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NTO Decomposition Products Tracked with ^{15}N Labels

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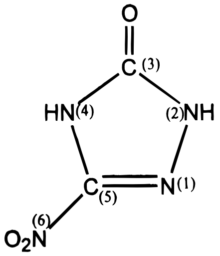
Isotopically labeled 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO) was used to determine the origins of nitrogen atoms in its decomposition gases. NTO samples with ^{15}N labels at 1 and 2 positions, the 4 position, and the 6 position of NTO were synthesized.[1] The thermolysis of NTO yields a brown insoluble residue and the nitrogen-containing gases dinitrogen, nitrous oxide, nitric oxide, and hydrogen cyanide. The analysis of these nitrogen-containing gases is reported, and the mechanistic implications are considered.

Introduction

NTO (5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one) is a candidate for an effective insensitive high explosive. For this reason we have examined its thermal stability, studying the kinetics of NTO decomposition and identifying decomposition products in both condensed phase and solution.[2]



Over the temperature range 220−280 °C, neat NTO exhibited a global activation energy of 78.6 kcal/mol with frequency factor of 2.53×10^{29}/s; NTO in water or methanol (4%, by weight) showed lower activation energies, 48.8 kcal/mol (6.53×10^{17}/s) and 38.4 kcal/mol (1.05×10^{13}/s), respectively. Below 255 °C the kinetics of NTO, neat and in solution, were first order. Above 255 °C autocatalytic decomposition of neat NTO was evident. The decomposition of neat NTO in open thermolysis tubes and solutions of NTO in sealed thermolysis tubes was strictly first order. This was also true for the decomposition of 2,4-dihydro-3*H*-1,2,4-triazol-3-one (TO) which lacks the nitro group present on C5 in NTO. The homolysis of the nitro groups (NO_2) at the 5 position of NTO is believed to contribute to autocatalytic decomposition of NTO. Above 255 °C, this pathway becomes dominant. Our studies of NTO and 10 compounds with triazole-like rings showed that those with a carbonyl or an amino group (NH_2) substituent at C3 experienced enhanced decomposition rates in the presence of exogenous NO_2. Therefore, we concluded that NO_2 attacked at the carbonyl position (C3). When NTO was deuterated at positions 2 and 4 the decomposition rate was slower, indicative of an intramolecular deuterium kinetic isotope effect (DKIE). An intermolecular DKIE was observed when decomposition of NTO was in deuterated solvent. The 10 compounds with triazole-like rings exhibited intermolecular DKIE only when there was a nitro group or an amino group substituent at what would be the 5 position of NTO. This is interpreted as evidence that hydrogen and the nitro group must be associated with the rate-determining step of NTO thermal decomposition.

When the thermal stabilities of molten mixtures of NTO and 2,4,6-trinitrotoluene (TNT) were studied, it was found that at temperatures below 230 °C NTO decomposed at a slower rate than TNT.[2] However, the situation was reversed at higher temperatures. A clue to understanding these observations was the autocatalytic behavior of pure NTO above 255 °C. A dominant decomposition pathway at higher temperatures may involve the generation of nitrogen dioxide via $C-NO_2$ homolysis at the 5 position of NTO. At lower temperatures it was speculated that hydrogen transfer to the nitro group substituent at position 5 was followed by loss of nitrous acid (HONO). Although both mechanisms involve loss of the nitro group from the 5 position of NTO, we only detect slight quantities of TO and large amounts of an intractable tar with an empirical formula comparable to TO in addition to the decomposition gases. The thermal decomposition of TO resulted in the formation of 1,2,4-triazole and a polymeric residue which is clearly different from that produced by NTO. Therefore, a mechanism involving loss of a nitro group by NTO to form TO followed by a pathway comparable to that of TO decomposition is not likely to be a principal mechanism in the thermal decomposition of NTO.

NTO samples with ^{15}N labels at specific positions in the triazole ring (6 position, 4 position, and 1 and 2 positions) were prepared.[1] Isotopic distributions of these labels were determined in the nitrogen-containing gases (dinitrogen, nitrous oxide, nitric oxide, and hydrogen cyanide) produced as a result of the thermal decomposition of these NTO samples. A temperature of 250 °C was selected since decomposition prior to autocatalysis could be studied. Data at 270 °C is also presented in which NTO decomposition was predominantly autocatalytic. These results were used for further clarification of possible mechanisms for the thermal decomposition of NTO.

Experimental Section

Synthesis procedures for preparation of NTO and its isotopomers have been previously reported.[1] Milligram amounts of NTO were accurately weighed into Kimax-51 glass melting point capillary tubes (0.8−1.10 mm) using a Mettler MT5 microbalance. The capillary tubes, containing NTO samples, were evacuated and sealed with a small welding torch. The decompositions were conducted in Wood's metal baths at 200, 220, 250, and 270 °C.

NTO samples were removed from the Wood's metal bath at time intervals of 14, 25.5, and 30 min corresponding to 10, 24, and 100% NTO decomposition, respectively. These percent decompositions were determined from samples of unlabeled NTO which were prepared and decomposed under conditions

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TABLE 1: Isotopic Distributions of Decomposition Gases of ^{15}N(4)-, ^{15}N(6)-, and ^{15}N(1,2)-labeled NTO at 250 and 270 °C[a]

		10% decomp at 250 °C			24% decomp at 250 °C			>99% decomp at 250 °C			>99% decomp at 270 °C		
		^{15}N(4)	^{15}N(6)	^{15}N(1,2)	^{15}N(4)	^{15}N(6)	^{15}N(1,2)	^{15}N(4)	^{15}N(6)	^{15}N(1,2)	^{15}N(4)	^{15}N(6)	^{15}N(1,2)
N_2	28	71.7	50.9	23.7	71.7	50.6	23.8	70.7	50.8	24.6	69.3	53.4	27.2
	29	28.1	42.6	16.5	28.0	42.8	16.8	29.1	42.7	16.5	30.4	41.8	17.2
	30	0.2	6.6	59.8	0.2	6.5	59.3	0.2	6.5	58.8	0.3	4.7	55.6
N_2O	44	92.1	0.5	14.8	93.3	0.9	15.2	93.8	0.7	16.5	90.7	9.4	22.5
	45	7.7	80.7	84.7	6.5	81.4	84.4	5.9	81.2	83.1	7.6	69.3	74.9
	46	0.25	18.7	0.5	0.2	17.7	0.5	0.2	17.6	0.4	1.8	21.3	2.5
NO	30	99.5	0.9	99.5	99.5	1.2	99.5	99.5	0.8	99.5			
	31	0.5	99.1	0.5	0.5	98.8	0.5	0.5	99.2	0.5			
HCN	27	26.1	92.1	86.5	28.5	91.1	85.1	28.0	91.2	85.5			
	28	73.9	7.9	13.5	71.5	8.9	14.9	72.0	8.8	14.5			

[a] The analytical method used to obtain the data at 270 °C was not able to detect nitric oxide or hydrogen cyanide gases.

identical to those of the isotopically labeled samples. Analyses for percentages of decomposition were accomplished using a Hewlett Packard (HP) 5890 gas chromatograph (GC) equipped with a thermal conductivity detector and a Hayesep DB packed column (30 feet × 1/8 inch, 100/120 mesh). The oven temperature was held at 35 °C for 6 min, ramped at 40 °C per minute to 140 °C, held for 8 min, and finally ramped at 40 °C per minute to 180 °C. The injector and detector temperatures were 120 °C and 190 °C, respectively. The sum of the peak areas from a chromatogram was used to obtain the total moles of gas per mole NTO at the above specified time intervals. Division by the sum of the peak areas of a chromatogram which gave the total moles of gas per mole NTO after 100% decomposition yielded the fraction decomposition. The above gas chromatography system was also used to determine the initial rates of production of carbon monoxide, carbon dioxide, dinitrogen, nitrous oxide, and nitric oxide at 200, 220, 250, and 270 °C. The moles produced per minute for each gas was obtained by comparison with gas calibration standards obtained from Scotts Specialty Gases.

A HP 5890 GC equipped with an electronic pressure control injection system and model 5971 electron impact quadrupole mass spectrometer were used for the analyses of isotopically labeled nitrogen-containing decomposition gases of NTO. A narrow internal diameter (0.25 mm) porous layer open tubular (PLOT) fused silica capillary column with poraPLOT Q stationary phase (25 m length), obtained from Chrompack, was used to separate gaseous components of NTO decomposition which included dinitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), nitric oxide (NO), water (H_2O) and small quantities of hydrogen cyanide (HCN). The GC oven temperature was held at −80 °C for 6 min and then ramped at 15 °C per minute to 150 °C. The injector temperature was 150 °C, and the transfer line temperature was 180 °C. Following decomposition the sealed capillaries containing the isotopically labeled NTO samples were placed in a flexible Teflon tube (0.125 inch, id.) connected in line with the carrier gas and just before the injector. The capillary tubes were broken allowing decomposition gases to enter the injector and be separated by the poraPLOT Q capillary column. Base line resolution of all the above mentioned gases was achieved with this column. Mass spectral analyses were used to obtain distributions of ^{14}N and ^{15}N isotopes in the nitrogen-containing gases, N_2, N_2O, NO, and HCN. Selected ion monitoring was used to obtain percentages of unlabeled and ^{15}N-labeled molecular ions based on their relative intensities. The total amount of gas produced with complete decomposition of 1 mol NTO was determined by breaking sealed capillary tubes containing known amounts of completely decomposed NTO into a mercury manometer.

TABLE 2: Consolidation of the Isotopic Distributions[a]

gas	label	^{15}N(4)	^{15}N(6)	^{15}N(1,2)
N2	^{15}N−^{15}N	0.2	6.5	59.3
	^{15}N−^{14}N	28.4	42.7	16.6
	^{14}N−^{14}N	71.4	50.8	24.0
N_2O	^{15}N−^{15}N	0.2	18.0	0.5
	^{15}N−^{14}N	6.7	81.1	84.1
	^{14}N−^{14}N	93.1	0.7	15.5
NO	^{15}N−O	0.5	99.0	0.5
	^{14}N−O	99.5	1.0	99.5
HCN	^{15}N−C	72.5	8.5	14.3
	^{14}N−C	27.5	91.5	85.7

[a] The numbers are averages of the three decomposition percentages given in Table 1.

Results

Isotopic distributions of nitrogen atoms in the decomposition gases of NTO samples labeled with ^{15}N atoms at the 1 and 2 positions, the 4 position, and the 6 position were determined at 10, 24, and 100% NTO decomposition. Thermal decomposition of the ^{15}N-labeled NTO samples were conducted at 250 and 270 °C. The isotopic distributions of nitrogen atoms in N_2, NO, N_2O, and HCN gases at different percentages of NTO decomposition are given in Table 1. There were no significant changes in the isotopic distributions of any of the labeled samples as decomposition progressed from 10% to complete decomposition (i.e. 100%). Even at 270 °C, where autocatalytic behavior is more marked than at 250 °C, at complete decomposition the isotopic distribution in the gases varies only slightly from that observed at 250 °C (Table 1). The data in Table 2 summarizes Table 1 results as averages over the three decomposition percentages obtained at 250 °C. According to the results in Table 2, nitrogen atoms from all four positions of NTO contribute to the formation of N_2 gas. Approximately 59% of the N_2 gas from the N(1,2)-labeled NTO has mass 30, meaning the nitrogens come exclusively from the 1 and 2 positions. Additional nitrogen atoms from the 1 or 2 positions of ^{15}N-(1,2)-labeled NTO make up half of the 17% of N_2 gas molecules having mass 29. This means that 68% (i.e. 59% + 17%/2 = 68%) of the nitrogen atoms are from the 1 and 2 positions of the NTO ring. The NTO samples labeled with ^{15}N at the 6 position also contribute to the formation of N_2 gas during thermal decomposition. About 7% of the N_2 molecules have both nitrogen atoms coming from the 6 position, and 43% have one atom of nitrogen coming from the 6 position. This implies that approximately 28% (i.e. 7% + 43%/2) of the nitrogen atoms in the N_2 gas come from position 6. The NTO samples with ^{15}N at the 4 position show insignificant amounts of N_2 gas being formed with both nitrogen atoms having a label from the 4 position (i.e. 0.2%). However, about 28% of the N_2 gas has one nitrogen atom from the 4 position. This suggests that about

TABLE 3: Origins of the Nitrogen Atoms in the Decomposition Gases of ^{15}N(4)-, ^{15}N(6)-, and ^{15}N(1,2)-labeled NTO

	sources of nitrogen atoms (%)			
gas	N(4)	N(6)	N(1,2)	total
N_2	14	28	68	110
N_2O	3.6	59	43	104[a]
NO	0.5	99	0.5	100
HCN	73	8.5	14	95

[a] This is the value used for normalizations. The sum of this row, 105.6, is higher due to rounding errors.

TABLE 4: Isotopic Distributions of Decomposition Gases of ^{15}N(1,2) NTO and Unlabeled NTO[a]

gas	mass	10% decomp	24% decomp	>99% decomp
N_2	28 (^{14}N−^{14}N)	58.9	58.3	58.2
	29 (^{14}N−^{15}N)	9.9	9.6	9.7
	30 (^{15}N−^{15}N)	31.2	32.1	32.1
N_2O	44 (^{14}N−^{14}N−O)	54.6	56.4	54.7
	45 (^{14}N−^{15}N−O)	45.0	43.3	45.0
	46 (^{15}N−^{15}N−O)	0.3	0.3	0.3
NO	30 (^{14}N−O)	99.5	99.5	99.5
	31 (^{15}N−O)	0.5	0.5	0.5
HCN	27 (H−C−^{14}N)	91.5	91.3	90.8
	28 (H−C−^{15}N)	8.5	8.7	9.2

[a] 50/50 weight percent mixture; 250 °C.

TABLE 5: Isotopic Distributions of Decomposition Gases of ^{15}N(4) NTO and ^{15}N(6) NTO[a]

gas	mass	10% decomp	24% decomp	>99% decomp
N_2	28 (^{14}N−^{14}N)	66.7	66.8	67.4
	29 (^{14}N−^{15}N)	25.3	25.1	24.8
	30 (^{15}N−^{15}N)	8.1	8.0	7.9
N_2O	44 (^{14}N−^{14}N−O)	47.5	47.3	45.4
	45 (^{14}N−^{15}N−O)	48.0	48.3	49.7
	46 (^{15}N−^{15}N−O)	4.5	4.4	4.9
NO	30 (^{14}N−O)	46.2	46.7	46.8
	31 (^{15}N−O)	53.8	53.3	53.2
HCN	27 (H−C−^{14}N)	56.3	56.8	56.6
	28 (H−C−^{15}N)	43.7	43.2	43.4

[a] 50/50 weight percent mixture; 250 °C.

14% (i.e. 28%/2 = 14%) of the nitrogen atoms in N_2 gas are from position 4 of the NTO ring.

Using the above analytical method it was possible to evaluate the contributions that nitrogen atoms from the labeled positions made to the formation of the other decomposition gases (i.e. NO, N_2O, and HCN) as well. These results are summarized in Table 3. For NO gas, 99% of the nitrogen atoms come from the 6 position; contributions from other positions are probably not significant (0.5%). The results for N_2O gas indicate that 43% of the nitrogen atoms are from the 1 and 2 positions, 59% from the 6 position, and only 4% from the 4 position. Nitrogen atoms from the 4 position predominate in HCN gas by contributing 73%, while the 6 and 1,2 positions contribute 9% and 14%, respectively. The total percentages in Table 3 do not add up to a perfect 100%. We attribute deviations to the uncertainties associated with independent mass spectral measurements used to obtain these results. Tables 4−7summarize isotopic distributions of the decomposition gases, at different percents of NTO decomposition, of approximately equal molar amounts of ^{15}N(1,2) NTO/unlabeled NTO, ^{15}N(4) NTO/^{15}N(6) NTO, ^{15}N(1,2) NTO/^{15}N(6) NTO, and ^{15}N(1,2) NTO/ ^{15}N(4) NTO.

TABLE 6: Isotopic Distributions of Decomposition Gases of ^{15}N(1,2) NTO and ^{15}N(6) NTO[a]

gas	mass	10% decomp	24% decomp	>99% decomp
N_2	28 (^{14}N−^{14}N)	40.4	40.2	39.9
	29 (^{14}N−^{15}N)	23.9	23.9	23.9
	30 (^{15}N−^{15}N)	35.8	36.0	36.2
N_2O	44 (^{14}N−^{14}N−O)	24.2	25.0	26.2
	45 (^{14}N−^{15}N−O)	51.9	52.0	51.3
	46 (^{15}N−^{15}N−O)	23.9	23.1	22.5
NO	30 (^{14}N−O)	45.9	46.5	46.6
	31 (^{15}N−O)	54.1	53.5	53.4
HCN	27 (H−C−^{14}N)	89.9	89.3	89.5
	28 (H−C−^{15}N)	10.2	10.7	10.5

[a] 50/50 weight percent mixture; 250 °C.

TABLE 7: Isotopic Distributions of Decomposition Gases of ^{15}N(1,2) NTO and ^{15}N(4) NTO[a]

gas	mass	10% decomp	24% decomp	>99% decomp
N_2	28 (^{14}N−^{14}N)	46.2	46.0	46.2
	29 (^{14}N−^{15}N)	21.0	22.4	21.9
	30 (^{15}N−^{15}N)	32.8	31.6	31.9
N_2O	44 (^{14}N−^{14}N−O)	53.7	54.5	53.1
	45 (^{14}N−^{15}N−O)	45.9	45.2	46.5
	46 (^{15}N−^{15}N−O)	0.3	0.3	0.3
NO	30 (^{14}N−O)	99.6	99.5	99.5
	31 (^{15}N−O)	0.4	0.5	0.5
HCN	27 (H−C−^{14}N)	54.6	55.1	54.4
	28 (H−C−^{15}N)	45.4	44.9	45.6

[a] 50/50 weight percent mixture; 250 °C.

TABLE 8: Normalized Mass Spectral Data for N_2 and N_2O Gases with Assignments and Evaluations of Interaction Parameters

				interaction parameters[a]		
					evaluations	
labeled samples	label	norm N_2	norm N_2O	assignments	N_2	N_2O
^{15}N(1,2)	^{15}N−^{15}N	54	0.5	A	$A = 54$	$A = 0.5$
	^{15}N−^{14}N	15	81	$D + E$	$B = 0.2$	$B = 0.2$
	^{14}N−^{14}N	31	19	$B + C + F$	$C = 6$	$C = 17$
^{15}N(4)	^{15}N−^{15}N	0.2	0.2	B	$D = 14$	$D = 76$
	^{15}N−^{14}N	26	6	$E + F$	$E = 0.8$	$E = 4$
	^{14}N−^{14}N	74	93	$A + C + D$	$F = 25$	$F = 2.5$
^{15}N(6)	^{15}N−^{15}N	6	17	C		
	^{15}N−^{14}N	39	78	$D + F$		
	^{14}N−^{14}N	55	5	$A + B + E$		

[a] A = [N(1,2)] = interactions that specifically involve nitrogen atoms from positions 1 and 2. B = [N(4,4)] = interactions that specifically involve nitrogen atoms from position 4. C = [N(6,6)] = interactions that specifically involve nitrogen atoms from position 6. D = [N(1,2,6)] = interactions that specifically involve nitrogen atoms from positions 1, 2, and 6. E = [N(1,2,4)] = interactions that specifically involve nitrogen atoms from positions 1, 2, and 4. F = [N(4,6)] = interactions that specifically involve nitrogen atoms from positions 4 and 6.

It was possible to use a quantitative approach to evaluate the extent of interactions between nitrogen atoms at the four positions of NTO associated with the formation of N_2 and N_2O gases. A normalization of the raw data sets in Table 2 was required in order to generate unique solutions for the interaction parameters (A−F) assigned in Table 8. The interaction parameters for N_2 and N_2O gases are unique solutions to sets of simultaneous equations given in Table 8. The assignments of interaction parameters A−F are also given in Table 8. The parameters distinguish between the various combinations of nitrogen atoms that contribute to the formation of the two gases. They indicate percentages of the N_2 or N_2O formed by the specified interactions. The raw data in Table 2 was divided by a normalization factor (110 for N_2 and 104 for N_2O, Table 3), and the raw numbers for the unlabeled molecules were then adjusted to give a total of 100. The normalized data and

TABLE 9: Summary of the Origins of Nitrogen Atoms in the Decomposition Gases Produced During the Thermal Decomposition of NTO at 250 °C

Percent for Each Interaction

type of N/N interaction	*A* N(1,2)	*B* N(4,4)	*C* N(6,6)	*D* N(1,2,6)	*E* N(1,2,4)	*F* N(4,6)	sum
N_2	54	0.2	6.0	14	0.8	25	100
N_2O	0.5	0.2	17	76	4.0	2.5	100

$10NTO \rightarrow 10N_2 + 1N_2O + 2NO$

type of N/N interaction	*A* N(1,2)	*B* N(4,4)	*C* N(6,6)	*D* N(1,2,6)	*E* N(1,2,4)	*F* N(4,6)	sum
N_2	5.40	0.02	0.60	1.40	0.08	2.50	10 N_2
N_2O	0.01	0.00	0.17	0.76	0.04	0.03	1 N_2O
NO	0.10	0.10	1.98				2 NO

fate N atoms	molecules	N_2	N_2O	NO	% N atoms[a]
N(1,2)	$A + D/2 + E/2$	6.14	0.41	0.10	66
N(4)	$B + E/2 + F/2$	1.31	0.04	0.10	28
N(6)	$C + D/2 + F/2$	2.55	0.57	1.98	82

[a] The percentage of nitrogen atoms coming from the designated position. For example, the percentage of nitrogen atoms coming from the 1 and 2 positions of NTO which are incorporated into N_2, N_2O, and NO is as follows: $[2(6.14) + 2(0.41) + 0.10]100/20 = 66\%$.

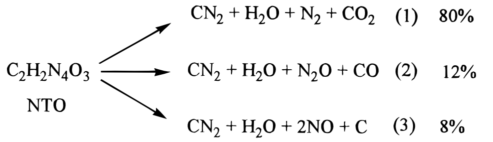
interaction parameters, with specified assignments and relationships to the normalized data, are given in Table 8. The distribution of ^{15}N labels, from NTO, into the decomposition gases is summarized in Table 9.

Manometric analyses for the total gas production accompanying complete decomposition of NTO yielded 2.24 mol of gas per mole of NTO as an average value for 11 experiments (standard deviation = 0.32). The average value as percent, by weight, of the insoluble solid residue remaining after thermal decomposition of NTO was 30.9% with standard deviation of 1.9% (14 replicate experiments). Gas chromatography with thermal conductivity detection yielded 43 mol % N_2, 6 mol % N_2O, 8 mol % NO, 37 mol % CO_2 and 6 mol % CO for the main decomposition gases. The small amount of HCN gas produced during decomposition of NTO was not quantified in this study.

Discussion

We have previously reported the condensed-phase products of NTO decomposition.[2] Since only trace amounts of TO and 1,2,4-triazole were observed, neither was considered to be a major decomposition product. The main condensed-phase product was an insoluble residue representing about 31% of the mass of the original NTO. The elemental analysis of the insoluble residue yielded an empirical formula of $C_{2.12}H_{2.23}N_{3.36}O$.[2] This is suggestive of "polymerized TO," for which the repeating unit would be given by $C_2H_2N_3O$. However, when TO was thermolyzed, the residue produced had the empirical formula $C_{4.5}H_5N_{7.7}O$. There are numerous other possibilities for the identity of the NTO residue, $C_2H_2N_3O$, including mixtures of cyclic azines such as melamine ($C_3N_6H_6$) and cyanuric acid ($C_3N_3O_3H_3$). Brill et al.[3] have reported azines, melamine, and melon as NTO decomposition products. Using the indicated stoichiometry for the production of dinitrogen, nitrous oxide, and nitric oxide, we report in Table 9 the percentages of the designated labels from NTO which appear in the decomposition gases. About 66% of the nitrogen atoms from the 1 and 2 positions of NTO are incorporated into the three decomposition gases (N_2, N_2O, and NO, Table 9). We suspect that most of the remaining 34% of nitrogen atoms make up the insoluble residue remaining after decomposition of NTO. Likewise, only 28% of the nitrogen atoms at the 4 position in NTO become associated with the decomposition gases, while most of the remainder (about 72%) incorporate into the solid residue. The nitrogen atom from the 6 position of NTO exhibits the greatest incorporation into the decomposition gases (82%).

SCHEME 1: Decomposition of NTO is Shown to Involve Formation of a Hypothetical Polymer Precursor (CN_2)[a]



[a] Three decomposition pathways are then postulated based on the compositional analyses of the gaseous products. The percentages express the extent to which each route contributes to the thermal decomposition of NTO. They are based on the relative amounts of the decomposition gases assigned to each route as determined by gas chromatography.

SCHEME 2: A Stoichiometric Equation for the Thermal Decomposition of NTO from the Gas Composition Data, Volumetric Data, and the Amount of Solid Residue

$$\underset{\text{NTO}}{10C_2N_4H_2O_3} \longrightarrow C_{11}H_8N_{16}O_4 + 10H_2O + 10N_2 + N_2O + 2NO + 8CO_2 + CO$$

	$C_{11}H_8N_{16}O_4$	N_2	N_2O	$2NO$	$8CO_2$	CO	
Calculated	33wt%	(45	5	9	36	5)	mol%
Observed	31wt%	(43	6	8	37	6)	mol%

A stoichiometric relationship for NTO decomposition in terms of the observed gaseous products was obtained assuming the production of a polymer precursor (CN_2) and water by three separate routes. This is shown in Scheme 1. On the basis of the gas composition analyses, about 80% of the decomposition proceeds via route 1 while 12% and 8% are by routes 2 and 3, respectively. It was also possible to deduce a stoichiometric equation for the decomposition of NTO from the gas composition data, volume data (i.e. total moles of gas), and the amount of residue formed. The stoichiometric equation, shown in Scheme 2, is atomically balanced by adjustment of the empirical formula of the residue. The calculated value is in good agreement with the observed results. The stoichiometry obtained in Scheme 2 was used for the interpretation given in Table 9.

On the basis of the results of decomposition kinetics and analysis of condensed phase products of NTO, a mechanism was proposed which is initiated by loss of nitrous acid or a nitro group. This is shown in Scheme 3. We have previously reported considerable evidence to support this mechanism.[2] First, above 255 °C, the autocatalytic decomposition of NTO is attributed to the evolution of nitrogen dioxide because exogenous nitrogen dioxide increases the NTO decomposition rate. This was also true of compounds with triazole-like rings containing amino groups or carbonyl groups. Second, intramolecular and intermolecular deuterium kinetic isotope effects were observed for NTO. Furthermore, compounds with triazole-like rings containing amino groups or nitro groups also exhibited intermolecular DKIE. Third, although TO (essentially NTO less NO_2) was a minor product, its presence is consistent with the proposed mechanism. The homolysis of the $X-NO_2$ bond is common to many classes of explosives—nitroarenes, nitramines, and nitrate esters. Other researchers also conclude that loss of nitrous acid or nitrogen dioxide is a likely route for NTO decomposition.[4-6] Menapace et al. based this on an observed DKIE.[4] Beard and Sharma used photoelectron spectroscopy to document the loss of the nitro group in radiation-damaged NTO. They observed a decrease in the binding energy of the nitrogen

SCHEME 3: A Previously Reported Mechanism for the Thermal Decomposition of NTO[2]

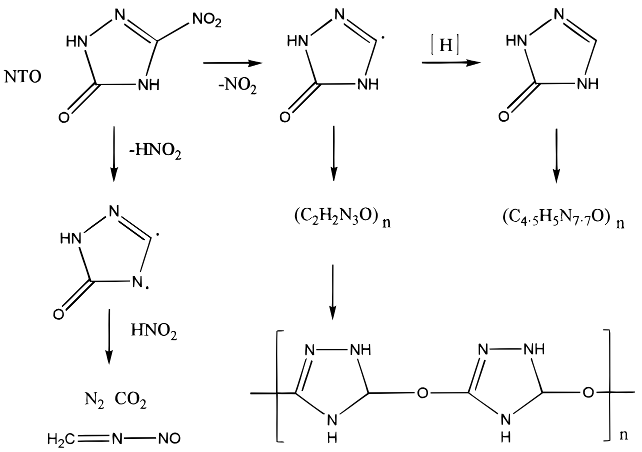


TABLE 10: Initial Rates of Production of CO, CO_2, N_2, N_2O, and NO Gases for Thermal Decompositions of NTO at 200, 220, 250, and 270 °C

	initial rate (mol/min)			
gas	200 °C	220 °C	250 °C	270 °C
CO	1.75×10^{-6}	1.35×10^{-5}	7.74×10^{-4}	1.45×10^{-2}
CO_2	1.97×10^{-5}	1.31×10^{-4}	8.52×10^{-3}	9.12×10^{-2}
N_2	2.28×10^{-5}	1.49×10^{-4}	7.69×10^{-3}	9.45×10^{-2}
N_2O	2.23×10^{-6}	1.11×10^{-5}	7.80×10^{-4}	1.34×10^{-2}
NO	3.76×10^{-6}	1.89×10^{-5}	1.10×10^{-4}	3.26×10^{-2}

atom at the 2 position of NTO which they attributed to loss of the electron-withdrawing nitro group.[5] Ostmark detected a mass fragment assigned to NO_2 (*m*/*z* 46) by laser-induced decomposition of NTO in a mass spectrometer.[6] Rothgery et al. used thermogravimetry coupled mass spectrometry and infrared spectroscopy to analyze gases evolved during NTO decomposition.[7] Mass spectroscopy showed major products at *m*/*z* 18, 30, and 44 with minor products at *m*/*z* 28 and 46. The IR spectrum detected H_2O, NO, CO_2, CO, and N_2O immediately after decomposition of NTO. The presence of nitrogen dioxide was not detected until about an hour after decomposition was initiated. They concluded that the nitrogen dioxide was formed from the oxidation of nitric oxide during the equilibration of the NTO decomposition products. Their elemental analysis of the NTO solid residue is in agreement with our previous study.[2]

Botcher et al., using infrared spectroscopy, have reported that they observe CO_2 as the first decomposition product.[8] They conclude that the CO_2 results from intermolecular oxidation of the carbonyl by the nitro group. Their mechanism would result in the formation of 1 mol each of dinitrogen and carbon dioxide per mole of NTO and produces nitroisocyanide radicals to serve as precursors of the solid polymeric residue. Furthermore, all the dinitrogen would be derived from nitrogen atoms from the 1 and 2 positions of NTO. Since infrared spectroscopy cannot detect dinitrogen, assignment of its nitrogen atoms to specific positions in NTO and verification that the evolution of carbon dioxide precedes that of dinitrogen are not possible.

The initial rates (mol/min) from the slopes of plots of moles of gas versus time for the production of CO_2, CO, N_2, N_2O, and NO gases, obtained from gas chromatography at decomposition temperatures of 200, 220, 250, and 270 °C, are reported in Table 10. It is apparent that the rates of formation of N_2 and CO_2 are comparable and about a factor of 10 greater than the rates of formation of the other three gases at all four decomposition temperatures. This seems to indicate that route 1 (Scheme 1) is fastest. Our ^{15}N-labeling experiments give evidence for the origins of the nitrogen atoms in dinitrogen. The ratio, $^{15}N-^{15}N/^{15}N-^{14}N$, from Table 2 for $^{15}N(1,2)$-labeled NTO was approximately 3.6. Fan et al. have reported a higher value of 4.4 for the thermal decomposition of NTO at 270 °C.[11] Their method involved an extrapolation based on a mole percent ratio, NO/N_2 of 0.27, to remove a contribution from $^{14}N-O$ which they were unable to chromatographically resolve from the $^{15}N-^{15}N$ peak. Our NO/N_2 mole percent ratio was about 0.19. The results given in Table 9 show that 61% of nitrogen atoms in dinitrogen are from the 1 and 2 positions of NTO while the remainder are from the 4 and 6 positions (13% and 26%, respectively).

It is evident from Tables 5 and 6 for decomposition studies involving equal molar mixtures of $^{15}N(6)$ NTO/$^{15}N(4)$ NTO and $^{15}N(1,2)$ NTO/$^{15}N(6)$ NTO that interactions involving the nitro group at the 6 position of NTO with other ring nitrogens do occur and are responsible for the formation of some of the dinitrogen. This is directly evident in Table 5 ($^{15}N(6)$ NTO/$^{15}N(4)$ NTO) where the formation of 8% double-labeled dinitrogen could only be accomplished by direct interaction of nitro groups. In Table 4 where unlabeled NTO is mixed with $^{15}N(1,2)$-labeled NTO about 32% of the dinitrogen is double labeled. On the other hand, when $^{15}N(1,2)$-labeled NTO is mixed with $^{15}N(6)$-labeled NTO, about 36% of the dinitrogen is doubly labeled. The difference for double-labeled dinitrogen of 4% is probably due to interactions involving the nitro group of one NTO molecule with a nitrogen from the 1 or 2 position of another NTO molecule, while most of the dinitrogen (about 32%) is likely to result from elimination of the two nitrogens from the 1 and 2 positions of a single NTO molecule. Comparison of Table 1 with Table 4, consisting of an equal molar mixture of $^{15}N(1,2)$ NTO and unlabeled NTO, shows that the percent of double- and single-labeled N_2 molecules are approximately half that of pure labeled $^{15}N(1,2)$ NTO while the unlabeled N_2 in Table 4 was roughly doubled. This was expected from a simple half dilution of the labeled NTO molecules and suggests that the double-labeled N_2 molecules form from ^{15}N atoms at the 1 and 2 positions of a given NTO molecule. Interactions between these nitrogen atoms from different NTO molecules would produce additional scrambling of ^{15}N labels and reduce the amount of double-labeled N_2. Table 9 shows that dinitrogen is about 13% nitrogen atoms from the 4 position of NTO and 26% nitrogen atoms from the 6 position of NTO. These results do not rule out the Botcher et al. mechanism, but they do suggest that alternate pathways are needed to account for about 39% of the nitrogen atoms in dinitrogen originating from the 4 and 6 positions of NTO. The relatively large production of N_2, which appears to be coupled with the production rate of CO_2, is evidently the result of multiple decomposition pathways.

Scheme 3 shows a decomposition pathway that accounts for the acceleratory effect of NO_2, a DKIE, 31% solid residue, and the major decomposition gases. Our results show that almost 40% of the observed dinitrogen could be generated by the nitro group as it undergoes homolysis from the carbon atom at the 5 position of NTO and attacks nitrogen atoms at the 1, 2, and 4 positions of NTO. Dinitrogen gas constitutes about 43% of total gas produced as a result of NTO decomposition. The other nitrogen-containing gases, nitrous oxide (N_2O) and nitric oxide (NO), make up approximately 6 mol % and 8 mol %, respectively. It is evident from Table 9 that for nitrous oxide approximately half the nitrogen atoms are from the nitro group of NTO and the other half are from the nitrogen atom at the 1 and 2 positions of NTO. The single nitrogen atom in nitric oxide is almost exclusively from the nitro group of NTO. The nitrogen atoms in the trace amounts of hydrogen cyanide gas

(Table 2) are derived predominantly from nitrogen atoms from the 4 position of NTO (about 73%), but nitrogen atoms from the 6, 1, and 2 positions of NTO are appreciable. McMillen et al. have used a surface analysis by ionization apparatus to obtain real-time photoionization mass spectra of shear-induced emission from NTO.[12] They have deduced a mechanism which involves an initial weakening of the O−NO bond followed by direct loss of NO. Our results support this in that almost exclusively ^{15}NO gas is obtained when the ^{15}N(6) (i.e. the nitro group)-labeled NTO is thermally decomposed (see Tables 2 and 9). Initial loss of either NO or NO_2 is followed by subsequent interaction with the remaining nitrogen atoms of the NTO ring. This is evident from the results in both Tables 2 and 9. The nitrogen atom of the nitro group of NTO contributes substantially to the formation of all the nitrogen-containing gases.

Summary

A series of NTO compounds specifically labeled with ^{15}N at N(1,2), N(4), and N(6) positions were synthesized and thermolyzed at 250 °C. Decomposition gases were identified and quantified, and the isotopic distributions in dinitrogen, nitrous oxide, nitric oxide, and hydrogen cyanide gases were determined. The quantitative assignments of interaction parameters given in Table 8 summarize origins of nitrogen atoms in dinitrogen and nitrous oxide. In the dinitrogen gas about 54% of the nitrogen atoms are from the 1 and 2 positions of NTO. About 25% of nitrogen atoms in dinitrogen are from the 4 and 6 positions, 14% are from interaction of the 1 or 2 position with the 6 position of NTO, and 6% involve exclusively nitrogen atoms from the 6 position of NTO. For nitrous oxide most of the nitrogen atoms (about 76%) are the result of interactions between nitrogens at the 1 or 2 position of NTO and those at the 6 position, and approximately 17% are exclusive from the 6 position. Small contributors to nitrous oxide are N(1,2,4) interactions (about 4%) and N(4,6) interactions. A mechanism, such as Scheme 1, involving homolysis of the nitro group from the NTO ring is consistent with our results.

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