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Registry No. $[(MeO)_3P]_3CuCl$, 67784-65-0; $[(MeO)_3P]_2CuBH_4$, 67784-66-1.

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Reaction between Nitric and Sulfamic Acids in Aqueous Solution[1]

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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 Lachman[2] and confirmed by Divers and Haga:[3]

$$HNO_3 + NH_2SO_3H \rightarrow N_2O + H_2SO_4 + H_2O \qquad (1)$$

Baumgarten[4] reported quantitative yields of N_2O upon treating solid sulfamic acid with HNO_3 of weight percent concentrations 73 and above. While the possible formation of nitramide (H_2NNO_2) was considered,[3] it was not detected as product in early investigations. Nitramide is known to decompose to N_2O and would appear to be a likely intermediate species in this reaction, however, and Heubel and Canis[5] detected formation of this species in a series of reactions between sulfamates and nitrates studied by thermogravimetry. In a subsequent study Canis[6] reported the production of H_2NNO_2 in low yield (<5%) upon treatment of solid NH_2SO_3H with 95% HNO_3 in the temperature range −50 to −20 °C and higher yields upon addition of $NaNO_3$. Because small changes in HNO_3 concentration between 93 and 100% have a large effect on the reaction rate, Canis postulated a mechanism involving attack of the species NO_2^+ on sulfamate. She also reported an increase in the rate and proportion of N_2O production upon addition of concentrated H_2SO_4.

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 HNO_3 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 NO_2^+. These authors have suggested alternative schemes, in each of which H_2NNO_2 is postulated to be the immediate precursor to product N_2O. We report here experiments with ^{15}N tracer which bear on this point.

Table I. Mass Spectra of N_2O Product in the $H^{15}NO_3$-NH_2SO_3H Reaction

mass	t = 7 days[a]	t = 21 days[a]	t = 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] $[HNO_3] = 12.7 \pm 0.5$ M, $[NH_2SO_3H] = 0.091 \pm 0.003$ M, % $^{15}N(HNO_3) = 12.8 \pm 0.5$. [b] $[HNO_3] = 5.9 \pm 0.2$ M, $[NH_2SO_3H] = 0.50 \pm 0.02$ M, % $^{15}N(HNO_3) = 6.9 \pm 0.3$. [c] % ^{15}N.

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 $[NH_2SO_3H] = 0.50$ M and $[HNO_3]$ 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 $[HNO_3] = 12.5$ M, $[NH_2SO_3H] = 0.091$ M, and reaction time 7 days. In each of these cases, the gas proved to be a mixture of N_2 and N_2O, the latter predominating. With a reaction mixture at $[HNO_3] = 12.7$ M and $[NH_2SO_3H] = 0.088$ M, product gas samples were withdrawn at intervals over a 2-week period, revealing a gradual increase of N_2 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 N_2 was not of atmospheric origin.

Tracer experiments were carried out at two different $H^{15}NO_3$ concentration levels, and the mass spectra of resulting separated N_2O product gases are shown in Table I. The unchanging isotopic composition at $[HNO_3] = 12.7$ 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 ^{15}N 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 HNO_3, within the error of measurement. This is the result that would be expected for N_2O produced by decomposition of an asymmetric, bound intermediate, e.g., nitramide:

$$H_2N^*NO_2 \rightarrow N^*NO + H_2O \qquad (2)$$

Clusius[9] has shown that nitramide decomposes to N_2O without rearrangement, and with all ^{15}N above natural abundance arising from HNO_3, the decay product at mass 45 should be almost entirely $^{14}N^{15}N^{16}O$ for reaction 2. However, the data in Table I show mass 45 abundances at both HNO_3 concentrations that are substantially greater than predicted for a nitramide precursor; this is reflected in the fact that the percentage of ^{15}N in N_2O (masses 44–46) is significantly greater than half the isotopic content of reactant HNO_3. In addition, N_2O of mass 46, largely $^{15}N^{15}N^{16}O$, 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 N_2O 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

	12.7 M HNO_3, 12.8% ^{15}N		5.9 M HNO_3, 6.9% ^{15}N	
mass	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 $H_2N^*NO_2$. [b] Assuming 57 mol % arises from $H_2N^*NO_2$. [c] % ^{15}N.

metric, bound precursor $H_2N^*NO_2$ and the other from an unbound intermediate whose nitrogen comes from HNO_3. The latter prescription is met by HNO:

$$H^*NO + H^*NO \rightarrow {}^*N^*NO \qquad (3)$$

Reaction 3 would account for the presence of $^{15}N^{15}N^{16}O$ and would also result in production of $^{15}N^{14}N^{16}O$ as well as $^{14}N^{15}N^{16}O$, 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 $[HNO_3] = 12.7$ M and 57 mol % from (2) plus 43 mol % from (3) at $[HNO_3] = 5.9$ 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–NH_2SO_3H reaction itself, a conclusion that is reinforced by the apparent constancy of N_2O isotopic composition with time in the experiment at $[HNO_3] = 12.7$ 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 $ONNHOSO_3H$ 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 $[HNO_3] = 12.7$ M was found to contain 7.3 ± 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 NH_2SO_3H, 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]

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

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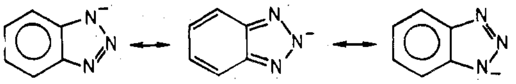
We wish to report some experimental results with the title compound (I) which strongly suggest unique tridentate bonding for each of the benzotriazole anions (BTA^-)



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 $Cu_5BTA_6^{4+}$ cation neutralized by four $acac^-$ anions.

Compound I is prepared by mixing equimolar amounts of 0.1 M methanol solutions of $Cu(NO_3)_2 \cdot 3H_2O$, 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 $C_{56}H_{52}N_{18}O_8Cu_5$: 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

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