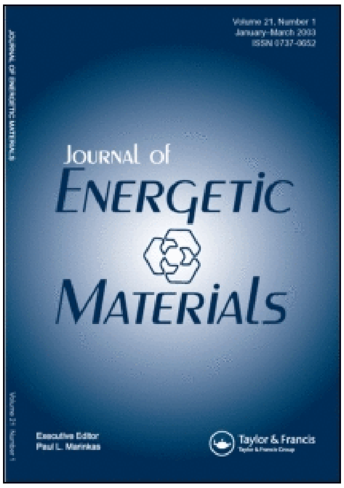

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Early Decomposition Chemistry of NTO,
(3-Nitro-1,2,4-triazol-5-one)

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ABSTRACT

The early reaction chemistry of NTO, (3-Nitro-1,2,4-triazol-5-one) induced by, drop weight impact, shock, heat and radiation has been investigated. X-ray photoelectron spectroscopy XPS and chemical ionization mass spectrometry CIMS were employed to observe and identify the partial decomposition products in the damaged samples. Several reaction intermediates have been identified, the focus of the reaction being the single nitro group present on this molecule. XPS spectra indicated in all cases the loss of NO_2 concentration in response to damage. Additional chemical states were suggested in the XPS N(1s) spectrum by the appearance of a new peak at a binding energy below that of the triazol ring nitrogens. Mass spectrometry provided the molecularly specific information needed to identify molecular species resulting from the decomposition reactions. Relative to the parent NTO molecule, mass peaks were observed that corresponded to the loss of one O atom, an NO fragment, and a HONO.

INTRODUCTION

NTO (3-Nitro-1,2,4-triazol-5-one) is a new energetic molecule that offers attractive explosive performance with a high degree of insensitivity.[1] As a result, NTO is being considered as an energetic component in insensitive high explosive formulations. In the face of potential large scale utilization of NTO, decomposition chemistry and sensitization of NTO need to be addressed.

Very little work has been done to date in the study of the solid state decomposition of NTO. Rothgery et al[2] discussed the thermal decomposition behavior of NTO by classical thermal analysis methods. Gaseous products of H_2O, NO, NO_2, N_2 and CO_2 were identified by a mass spectrometer attached in tandem to the thermogravimetric analysis (TGA) cell. Chemical analysis was performed on the solid residue remaining after the TGA run, identifying a composition of $C_2H_3N_3O$. Infra-red spectrophotometric examination of this residue determined, however, that it was not 1,2,4-triazol-3-

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one (TO) the precursor of NTO.

Ostmark[3] investigated the decomposition of NTO by mass spectrometry. Fragmentation of NTO under high energy (70 eV) electron impact ionization produced fragmentation by the loss of NO_2 and cleavage of the triazol ring. Laser induced mass spectrometry produced similar results where dissociation of NTO began with the loss of NO_2 from the triazol ring. The mechanistic conclusion in this work was that the first step in the dissociation of NTO was through the loss of NO_2 followed by fragmentation of the triazol ring.

The work described in this paper is a follow-up of our previous work that investigated the relative radiation sensitivity of NTO in comparison to the well known explosives, TATB, HMX and RDX.[4] In this earlier work several partial decomposition products of NTO were suggested based upon the observed changes in the x-ray photoelectron spectra (XPS) of radiation decomposed NTO. The product assignments in this earlier work were tentative due to the inability of XPS to uniquely identify the molecular nature of a sample. To overcome this limitation and reinforce the previous conclusions, mass spectrometry has been added in the study of partially decomposed NTO.

The partially decomposed samples to be discussed in the present report were generated by radiation, shock, impact and thermal degradation. The similarity of the intermediate products formed by these different degrading stimuli are noted. Additional XPS data and the supporting mass spectrometry extend the previous work and permit definitive identification of the solid state partial decomposition products of the NTO molecule.

EXPERIMENTAL

X-ray Photoelectron Spectroscopy

A Kratos ES-300 x-ray photoelectron spectrometer incorporating a dual anode Al/Mg x-ray source was employed for the XPS analysis. The Mg x-ray source was operated at 15 KeV and 12 ma (180W), producing characteristic Mg Kα x-rays with an energy of 1253.6 eV. Binding energies were corrected for surface charging by setting the binding energy of the adventitious hydrocarbon contamination peak to 285.0 eV. The analysis chamber pressure was maintained to less than 1.33 x 10^{-6} Pa. A samples of the control NTO material was ground into a fine powder then deposited as a thin even layer onto nitrogen-free cellophane tape. The samples subjected to impact, shock, thermal and radiation damage were investigated without disrupting the surface. For a thorough discussion of XPS and its application to energetic materials the reader is referred to Sharma and Beard[5].

Mass Spectrometry

Chemical ionization mass spectra (CIMS) were collected with a Finnigan 2000 GC/MS instrument equipped with a solids probe. A 1.5 mm diameter by 6 mm long glass capillary containing a few particles of the sample was inserted into the end of the solids probe. The solids probe was inserted into the instrument entering the ionization chamber for the mass spectrometer. The sample temperature was rapidly raised to 100°C then increased at a rate of 20°C/min to a maximum temperature of 250°C. During the temperature program the relative intensities of the mass spectral peak can vary due to differences in volatility. This variation was not closely followed in this work. The increased temperature volatilized the solid sample into the mass spectrometer vacuum chamber where repetitive mass scans from 50 to 300 amu were collected. The selection of this mass range was due to our interest in the early partial decomposition products of NTO as opposed to the low mass fragments. Unique assignment of such low mass peaks is also fraught with difficulties due to their presence arising from contamination in the mass spectrometer vacuum system and of the solids probe surfaces.

Based on initial evaluation of mass spectra of control NTO with both Electron Impact (EI) and Chemical Ionization techniques (CI) the CI method was found to be superior for this work due to a great reduction in the amount of molecular fragmentation. An attribute of CI is addition of 1 amu to each peak, arising from the ionizing mechanism;

$$CH_5^+ + M \longrightarrow M\text{-}H^+ + CH_4$$

Impacted Samples

Impact damaged samples of NTO were generated with a 10 Kg drop weight machine. Heat sensitive films were placed above and below the 30 mg sample. The areas of greatest compressive and shear heating are therefore highlighted by darkening of the films. The impacts were run up to the 300 cm limit of the machine, attained by dropping from 150 cm and accelerating the weight with rubber bands. Samples of the impacted powder for XPS analysis were taken from between the heat sensitive films adjacent to the darkest areas. This impacted material was then mounted onto nitrogen free tape for analysis. An alternative mounting method used cut portions of the heat sensitive film mounted directly on to the sample holder to observe directly the impact residue remaining on the surface of the heat sensitive film.

Shocked Samples

Shocked samples were generated with a micro-flyer plate apparatus similar to that described previously[6]. The mylar flyer (7.5×10^{-4} g) was accelerated by an exploding foil down a 0.144" diameter barrel onto a 0.144" dia. x 0.125" thick pellet pressed to 98% TMD. The energy imparted to the sample is varied through the velocity of the flyer which in-turn is controlled by the electrical energy deposited into the exploding foil.

Radiation Damaged Samples

Radiation damaged samples of NTO were generated within the XPS instrument by prolonged exposure to the x-ray beam. The longest exposure was 11 hours resulting in a dose of 3.3×10^{8} Rad. During the extended x-ray irradiation the sample temperature was monitored by a thermocouple within the sample holder. The temperature rise from the irradiation was no greater than 5°C.

Thermally Decomposed Samples

Thermal decomposition was performed on a DuPont 1090 thermogravimetric apparatus. The heating rate during the TGA analysis was 20°K/min under a constant flow of 50cc/min He. Initial sample size was held to ~ 10 mg. The first TGA run was taken to a stable orange-red residue which was 11.9% of the original sample weight. There was a single weight loss step occurring at 286 °C. To obtain a more intermediate level of decomposition a sample was removed from the heater after a 6.9% weight loss.

RESULTS

Control Samples

XPS spectra of the C(1s), N(1s), and O(1s) photoelectron transitions from control NTO were collected. Atomic concentrations were found to be in agreement with the molecular formula, ($C_2H_2N_4O_3$) of NTO. The oxygen (1s) data from the control NTO had two peaks appearing at 533.7 eV and 532.2 eV. Peak ratios from the oxygen spectra were 1:2, representing the one ketone oxygen (533.6 eV) and the two oxygens in the nitro group (532.2 eV). The carbon data had only one peak from the two carbons in the NTO, suggesting that the carbons have similar electronic environments. The four nitrogen atoms in NTO produce two peaks at 406.5 eV and 401.3 eV, Figure 1. The peak area ratio is 1:3 indicative of the one nitro nitrogen (406.5 eV) and the three ring nitrogens (401.3 eV).

Figure 2 is a CIMS of control NTO. The parent peak M+1 = 131 amu is the predominant peak in the spectrum. Minor peaks appearing in this spectrum (57 and 71 amu) arise from carbonaceous contaminants in the mass spectrometer vacuum system or from small levels of decomposition occurring under the CI conditions. The observed peaks, their intensity and suggested molecular identity are given in Table I.

In the evaluation of the ionization techniques (CI vs EI) of control NTO referred to earlier, there were several fragmentation products observed in the EI spectra, Figure 3. The molecular ion m/e=130 amu was observed, however, not as the predominant peak. Peaks at 44, 46, 54, 68, 83, 91 and 114 amu were observed. The peaks at 44, 46, and 83 amu were greater than the parent peak; the 54 amu peak was approximately equal to the parent peak; while the 68, 91 and 114 amu peaks were just above the noise.

Damaged Samples

Impacted

Under no set of conditions on the drop weight impact machine could an ignition be attained, despite a 300 cm drop height. Localized areas of the NTO powder were discolored yellow-brown, however, the heat sensitive film showed no evidence for exothermic reaction of the NTO. In most cases the material caked together into thin flakes from the impact. At the periphery of the most violently impacted sample, partial decomposition was observed by XPS, Figure 1. The decomposition was manifested by a new low binding energy peak 1.6 eV below the 401.3 eV peak of the ring nitrogens. Curve fitting this spectrum determined that the 406.5 eV (nitro group) peak decreased as much as 36% relative to the control sample. These changes are identical to those observed and discussed in the radiation damage study[2]. Due to the presence of the polymeric heat sensitive film, the carbon and oxygen spectra collected from the impacted NTO could not be uniquely assigned. Mass spectra of the impacted NTO demonstrated no clear evidence for the presence of decomposition products.

Since the impacting experiment was carried out with powder, the compressional and shearing forces between particles is concentrated at their surfaces. The surface specific XPS technique is therefore at a great advantage for observing the low levels of reactivity in this case. CIMS is a bulk technique where the amount of reacted material is greatly diluted by the strong signal from the bulk.

Shocked

Mass spectral analysis of shocked NTO, Figure 4., identified little if any change relative to the control sample The intensity of the 101 and 84 amu peaks were slightly greater than those observed in the control sample, however, this was not significant compared to the variation from one analysis to the next.

The shock levels imparted by the micro-flyer apparatus were rather limited, particularly for a material as insensitive as NTO. XPS, however, was able to identify a low level of decomposition. In a 4.76 km/s micro-flyer shot, there was material collected and analyzed that displayed a 10% loss of nitro concentration and the development of a weak shoulder below the 401.3 eV peak, as observed in the impacted sample.

Thermal

The first TGA run (20°K/min) was taken to a stable orange-red residue which was 11.9% of the original sample weight. This result is in agreement with the 12% residue weight reported by Rothgery et al[3]. There was a single weight loss step occurring at 286°C. The XPS N(1s) spectrum of this residue had a strong component 1.7 eV below the nitrogens from the triazol ring, however, there was no indication of nitro nitrogen remaining in the residue. Intensity at a binding energy consistent with the triazol nitrogens continued to be present.

To obtain an intermediate level of decomposition a sample was removed from the TGA heater after a 6.9% weight loss. This sample had a slight yellow coloration. The N(1s) XPS spectrum demonstrated a decrease in nitro intensity and the development of a new component 1.6 eV below the triazol ring nitrogens.

Radiation

Figure 5 is a CIMS spectrum of the NTO residue following 11 hrs of x-ray irradiation as described in reference 2. In this sample there was significant evidence for partial decomposition leading to prominent peaks at 115, 101, 86 and 84 amu. The observed peaks, their intensity and suggested molecular identity are listed in Table II. XPS spectra from this sample can be found in reference 2.

DISCUSSION

Several of the observed peaks listed in Table I are due to contamination or artifacts of the CI method. Peaks at 57 and 71 arise from $C_xH_y^+$ species due to carbonaceous contamination in the instrument vacuum chamber. Peaks above the molecular ion, 145, 159 and 171 are due to adduct formation with the ionizing gas used for the CI process. Apart from the molecular ion and a molecular dimer, only four peaks remain. These peaks correspond to NTO after the loss of an oxygen atom, the loss of an NO, the loss of NO_2 and conversion back to TO.

Electron impact ionization (70 eV) mass spectra of control NTO produced significant fragmentation, with predominant peaks at 44, 46, and 83 amu. The 44 and 46 peaks can be assigned to CO_2 and NO_2 respectively. The 83 amu peak would result from the loss of 47 mass units from NTO, corresponding to HONO. Figure 6 displays the final 83 amu product. These results are in complete agreement with those presented by Ostmark [3].

XPS spectra of shocked, impacted and thermally decomposed NTO are very similar to those observed from the radiation damaged samples, Figure 3 of reference 2, changing only in the extent of decomposition. The change in the XPS N(1s) spectra of these samples is characterized by the loss of nitro intensity along with the development of intensity from a new peak below the 401.3 eV triazol ring nitrogen peak. Despite the differences in the rate and mode of energy deposition between thermal, shock, radiation and impact, no differences in the chemical response of NTO can be identified. The apparent conclusion from such an observation is that the mechanism of decomposition for NTO is uncomplicated with respect to possible side reactions and invariant with respect to the rate.

The presence of a nitroso derivative of TO was suggested in [2] based on the observed variations in the XPS spectra and reactions observed in nitramine decomposition chemistry.[7] Mass spectrometry confirmed this earlier supposition by the detection of the 114 amu product. The mechanism leading to this product can only be guessed. Liberation of an oxygen atom from the nitro group strongly suggests an intermolecular reaction. The strong H-bonding between the NTO molecules[1] the presence of H_2O as a major product and the observance of a primary isotope effect in the decomposition of NTO by Menapace et al[8] suggest an intermolecular oxidation step leading to the formation of H_2O and the nitroso TO as an early (perhaps initial) reaction step.

The structure of the molecule responsible for the 100 amu mass peak is difficult to pin down. Assuming the starting material of NTO, the new peak would result from the loss of an NO. As suggested in [2] this could be assigned to a urazole molecule, however, the mass is incorrect by one unit. One is forced into the discussion of rationalizing a structure for the mass 100 molecule or assuming error in the spectrometer calibration. If the mass scale were off, the peak should have appeared at 102 amu corresponding to urazole plus H^+ from the CI ionization. It is difficult to adhere to this assumption since all of the other mass peaks observed have consistent and reasonable assignments in-line with the kind of chemistry one would expect. To address the structure of the 100 amu specie, the result is a urazole molecule minus one proton with a resulting unbalanced molecular charge. The positive charge can be stabilized through a number of resonance structures with each of the ring atoms taking turn at bearing the unbalanced charge. The equal distribution of the charge could impart sufficient stabilization that the molecule could remain over a period of several days. As an alternative, urazole may have liberated an electron through an ionization process resulting in the peak mass equal to the molecular mass unlike the other peaks in the CI spectrum.

An additional aspect of the 100 amu product that needs to be discussed is the nature of the mechanism involved in going from a C-N to a C-O bond. Oxidation of this site following release of the NO_2 is one possibility, producing the observed fragment and NO. Alternatively nitrite ester with subsequent cleavage of the O-NO bond can form. Calculational[9] and experimental[10] precedence has been set for this later possibility.

The products appearing at 85 and 83 amu correspond to TO and dehydrogenated TO. The abstraction of NO_2 from the triazol ring leaves the remaining fragment with an unbalanced charge. By gaining a proton TO is formed, with the loss of a proton the 83 amu fragment is formed. The 83 fragment has a structure with doubly bonded nitrogens attached to the remainder of the ring by single C-N bonds, a structure that has been found to be relatively unstable due to the facile liberation of N_2.[11]

Figure 6 is a schematic representation of the decomposition pathways suggested by the products observed in this work. This is provided as a guide to the observed products and the possible steps along the total decomposition route. Certainly under severe conditions, the direct removal of NO_2 and subsequent fragmentation of the triazol ring would be anticipated. Under the more mild conditions employed in this study, alternative partial decomposition products arise with sufficient stability to be detected by sensitive analytical techniques.

One indication of the relative thermal stability of the damaged residue was obtained by the temperature of onset of ion counts in the mass spectrometer. As the temperature is raised in the solids probe the material begins to volatilize producing gaseous molecules that pass into the ionizer stage of the instrument. Signal is then observed in the mass spectrometer as these ions are detected. It is interesting to note that at 160°C the control sample produced its first ion counts, at ~ 135°C the shocked samples produced signal whereas the radiation damaged sample produced signal at less than 110°C. These observations indicate the relative thermal stability of the damaged materials and the increased volatility of the products.

As suggested in [2], NTO is unique among the secondary high explosives currently in use in that it possesses only one nitro group. The presence of a single nitro group may in large part be responsible for the simplicity of the reaction chemistry of this molecule compared to the polynitro explosives. Also as suggested in [2], once the nitro group from the NTO molecule is lost, the remaining molecule, (TO), possess no explosive nature whatsoever. The possibility of the formation of intermediate decomposition products of equal or greater sensitivity is unlikely, as indicated by the products observed in this study. Estimation of the impact sensitivity of these intermediate compounds from the Kamlet OB relation indicates them to be highly insensitive. Polynitro compounds may suffer the loss or conversion of one or even two nitro groups while yet displaying significant explosive performance, for example the formation of trinitro benzaldehyde or trinitro benzoic acid from TNT or the formation of furoxan derivatives of TATB.[12] In such molecules the possibility of sensitization through the formation of energetic intermediate decomposition products is much more likely. If the reaction of a molecule is to stop due to lack of ample stimuli or propagation at a point well away from the final products, the intermediate(s) observed must possess a fair degree of stability, (require an activation energy for further reaction) or it would not be present in that form. The important point with respect to polynitro compounds is that while the total potential chemical energy of the molecule available through chemical reaction may be reduced, a significant portion may remain, and it is the activation energy required to reignite the reaction and kinetics of subsequent reaction that dictate the sensitivity of the intermediate and violence of continued reaction.

The residue resulting from complete weight loss in the TGA experiment had a distinctive red-orange, (burnt-orange) color. In the paper by Rothgery et al a similar residue was found to have an empirical formula of $C_2H_3N_3O$. Infra-red inspection by these workers determined that the residue was not TO. Indeed TO is a colorless material, further indicating the final thermal decomposition residue to not be TO. The colored appearance of the residue may suggest a conjugated material, perhaps polymeric in nature. Menapace et al[8] noted that the residue from each of their isothermal decompositions yielded solid polymeric products or tars.

Acknowledgment

The authors would like to acknowledge the NAVSWC Independent Research Program, which has provided most of the funding for the present work.

TABLE I

Major Mass Spectral peaks from Control NTO

Observed AMU	Molecular Mass	Peak Intensity	Molecular Formula	Comment
57	56	1.6%	C_4H_8	Contamination
71	70	2.1%	C_5H_{10}	Contamination
84	83	3.6%	C_2HN_3O	NTO - 47 amu, HONO
86	85	1.5%	$C_2H_3N_3O$	1,2,4-Triazol-5-one, TO
101	100	3.6%	$C_2H_2N_3O_2$	NTO - 30 amu, NO
115	114	2.3%	$C_2H_2N_4O_2$	NTO - 16 amu, O
131	130	100.0%	$C_2H_2N_4O_3$	NTO
145		0.6%		NTO + CH_{3+}, CI artifact
159		1.2%		NTO + C_2H_{5+}, CI artifact
171		1.9%		NTO + Ar^+, CI artifact
261	260	1.0%	$C_4H_4N_8O_6$	NTO dimer

TABLE II

Major Mass Spectral peaks from Radiation Damaged NTO

Solids Probe Temperature 130°C

Observed AMU	Molecular Mass	Peak Intensity	Molecular Formula	Comment
84	83	4.6%	C_2HN_3O	NTO - 47 amu, HONO
86	85	22.2%	$C_2H_3N_3O$	1,2,4-Triazol-5-one, TO
101	100	81.0%	$C_2H_2N_3O_2$	NTO - 30 amu, NO
115	114	19.0%	$C_2H_2N_4O_2$	NTO - 16 amu, O
131	130	100.0%	$C_2H_2N_4O_3$	NTO

TABLE III

COMPARISON OF CONTROL AND DAMAGED SAMPLES

CIMS DATA, Percent Intensity

AMU	CONTROL	SHOCKED	RADIATION
131	100.0	100.0	100.0
115	2.3	4.2	19.0
101	3.6	4.2	81.0
86	1.5	1.4	22.2
84	3.6	6.1	4.6

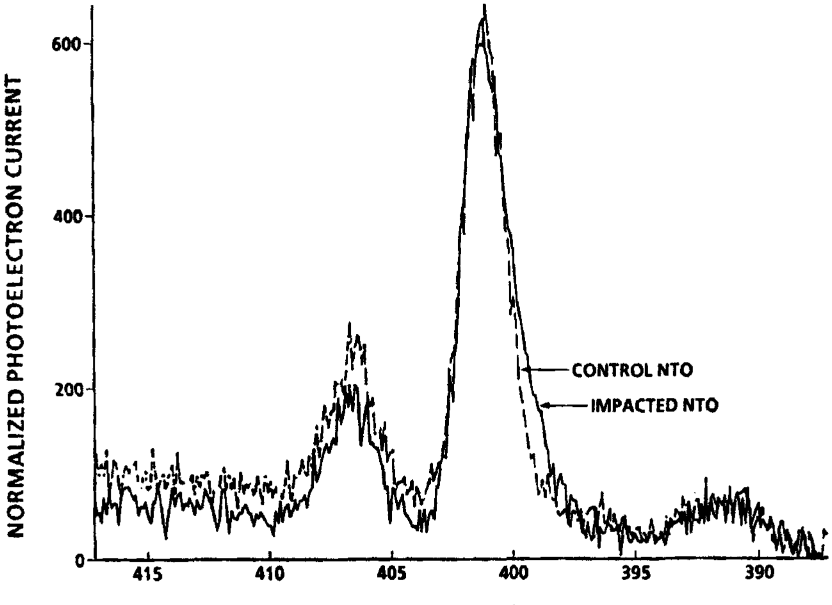

Figure 1. N(1s) XPS spectrum of control NTO and NTO impacted with a 10 kg. weight dropped from a height of 3 meters. The spectrum reveals that in the impacted sample the nitro peak at 406.5 eV has decreased and a new peak 1.6 eV below that of the ring nitrogen(401.3 eV) has appeared.

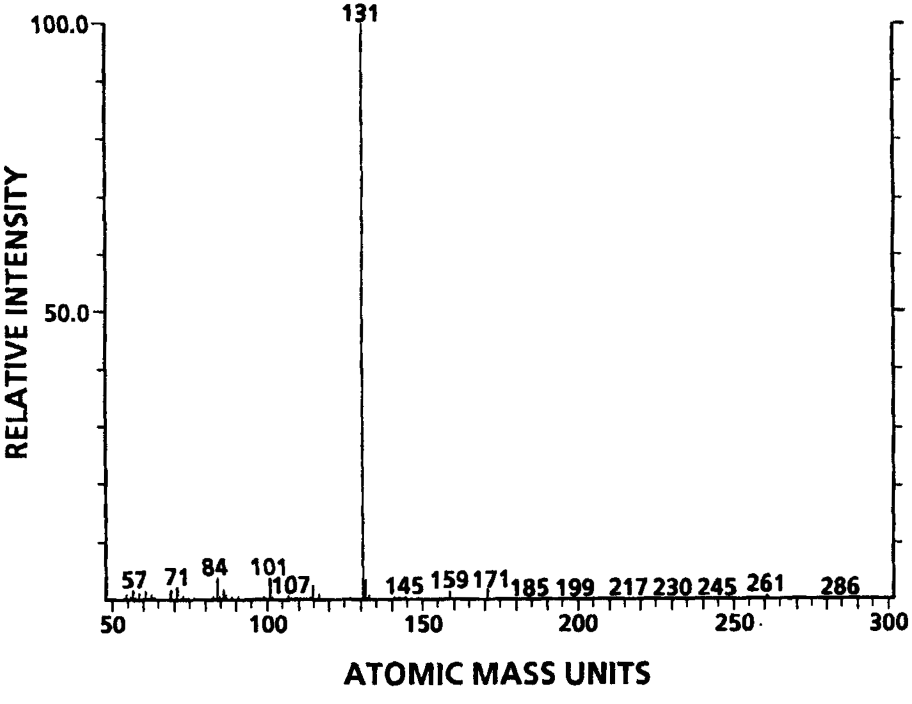

Figure 2. Chemical ionization mass spectrum (CIMS) of control NTO.

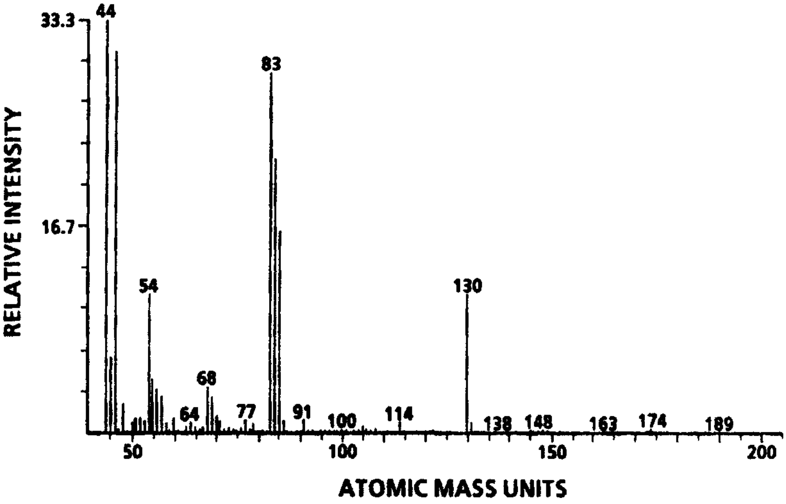

Figure 3. Electron impact ionization mass spectrum of control NTO.

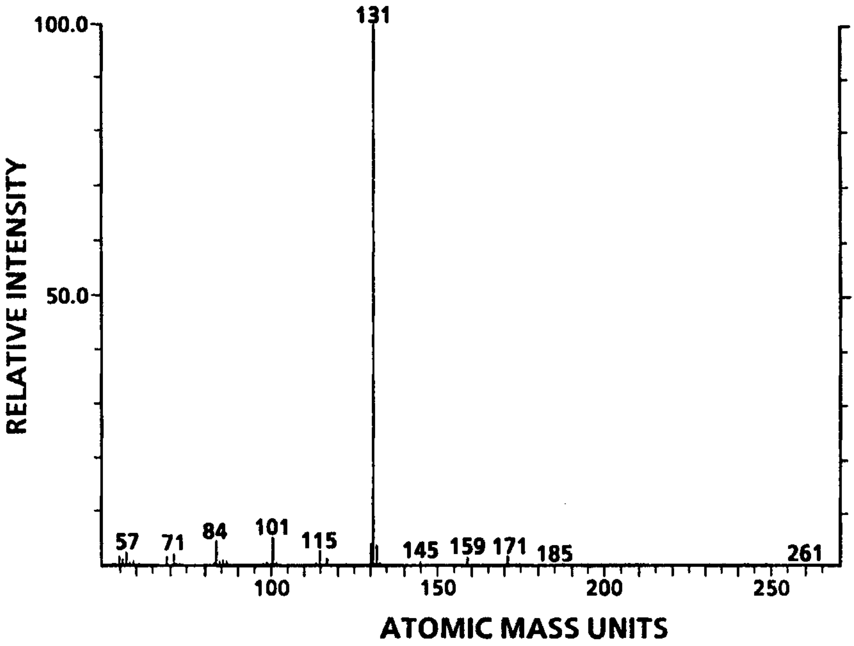

Figure 4. Electron impact ionization mass spectrum of shocked NTO.

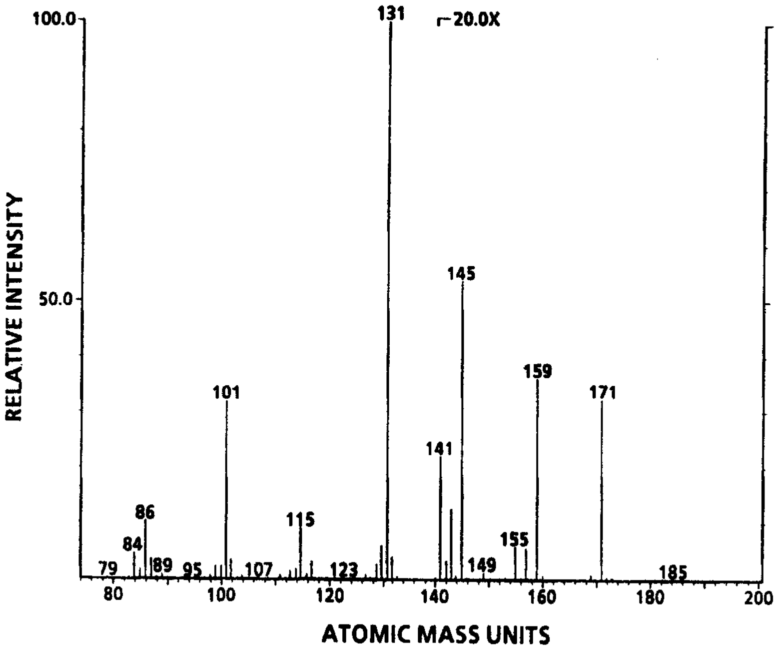

Figure 5. Chemical ionization mass spectrum of NTO following 11 hrs. of x-ray irradiation within the XPS instrument(3.3X10^8 Rad).

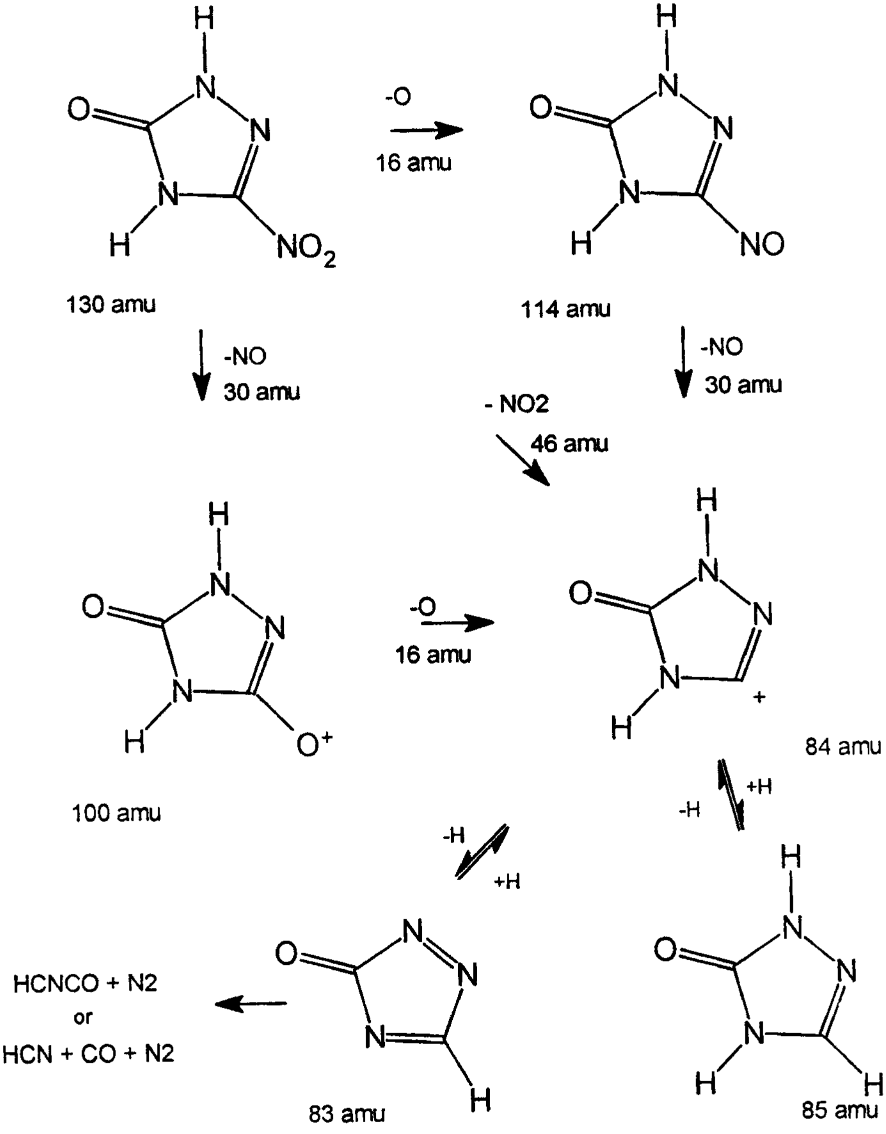

Figure 6. Schematic representation of the decomposition pathways suggested by the products observed in this work.

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