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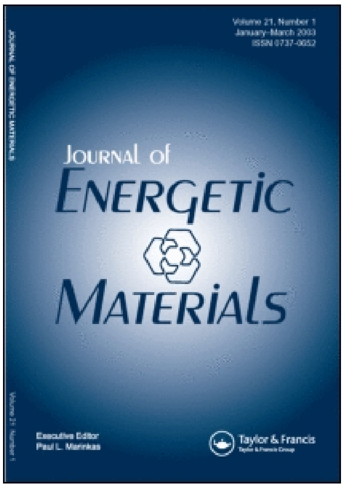

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
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The radiation sensitivity of NTO (3-Nitro-1,2,4-Triazol-5-One)

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To cite this Article Beard, B. C. and Sharma, J.(1989) 'The radiation sensitivity of NTO (3-Nitro-1,2,4-Triazol-5-One)', Journal of Energetic Materials, 7: 3, 181 — 198

To link to this Article: DOI: 10.1080/07370658908014895

URL: http://dx.doi.org/10.1080/07370658908014895

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THE RADIATION SENSITIVITY OF NTO
(3-Nitro-1,2,4-triazol-5-one)

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ABSTRACT

NTO and the better known molecular explosives, TATB, RDX, and HMX, were subjected to X-ray and Ultra-violet radiation to determine the relative sensitivity of NTO to radiation damage. X-ray Photoelectron Spectroscopy, (XPS) detected damage induced chemical changes. RDX was the most sensitive molecule to both the X-ray and UV radiation while HMX was only slightly less sensitive. NTO was found to be 1.5 to 3.0 times more sensitive to x-ray and UV damage than TATB. The resulting hierarchy of radiation sensitivity is therefore RDX > HMX >> NTO > TATB. XPS analysis of the x-ray damaged residue suggested three decomposition products resulting from loss of nitro, reduction of nitro to nitroso, and loss of NO.

INTRODUCTION

The molecule NTO [3-Nitro-1,2,4-triazol-5-one], Fig. 1, has recently been suggested as a high performance insensitive energetic material[1]. The initial evaluation of NTO, established its sensitivity to thermal, impact, and spark initiation[1]. The work reported here continues the characterization of NTO by determining its radiation sensitivity to x-ray and UV radiation. Gamma ray damage data[2] of the molecular explosives, TATB, RDX, and HMX demonstrate a wide range of sensitivity to radiation damage. To cover a broad range for comparison, these explosives were chosen as reference compounds for the determination of the relative radiation sensitivity of NTO.

The radiation damaged NTO was analyzed to determine the level of decomposition, and to gain insight into the chemical nature of the decomposition products. Extensive work by one of us (JS) has established XPS as an indispensable tool for the study of propellants and explosives. Stable intermediate compounds have been identified in several molecular explosives[3,4,5]. Products resulting from the first endothermic and first exothermic steps in the decomposition of TATB have recently been identified[5]. The role of these products in sensitization of TATB has also been demonstrated[6]. The chemical nature and sensitivity of the tentatively identified decomposition products of NTO will be discussed.

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EXPERIMENTAL

A Kratos ES-300 X-ray photoelectron spectrometer incorporating a dual anode Al/Mg x-ray source and an x-ray monochromator was employed for analysis. Operating conditions of the Al x-ray source were 15 KeV and 15 ma (225W), producing characteristic lines of Al and Bremsstrahlung radiation up to 15KV in energy. The x-ray monochromator (operated at 15KV and 12 ma, 180W) transmitted only the Al $K\alpha_1$ characteristic x-ray line yielding higher resolution photoelectron spectra. The x-ray radiation dose from the Al x-ray source was determined by the use of radiation sensitive chlorostyrene film (Cl-1) which darkens as a function of radiation dose[7]. The x-ray flux in the XPS instrument was found to be 0.5×10^6 rad/min. The analysis chamber pressure was maintained to less than 1×10^{-8} torr. Each material was ground into a fine powder then deposited as a thin even layer onto nitrogen-free cellophane tape.

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The explosive samples accumulated radiation damage as they were simultaneously analyzed within the XPS spectrometer. Total accumulated dose during the x-ray exposure, (11 hrs), was on the order of 3.3×10^8 rad. During the extended x-ray irradiation the sample temperature could be monitored by a thermocouple within the sample holder. The temperature rise from the irradiation was 5°C.

Ultra-violet exposures were performed in air using the total transmitted radiation from a low pressure quartz Hg lamp. Exposure times ranged from 15 min to 8 hours. Damage was measured by XPS analysis of the UV irradiated sample. Additional damage from the XPS x-ray was minimized by collecting the N(1s) spectrum in less than 10 min.

RESULTS

Figure 2 compares the damage sustained by the four molecular explosives as a function of x-ray exposure time. Damage is plotted in Fig. 2 as the percentage NO_2 loss, calculated from the XPS peak areas using the relation,

$$[\{NO_2/\text{Total N}\}_t/\{NO_2/\text{Total N}\}_{t=0}].$$

The decomposition reactions were found to follow first order kinetics with the rate constants listed in Table I. RDX is the most sensitive, with HMX displaying very similar damage sensitivity. RDX and HMX have x-ray induced decomposition rates 6.9, and 4.9 times greater than TATB. The damage rate of NTO is only 1.5 times greater than TATB.

TABLE I

FIRST ORDER RATE CONSTANT (min^{-1})*

SAMPLE	X-RAY	UV
RDX	-5.4×10^{-3}	
HMX	-3.8×10^{-3}	
NTO	-1.2×10^{-3}	-1.3×10^{-3}
TATB	-7.8×10^{-4}	-4.1×10^{-4}

* Note that these rate values are specific only for the irradiation conditions used in these experiments.

Damage to NTO is manifested by loss of XPS N(1s) signal intensity from the high binding energy peak (407.6 eV) of the nitro functionality. A composite plot of N(1s) spectra from x-ray

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damaged NTO is shown in Figure 3. The spectrum (3a.) exhibits well separated peaks for the nitro and ring nitrogens (401.3 eV) in the expected peak area ratio of 1:3. In the damaged sample spectra (3b & 3c) the nitro to ring nitrogen ratio drops significantly, to 1:4.6 and 1:7.8 respectively. The loss of nitro peak intensity is accompanied by the appearance of a new peak on the low binding energy side (~400.0 eV) of the ring nitrogens. Following 11 hours of x-ray irradiation 17% of the nitrogen was observed in the damaged state.

The nitrogen spectra from NTO and TO (the precursor of NTO, see Fig.1) were carefully examined to clarify the peak assignments for damaged NTO. Figure 4 is a bar chart representation of the N(1s) XPS spectra from NTO, NTO (collected with an X-ray monochromator), TO, and x-ray damaged NTO. The added spectral resolution of monochromatic XPS disclosed the inequivalency of the ring nitrogens in NTO. The 402.0 eV peak from NTO corresponds to N^4 and the 400.9 eV peak is from N^1 and N^2. The assignment of N^4 as the highest binding energy ring nitrogen is consistent with the reported strong acidity[1,8,,9] of the proton attached to N^4. Nitrogen (1s) spectra from TO also demonstrate ring nitrogen inequivalency. For TO, however, the signal from N^4 is coincident with the peak from N^1. A decrease in N^2 binding energy to 399.9 eV is observed due to the absence of the strongly electron withdrawing NO_2. The peaks observed from the damaged sample suggest a mixture of NTO and TO. The ring nitrogen peak splitting

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from the monochromator NTO data was used as the starting point for the curve fit of the damaged NTO spectra.

Figure 5 is a plot of the intensity of each nitrogen component in the N(1s) XPS spectra as a function of x-ray exposure time. The numbers assigned to the components are illustrated in Fig.4. If loss of NO_2 (degradation back to TO) were the sole mode of decomposition, peak 2 (N^4 in NTO) should decrease in lock-step with peak 1. However, the intensity of component 2 in the fitted XPS N(1s) spectrum of damaged NTO does not follow component 1. Therefore, there must be additional decomposition pathways.

UV damage of the explosives is plotted in Fig. 6. The radiation sensitivity trend is RDX > HMX >> NTO > TATB. The precision of the decomposition rate constant values is not as good as those for the x-ray data, due to the limited number of data points. First order decomposition rates for NTO and TATB are given in Table I. NTO decomposition is ~3.0 times faster than that of TATB. XPS spectra of UV damaged NTO showed identical chemical changes as those observed from the x-ray damaged samples.

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DISCUSSION

It is of interest to identify decomposition products which are consistent with the observed XPS data. As suggested in the results section, the direct loss of NO_2 to produce TO is one possible mode of decomposition. Another product could be urazole resulting from elimination of NO via a cyclic intermediate as suggested by Dewar et al[15]. Reduction of nitro to nitroso is also a possible decomposition mechanism as observed in decomposition studies of RDX[10,11].

Spectra from NTO, TO, and urazole are shown with the predicted spectrum for the nitroso product, Fig.7. Since a sample of the nitroso derivative of NTO was not available, the anticipated spectrum was extrapolated from available data. The >N-<u>N</u>O (nitroso nitrogen in the nitrosamine) nitrogen has a reported binding energy of ~402 eV[12]. Nitroso bonded to carbon should have a lower binding energy (~-0.6 eV),[13] placing the nitroso in the peak 2-3 area (401.4 eV) of the damaged NTO spectrum. Decreased electron withdrawing strength of the nitroso group relative to the nitro[14] would increase the total electron density in the five membered ring, resulting in the lowering of the ring-nitrogen's binding energy (specifically, the binding energy of N^2 would decrease toward the N^2 value in TO).

The spectra in Fig. 7 demonstrate how the predicted products could lead to the observed N(1s) spectrum from x-ray damaged NTO. Estimates of the relative amounts of these products can be made by using the changes in the chemical forms of nitrogen depicted in Fig.5. Mass spectrometry would be most helpful in establishing the relative priority of the decomposition pathways.

The observed decomposition is thought to be purely photochemical not thermal. As noted in the experimental section, the observed temperature rise of the sample holder was only 5°C. The energy deposited onto the sample can be estimated based upon

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the conversion efficiency of the x-ray tube and area of the sample. This result is 1.22 x 10^{-4} cal/s. Using the x-ray extinction coefficient for NTO (15KeV x-rays) the portion of this energy deposited in the NTO layer (assume one micron) is 3.01 x 10^{-6} cal/s. The high thermal conductivity of the metallic sample holder and probe would easily carry away the heat at this rate of deposition. Photochemical decomposition is dependant upon a materials inherent photoionization relaxation mechanism back into the original electronic arrangement. Those materials with low energy pathways of relaxation leading to products other than the starting material will suffer decomposition more rapidly.

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An interesting distinction can be made between NTO and typical highly nitrated energetic materials. TATB for example, is known to generate furazan and furoxan derivatives in response to damage[5]. Highly nitrated explosives can retain as many as two of the original three nitro groups following damage and therefore possess significant energetic potential. Furoxan formation, in particular, constitutes a hazard because furoxans have been identified as sites of increased sensitivity[6]. Many of the identified decomposition products of TNT also retain all three nitro groups[16,17]. Such compounds as trinitrobenzalcohol and trinitrobenzaldehyde are more sensitive than the parent TNT. The existence of only a single nitro group on NTO, however, implies that removal of NO_2 should leave little if any energetic potential and, therefore, no explosive hazard. Based on the Kamlet[18] oxygen balance (OB) to impact sensitivity relation, TO, 3-nitroso-1,2,4-triazol-5-one, and urazole all are predicted to be more stable than NTO. While this calculation is not definitive proof of insensitivity, it appears unlikely that the presence of decomposition products in damaged NTO will increase the sensitivity. NTO is therefore unique among commonly used energetic materials in that it may not be sensitized by molecular degradation.

SUMMARY

The x-ray and UV radiation sensitivity of NTO has been determined relative to RDX, HMX, and TATB. NTO suffers damage at a slightly greater rate (1.5 to 3.0 times) than TATB but much lesser rate than RDX or HMX. The damage imparted to the NTO by both x-rays and UV irradiation is manifested by loss of the nitro functionality and/or its transition to a more reduced chemical state. The formation of TO, urazole and the nitroso derivative of NTO are suggested. These decomposition products are expected to have lower sensitivity than NTO based on Kamlet's oxygen balance/sensitivity relations. We were therefore led to the conclusion that NTO is a unique new energetic material that should not display chemical sensitization in response to damage.

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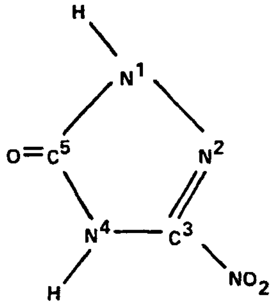
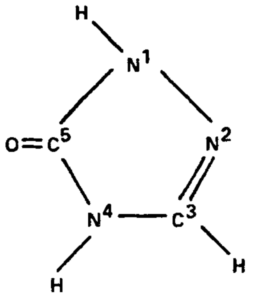


NTO, 3 NITRO-1, 2, 4-TRIAZOL-5-ONE



TO, 1, 2, 4-TRIAZOL-5-ONE

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FIGURE 1
Diagram of the chemical structure of a.) NTO (3-Nitro-1,2,4-Triazol-5-one), and b.) TO (1,2,4-Triazol-5-one).

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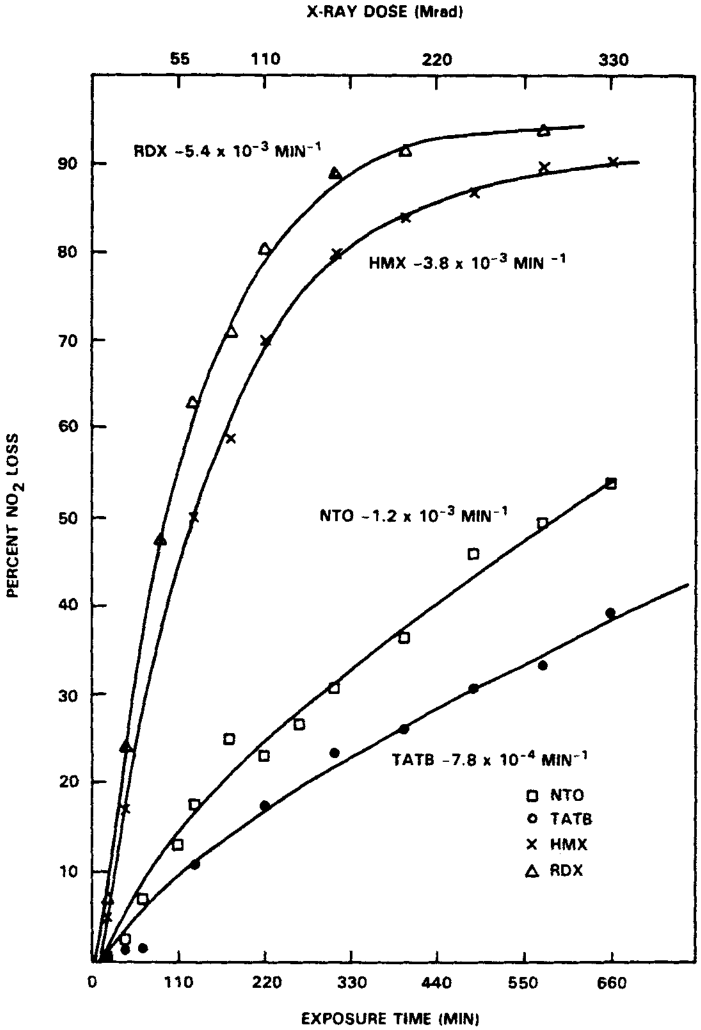

FIGURE 2
Plot of x-ray damage versus time for the four explosives. Damage represented as, Percent NO_2 Loss, is calculated from the XPS peak areas using the relation,

$$[\{NO_2/\text{Total N}\}_t/\{NO_2/\text{Total N}\}_{t=0}].$$

First order rate constants under the radiation conditions used are shown.

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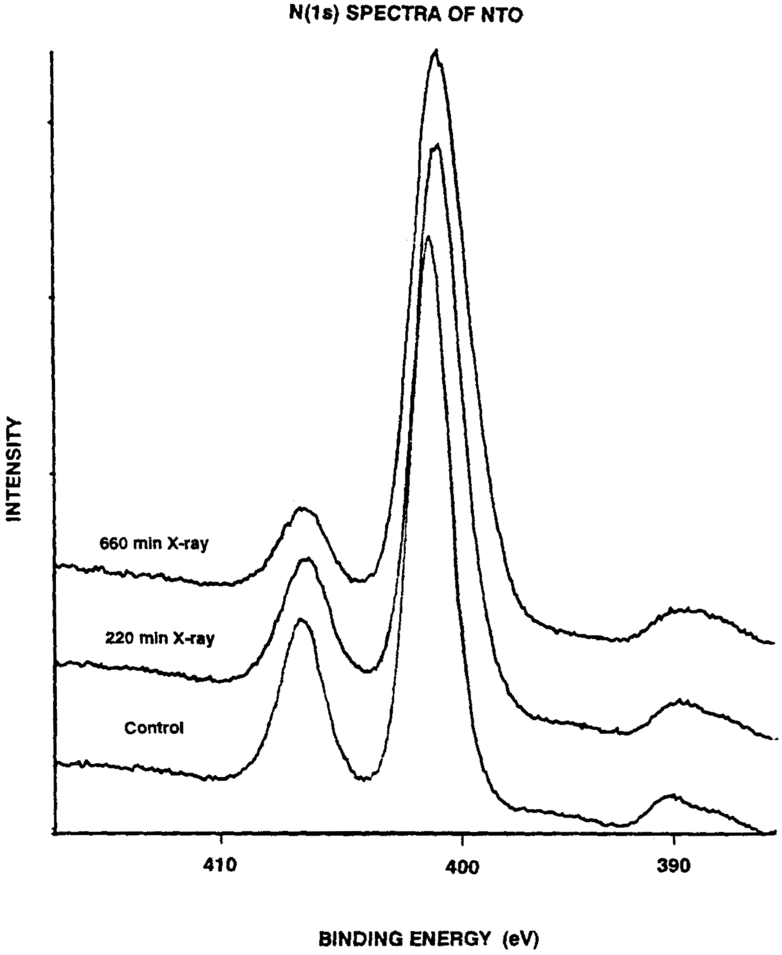

FIGURE 3
Composite plot of N(1s) XPS spectra from NTO, exposed to 15KV, 15ma x-ray photons for 0 min., 220 min., and 660 min.

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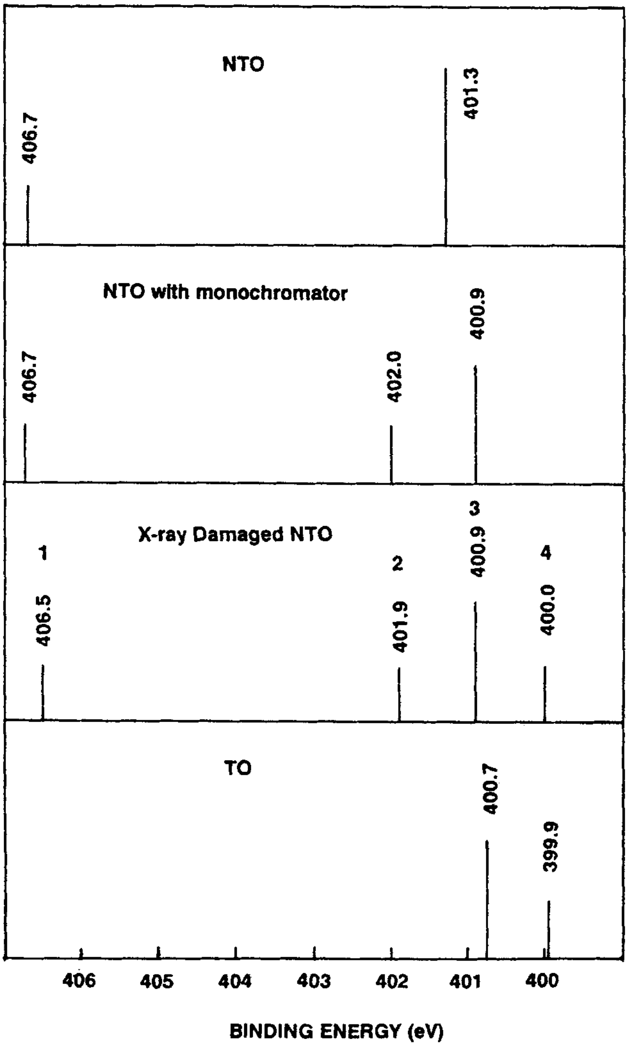

FIGURE 4
Bar chart representation of N(1s) XPS spectra from, a.) NTO, b.) NTO collected with an x-ray monochromator, c.) x-ray damaged NTO, and d.) TO.

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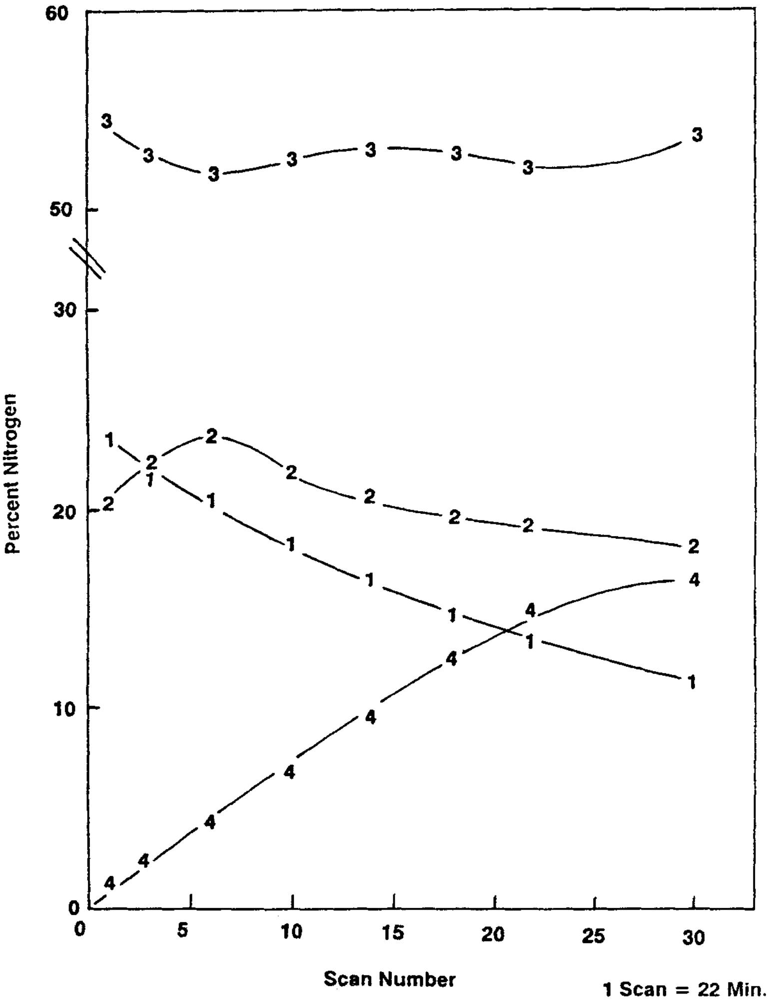

FIGURE 5
Plot of the chemical states of nitrogen in NTO as a function of x-ray irradiation time. Numbered curves correspond to the numbered peaks in the damaged NTO spectrum shown in Fig. 4.

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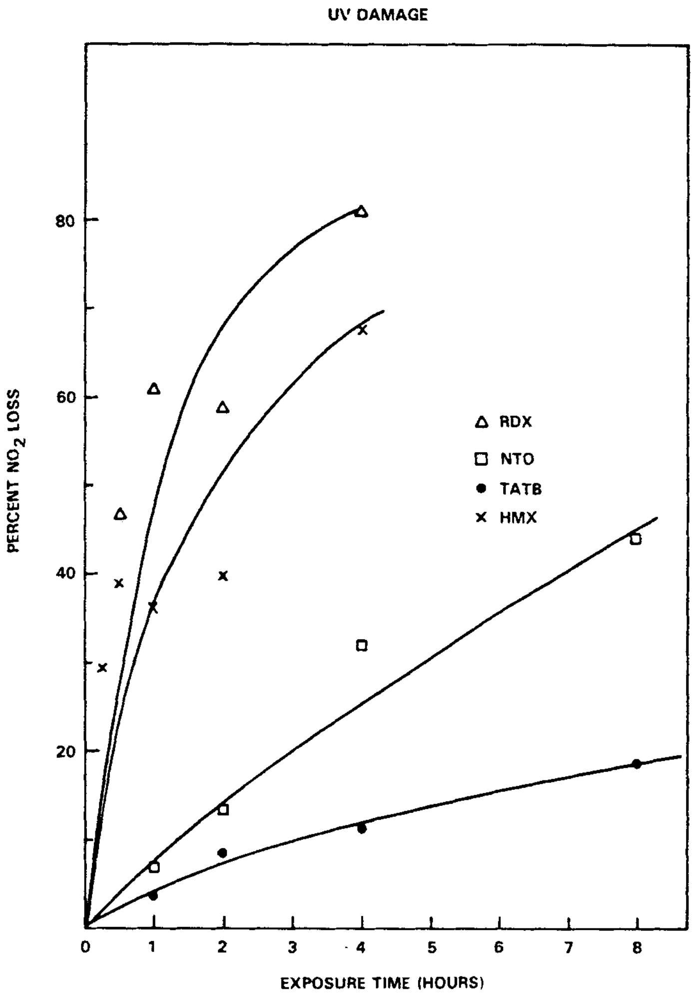

FIGURE 6
Plot of Ultra-violet damage versus time for the four molecular explosives. Percent NO_2 loss was calculated as in the case for x-ray damage.

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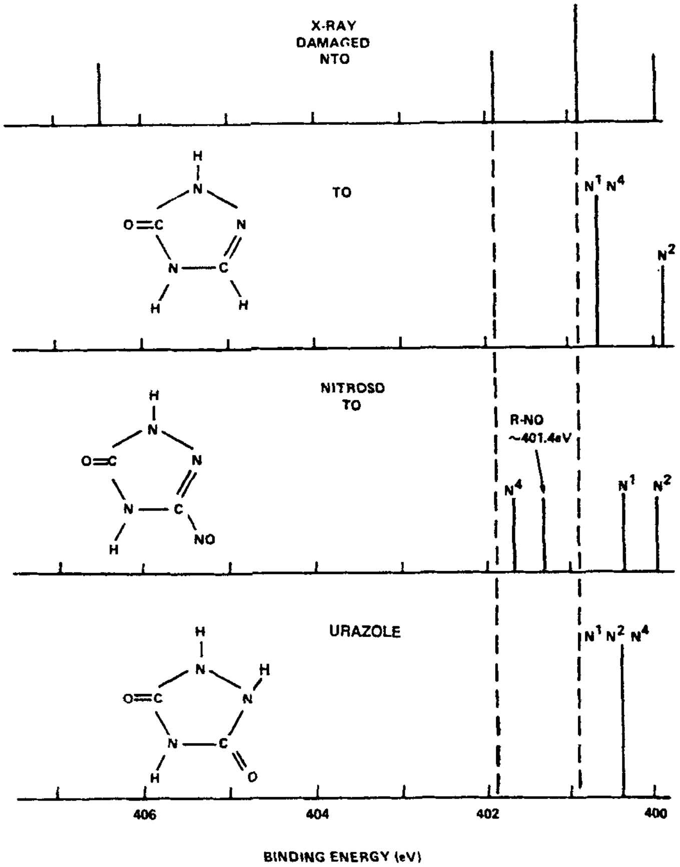

FIGURE 7
Predicted XPS N(1s) spectra of the speculated decomposition products, in comparison to the observed spectra from x-ray damaged NTO.