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Registry No. [(MeO)₃P]₃CuCl, 67784-65-0; [(MeO)₃P]₂CuBH₄, 67784-66-1.

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Reaction between Nitric and Sulfamic Acids in Aqueous Solution¹

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The production of nitrous oxide when sulfamic acid is treated with nitric acid in the presence of sulfuric acid was first reported by Thiele and Lachman² and confirmed by Divers and Haga.³



Baumgarten⁴ reported quantitative yields of N₂O upon treating solid sulfamic acid with HNO₃ of weight percent concentrations 73 and above. While the possible formation of nitramide (H₂NNO₂) was considered,³ it was not detected as product in early investigations. Nitramide is known to decompose to N₂O and would appear to be a likely intermediate species in this reaction, however, and Heubel and Canis⁵ detected formation of this species in a series of reactions between sulfamates and nitrates studied by thermogravimetry. In a subsequent study Canis⁶ reported the production of H₂NNO₂ in low yield (<5%) upon treatment of solid NH₂SO₃H with 95% HNO₃ in the temperature range -50 to -20 °C and higher yields upon addition of NaNO₃. Because small changes in HNO₃ concentration between 93 and 100% have a large effect on the reaction rate, Canis postulated a mechanism involving attack of the species NO₂⁺ on sulfamate. She also reported an increase in the rate and proportion of N₂O production upon addition of concentrated H₂SO₄.

In more recent studies,^{7,8} the kinetics of the nitric acid-sulfamic acid reaction have been measured at somewhat elevated temperatures and over a broad range of HNO₃ concentrations. Hughes et al.⁸ have made the surprising observation that the reaction proceeds through two initial stages, each involving apparent intermediate formation, and reported that nitrous oxide and sulfate products appear in a third (and slowest) stage which is first order in both sulfamate and nitrate concentrations and whose acidity function dependence indicates involvement of NO₂⁺. These authors have suggested alternative schemes, in each of which H₂NNO₂ is postulated to be

Table I. Mass Spectra of N₂O Product in the H¹⁵NO₃-NH₂SO₃H Reaction

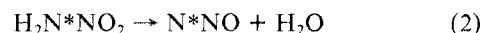
mass	<i>t</i> = 7 days ^a	<i>t</i> = 21 days ^a	<i>t</i> = 19 days ^b
46	0.0038	0.0039	0.0037
45	0.164	0.164	0.107
44	1.00	1.00	1.00
31	0.0113	0.0105	0.0064
30	0.0794	0.0734	0.0823
44-46 ^c	7.35	7.36	5.15
30 + 31 ^c	12.5	12.5	7.2

^a [HNO₃] = 12.7 ± 0.5 M, [NH₂SO₃H] = 0.091 ± 0.003 M, % ¹⁵N(HNO₃) = 12.8 ± 0.5. ^b [HNO₃] = 5.9 ± 0.2 M, [NH₂SO₃H] = 0.50 ± 0.02 M, % ¹⁵N(HNO₃) = 6.9 ± 0.3. ^c % ¹⁵N.

the immediate precursor to product N₂O. We report here experiments with ¹⁵N tracer which bear on this point.

Experiments were carried out on degassed solutions in Y-shaped reaction vessels at room temperature (25 ± 2 °C), employing vacuum-line techniques. Gas products were collected by Toepler pump and analyzed by gas chromatography (Varian Aerograph 920 with a 12-ft Porapak Q column and a Varian A-25 integrator/recorder) or, in the cases of isotopic analyses and gas analyses at very low pressure, on an AEI MS-30 mass spectrometer. Extremely small quantities of gas product were found after extended reaction periods, indicating low rates consistent with the rate constants and activation energy reported by Hughes et al.⁸ Yields of <2 μmol were produced in 10 mL of solution at [NH₂SO₃H] = 0.50 M and [HNO₃] in the range 0.50-4.5 M, with reaction times between 2.5 and 21 days. Increasing quantities were obtained at higher nitric acid concentrations, up to 114 μmol with [HNO₃] = 12.5 M, [NH₂SO₃H] = 0.091 M, and reaction time 7 days. In each of these cases, the gas proved to be a mixture of N₂ and N₂O, the latter predominating. With a reaction mixture at [HNO₃] = 12.7 M and [NH₂SO₃H] = 0.088 M, product gas samples were withdrawn at intervals over a 2-week period, revealing a gradual increase of N₂ content from 1.0% of total gas product at 24 h to 4.7% at 2 weeks. Vacuum line conditions were such that we are confident the observed N₂ was not of atmospheric origin.

Tracer experiments were carried out at two different H¹⁵NO₃ concentration levels, and the mass spectra of resulting separated N₂O product gases are shown in Table I. The unchanging isotopic composition at [HNO₃] = 12.7 M between 7 and 21 days of reaction time indicates that no shift of pathway occurred within this period. At both concentration levels the percentage of ¹⁵N observed at masses 30 and 31, i.e., in NO produced by electron impact cracking in the mass spectrometer, is the same as its initial abundance in reactant HNO₃, within the error of measurement. This is the result that would be expected for N₂O produced by decomposition of an asymmetric, bound intermediate, e.g., nitramide:



Clusius⁹ has shown that nitramide decomposes to N₂O without rearrangement, and with all ¹⁵N above natural abundance arising from HNO₃, the decay product at mass 45 should be almost entirely ¹⁴N¹⁵N¹⁶O for reaction 2. However, the data in Table I show mass 45 abundances at both HNO₃ concentrations that are substantially greater than predicted for a nitramide precursor; this is reflected in the fact that the percentage of ¹⁵N in N₂O (masses 44-46) is significantly greater than half the isotopic content of reactant HNO₃. In addition, N₂O of mass 46, largely ¹⁵N¹⁵N¹⁶O, is present in both experiments at levels that are small but unmistakably greater than predicted on the basis of reaction 2.

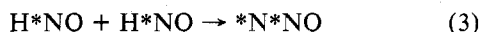
The only way that the apparent contradictions posed by these data can be reconciled is to assume that the observed N₂O is a mixture of two kinds, one arising from the asym-

Table II. Isotopic Composition (%) of N_2O As Calculated for Assumed Reaction Source Mixtures and Compared with Observed Values

mass	12.7 M HNO_3 , 12.8% ^{15}N		5.9 M HNO_3 , 6.9% ^{15}N	
	calcd ^a	obsd	calcd ^b	obsd
46	0.38	0.33	0.40	0.33
45	14.0	14.0	9.62	9.63
44	85.6	85.6	90.0	90.0
44-46 ^c	7.37	7.36	5.21	5.15
30 + 31 ^c	12.8	12.5	6.91	7.20

^a Assuming 90 mol % arises from $\text{H}_2\text{N}^*\text{NO}_2$. ^b Assuming 57 mol % arises from $\text{H}_2\text{N}^*\text{NO}_2$. ^c % ^{15}N .

metric, bound precursor $\text{H}_2\text{N}^*\text{NO}_2$ and the other from an unbound intermediate whose nitrogen comes from HNO_3 . The latter prescription is met by HNO :



Reaction 3 would account for the presence of $^{15}\text{N}^{15}\text{N}^{16}\text{O}$ and would also result in production of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ as well as $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, which in turn can account for the elevation of the overall ^{15}N content of the N_2O . To test this idea we have calculated the detailed isotopic composition of N_2O expected from reactions 2 and 3 separately, at the two different levels of ^{15}N enrichment in HNO_3 , by taking into account all possible isomers at masses 44-46 and without neglecting natural abundances of ^{15}N and ^{18}O . As shown in Table II, a very close match between observed and calculated isotopic compositions is obtained when we assume a product containing 90 mol % from (2) and 10 mol % from (3) at $[\text{HNO}_3] = 12.7 \text{ M}$ and 57 mol % from (2) plus 43 mol % from (3) at $[\text{HNO}_3] = 5.9 \text{ M}$. The closeness of comparison extends to the electron-impact-produced NO composition (mass 30-31) as well as the individual masses 44-46 and overall N_2O composition.

We conclude that the predominant immediate precursor to N_2O product of the nitric acid-sulfamic acid reaction is indeed nitramide, as proposed by Hughes et al.⁸ but that, at least under the slow reaction conditions of our experiments, substantial proportions also arise from the dimerization of an unbound intermediate whose nitrogen atoms come from HNO_3 and which we presume to be HNO . Since N_2O is not a reported or expected product of self-decomposition in HNO_3 , we presume that the HNO must have its origins within the HNO_3 - $\text{NH}_2\text{SO}_3\text{H}$ reaction itself, a conclusion that is reinforced by the apparent constancy of N_2O isotopic composition with time in the experiment at $[\text{HNO}_3] = 12.7 \text{ M}$ (Table I). HNO could be a product of sequential redox processes, but this seems unlikely since unlabeled hydroxylamine and labeled HNO_2 would also be products; interaction of these species would produce N_2O of isotopic composition substantially different from that of either reactions 2 or 3.¹⁰ (Hughes et al.⁸ have also considered the possibility of N_2O production by an NH_2OH - HNO_2 reaction; our results appear to rule this out definitively.) We believe it most likely that HNO is produced via decomposition of or a competing reaction with an intermediate which precedes the formation of nitramide. In Scheme 2 of Hughes et al.,⁸ for example, it is postulated that the species $\text{ONNHOSO}_3\text{H}$ is formed and subsequently reacts with HNO_3 on the route to H_2NNO_2 . HNO containing nitrogen of the same isotopic content as initial HNO_3 could be formed from this species by N-N cleavage by hydrolysis or some other means. The higher proportion of N_2O from HNO dimerization observed at the lower HNO_3 concentration could then be interpreted in terms of a weaker competition of HNO_3 for reaction with the intermediate.

Separated N_2 produced at $[\text{HNO}_3] = 12.7 \text{ M}$ was found to contain $7.3 \pm 0.9\%$ ^{15}N , i.e., just half of the initial H^{15}NO_3 abundance within error. This product probably arises from

reaction between HNO_2 and $\text{NH}_2\text{SO}_3\text{H}$, which is consistent with the isotopic result. The source of HNO_2 can be self-decomposition of HNO_3 to NO_2 followed by disproportionative hydrolysis and also the nitric acid-sulfamic acid reaction itself, if Scheme 2 of Hughes et al.⁸ should be correct. An additional reaction source possibility, which would have the same isotopic consequence, is interaction between HNO_2 and H_2NNO_2 .¹¹

Acknowledgment. We thank Dr. Charles Iden and the Stony Brook mass spectrometry facility for assistance with isotopic analyses.

Registry No. HNO_3 , 7697-37-2; $\text{NH}_2\text{SO}_3\text{H}$, 5329-14-6; N_2O , 10024-97-2.

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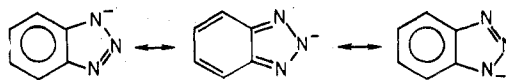
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Preparation and Characterization of Tetrakis(2,4-pentanedionato)hexakis(benzotriazolato)-pentacopper(II)

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We wish to report some experimental results with the title compound (I) which strongly suggest unique tridentate bonding for each of the benzotriazole anions (BTA^-)



One structure for I consistent with our results is a tetrahedral array of Cu(II) ions surrounding a central Cu(II) ion held together by bridging tridentate BTA^- and terminated by 2,4-pentanedionato (acac^-) end caps (Figure 1).¹ It is easily built from molecular models and may be viewed as a $\text{Cu}_5\text{BTA}_6^{4+}$ cation neutralized by four acac^- anions.

Compound I is prepared by mixing equimolar amounts of 0.1 M methanol solutions of $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2,4-pentanedione, and BTA followed by addition of ammonia to basic pH or by mixing dichloromethane solutions of Cu(acac)_2 and BTA in equimolar proportions.² If the former method is employed, the clear dark green solution is extracted with cyclohexane and the cyclohexane extracts are washed with H_2O and then dried with anhydrous Na_2SO_4 . The cyclohexane is removed by evaporation, the green solid is recrystallized from 1,2-dichloroethane-acetonitrile (ca. 1:20), and the deep green crystals are heated overnight in vacuo at 80°C . Anal. Calcd for $\text{C}_{56}\text{H}_{52}\text{N}_{18}\text{O}_8\text{Cu}_5$: C, 47.26; H, 3.69; N, 17.73; Cu, 22.33. Found: C, 47.22; H, 3.69; N, 17.65; Cu, 23.12.³ Osmometric molecular weight determinations yielded 993 (CHCl_3)⁴ and 1335 (benzene); 1423 is calculated for I.⁵ Yields of I based