

Notes

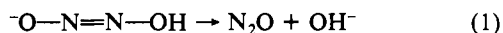
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Reaction of Nitric Oxide with Hyponitrous Acid: A Hydrogen Atom Abstraction Reaction

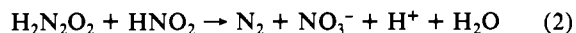
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and Martin N. Hughes^{*1b}

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The decomposition 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 ($k_1 = 7.2 \times 10^{-4} \text{ s}^{-1}$ at



pH 9.2 and 25 °C).² In acid solution, hyponitrite is present as hyponitrous acid and is considerably more stable (e.g., $k_1 = 1.6 \times 10^{-4} \text{ s}^{-1}$ 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 Powell⁵ found this reaction to be inhibited by $\text{C}_2\text{H}_5\text{OH}$ and reported it to proceed via an initial buildup of HNO_2 followed by the HNO_2 - $\text{H}_2\text{N}_2\text{O}_2$ reaction (eq 2), with the NO product ascribed



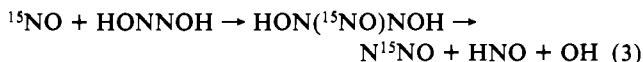
to HNO_2 disproportionation and N_2O to simultaneous occurrence of the "normal" path (eq 1). Recent studies of the reaction (2) beyond those previously published^{5,9} have suggested that an additional reaction may occur in these systems, i.e. a reaction between NO and $\text{H}_2\text{N}_2\text{O}_2$. In particular, it has been observed that NO is absent in reaction systems containing HClO_4 and characterized by high $\text{H}_2\text{N}_2\text{O}_2$ 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 $\text{H}_2\text{N}_2\text{O}_2$ 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 - $\text{H}_2\text{N}_2\text{O}_2$ reaction, its origin cannot be entirely from HNO_2 disproportionation because a significant proportion of its N atoms arise from $\text{H}_2\text{N}_2\text{O}_2$.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 $\text{H}_2\text{N}_2\text{O}_2$, 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

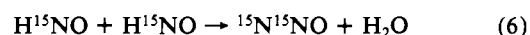
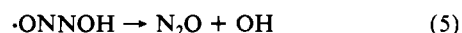
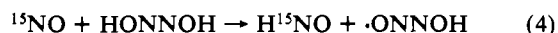
To establish whether or not a direct NO - $\text{H}_2\text{N}_2\text{O}_2$ reaction occurs, gas products of $\text{H}_2\text{N}_2\text{O}_2$ decomposition in 5 M HClO_4 with and without $\text{C}_2\text{H}_5\text{OH}$ as chain inhibitor, and in the absence and presence of added NO gas, were measured 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 $\text{H}_2\text{N}_2\text{O}_2$ occurs, both with and without chain inhibitor. With no $\text{C}_2\text{H}_5\text{OH}$ 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 $\text{C}_2\text{H}_5\text{OH}$ 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 $(\text{H}_2\text{N}_2\text{O}_2)_0$ alone and the product ratio $n_{\text{N}_2}/n_{\text{N}_2\text{O}}$ 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 $\text{C}_2\text{H}_5\text{OH}$, on the other hand, formation of the two singly labeled species $^{14}\text{N}^{15}\text{NO}$ and $^{15}\text{N}^{14}\text{NO}$ (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 $\text{H}_2\text{N}_2\text{O}_2$ (eq 3) as anything more than a minor reaction pathway. The only



attack that appears to explain the observations is a reaction of H atom abstraction at NO , forming H^{15}NO and the radical $\cdot\text{ONNOH}$. 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 $\text{C}_2\text{H}_5\text{OH}$.



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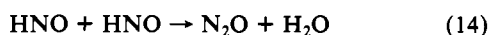
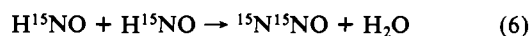
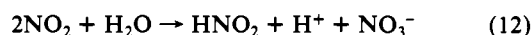
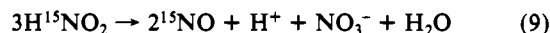
Table I. Gas Products of Reaction Systems Containing $\text{H}_2\text{N}_2\text{O}_2$ in 5.0 M HClO_4 at 25 °C, with and without Added NO and with and without $\text{C}_2\text{H}_5\text{OH}$ as Chain Inhibitor

	t, h	$n_{\text{N}_2\text{O}}/$ $(n_{\text{H}_2\text{N}_2\text{O}_2})_0$	$n_{\text{N}_2}/$ $n_{\text{N}_2\text{O}}$	$(n_{\text{N}_2} + n_{\text{N}_2\text{O}})/$ $(n_{\text{H}_2\text{N}_2\text{O}_2})_0$	$10^5 \Delta n_{\text{NO}},$ mol
A. No $\text{C}_2\text{H}_5\text{OH}$ Added ^a					
1. $(P_{\text{NO}})_0 = 0; 10^5(n_{\text{H}_2\text{N}_2\text{O}_2})_0 = 5.93$	18	0.28	0.48	0.41	
	24	0.31	0.43	0.45	
	87	0.55	0.22	0.67	
2. $(P_{\text{NO}})_0 = 43.8 \text{ torr}; 10^5(n_{\text{H}_2\text{N}_2\text{O}_2})_0 = 4.44$	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 $\text{C}_2\text{H}_5\text{OH}$ Added ^a					
1. $P_{\text{NO}}^\circ = 0; 10^5(n_{\text{H}_2\text{N}_2\text{O}_2})_0 = 4.42$	46	0.47	0.17	0.55	
	170	0.75	0.10	0.83	
	210	0.98	0.075	1.06	
2. $P_{\text{NO}}^\circ = 50.9 \text{ torr}; 10^5(n_{\text{H}_2\text{N}_2\text{O}_2})_0 = 5.26$	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

^aTotal solution volume 10.0 mL.**Table II.** Mass Spectrometric Analyses of N_2O Product of $\text{H}_2\text{N}_2\text{O}_2$ 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 $\text{C}_2\text{H}_5\text{OH}$ Added			
$P_{\text{NO}}^\circ = 45.0 \text{ torr};$ $10^5(n_{\text{H}_2\text{N}_2\text{O}_2})_0 = 4.59; t = 190 \text{ h}$	46	0.1725	
	45	0.4547	40.0
	44	0.3728	
B. 0.5 mL of $\text{C}_2\text{H}_5\text{OH}$ Added			
$P_{\text{NO}}^\circ = 36.0 \text{ torr}; t = 250 \text{ h}$	46	0.1542	
	45	0.0239	16.6
	44	0.8219	

In the absence of chain inhibition, the free radical OH may interact with $\cdot\text{ONNOH}$ to yield NO (eq 7) and with NO to yield HNO_2 (eq 8). The latter will in turn be expected to undergo disproportionation to yield NO and NO_3^- (eq 9), so that some nitrate should be found among the $\text{NO}-\text{H}_2\text{N}_2\text{O}_2$ 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 $\cdot\text{ONNOH}$ 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

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.



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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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