

## Synthesis and Thermal Decomposition of <sup>15</sup>N-labelled NTO

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### SUMMARY

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) has been synthesized in good yield with <sup>15</sup>N at the 1 and 2 positions. The N-H coupling provides unequivocal assignments for <sup>1</sup>H and <sup>15</sup>N NMR spectra and the acidic proton. The products of thermal decomposition at 270 °C were identified spectroscopically. NMR spectra reveal that thermal decomposition results in the formation of 2,4-dihydro-3H-1,2,4-triazol-3-one and ammonia (the latter observed as ammonium ion). The production of ammonia from the thermal decomposition of an energetic material is unprecedented. The gas products HCN, <sup>15</sup>N<sup>14</sup>N, <sup>15</sup>N<sub>2</sub>, and CO were detected by mass spectrometry. Some possible mechanisms of thermal decomposition are discussed.

KEYWORDS: NTO, thermal decomposition, nitrogen isotopic label

### INTRODUCTION

NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) is an energetic material with a high density and a low sensitivity to shock (1). Although NTO has a high melting point (262–3 °C), free radicals from NTO are formed below 100 °C in mixtures of NTO and trinitrotoluene (2). Mechanistic studies of NTO thermal decomposition are hampered by self-heating and autocatalytic reactions that make it difficult to control sample temperatures and to trap reaction intermediates. Thus experiments with <sup>15</sup>N-labelled NTO can provide important mechanistic information that is not easily obtained otherwise.

We report here the good synthetic yield and spectra (<sup>1</sup>H and <sup>15</sup>N NMR) of NTO-1,2-<sup>15</sup>N<sub>2</sub>. Solid and gaseous thermal decomposition products of NTO-1,2-<sup>15</sup>N<sub>2</sub> were detected by NMR spectroscopy and mass spectrometry, respectively. For the first time for any

energetic material, ammonia is reported as a product. The isotopic distribution in ammonia and nitrogen gas indicate there are at least two competing pathways for thermal decomposition of NTO(3,4).

## EXPERIMENTAL SECTION

**Materials.** Fuming nitric acid, potassium permanganate, hydrazine sulfate ( $\text{H}_6\text{N}_2\text{O}_4\text{S}$ ), and sulfuric acid were obtained from J. T. Baker Chemical Co. Semicarbazide hydrochloride, dimethyl sulfoxide (DMSO),  $\text{DMSO-d}_6$ , and *p*-dimethylamino-benzaldehyde (DMBA) were purchased from Aldrich. Hydrazine- $^{15}\text{N}_2$  sulfate (99.7 atom %  $^{15}\text{N}$ ) was obtained from Isotec, Inc. Formic acid (97%) was obtained from Eastman Organic Chemicals. All chemicals were used as purchased.

**Instrumentation.** JEOL 270 MHz and Varian VXR 300 MHz magnetic resonance spectrometers were used to obtain NMR spectra.  $\text{NaNO}_3$ - $^{15}\text{N}$  in  $\text{D}_2\text{O}$  (7.9 M, sealed in a capillary tube) was placed in the NMR tube as an external reference ( $^{15}\text{N}$  chemical shift of  $\text{NaNO}_3$  is -3.7 ppm) (5). All spectra were obtained using  $\text{DMSO-d}_6$  as the solvent. Mass spectral data were obtained with an AutoSpec Q hybrid tandem mass spectrometer interfaced to a Digital Vax Station 3100. Gaseous samples were introduced via the PKF inlet system and ionized by bombarding with a beam of 70 eV electrons. The emission current was adjusted to 100  $\mu\text{A}$ . Thermal decomposition products were mass analyzed at a mass resolution of 3,000 and an accelerating potential of 8,000 V. The magnet was scanned in the mass range of 20-50 amu at a scan rate of 7 s per decade. Gas chromatograms were obtained with a Hewlett-Packard 5890 Series II GC with a thermal conductivity detector and a 30'x1/8" HayesSep DB 100/120 Mes packed column.

**Standard synthesis.** NTO-1,2- $^{15}\text{N}_2$  was synthesized by a modification of Chipen's method (Scheme 1) (6). Unlabelled NTO, used as an analytical control, was synthesized by an identical procedure prior to the synthesis of NTO-1,2- $^{15}\text{N}_2$ .

**Semicarbazide.** In a 100-mL round-bottom flask, 2.0 g (15.4 mmol) of hydrazine sulfate was mixed with 6.0 g (19.0 mmol) of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in 12 mL of  $\text{H}_2\text{O}$ .  $\text{BaSO}_4$  precipitated immediately after which the mixture was refluxed for 10 minutes. Hydrazine hydrate (15 mL) was recovered by trap-to-trap distillation. Watt and Chrisp's method was used to determine the yield of hydrazine (14.6 mmol, 95% yield) (7). Urea (1.20 g, 20.0 mmol) was added to the hydrazine hydrate, and the mixture was refluxed at 110 °C for four hours in a 100-mL round-bottom flask. Unreacted hydrazine (2.5 mmol, 17%) was recovered by

another trap-to-trap distillation. The residue remaining after distillation was dissolved in 20 mL of water. This solution was filtered, and 3 mL of concentrated HCl was added. After evaporation, a white solid remained and was extracted with 20 mL of absolute ethanol to remove urea. Upon drying under vacuum overnight, the sample weighed 1.248 g (11.2 mmol). An NMR spectrum of the product matched the spectrum of authentic semicarbazide hydrochloride with no other proton peaks:  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  10.0 (br s, 2H) 8.9 (br s, 1H) 6.5 (br s, 3H). The yield of semicarbazide was 73% from hydrazine sulfate and 93% from unrecovered hydrazine hydrate. The hydrazine hydrate, recovered from the trap-to-trap distillation, was treated with 3 mL of 4.0 M  $\text{H}_2\text{SO}_4$  to convert it to hydrazine sulfate. The water was evaporated, and 2.0 g of hydrazine sulfate, 10.0 g of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and 12 mL of  $\text{H}_2\text{O}$  were added. Additional semicarbazide hydrochloride (1.61 g, 14.4 mmol) was prepared as above using urea (1.30 g, 20.6 mmol). The yield was 81% from 17.9 mmol hydrazine sulfate.

TO (2,4-dihydro-3H-1,2,4-triazol-3-one). Semicarbazide hydrochloride (4.00 g, 35.9 mmol) in 10 mL of 97% formic acid was refluxed at 106 °C for 4 hours. The liquid was evaporated under vacuum, and the residue was washed with 10 mL of ethanol. A white solid product (TO, 2.9 g, 34.1 mmol) was obtained. The yield was 95% from semicarbazide hydrochloride.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  11.4 (br s) 11.3 (br s) 7.7 (s).

NTO. A mixture of 10 mL of 70%  $\text{HNO}_3$  and 5 mL of fuming  $\text{HNO}_3$  was added to a 100-mL flask containing 3.00 g (35.3 mmol) of TO; all were at -20 °C. The flask was heated to 50 °C until the TO dissolved and then to 85 °C for 30 minutes. The flask was cooled in a ice-water bath, and ice-water (10 mL) was added. A pale yellow-white precipitate was filtered and vacuum dried overnight (3.86 g, 29.7 mmol). The yield of NTO from TO was 84%. Anal. Calcd. for  $\text{C}_2\text{H}_2\text{N}_4\text{O}_3$ : C, 18.47; H, 1.55. Found: C, 18.15, H 1.60.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  13.5 (br s) 12.8 (br s).

NTO-1,2- $^{15}\text{N}_2$ . Semicarbazide-1,2- $^{15}\text{N}_2$  hydrochloride was synthesized by the above procedure in three consecutive experiments by using three, 2.0 g samples of hydrazine- $^{15}\text{N}_2$  sulfate (45.45 mmol total). The hydrazine- $^{15}\text{N}_2$  recovered from the first and second experiments were used subsequently in the second and third experiments, respectively. The yield of semicarbazide-1,2- $^{15}\text{N}_2$  hydrochloride was 73% (3.77 g, 33.2 mmol). From 4.01 g of semicarbazide-1,2- $^{15}\text{N}_2$ , 3.36 g crude TO-1,2- $^{15}\text{N}_2$  was obtained. The NMR spectrum showed ammonia, formate, and water peaks, but no further purification was

performed.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  11.44 (br d,  $J = 106$  Hz) 11.3 (b s), 7.7 (dd  $J = 13.2, 4.3$  Hz).  $^{15}\text{N}$  NMR (DMSO- $d_6$ )  $\delta$  -212.5 (br d,  $J = 103$  Hz) -114.6 (t,  $J = 13$  Hz). NTO-1,2- $^{15}\text{N}_2$  (3.48 g, 26.4 mmol) was prepared with an overall yield of 58% from hydrazine- $^{15}\text{N}_2$  sulfate.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  13.5 (br s) 12.8 (d d,  $J = 105.5$  Hz, 8 Hz).  $^{15}\text{N}$  NMR (DMSO- $d_6$ )  $\delta$  -202.7 (dd,  $J = 106, 13$  Hz) -109.5 (dd,  $J = 13, 7$  Hz).

Alternate semicarbazide syntheses. Hydrazine sulfate (2.0 g) was neutralized with 15 mL of hot aqueous barium hydroxide (4.85g  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , 15.4 mmol). The solution was centrifuged to separate the barium sulfate, and the aqueous hydrazine supernatant was decanted and transferred with 1.00 g urea (16.7 mmol) to either a 100-mL flask and refluxed or to a Teflon-lined Parr bomb (model 4745) and heated to 100 °C for 6 hours. Yields of semicarbazide after 2.5, 4 and 5 hr of refluxing were 45, 55 and 53%, respectively. The yield for heating 6 hours in the bomb was 53%.

Thermal Decomposition. NTO-1,2- $^{15}\text{N}_2$  (1.0 g, 7.5 mmol) was placed in a 50-mL flask fitted with a stopcock that was connected to a vacuum line by an o-ring joint. The flask was evacuated, filled with He, and heated to 270 °C for 5 minutes. The flask was transferred to the mass spectrometer for analysis of the gas products. The residue in the flask was analyzed by NMR.

## RESULTS

The thermal decomposition of NTO-1,2- $^{15}\text{N}_2$  in a He atmosphere resulted in the evolution of gases and the formation of a non-volatile brown residue. A 1:1:1 triplet ( $J = 51.2$  Hz) and 1:1 doublet ( $J = 71.9$  Hz), both at 7.10 ppm were observed in the  $^1\text{H}$  NMR spectrum of the residue. The triplet is assigned to  $^{14}\text{NH}_4^+$  by comparison with various ammonium salts. By analogy the doublet is assigned to  $^{15}\text{NH}_4^+$ . The integration ratio of the  $\text{NH}_4^+$  triplet and doublet peaks was 4.3. Only the triplet peak was observed when NTO was decomposed, and assignment of the triplet was confirmed by detection of ammonia by the Nessler Method (8). A doublet of doublets ( $J = 105.4, 8.4$  Hz) at 12.8 ppm is assigned to NTO-1,2- $^{15}\text{N}_2$ . The relative areas of the NTO-1,2- $^{15}\text{N}_2$  and  $\text{NH}_4^+$  peaks were 1.26:1 indicating a 4-fold excess of NTO-1,2- $^{15}\text{N}_2$ . Small peaks at 7.70 (dd,  $J = 13.2, 4.3$  Hz) and 11.41 ppm (dd,  $J = 105.7, 7.7$  Hz) were assigned to TO-1,2- $^{15}\text{N}_2$  (see Experimental

Section). A  $^1\text{H}$ -decoupled  $^{15}\text{N}$  NMR spectrum of the same sample shows NTO-1,2- $^{15}\text{N}_2$  doublets at -109.5 ( $J = 13$  Hz) and -202.7 ppm ( $J = 13$  Hz), one of the TO-1,2- $^{15}\text{N}_2$  doublets at -212.6 ppm, and an  $\text{NH}_4^+$  peak at -360.6 ppm (5). Preliminary experiments with NTO indicate that the yield of TO and ammonium ion were at least 13 and 10%, respectively.

The peak assignments for the mass spectra of the gaseous products from NTO-1,2- $^{15}\text{N}_2$  thermal decomposition are listed in Table 1. Under the resolution used,  $^{15}\text{N}_2$  and  $^{14}\text{NO}$  could not be resolved, and CO was not entirely resolved from the  $^{14}\text{N}_2$ . Substantial background peaks were observed at 28, 32, and 44 (presumably due to residual atmosphere and pump oil decomposition). In similar thermal decomposition experiments with NTO, the mole ratio of NO to  $\text{N}_2$  was found to be 0.27 by gas chromatography. This yields 4.4 for the ratio of  $^{15}\text{N}_2$  to  $^{14}\text{N}^{15}\text{N}$ .

Table 1. Mass spectroscopic data and assignments for the gas products from NTO-1,2- $^{15}\text{N}_2$  decomposition

| Mass m/e | Relative Intensity | Assignment                           | Expected Mass  |
|----------|--------------------|--------------------------------------|----------------|
| 27.014   | 0.08               | $\text{HC}^{14}\text{N}$             | 27.011         |
| *        | 0.21               | CO                                   | 27.995         |
| 28.006   | 0.70               | $^{14}\text{N}_2$                    | 28.006         |
| 29.001   | 0.17               | $^{14}\text{N}^{15}\text{N}$         | 29.003         |
| 29.996   | 1.00               | $^{15}\text{N}_2$ , $^{14}\text{NO}$ | 30.000, 29.998 |
| 31.988   | 0.06               | $\text{O}_2$                         | 31.990         |

\*low mass shoulder of the 28.006 peak

## DISCUSSION

The yield of NTO-1,2- $^{15}\text{N}_2$  from hydrazine sulfate (58%) is a significant improvement over the 9% recently reported (4). Extended reaction between urea and hydrazine leads to low semicarbazide yields that are probably due to further reactions of semicarbazide with urea, hydrazine or another semicarbazide. Since there is an equilibrium in the first step of Scheme 1, the removal of ammonia during reflux could drive the reaction to completion, yet no marked change in yields were noted when the experiments with unlabelled hydrazine

were carried out in a sealed bomb instead of an open flask. (Note that the semicarbazide yields for the alternate syntheses were lower than that of the standard synthesis because hydrazine was decanted instead of distilled from the barium sulfate). Particular care must be taken during the nitration of TO.

Extended exposure of NTO to nitric acid

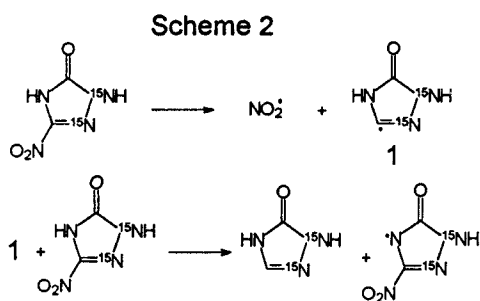
at high temperatures will result in

decomposition. We find that NTO (1g) can be completely decomposed by heating in

fuming nitric acid (5 mL) for 30 min at 80 °C. Thus, the TO nitration yields are improved by starting at low temperatures.

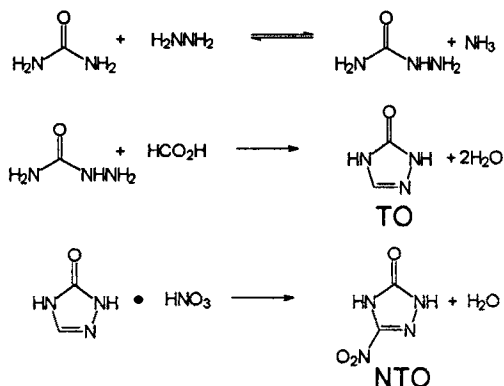
Assignment of the NTO-1,2-<sup>15</sup>N<sub>2</sub> proton peaks are straightforward. The 12.8 ppm peak shows 1 and 2 bond coupling to <sup>15</sup>N nuclei, so it is assigned to the hydrogen at the 2 position. The broad peak at 13.5 ppm must therefore be at the 4 position. The broadening is likely to be due primarily to proton exchange. In accord with this explanation, this peak was not observed in the decomposition mixture which contains ammonia. Taken together, these observations indicate that the acidic proton is at the 4 position. These assignments are in agreement with those made previously (4,9). Note that a recently published tautomeric structure where a hydrogen is at the 1 and 2 position but not the 4 position is not consistent with our results (10).

NTO thermal decomposition has been reported to produce N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, NO<sub>2</sub>, NO, and H<sub>2</sub> (11,12). TO formation after partial NTO decomposition suggests that NO<sub>2</sub> and TO radicals (I) are formed (Scheme 2). TO could be formed by hydrogen abstraction from other intermediates or NTO. In fact, kinetic isotope effects indicate that an N-H scission occurs in the global rate-determining step for thermal decomposition (2,4).

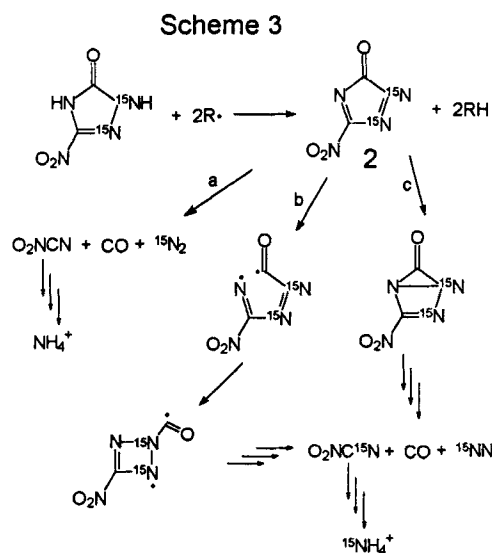


The production of ammonia as a thermal decomposition product from an energetic material is surprising. The ammonia is detected as ammonium ion, and we believe that the major counter anion is the conjugate base of NTO. This assumption seems reasonable since NTO

**Scheme 1**



was present in excess and has a low  $\text{pK}_a$  (3.67) (1). Elemental analysis of the ammonium salt was not consistent with any simple stoichiometry. This was probably due to the presence of other anions such as nitrite or nitrate. We find that the yield of ammonia varies from 5 to 10%. The yield of ammonium ion is probably limited by the availability of water for hydrolysis of the CN group (see Scheme 3).



The loss of two hydrogens would result in the formation of **2** (5-nitro-3H-1,2,4-triazol-1,2,15 $\text{N}_2$ -3-one, Scheme 3,  $\text{R} = \text{I}$ , or  $\text{NO}_2$ , or other radical). The electronic structure of **2** is not certain. The hydrogen abstraction initially forms a  $\sigma$  radical, but if **2** is spin paired (as indicated), it is formally an antiaromatic species similar to cyclopentadienone, a highly reactive diene (13). A symmetry allowed cheletropic reaction (14) (path a) would provide a potential pathway for formation of  $^{15}\text{N}_2$  and 3 other gaseous products since  $\text{NCNO}_2$  will

likely fragment to  $\text{CN}$  and  $\text{NO}_2$  radicals at elevated temperatures (15). Possible mechanisms that account for the formation of  $^{14}\text{N}^{15}\text{N}$  involve either an initial C-N bond homolysis (path b) or the formation of a bicyclic species that extrudes  $\text{CO}$  and ring opens to give the gaseous products (path c). Scheme 3 is offered to explain the formation of ammonium ion and nitrogen gas. Other mechanisms are possible, and concurrent reactions must account for some of the other products. The formation of the bicyclic product by a concerted disrotatory process appears to be symmetry forbidden. This, along with the added strain, makes this path unlikely. Our data are consistent with a stepwise mechanism involving the homolysis of the C-N bond followed by ring closure to form the  $^{14}\text{N}$ - $^{15}\text{N}$  bond. Note that Scheme 3 explains why the ratios for  $^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$  and  $^{15}\text{NH}_4^+/\text{NH}_4^+$  are equal.  $^{14}\text{N}^{14}\text{N}$  apparently is also a major product. Assuming oxygen was an atmospheric contaminant, less than 40% of the observed  $^{14}\text{N}^{14}\text{N}$  could originate from the atmosphere. Hydrogen abstraction by  $\text{NO}_2$  could form  $\text{HNO}_2$  leading to the well known reaction between  $\text{HNO}_2$  and  $\text{NH}_3$  that forms  $\text{N}_2$  and  $\text{H}_2\text{O}$ . (16) Further work is planned to determine the temporal behavior of these reactions.

## ACKNOWLEDGMENTS

This work was supported in part by the Air Force Office of Scientific Research.

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