solution has been achieved only by pulse radiolysis.[27] The pK_a value of HNO observed in this way is 4.7.[27] The conjugate base NO^-, which we shall refer to as nitroside anion, reacts rapidly and sequentially with NO to form $N_2O_2^-$ and $N_3O_3^-$; the latter species and its conjugate acid decay rapidly to form NO_2^- and N_2O.[27]

Prior to its first direct observation in 1958, HNO had already enjoyed a long history as a hypothetical intermediate species. The origin of HNO can be traced to Angeli's interpretation[28] of the self-decomposition of sodium trioxodinitrate ($Na_2N_2O_3$, "Angeli's salt") in weakly acidic to weakly alkaline solution (Eq. (7)),

$$2N_2O_3^{2-} + 2H^+ \longrightarrow N_2O + 2NO_2^- + H_2O \qquad (7)$$

as occurring via a primary split into HNO and NO_2^- (Eq. (8)),

$$N_2O_3^{2-} + H^+ \longrightarrow HNO + NO_2^- \qquad (8)$$

followed by rapid dimerisation of HNO (Eq. (2)). Angeli also postulated that the self-decomposition of N-hydroxybenzenesulfonamide ("Piloty's acid," Eq. (9))

$$2C_6H_5SO_2NHOH \longrightarrow 2C_6H_5SO_2H + N_2O + H_2O \qquad (9)$$

involves HNO intermediacy, and interpreted the role of both this compound and trioxodinitrate as aldehyde test reagents, and in the conversion of alkyl halides to oximes, as reactions of HNO. While these particular instances have been proven unlikely by Smith and Hein,[29] the literature of organic chemistry includes many examples of reactions for which HNO elimination is strongly indicated (see, e.g., Smith and Pars[30] and references therein), and in some cases even directly detected.[31,32] Numerous plausible assumptions of HNO intermediacy also appear in the literature of inorganic chemistry, including the hydrolysis of hydroxylamine Nsulfonate,[33,34] hydroxylamine oxidation (e.g., Refs. 35 and 36), and both chemical (e.g., Ref. 37) and electrolytic[38] reduction of nitrite. The literature of inorganic chemistry also includes examples of early postulates of HNO intermediacy, e.g., in the reaction between HNO_2 and NH_2OH,[39] that have been subsequently disproven.[40,41]

The directly proven chemical properties of HNO and its conjugate NO^- include dehydrative dimerisation (Eq. (2)), and the sequential reactions with NO in which $N_2O_2^-$, $N_3O_3^-$ and their conjugates are formed.[27] Accepting the trioxodinitrate decomposition reaction (Eq. (7)) as a demonstrated souce of HNO (Eq. (8), *vide infra*), reduction by hydroxylamine to form N_2 (Eq. (10))

$$HNO + NH_2OH \longrightarrow N_2 + 2H_2O \qquad (10)$$

is also a known property of HNO, because addition of NH_2OH to $HN_2O_3^-$ in solution does not alter its decomposition rate but results in a mixture of N_2 and N_2O as products, due to competition between dimerisation (Eq. (2)) and reduction (Eq. (10)).[42] The NO^- product of $HN_2O_3^-$ decomposition has also been shown to cause nitrosylation of $[Ni(CN)_4]^{2-}$ in a direct displacement process (Eq. (11)).[43]

$$[Ni(CN)_4]^{2-} + NO^- \longrightarrow [Ni(NO)(CN)_3]^{2-} + CN^- \qquad (11)$$

This reaction was initially postulated by Nast[44,45] in interpretation of the reaction between $[Ni(CN)_4]^{2-}$ and alkaline hydroxylamine, a reaction that is known to be an independent pathway to the nitrosyl compound.[43] However, Nast's interpretation depended upon a postulate of HNO formation via NH_2OH disproportionation[45] that remains unsubstantiated.

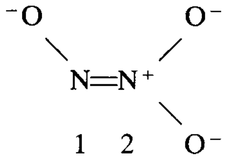
In a reaction analogous to the trapping of NO^- by nickel cyanide, Bazylinski and Hollocher[46] have shown that the Fe(III) heme proteins methemoglobin (Hb^+) and metmyoglobin (Mb^+) are capable of acting as traps for the NO^- released by $HN_2O_3^-$ decomposition in neutral aqueous solution (Eq. (12)).

$$Hb^+ + NO^- \longrightarrow HbNO \qquad (12)$$

Trapping efficiencies as high as 80% were observed in the competition between nitrosylhemoglobin and N_2O formation,[46] in contrast to a maximum of 30% in the case of $[Ni(CN)_4]^{2-}$.[43] Additional proven instances of HNO intermediacy are discussed further on.

4. TRIOXODINITRATE, $Na_2N_2O_3$

Although formally a +2 nitrogen compound, the dianion $^-ONNO_2^-$ effectively bears both +1 (nitroso) and +3 (nitro) halves. Its solid state structure is the unequivocally double bonded form[47]



The chemistry of trioxodinitrate, and in particular its decomposition reaction, has been the subject of a number of investigations since the time of Angeli[28] (e.g., Refs. 32 and 48), and its role as an HNO source has stimulated much recent research on this interesting compound. Kinetic studies of the decomposition reaction[49,50] show it to be a rigorously first order ($k_1 = 6.8 \times 10^{-4}$ s^{-1} at pH 6.2, 25°C), and essentially independent of pH in the interval ca. 4–8 corresponding to monoprotonation (pK_I and pK_{II} = 2.5 and 9.7, respectively[51]). Thus it is the monoanion $HN_2O_3^-$ that is destabilized and undergoes cleavage to produce HNO (Eq. (8)). Nitrogen-15 introduced at nitrogen position 2 via alkyl nitrate in the synthetic reaction[1,52] (Eq. (13))

$$NH_2OH + RONO_2 \xrightarrow{(C_2H_5ONa)} Na_2(ONNO_2) + ROH \tag{13}$$

appears in the nitrite product.[53] Nitrogen-15 introduced via NH_2OH appears exclusively in the N_2O product and in random distribution among the four expected isotopomers, confirming the formation of N_2O from a monomeric precursor (i.e., Eq. (2)).[49] The decomposition reaction is kinetically inhibited by addition of nitrite,[54] demonstrating reversibility in the primary step (Eq. (14)),

$$HN_2O_3^- \rightleftharpoons HNO + NO_2^- \tag{14}$$

a conclusion that has been confirmed by an observation that $^{15}NO_2^-$ added to a decomposing $HN_2O_3^-$ solution becomes incorporated at N-2 position in the unreacted compound.[55] Reversibility has been further confirmed by ^{15}N NMR.[56]

Since trioxodinitrate resembles hyponitrite in having a dianion that is stable in solution and a monoanion that is unstable, by further analogy the free acid $H_2N_2O_3$ might be expected to exhibit a relatively high degree of stability.[8] However, at pH ca. 3 a new reaction pathway appears, leading to NO[48-50] (Eq. (15)).

$$N_2O_3^{2-} + 2H^+ \longrightarrow 2NO + H_2O \qquad (15)$$

The existence of this pathway led to an early, widespread assumption that a true chemical anhydride relation exists between NO and $H_2N_2O_3$,[57] an assumption that still appears in the literature from time to time (e.g., Ref. 38) despite the fact that UV spectrophotometric[58] and isotopic exchange[59] studies have demonstrated the complete absence of hydrated forms of NO in solution. The NO-producing decomposition reaction has been shown to result from the nitrosation of trioxodinitrate by nitrous acid, either adventitiously present in solution or derived from the nitrite-producing decomposition reaction (Eq. (14)). In the complete absence of nitrite (an unobtainable condition) the diprotonated species would be stable relative to the monoanion.[54] The NO-producing reaction itself is a complex chain reaction that is catalytic in nitrous acid.[54]

A complete infrared spectroscopic study and normal coordinate analysis of $Na_2N_2O_3$ and its three ^{15}N isotopic variants has provided detailed knowledge of the complex motions associated with each of the nine vibrational modes.[60] Raman spectroscopic measurements in the monoprotonation pH interval show that the single added proton attaches itself at the nitroso side of the anion.[60] Nitrogen-15 NMR measurements confirm this, showing a substantial (24 ppm) upfield shift of the N-1 resonance between pH 13 and pH 6, but negligible shift at N-2 over the same interval.[61] The protonation effect at N-1 is very much greater than that observed for O-protonation in the most closely analogous case of hyponitrite[10]; this circumstance, in combination with a very large NOE (−2.1) measured for N-1 at pH 8, led to a conclusion that protonation occurs at the N-1 nitrogen lone pair rather than at nitroso oxygen.[61] While this interpretation has been questioned[62] and further work is needed, the NMR studies clearly show extensive involvement of N-1 nitrogen in the protonation, at the very least via tautomerisation, a high degree of which reveals itself in the line broadening observed in the ^{15}N NMR spectra.[61]

A revision of the mechanism expressed in Eqs. (14) and (2) for trioxodinitrate decomposition was proposed in 1984 by Doyle *et al.* in their interpretation of a newly observed reaction with hemoglobin.[63] According to this proposal the primary decomposition products are HNO_2^- and NO (Eq. (16)),

$$HN_2O_3^- \longrightarrow HNO_2^- + NO \qquad (16)$$

rather than HNO and NO_2^- (Eq. (14)). The rare hydronitrite anion NO_2^{2-}, known for its violent reactivity, has been observed in aqueous solution only as a product of radiolysis, along with its conjugates HNO_2^- and H_2NO_2.[64] The mechanism postulated in Ref. 63 requires three steps subsequent to Eq. (16) for formation of the final products N_2O and nitrite, involving the unknown species $HN_2O_3^{2-}$ and $ONN(OH)NO_2^{2-}$. This mechanism has been decisively disproven by Hollocher *et al.* in experiments on the interaction of ^{15}NO with the $HN_2O_3^-$ decomposition product,[12] a demonstration that Fe(III) hemoglobin (Hb^+) and myoglobin (Mb^+) are efficient trapping reagents for NO^-,[46] and detailed kinetic and stoichiometric studies of the $HN_2O_3^-$–Hb reaction.[65] The latter is first order in $HN_2O_3^-$ but zero order in Hb, and occurs in a 2:1 stoichiometry ($HN_2O_3^-$:Hb); a rate determining conversion between two forms of trioxodinitrate was postulated in accounting for the observed kinetics.[65]

Trioxodinitrate has been found to react with the hexaammineruthenium(III) cation $Ru(NH_3)_6^{3+}$, in a process that involves direct interaction between that species and the dianion $N_2O_3^{2-}$.[66] The gas products are N_2O and NO, arising principally from the N-1 nitrogen atom. A principal reductive pathway leading to Ru(II), NO (from N-1) and NO_2^- (from N-2) has been identified, along with a secondary pathway that yields NO^- (from N-1) and NO_2.

Important progress has been achieved in recent years in alkaline solution nitrosation, e.g., by N_2O_3 formed directly in solution via reaction between NO and NO_2, ascribed to the rare symmetric isomer ONONO.[67] Nitrosyl complexes bearing the NO^+ group are also potential agents of nitrosation under high pH conditions, as has recently been demonstrated in comparative studies of the reactions between trioxodinitrate and the complex ions $[Ru(NH_3)_5NO]^{2+}$ and $[Fe(CN)_5NO]^{2-}$.[68,69] Trioxodinitrate is known to be subject to nitrous acid nitrosation under acidic conditions[50]; consistent with that observation but under alkaline conditions, the NO^+ group in each of these nitrosyl complexes is found to attack the N═N bond, causing rapid cleavage. Both reactions appear to involve intermediates containing coordinated NO rather than NO^+ or NO^-. In the case of reaction with the Ru(II) nitrosyl complex this is derived from the NO^+ group, whereas in the nitroprusside reaction the NO ligand derives from the NO^- fragment of $N_2O_3^{2-}$. A further interesting and fundamental difference is that opposite sides of the trioxodinitrate anion become associated with the metal center: reaction with the Ru(II) complex yields free NO (from NO^-) and bound NO_2^-, while reaction with nitroprusside yields free nitrite and bound NO^-.

5. NITRIC OXIDE, NO

The reduction of nitric oxide is of general interest, and relates to N(I) chemistry in particular with respect to its potential for formation of HNO. In a detailed study of the reduction of NO to N_2O by Fe(II), the intermediate formation of HNO has been demonstrated by an isotopic method in which cross-dimerisation has been observed to occur between single-electron reduced NO and HNO simultaneously supplied by decomposition of $HN_2O_3^-$ in the same solution system.[70] A threshold of pH 4 for reduction of NO to N_2O by Fe(II) was found to be related to the existence of a reactive dinitrosyl complex, the familiar "brown ring" mononitrosyl complex being redox inert in this system.[71] Kinetically, the reaction is characterized by a rate law containing both first and second order terms with respect to the dinitrosyl complex $Fe(NO)_2^{2+}$, with the second order pathway predominant at pH 6. This kinetic feature seems remarkable, since interaction between dinitrosyl cations might be expected to encourage N═N bond formation within the Fe(II) coordination sphere, a process that appears to be unlikely in view of the demonstrated ability of the primary NO reduction product to interact with HNO from a second source.

Reduction of NO by hydroxylamine proceeds by the stoichiometry of Eq. (17) at pH ≥ 13.[72]

$$2NO + 2NH_2OH \longrightarrow N_2 + N_2O + 3H_2O \qquad (17)$$

The mechanism of this reaction initially proposed by Cooper *et al.*,[72] as shown in Eqs. (18)–(20),

$$NO + NH_2OH \longrightarrow HNO + NHOH \qquad (18)$$

$$HNO + NH_2OH \longrightarrow N_2 + 2H_2O \qquad (19)$$

$$NO + NHOH \longrightarrow [ON{-}NHOH] \longrightarrow N_2O + H_2O \qquad (20)$$

has been confirmed in experiments employing $^{15}N^{18}O$.[42] As pH is reduced below 13, the molar product ratio η_{N_2O}/η_{N_2} is found to increase. While the high pH product formed with $^{15}N^{18}O$ contains N_2O of masses 47 and 45 but none of mass 48, the increase in N_2O content correlates with the first appearance of the latter species, showing that HNO dimerisation (Eq. (2)) enters into competition with reduction (Eq. (19)). At pH 8 the HNO produced in this reaction system is predominantly dimerised to form N_2O; in contrast, the HNO released by $HN_2O_3^-$ decomposition in the presence of excess hydroxylamine at the same pH is predominantly reduced to N_2. The active reducing agent in this reaction is the O-deprotonated anion NH_2O^-; the reaction is first order in both this species and in NO ($k_2 = 6.68 \times 10^{-3}\ M^{-1}s^{-1}$ at 25°C).[73]

Reactions of NO with the alkylated hydroxylamines show that HNO is formed in an initial hydrogen atom abstraction reaction in each case (as in Eq. (18)), surprisingly including the N,N-dialkyl compounds, in which the abstraction occurs at α-carbon.[74] The radical species formed attaches an NO molecule in each case, forming stable nitrosohydroxylamine products in the cases of N-alkyl, N,O- and N,N-dialkyl compounds, so that any N_2O product observed must arise entirely via HNO dimersation. The importance of anionic charge is accepted by the observation that the reactions of NO with O-alkylated hydroxylamines exhibit extreme kinetic inhibition, to an extent such that the reactivity of NH_2O^- toward NO is estimated to be at least 3.4×10^5 times greater than that of NH_2OH.[74]

Hydrogen atom abstraction by NO, which has been amply demonstrated in the reactions with hydroxylamine,[73,74] and also in a recent report of a reaction with $H_2N_2O_2$,[75] is not a property generally associated with NO. Reaction between NO and amines, for example, leads preferentially to the formation of N_2O_2 adducts,[76-78] and NO exhibits vanishing power of nitrosation in solution, a feature that has been attributed to its lack of capacity to abstract amino hydrogen atoms.[79] The greatly enhanced reactivity of hydroxylamine toward NO upon O-deprotonation indicates that N–H bond activation is related to the presence of charge on the neighboring O atom, an effect that appears to be transmissible to α-carbon as well.

6. NITROAMINE, NH_2NO_2

The compound nitroamine (also known as nitroamide) was once thought, incorrectly, to be an isomeric form of hyponitrous acid. In practice it contains N atoms in the formal oxidation states −1 and +3, and represents an extremely interesting combination of chemical groups. The base-catalyzed decomposition of nitroamine to nitrous oxide and water is of classical significance, because this reaction was used extensively in the development of theories of base catalysis in view of its apparent simplicity. The reaction was generally believed to involve the base-catalyzed elimination of H^+ from the *aci*-form of nitroamine (Eq. (21)).

$$H_2NNO_2 \rightleftharpoons HN{=}NO_2H \xrightarrow{B} N_2O + BH^+ + OH^- \quad (21)$$

However, this reaction appears to be more complex than originally thought. Not only is there a second pathway for decomposition via the nitroamine anion $HNNO_2^-$,[80] but studies in more strongly basic solutions in association with a consideration of isotope effects have revealed new mechanistic details for the pathway shown in

Eq. (21).[81] Neutral primary amine catalysts and negatively charged oxygen bases give linear Brønsted relationships for increasing catalyst strength, but eventually, at higher catalyst strength, show curvature. These results imply that proton transfer precedes heavy atom reorganization, as shown in Eqs. (22)–(24).

$$B + HN{=}NO_2H \rightleftharpoons B \cdot HN{=}NO_2H \qquad (22)$$

$$B \cdot HN{=}NO_2H \rightleftharpoons \overset{+}{B}H \cdot \overset{-}{N}{=}NO_2H \qquad (23)$$

$$\overset{+}{B}H \cdot \overset{-}{N}{=}NO_2H \longrightarrow BH^+ + N_2O + OH^- \qquad (24)$$

For weak catalysts, the reverse of Eq. (23) is fast, and heavy atom reorganization is rate determining. For stronger catalysts, proton transfer to the base is favored, the reverse of Eq. (23) is slow, and proton transfer begins to be rate determining.

The decomposition of nitroamine is also subject to acid catalysis. Recent studies[82,83] have centered on concentrated mineral acids, and arose partly out of investigations of the role of nitroamine as an intermediate in the oxidation of sulphamic acid by concentrated nitric acid.[84] The acid hydrolysis of nitroamine in concentrated $HClO_4$, HCl and H_2SO_4 followed a similar pattern in all cases, with a linear correlation between log k_1 (first order rate constant for the acid-catalyzed reaction) and the Hammett acidity function H_0 with a slope of ca. 0.34. This has been interpreted in terms of a rate-determining nucleophilic attack by water on protonated nitroamine, in accord with results obtained using ^{18}O labeled H_2O.[83] Decomposition of nitroamine at pH 7 gives unlabeled N_2O, but as the acidity of the reaction solution is increased the ^{18}O content of the N_2O rises, reaching a saturation value, in which the ^{18}O content of N_2O is equal to that of solvent H_2O, at 7M $HClO_4$. In the scheme shown in Eqs. (25) and (26)

$$NH_2NO_2 + H^+ \rightleftharpoons {}^+NH_3NO_2 \qquad (25)$$

$$\begin{aligned}{}^+NH_3NO_2 + H_2O &\xrightarrow{\text{(slow)}} {}^+NH_3OH\\ &+ HNO_2 \longrightarrow N_2O + 2H_2O + H^+ \qquad (26)\end{aligned}$$

it is assumed that N–N cleavage occurs giving hydroxylamine and nitrous acid which then react to give N_2O. The nitrous acid must undergo rapid oxygen exchange with the oxygen-18 labeled water to account for the levels of label in the N_2O. N–N bond cleavage results from the presence of the strongly conjugating and electron-withdrawing nitro group. Protonation of nitroamine enhances nucleophilic attack of water, while having little effect on the leaving of HNO_2, particularly if the nitronic acid species $^+NH_2NO_2H$ is involved. This reaction scheme contrasts with the base-catalyzed reaction, where N–N bond cleavage does not occur.

Nitroamine and nitrous acid react in aqueous acidic solution to give nitrate and nitrogen,[85] with a rate law at 0°C: Rate $= (2.8 \times 10^{-3}[H_2NNO_2] + 1.6 \times 10^3[HNNO_2^-])[H^+][HNO_2]$. The two terms correspond to nitrosation of the neutral and deprotonated nitroamine molecules. The rate constant for attack at the anion compares well with those for similar nitrosation reactions at other negative substrates, which are thought to be diffusion controlled. Attack at neutral substrates is usually 10–100 times slower, reflecting the effect of charge on the encounter rate, but attack at H_2NNO_2 is slower by a factor of 10^6. This must result from the presence of the adjacent nitro group. The nitroamine–nitrous acid reaction is catalyzed by halide and thiocyanate ions,[86] and involves rate determining attack of the covalent nitrosyl compound (NOX) on deprotonated nitroamine. In the case of catalysis by bromide, there is a rapid increase in the rate of reaction after an induction period due to the reaction of Br_2 (formed by decomposition of NOBr) with nitroamine.

Little other work has been carried out on nitroamine, but it has been shown[87] that the compound is reduced rapidly to N_2 by V(II), and to N_2 and NH_3 by Cr(III), with ammonia as major product. In the latter case there is no evidence for the formation of hydrazine.

7. CONCLUSION AND CONTINUATION

The observation that the HNO intermediate formed in the NO–NH_2OH reaction is predominantly dimerised to N_2O at pH 8, while that released via $HN_2O_3^-$ decomposition is largely reduced to N_2

under comparable conditions,[42] poses an interesting question. In view of the known pK_a value 4.7 for HNO,[27] the anion NO^- should be the overwhelmingly predominant form of the intermediate at pH 8. Assuming the hydroxylamine species that is reactive toward NO^- to be NH_2O^-, as it is known to be in the case of NO, it is estimated that $HN_2O_3^-$-generated NO^- is more reactive than the ($NO-NH_2OH$)-generated species by a factor $>10^6$.[73] A difference of reactivity has also been observed in the nitrosylation of $[Ni(CN)_4]^{2-}$ by NO^-.[43] It has been postulated that the difference between the two forms of NO^- is one of electronic state, the reactive form being singlet and the other triplet,[42,73] analogous to the well-known isoelectronic case of O_2. The $^3\Sigma$-$^1\Delta$ energy separation in NO^- (0.68 ev)[88] is so large in relation to the electron affinity of NO (0.024 ev)[89] that a direct spectroscopic test of this postulate is precluded, but recent observations in the photochemistry of trioxodinitrate appear to lend support, indicating that photolytically produced NO^-, which is expected to be a triplet, readily reacts with triplet O_2 to form peroxonitrite.[90] The preparation of singlet nitroside anion, if confirmed and extended, may open a significant new area of chemistry to exploration, as has proven to be the case for the isoelectronic species singlet dioxygen.[91]

The thermal decomposition reactions of the monoprotonated hyponitrite and trioxodinitrate anions exhibit essentially identical kinetic properties (as detailed and compared in Ref. 10), despite the fact that they involve N–O and N–N bond cleavages, respectively. This may suggest the presence of a fundamental, rate-controlling process prior to decomposition that is common to the two reactions. It is clear that tautomerism is essential to $HN_2O_3^-$ self-decomposition,[54,91] and recent evidence also points to tautomer-induced isomerisation as a precursor to the decomposition of $HN_2O_2^-$.[20] Further exploration, in which ^{15}N NMR may well play a role,[10,61] will be needed to determine whether an underlying mechanistic feature is shared by these two seemingly dissimilar processes.

Finally, we draw attention again to the essential role that the redox chemistry of nitrogen plays in such fundamental biological processes as nitrification, denitrification, assimilatory nitrogen reduction and nitrogen fixation. Along with numerous more strictly inorganic processes, these play a central part in the nitrogen cycle, and bear crucially on the nature, content and interactive properties of nitrogen-containing substances in the earth's aquatic, atmospheric and stratospheric envelopes. A number of important, current problems in nitrogen cycle research focus on the identity and reactivity of nitrogen compounds in intermediate oxidation states. In the investigation of denitrification, for example, a microbiological process in which nitrate is reduced to dinitrogen via nitrite and nitrous oxide (Eq. (27)),

$$NO_3^- \longrightarrow NO_2^- \longrightarrow ? \longrightarrow N_2O \longrightarrow N_2 \qquad (27)$$

current controversy centers around the pathway between nitrite and nitrous oxide in terms of the identity of any other intermediates and the mechanism of N–N bond formation. The existence of an NO^+ nitrosyl intermediate has been demonstrated,[92] but the fate of this species is not yet conclusively resolved. One proposal is that the NO^+ group is reduced to NO^-, and lost from the enzyme, dimerising to yield N_2O.[92] An alternative view is that the NO^+ group reacts with free nitrite to give bound N_2O_3 which is then reduced to N_2O via $N_2O_3^{2-}$ (Eq. (28)).[93,94]

$$E \cdot NO_2^- \rightleftharpoons E \cdot NO^+ \xrightleftharpoons{NO_2^-} E \cdot N_2O_3 \longrightarrow N_2O \qquad (28)$$

Evidence against the intermediacy of trioxodinitrate has been presented,[56] but recently isotopic evidence has been put forward to support attack of a second nitrite on an enzyme-bound NO^+ intermediate.[95]

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