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Reaction of Nitric Oxide with Hyponitrous Acid: A Hydrogen Atom Abstraction Reaction

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The decompositon of hyponitrite in aqueous solution systems has been investigated over a broad acidity range.[2-8] In the pH region in which $HN_2O_2^-$ is dominant, this species is known to undergo heterolysis at an N–O bond to yield N_2O and OH^- as products (eq 1) in a first-order process ($k_1 = 7.2 \times 10^{-4}$ s^{-1} at

$$^{-}O{-}N{=}N{-}OH \rightarrow N_2O + OH^- \tag{1}$$

pH 9.2 and 25 °C).[2] In acid solution, hyponitrite is present as hyponitrous acid and is considerably more stable (e.g., $k_1 = 1.6 \times 10^{-4}$ s^{-1} in 1.24 M $HClO_4$ at 70 °C),[3] although an acidity dependent pathway that appears above about 1 M H^+ reduces this stability substantially in concentrated acid.[3,4] In addition to the "normal", N_2O-producing reaction, an additional chain reaction has been reported and investigated,[3,5] for which the products N_2, NO_3^-, N_2O, and NO have been observed. Buchholz and Powell[5] found this reaction to be inhibited by C_2H_5OH and reported it to proceed via an initial buildup of HNO_2 followed by the HNO_2–$H_2N_2O_2$ reaction (eq 2), with the NO product ascribed

$$H_2N_2O_2 + HNO_2 \rightarrow N_2 + NO_3^- + H^+ + H_2O \tag{2}$$

to HNO_2 disproportionation and N_2O to simultaneous occurrence of the "normal" path (eq 1). Recent studies of the reaction (2) beyond those previously published[5,9] have suggested that an additional reaction may occur in these systems, i.e. a reaction between NO and $H_2N_2O_2$. In particular, it has been observed that NO is absent in reaction systems containing $HClO_4$ and characterized by high $H_2N_2O_2$ concentration, despite its expected presence as a product of HNO_2 disproportionation, and that an induction period that is normally observed for the overall reaction in the presence of excess $H_2N_2O_2$ over HNO_2 disappears when NO is bubbled into the reaction system.[10] The reaction rate is also increased by the presence of NO. Isotopic studies indicate that, under conditions in which NO is observed as a product of the HNO_2–$H_2N_2O_2$ reaction, its origin cannot be entirely from HNO_2 disproportionation because a significant proportion of its N atoms arise from $H_2N_2O_2$.[10] Buchholz and Powell commented without elaboration that "NO is rapidly absorbed by hyponitrous acid solutions at 1 M H^+". If there is a direct reaction between NO and $H_2N_2O_2$, the possibility is raised that H atom abstraction by NO may be involved, as has been reported previously in the case of NO reduction by hydroxylamine in alkaline solution.[11]

To establish whether or not a direct NO–$H_2N_2O_2$ reaction occurs, gas products of $H_2N_2O_2$ decomposition in 5 M $HClO_4$ with and without C_2H_5OH as chain inhibitor, and in the absence and presence of added NO gas, were measured at extended time intervals in a reaction vessel with phase mixing by mechanical vibration and analysis by gas chromatography employing CF_4 as a reference gas, all as reported elsewhere.[12,13] As shown in Table I, the results of these experiments provide a clear indication that reaction between NO and $H_2N_2O_2$ occurs, both with and without chain inhibitor. With no C_2H_5OH added, a very large increase in the yield of N_2 is observed when NO is present, and the N_2O yield remains approximately constant, rather than increasing with time as it does in the absence of NO. Column 5 of Table I shows that substantial NO has been consumed, although the actual molar amount is unknown because a potential for NO production exists within the reaction system. With C_2H_5OH added, column 5 again indicates that net NO has been consumed, although considerably less than in the non-chain-inhibited case. The apparent yield of N_2O based upon $(H_2N_2O_2)_0$ alone and the product ratio n_{N_2}/n_{N_2O} do not appear strongly affected by the presence of NO in this case.

Tracer experiments were carried out under conditions similar to those described above, with ^{15}NO added (96.2% ^{15}N, Stohler) as reactant. The results, as shown in Table II, reveal a dramatic difference between the N_2O products formed in the two cases. Without chain inhibitor present, all the varieties of doubly labeled, singly labeled, and unlabeled N_2O were observed, at a somewhat greater than twofold isotopic dilution relative to the initial reactant gas. The isotope distribution observed in case A is not far removed from complete randomness at the observed level of 40.0% ^{15}N (values expected for random distribution (e/m, fraction): 46, 0.160; 45, 0.480; 44, 0.360). In the presence of C_2H_5OH, on the other hand, formation of the two singly labeled species $^{14}N^{15}NO$ and $^{15}N^{14}NO$ (mass 45) is virtually suppressed, and the N_2O product consists almost entirely of doubly labeled (mass 46) and unlabeled molecules (mass 44). In both cases, mass spectrometry showed no more than a small extent of incorporation of ^{15}N into N_2 product, and unreacted NO showed very little isotopic dilution in both cases (to 94.1% in case A and 94.7% in case B).

The results show that under chain-inhibited conditions a substantial proportion of the N_2O product consists of reduced NO, since both N atoms in N_2O at mass 46 arise from ^{15}NO. The small percentage of singly labeled N_2O (mass 45) immediately rules out the possibility of NO attack at an N atom of $H_2N_2O_2$ (eq 3) as anything more than a minor reaction pathway. The only

$$^{15}NO + HONNOH \rightarrow HON(^{15}NO)NOH \rightarrow N^{15}NO + HNO + OH \tag{3}$$

attack that appears to explain the observations is a reaction of H atom abstraction at NO, forming $H^{15}NO$ and the radical $\cdot ONNOH$. The $H^{15}NO$ then dimerizes to form doubly labeled N_2O(mass 46), while the radical decomposes to yield unlabeled N_2O(mass 44) and OH (eq 4–6). The latter species is then trapped by C_2H_5OH.

$$^{15}NO + HONNOH \rightarrow H^{15}NO + \cdot ONNOH \tag{4}$$

$$\cdot ONNOH \rightarrow N_2O + OH \tag{5}$$

$$H^{15}NO + H^{15}NO \rightarrow {}^{15}N^{15}NO + H_2O \tag{6}$$

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Table I. Gas Products of Reaction Systems Containing $H_2N_2O_2$ in 5.0 M $HClO_4$ at 25 °C, with and without Added NO and with and without C_2H_5OH as Chain Inhibitor

	t, h	$n_{N_2O}/(n_{H_2N_2O_2})_0$	n_{N_2}/n_{N_2O}	$(n_{N_2}+n_{N_2O})/(n_{H_2N_2O_2})_0$	$10^5\Delta n_{NO}$, mol
A. No C_2H_5OH Added[a]					
1. $(P_{NO})_0 = 0$; $10^5(n_{H_2N_2O_2})_0 = 5.93$	18	0.28	0.48	0.41	
	24	0.31	0.43	0.45	
	87	0.55	0.22	0.67	
2. $(P_{NO})_0 = 43.8$ torr; $10^5(n_{H_2N_2O_2})_0 = 4.44$	67	0.32	1.04	0.65	8.52
	98	0.32	1.56	0.83	4.98
	118	0.29	1.71	0.78	6.13
	166	0.29	1.77	0.81	6.80
B. 0.5 mL of C_2H_5OH Added[a]					
1. $P_{NO}° = 0$; $10^5(n_{H_2N_2O_2})_0 = 4.42$	46	0.47	0.17	0.55	
	170	0.75	0.10	0.83	
	210	0.98	0.075	1.06	
2. $P_{NO}° = 50.9$ torr; $10^5(n_{H_2N_2O_2})_0 = 5.26$	42	0.49	0.11	0.54	2.53
	96	0.69	0.095	0.76	3.55
	163	0.79	0.080	0.85	2.92
	250	0.94	0.054	0.99	3.47

[a] Total solution volume 10.0 mL.

Table II. Mass Spectrometric Analyses of N_2O Product of $H_2N_2O_2$ Decomposition and Reaction with ^{15}NO (96.2%) in 5.0 M $HClO_4$ at 25 °C

	e/m	fraction of total N_2O	% ^{15}N in total N_2O
A. No C_2H_5OH Added			
$P_{NO}° = 45.0$ torr;	46	0.1725	
$10^5(n_{H_2N_2O_2})_0 = 4.59$; $t = 190$ h	45	0.4547	40.0
	44	0.3728	
B. 0.5 mL of C_2H_5OH Added			
$P_{NO}° = 36.0$ torr; $t = 250$ h	46	0.1542	
	45	0.0239	16.6
	44	0.8219	

In the absence of chain inhibition, the free radical OH may interact with ·ONNOH to yield NO (eq 7) and with NO to yield HNO_2 (eq 8). The latter will in turn be expected to undergo disproprotionation to yield NO and NO_3^- (eq 9), so that some nitrate should be found among the NO–$H_2N_2O_2$ reaction products (but has not been observed directly by us). The near randomness of isotopic distribution observed in N_2O in the non-chain-inhibited case indicates that it is produced largely by HNO dimerization, so that H atom abstraction on the part of unlabeled NO clearly comes into play on an important scale in this case (eq 10). This downgrades the importance of eq 4 as an N_2O source. To account for this and to identify the major source of the very abundant N_2 product, as well as of OH radicals, we postulate attack of NO at oxygen on ·ONNOH to produce these two products, plus NO_2 (eq 11). Through its expected disproportionative hydrolysis (eq 12), the NO_2 will become a further source of both HNO_2 and NO_3^-. The reaction pathway described above is summarized in eq 7–14 of Scheme I.

Scheme I

$$\mathrm{OH} + \cdot\mathrm{ONNOH} \rightarrow 2\mathrm{NO} + \mathrm{H_2O} \qquad (7)$$

$$^{15}\mathrm{NO} + \mathrm{OH} \rightarrow \mathrm{H^{15}NO_2} \qquad (8)$$

$$3\mathrm{H^{15}NO_2} \rightarrow 2\,^{15}\mathrm{NO} + \mathrm{H^+} + \mathrm{NO_3^-} + \mathrm{H_2O} \qquad (9)$$

$$\mathrm{NO} + \mathrm{HONNOH} \rightarrow \mathrm{HNO} + \cdot\mathrm{ONNOH} \qquad (10)$$

$$\mathrm{NO} + \cdot\mathrm{ONNOH} \rightarrow \mathrm{ONONNOH} \rightarrow \mathrm{NO_2} + \mathrm{N_2} + \mathrm{OH} \qquad (11)$$

$$2\mathrm{NO_2} + \mathrm{H_2O} \rightarrow \mathrm{HNO_2} + \mathrm{H^+} + \mathrm{NO_3^-} \qquad (12)$$

$$\mathrm{H^{15}NO} + \mathrm{H^{15}NO} \rightarrow {}^{15}\mathrm{N^{15}NO} + \mathrm{H_2O} \qquad (6)$$

$$\mathrm{H^{15}NO} + \mathrm{HNO} \rightarrow {}^{1}/_{2}\,{}^{15}\mathrm{NNO} + {}^{1}/_{2}\,\mathrm{N^{15}NO} + \mathrm{H_2O} \qquad (13)$$

$$\mathrm{HNO} + \mathrm{HNO} \rightarrow \mathrm{N_2O} + \mathrm{H_2O} \qquad (14)$$

In addition to the above scheme, the possible reactions eq 15 and 16 have been postulated by Buchholz and Powell; however, these seem less plausible to us than eq 7–14.

$$\mathrm{HONNOH} + \mathrm{NO} \rightarrow \mathrm{HNO_2} + \mathrm{N_2} + \mathrm{OH} \qquad (15)$$

$$\mathrm{HONNOH} + \cdot\mathrm{ONNOH} \rightarrow 2\mathrm{NO} + \mathrm{N_2} + \mathrm{OH} + \mathrm{H_2O} \qquad (16)$$

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Synthesis and X-ray Structural Characterization of a Bimetallic Rh–Au Complex with Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

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Heterobimetallic complexes with bidentate phosphine and phosphine–pyridine type ligands to hold two metals in close proximity have received considerable attention in recent years.[1-10] Bifunctional ligands such as 2-(diphenylphosphino)pyridine, Ph_2Ppy, have proved to be particularly useful in constructing

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