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Radiation Stability of the Nitrate Ester Energetic Functional Group

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Abstract. High explosives (HEs) are used in a variety of applications that require them to be stable under a wide range of harsh environments, and understanding how HE is altered by ionizing radiation is of particular importance. This paper explores the radiolytic degradation of the nitrate ester (-ONO_2) functional group (FG) which is the energetic FG responsible for the explosive properties of the commonly used explosive pentaerythritol tetranitrate (PETN). Trace chemical analyses using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, ultra high pressure liquid chromatography (UHPLC), and gas chromatography-time of flight mass spectrometry (GC-TOFMS) were completed on control and γ-irradiated materials containing nitrate esters to assess chemical changes brought about by ionizing radiation. Results indicate that the nitrate ester FG is predominantly affected, and the most probable degradation pathway involves the scisson of the trigger linkage (O-NO_2). These results were found to be insufficient to explain changes in small scale sensitivity tests seen by other researchers.

INTRODUCTION

Pentaerythritol tetranitrate (PETN) is one of the most commonly used explosives, and it therefore must withstand a variety of harsh conditions both during storage and use. One such harsh condition is ionizing radiation, and the effects of ionizing radiation on explosives are not well understood. The energetic properties of PETN are partly supplied by the nitrate ester (-ONO_2) functional group (FG), and this study investigated the radiolytic degradation of the nitrate ester FG. This study was completed using both explosive (PETN) and nonexplosive (dodecane-based) configurations of the nitrate ester FG to probe the chemical degradation induced by ionizing radiation.

RESULTS AND DISCUSSION

PETN

PETN was processed and pressed into high density pellets at Los Alamos National Laboratory (LANL). The pellets were placed into glass ampoules hermetically bonded to stainless steel flanges, flushed with argon gas, and sealed before being transported to and irradiated at the Low Dose Rate Irradiation Facility (LDRIF) at Sandia National Laboratories (SNL) in Albuquerque, NM. Irradiations were carried out with a ^{137}Cs source (662 keV γ ray) and the total dose was 2 kGy-CaF_2. Headspace gas was sampled and analyzed using gas chromatography-mass spectrometry (GC-MS) at SNL, while solid phase chemical analyses were completed at LANL using both proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and ultra high pressure liquid chromatography (UHPLC). For more experimental details, see [1].

Analysis of the headspace gas of the irradiated PETN sample revealed that the atmosphere of the sample was closer to atmosphere than the argon flushed environment that was originally created, though there were still above atmospheric levels of both nitric oxide (NO) and carbon dioxide (CO_2) [1]. This result implies that some leaking occurred with the sample during the 2 year irradiation period. The presence of these species suggests that there was degradation both to the carbon backbone as well as the nitrate ester FG.

^{1}H-NMR spectra identified two new peaks (3.63 and 4.63 ppm) that are consistent with the formation of PETriN [1]. PETriN is a degradation product of PETN whereby a single nitrate ester FG is converted to a alcohol (-OH), and thus this result indicates a significant degradation of the energetic FG. UHPLC identified several new species, including various alcohols and aldehydes such as PETriN and PETriNal. These species also appear to be formed for the various PETN homologues, but a more rigorous analysis of this data is currently underway. For all the listed species, NO_2 must be removed from the nitrate ester FG, then the remaining O will either form a double bond (aldehyde) or obtain an hydrogen atom to form an alcohol. These same species were identified in heated PETN using similar methods employed in this study [2]. A schematic showing a summary of these results can be found in Fig. 1.

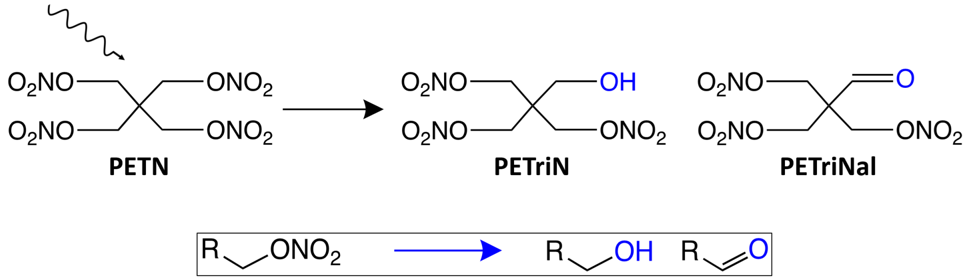

FIGURE 1. Summary of the chemical analysis results for irradiated PETN. A general scheme for the homologues is highlighted by the box.

Dodecyl Nitrate Ester

Dodecyl nitrate ester was synthesized at LANL. The liquid sample was placed into a similar vessel to the PETN irradiations, but were altered to allow for evacuation and the addition of a removable gas sample cylinder. Samples were evacuated using the freeze-pump-thaw methodology before being transported to the Gamma Irradiation Facility (GIF) at SNL. The samples were irradiated to a dose of 300 kGy-CaF_2 using ^{60}Co (1.17 and 1.33 MeV γ rays) before being transported back to LANL. Headspace gas was analyzed with GC-MS while the condensed phase was analyzed using both ^{1}H-NMR spectroscopy as well as gas chromatography-time of flight mass spectrometry (GC-TOFMS). For more experimental details, see [3].

After irradiation, headspace gas analysis revealed that dodecyl nitrate ester produced almost 5 times the amount of gas that dodecane produced despite the only difference in the samples being the addition of the nitrate ester FG at the end of the molecule. GC-MS of that gas found that 75 mol% was nitrous oxide (N_2O) while the rest was either H_2, volatile alkanes and alkenes containing the nitrate ester FG, or a degraded FG such as an alcohol or aldehyde. This result suggests that most of the radiolytic degradation occurs on the energetic FG, even when connected to a long chain hydrocarbon.

GC-TOFMS identified the formation of several products including various chain lengths containing aldehydes (C=O), various chain length containing alcohols (C-OH), and shorter chain nitrate ester alkanes. As with the GC-MS results of the headspace gas, these results indicate degradation of energetic FG as well as the carbon backbone molecule. ^{1}H-NMR spectroscopy was able to positively identify four signals: triplets at 2.35, 2.42, and 3.64 ppm and a singlet at 9.76 ppm. The triplets at 2.35 and 2.42 ppm along with the singlet at 9.76 ppm were identified as the aldehyde signal, and together integrated to a decomposition of about 2%. The triplet at 3.64 ppm was identified as the alcohol signal and it integrated to a decomposition of roughly 1%. A summary of these results can be found in Fig. 2.

Discussion

For the γ ray energies utilized in these studies, the predominant interaction between the photon and the material is Compton scattering [4], an incoherent scattering process that deposits roughly tens of eV per event [5]. The initial energy deposition is randomly distributed throughout the molecule (weighted by the electron density) and energetic enough to cause ionization. This initial energy deposition, however, does not necessarily indicate where a bond will break. Although headspace gas analysis for both PETN and dodecyl nitrate ester indicated that some degradation of the carbon backbone structure did take place, the majority of the degradation was concentrated on the nitrate ester FG. In particular, the bond most affected appeared to be the O-NO_2 bond. In fact, GC-TOFMS results did not find any indication of dodecane or dodecene, both of which would result from the removal of the entire nitrate ester FG. While this doesn't necessarily mean there was no removal of the entire FG, it does show that the likelihood of breaking the -ONO_2 bond is significantly less than breaking the O-NO_2 bond. The O-NO_2 bond is known as the trigger linkage for the nitrate ester FG. The trigger linkage of an energetic FG is often the weakest bond in the molecule, and it is thought

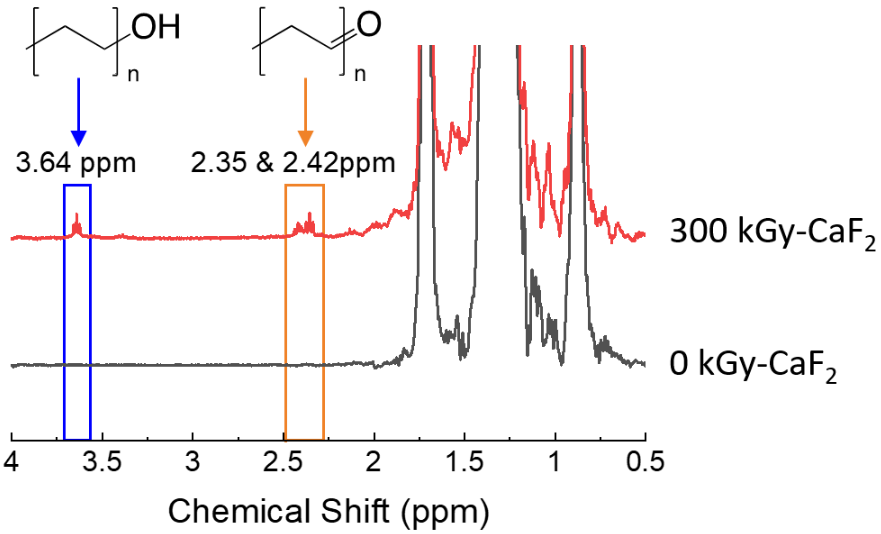

FIGURE 2. Summary of degradation products for irradiated dodecyl nitrate ester as measured by GC-TOFMS and ^{1}H-NMR spectroscopy.

to be the first bond to break during an explosive reaction [6, 7, 8, 9, 10, 11, 12]. Bond strength alone is not a good determination of radiolytic degradation pathways, however. In fact, the C-C bond is weaker than the C-H bond, but the C-H bond is the most likely bond to break in dodecane [13, 14]. The process of radiolytic degradation is complicated and several effects must be considered. For the dodecyl nitrate ester system, photolytic computations completed for excitation energies of 8 eV [15] can give some insight into this phenomenon. For an 8 eV excitation energy, the exciton is initially located on the dodecane backbone. The exciton quickly moves to the energetic FG, and it is there that the degradation occurs at the site of the trigger linkage. Radiolytic studies on *n*-alkanes have shown that they are very efficient at transferring energy along the C-C bonds [14], and thus energy deposited along the dodecane chain can be easily transferred to the nitrate ester FG. Although the same studies have not yet been completed on PETN, PETN is based on an alkane structure and thus it is reasonable to assume a similar process could happen which would lead to the observations seen in this study. Overall it appears that, at least chemically speaking, radiation predominantly affects the nitrate ester FG instead of the carbon backbone molecule it is attached to, leading to a scission of the trigger linkage.

The energetic FG is the primary source of the energetic properties in explosives, so a change to the energetic FG should result in a change to the performance of an explosive. For example, for each nitrate ester that is replaced with an alcohol in PETN, the sub-shock impact sensitivity, as measured by the drop-weight impact sensitivity test [16], decreases indicating that it becomes less sensitive to impact insults (see Fig. 3a). Interestingly, after irradiating PETN with ^{60}Co to a dose of 200 kGy, Lewis saw an increase in sub-shock impact sensitivity [17] which is in direct contradiction with the results of the chemical analyses completed in these studies. In an extreme example, doping 15% PETriN into a PETN matrix, a configuration more indicative of irradiated PETN, did not result in an increase in impact sensitivity (see Fig. 3b). It should be noted that although the impact test is commonly used to relatively quantify an explosive's sensitivity, the sensitivity of explosives is not well understood, nor are the small-scale sensitivity tests a perfect rendition of the potential initiation of explosives (see [16] for more details concerning what factors can influence sensitivity measurements done in this manner). The ignition of explosives during any of these tests is thought to be triggered by a variety of factors, and thus separating out potential causes for changes in sensitivity is no easy task. What can be taken away from the results presented here is that the increase in sensitivity seen by Lewis cannot be explained by the chemical changes taking place as a result of irradiation, and thus there must be physical changes occurring that have a significant effect on the sub-shock impact sensitivity of these materials.

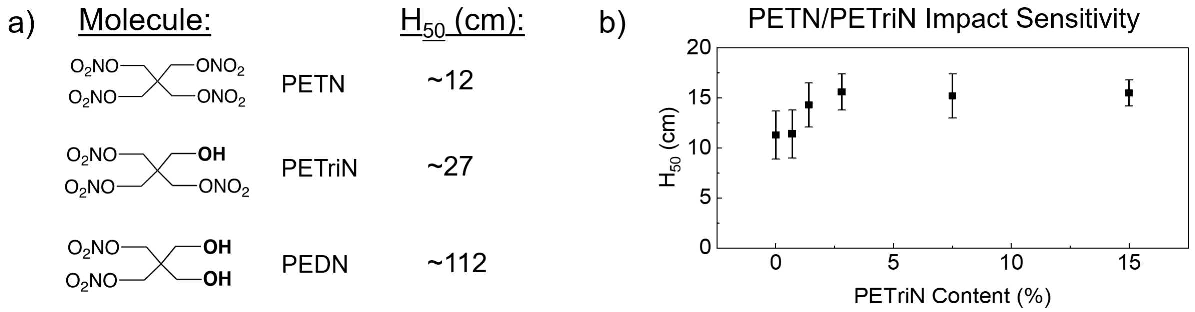

FIGURE 3. Results from sub-shock impact tests on the PETN-OH series showing the effects of a) wholly replacing energetic FGs with nonenergetic FGs and b) doping a less sensitive explosive (PETriN) into a more sensitive explosive (PETN).

CONCLUSIONS

The effects of ionizing radiation on explosives is not well understood, though it is an incredibly important topic from a safety perspective. This study utilized both explosive and nonexplosive forms of the nitrate ester FG, a commonly used energetic FG, to better understand the radiation-induced chemistry occurring when these materials were exposed to a γ ray radiation field. For both materials, energy was expected to be deposited randomly along the molecule but most of the degradation occurred at the nitrate ester FG, specifically at the trigger linkage. Both molecules therefore appear to be efficient at transporting energy from the carbon backbone to the nitrate ester FG where it can undergo degradation.

Current understandings of the radiation-induced chemistry of PETN do not appear to support what has been reported for changes in the small-scale sensitivity, hinting at yet unexplored physical changes that can lead to drastic consequences for handling scenarios, though more work must be done to elucidate possible mechanisms.

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