SAND-97-8684C
M98050608

Degradation Chemistry of PETN and its Homologues

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Introduction & Background

Pentaerythritol tetranitrate (PETN) is used throughout the stockpile as an energetic material. The formulation of PETN into XTX8003 (80% PETN, 20% Sylgard 182) creates an extrudable energetic composite. PETN and XTX8003 are used in the firesets for the retired W68 (MC2370) and the W76 (MC3028). When faced with potential lifetime extensions, energetic materials are naturally suspect regarding their output after prolonged aging. We have studied PETN and XTX8003 by looking at 25-year-old samples from retired MC2370's and newer materials. Both the old and new materials have also been placed in various accelerated aging protocols to investigate any decomposition that might occur over time. PETN is known to decompose autocatalytically even in the early stages of decomposition,[1] but the process is poorly understood.[2] Published values for the activation energy of decomposition vary by >40 kcal/mol. The 12 million year half life predicted for room temperature PETN[3] would be dramatically shortened by chemical influences that lead to lower energy decomposition pathways. Degree of confinement, purity, and crystal size all influence degradation rates.

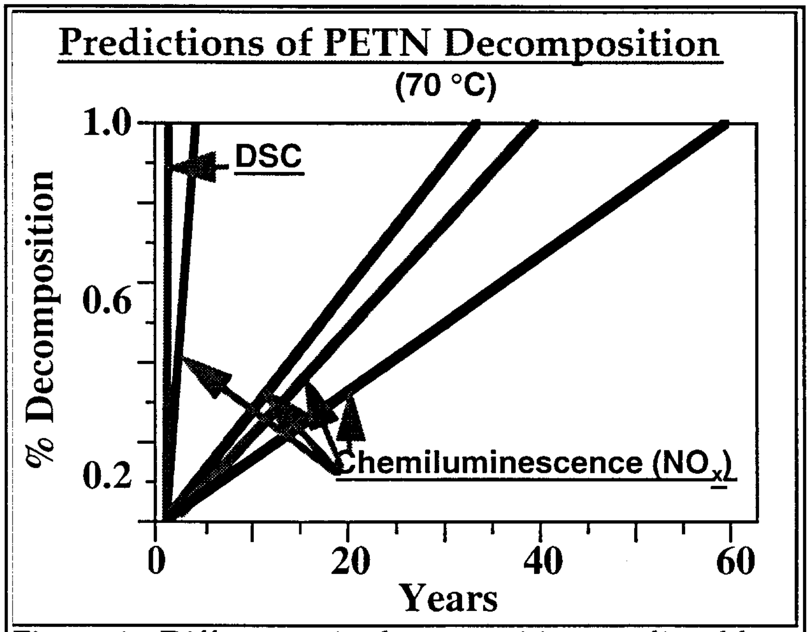

Figure 1: Differences in decomposition predicted by different literature values of the activation energy of decomposition for PETN.

In this paper, we observe the effects of chemical and thermal aging on PETN. We anticipate changes in mechanism at higher temperature aging, and before trying to extrapolate to lower temperatures, we want to make sure that we understand the different chemical processes involved.

Low Temperature Thermal Aging

Samples of PETN and XTX8003 (≈1 w% PETN) were aged at room temperature, 50 °C, and 65 °C in acetonitrile solution. Modifiers (≈0.05 M) were added to the solutions to observe the effects of various hydrolytic conditions on the PETN solutions including nitric acid, methane sulfonic acid, pure water, ammonia, and cesium hydroxide. These represent oxidizing acidic, acidic, neutral, basic, and strongly basic

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environments. At all of these temperatures and chemical conditions except pure water, cleavage of a single nitrate ester moiety was the first observed event. Pentaerythritol trinitrate (PETRIN) formation was also confirmed with authentic samples. Secondary chemistry was also observed under many conditions. PETN showed no signs of hydrolysis in aqueous acetonitrile. PETN shows no reaction with NO_2 at room temperature.[4]

High Temperature Thermal Aging

Samples of PETN and its fully ^2H and ^{15}N labeled analogs were heated under vacuum to temperatures near their melting points while monitoring the effluent of their reaction cell. The melting point of PETN is 141.3 °C. The samples were heated at 115-135 °C until significant decomposition occurred then rapidly quenched. Samples of the partially decomposed materials were dissolved in appropriate solvents and analyzed by liquid chromatography coupled to negative chemical ionization mass spectrometry detection (LCMS) or capillary electrochromatography coupled to ion-trap mass spectrometry detection (CEC/MS). Numerous decomposition intermediates were identified. In general, a wider distribution of decomposition products are generated in the high-temperature, solid phase decompositions than in those performed at 20-65 °C. The two analytical techniques, LC/MS and CEC/MS, are complimentary. Each is able to separate and identify different subsets of the decomposition products with corroborating results.

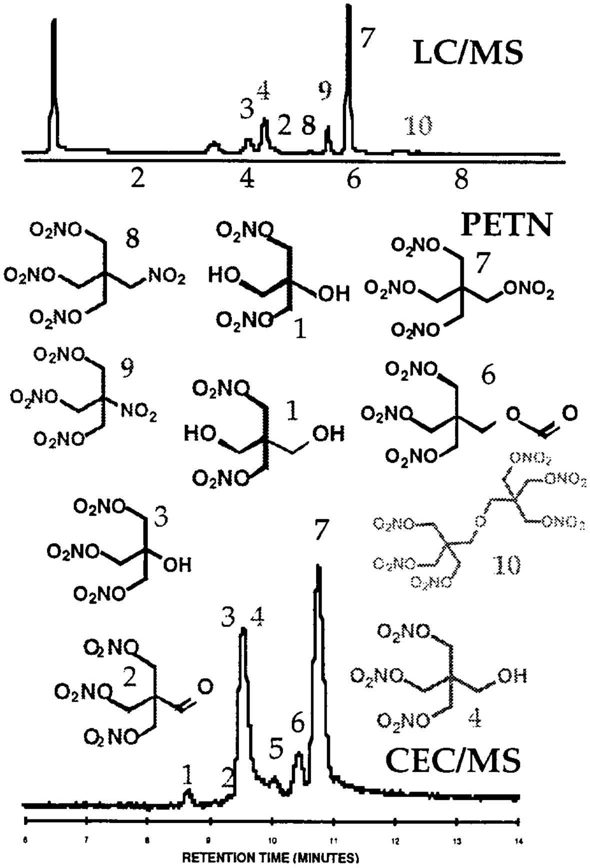

Figure 2: Analyses of PETN heated at 130 °C to partial decomposition. The numbers representing the structures and corresponding peaks of the decomposition products are shown above.

Discussion & Conclusions

The reversible loss of NO_2 is the first observed decomposition step for PETN and other nitrate esters in several literature studies.[5] PETN subsequently loses formaldehyde. Eventually, pyrolysis can lead to residual material consistent with a polyketo oxetane as well as complex gas evolution.[6] Our results at low conversion are consistent with those in the literature. The experiments in low-temperature solution should emphasize PETRIN formation. Recombination would be less likely to occur in solution than in a single crystal as free NO_2 would react elsewhere.

The experiments at higher temperatures yielded much more complex mixtures of products. Clearly, recombination of radical products was occurring. The dominant process at lower temperature was influence by numerous side reactions.

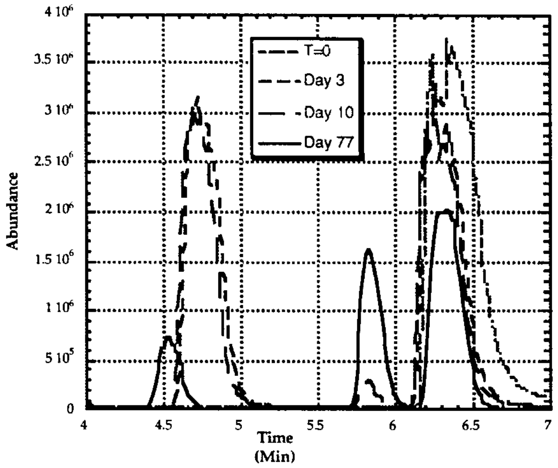

Figure 3: PETN exposed to methane sulfonic acid in acetonitrile solution. The peak at retention time 2.5-3 min. represents PETRIN from cleavage of a single nitrate ester. The peak at 3.8 min. is a secondary product.

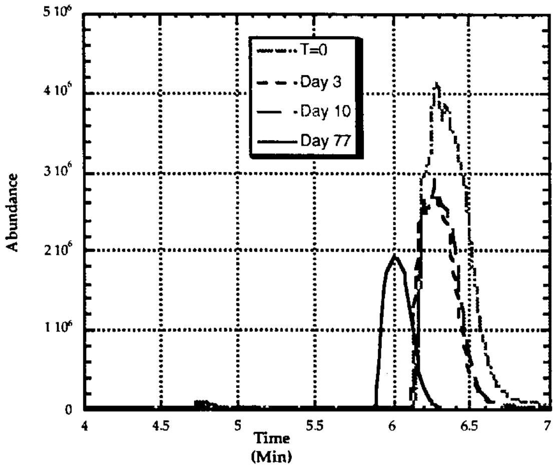

Figure 4: PETN exposed to nitric acid in acetonitrile solution. Formation of PETRIN is starting in the older samples. Retention time variability is an artifact of the autosampler. All peak identities are confirmed with mass spectrometry.

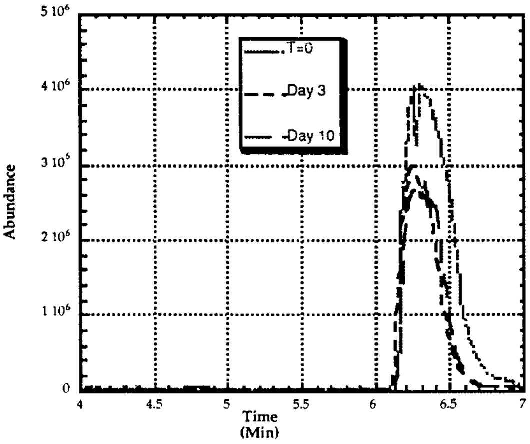

Figure 5: PETN exposed to aqueous ammonia in acetonitrile solution. PETRIN formation just started at the longest aging time.

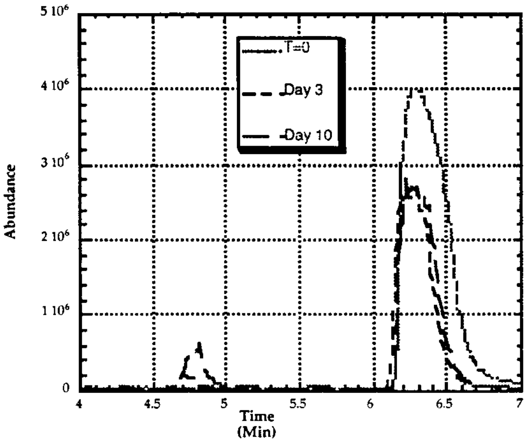

Figure 6: PETN exposed to aqueous cesium hydroxide in acetonitrile solution. PETRIN formation was obvious by the end of the experiment.

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*This work supported by U. S. Doe Contract DE-AC04-94AL85000

Type of Presentation: 20 min. Oral

M98050608

Report Number (14) SAND--97-8684C

ubl. Date (11) 199711

ponsor Code (18) DOE/DP, XF

JC Category (19) UC-701, DOE/ER

DOE