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Towards unraveling the photochemistry of TATB

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Abstract

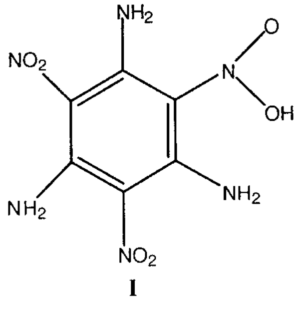
A combined theoretical and experimental chemical analysis has been conducted to unravel the mechanism, underlying the color change of yellow 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) to green upon UV irradiation. There is a strong evidence to show, for the first time, that the process is photochemical in nature and due to the formation of the mono nitroso derivative. We have identified a chemical synthesis by which this derivative compound can be produced in the laboratory, thus allowing for direct testing and determination of its chemical and physical properties. Calculations also show only a slight decrease in the sensitivity and performance of the irradiated materials, attributed to the formation of this previously unidentified species.

Keywords: Photochemistry; 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB); Mass spectroscopy; Green TATB

1. Introduction

A peculiar property of the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is a change in color, from yellow of the freshly prepared sample to green upon exposure to a radiation stimulus. This darkening is a surface phenomenon and increases with the penetrating radiation. If this effect is due to chemical decomposition, it certainly raises some concern and issues to consider regarding the bulk properties, such as performance and sensitivity. The differential scanning calorimetry (DSC) results [1], for example, showed a 10° decrease in the onset of reaction exotherm of the light-induced green material, and a 15° reduction [2] for gamma-induced dark green materials. As this explosive might be exposed to a penetrating radiation in the stockpile environment, the formation of green materials is an aging signature that is readily manifested, with consequences to the lifetime service. Identification of the mechanism and the species, if any, causing this aging trend is the object of this work.

There have been numerous, albeit inconclusive studies regarding the "greening" of TATB. In the early 1980s, Britt et al. [3] measured the ESR spectra of UV photolyzed TATB both in the solid phase and in solution. They proposed that the coloring is due to the formation of an unusually stable radical, with no evidence of decaying after 2 years, of H-adduct TATB (**I**). Their results were later contradicted [4] based on semi-empirical molecular orbital calculations of spin density.



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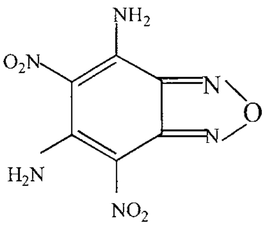
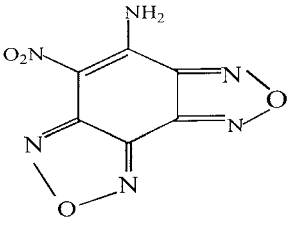
More recently, a group at LANL [2] found evidence for the formation of mono (**II**) and di (**III**) furazans in gamma and proton irradiated samples of doses 17 and 70 Mrad. These substances were not detected in a sample with 9 Mrad radiation, although lime green in color.



II



III

The above noted studies have thus determined that the greening effect is chemical in nature, due to the production of new species. Since this effect is a surface phenomenon, reliable identification of the new species is hindered by its low concentration in the bulk materials, and by the low solubility of both the original and contaminant materials. It is highly desirable and more advantageous to reproduce the new species directly by synthetic methods. We should note that decomposition products of TATB due to a variety of external stimuli (shock, impact, and heat) have also been identified [5,6].

The present work combines theoretical modeling and experimental chemical analysis of control (untreated), irradiated (a 70 Mrad dose and an UV irradiated), and green synthesized (see below) TATB samples. Spectroscopic determinations included infrared (IR), UV, and mass spectra (high resolution and positive electron impact, PEI).

2. Results and discussion

The visible region of the electromagnetic spectrum extends in the approximate range of 400–800 nm, the green color occurring at ~550 nm. The absorption of light can be modeled as electrons are excited to higher energy levels. We have calculated, using semi-empirical methods, the UV spectra of TATB and all previously proposed decomposition products (**I–III**). We note that due to the increase bond conjugation, the mono and di furazans should be primary suspects for coloration.

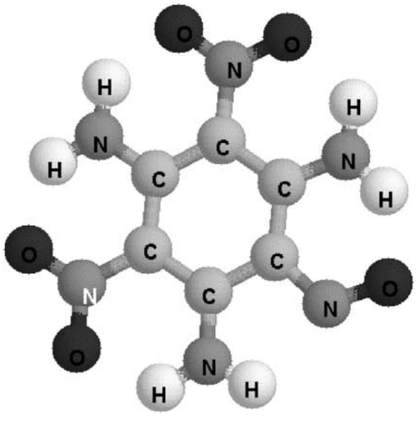
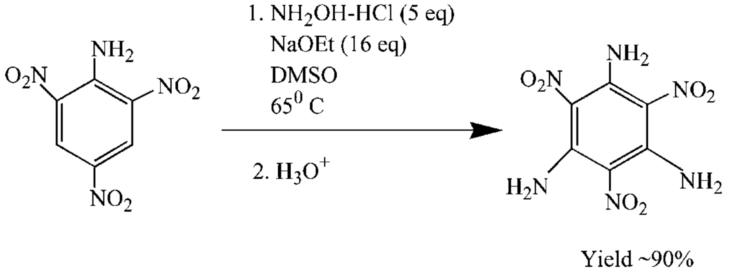


Fig. 1. Mono nitroso analog of TATB (TADNB).

We have also calculated that the UV spectra of the mono nitroso analog of TATB (Fig. 1, referred to thereafter as TADNB). Nitroso derivatives are known to be colored. Consider the simple case of nitrobenzene and nitrosobenzene. While both spectra show strong absorption in 250–300 nm region, the nitrosobenzene spectrum shows an additional weak absorption at 750 nm. Further, mono nitroso analogs have been determined to be major products in the thermal decomposition experiments of HMX and RDX [7,8]. Interestingly, the calculated UV spectrum of TADNB shows a weak absorption at 600 nm.

TADNB seems to be the major contaminant in a new, direct synthesis of TATB [9], using Scheme 1. The mass spectrum of untreated, yellow TATB (Fig. 2) shows peaks at 258 and 228 nm due to TATB and the loss of NO. The spectra of both light irradiated and the synthesized materials (as described in the above scheme) exhibit additional peaks at 242 and 225 nm (Fig. 3). The peak at 242 nm corresponds to the molecular weight of TADNB, and is of the same intensity for aged and synthesized species. High resolution mass spectroscopy recorded similar results. The peak at 242 nm is due to the loss of an oxygen atom and not, say, an amine group (NH_2) is accounted for on the basis of the definitive results obtained from the high resolution mass spectra, and taking into account that diaminotrintrobenzene (DATB) produces a different mass spectra. Note that, based on our ab initio quantum mechanical calculations, breaking the C–NH_2 bond requires 104 kcal/mol, significantly more than that required for the rupture of the N–O bond,



Scheme 1.

which is 76 kcal/mol. The UV spectrum recorded on the synthesized materials showed a very weak absorption at 600 nm. This is not definitive, however, due to relatively small concentration of the materials in the sample (which also seems to have the same solubility characteristics of TATB). Further analysis of the synthesized TADNB (purification, isolation, and X-ray characterization) is still needed for a definitive conclusion. Finally, we note that this species has been detected as a major product in early shock-induced decomposition of TATB [10].

The production of a di nitroso compound and the loss of OH radical can account for the presence of the peak at 225 nm from TADNB as in Scheme 2.

The mass spectrum of TADNB (MSMS) shown in Fig. 4, clearly identifies TADNB as the source for the production of the peak at 225 nm. The calculated IR spectrum of TADNB is shown in Fig. 5. We note strong absorption at 1361 and 1625 cm^{-1}. The strongest of the double peaks, around 1625 cm^{-1}, is due to the NO_2 asymmetric stretch and the weaker peak is due to the N=O stretch. Only one peak should be observed in non-irradiated TATB samples. It is doubtful, however, that these peaks can be resolved experimentally.

We also recorded the IR spectra of the four samples. It shows that the samples are similar in all aspects except for the synthetic byproduct, whose symmetric angle of deformation of the NH_2 group (1638.2 cm^{-1})

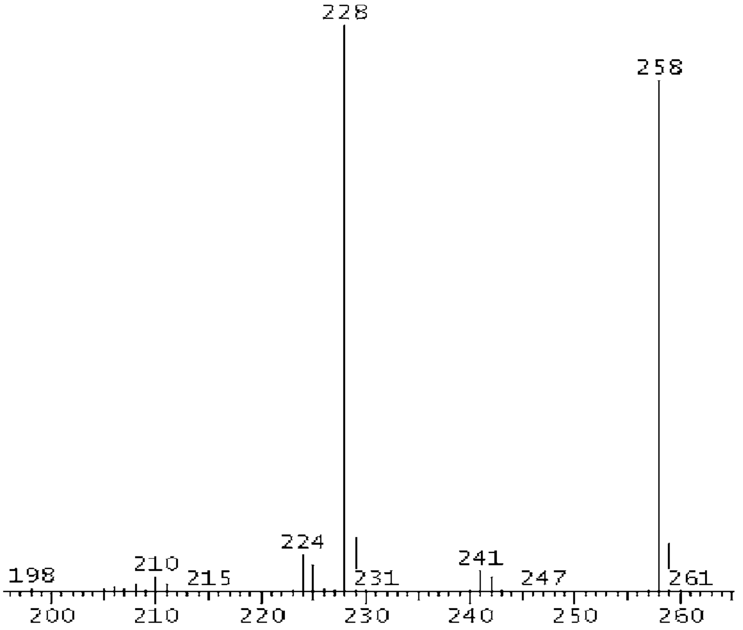


Fig. 2. The mass spectrum of untreated, yellow TATB.

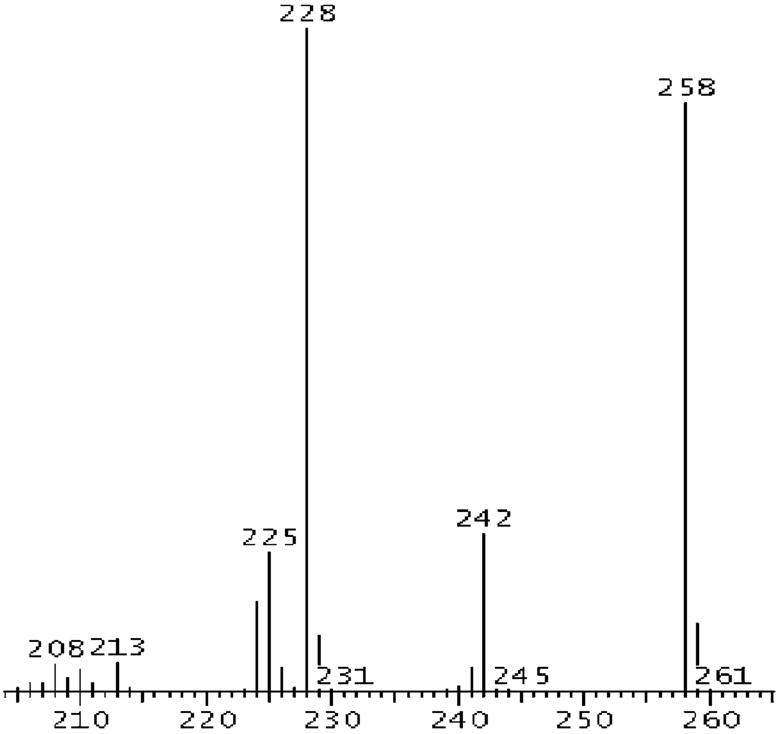
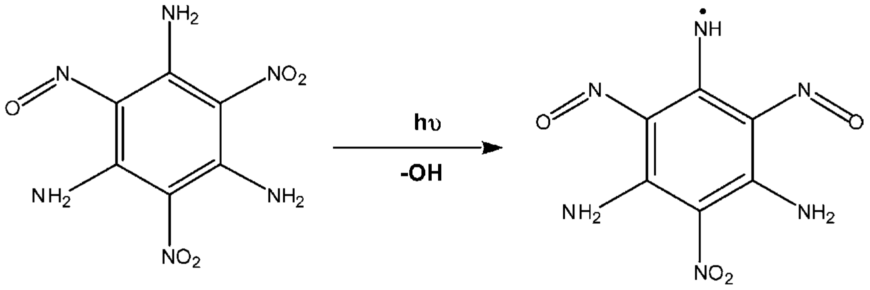


Fig. 3. The mass spectrum of synthesized DATNB. Similar spectrum is obtained from the aged, light irradiated TATB.

appears 5 cm^{-1} lower than the rest. To see the doublet around 1625 cm^{-1} may require Raman spectroscopy.

As for the H-adduct species (**I**), quantum chemical density functional calculations confirmed that it is unstable, having no minimum equilibrium potential energy. The formation of this species is, thus, precluded since no evidence of its existence appears in the mass spectra.

Finally, an estimate for the change to detonation sensitivity and performance, due to the formation of TADNB, has been determined using calculated heat of formation characteristics of this species and the thermochemical code CHEETAH. Performance calculations were based on the assumption that the density of TADNB is the same as that of TATB. The heat of formation of TADNB was calculated to be −19 kcal/mol. This compares with a heat of formation of −35 kcal/mol for TATB. In order to assess the difference in performance of the materials, we calculated the energy released at a relative volume expansion of



Scheme 2.

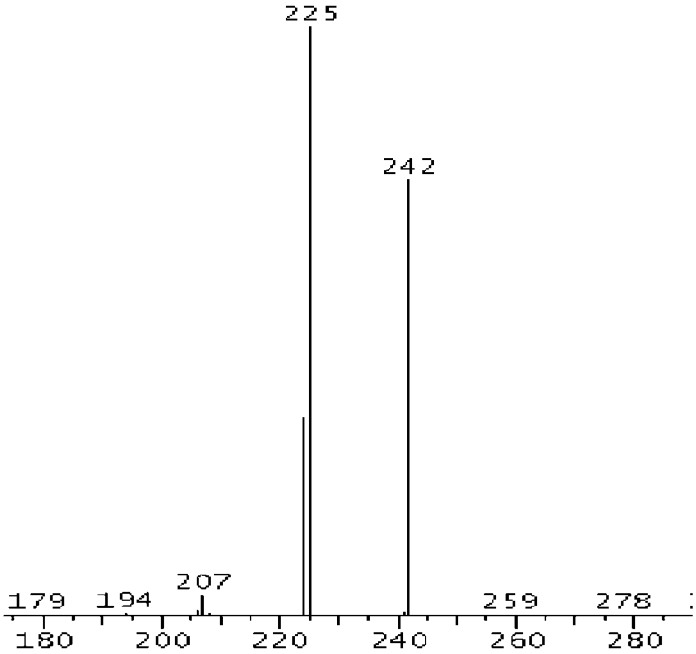


Fig. 4. MSMS, mass spectrum indicating the production of the peak at 225 nm fragment from TADNB.

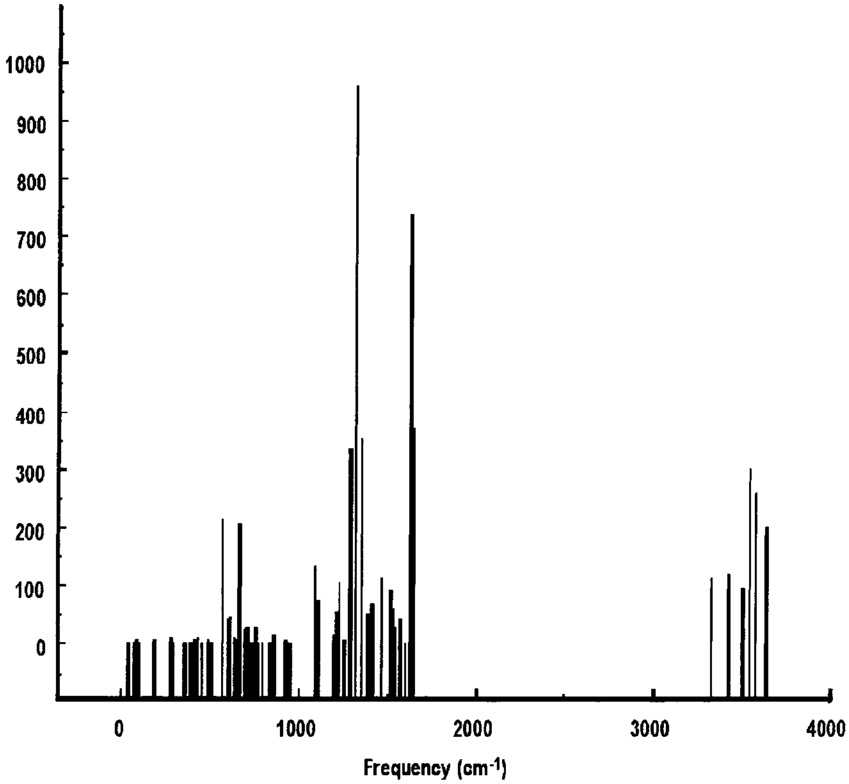


Fig. 5. Calculated harmonic frequencies of TADNB.

2.2. This is a common metric in determining the metal acceleration ability of an explosive. The calculated performance of TADNB at its crystal density was 6% less than that of TATB at the same density. This is due to the poorer oxygen balance of TADNB.

Safety calculations were based on calculating the strength of the weakest bond in the molecule. We have been able to show that this often correlates with explosive sensitivity. The calculated bond dissociation energy of 64 kcal/mol leads to a predicted drop hammer height of 100 cm. Thus, TADNB is predicted to be an insensitive high explosive, but more sensitive than TATB (>300 cm hammer height). Small quantities of TADNB are thus not expected to significantly sensitize TATB.

3. Summary

Our work indicates that there is considerable evidence, based on mass spectroscopic analysis, that the production of green TATB is a photochemical process accompanied with the formation of mono nitroso analog (TADNB). A synthetic route for the production of this species under controlled laboratory conditions has been identified. Additional work requires the isolation and purification of this material in appropriate quantities for conclusive identification and further testing.

Acknowledgements

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