Degradation Chemistry of PETN and its Homologues

Timothy Shepodd Daniel Miller MS9403
Rich Behrens Kraig Anderson MS9052
Deon Anex MS9671
Sandia National Laboratories, Livermore, CA 94550-0969

19980327 102

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 PETN³ 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.

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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 (PETN) 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 $141.3\text{ }^\circ\text{C}$. The samples were heated at $115\text{--}135\text{ }^\circ\text{C}$ 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 (LC/MS) 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 $20\text{--}65\text{ }^\circ\text{C}$. 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.

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.

References

- ¹Miller, G. D.; Haws, L. D.; Dinegar, R. H. Nineteenth Symposium (International) on Combustion/ The Combustion Institute, 1982, 701-705.
- ²Encyclopedia of Chemical Technology, Fourth Ed.; Kirk-Othmer, Ed.; John Wiley and Sons: New York, 1993; Vol. 10.
- ³Volltrauer, H. N. J. *Hazardous Mats*, 1982, 5(4), 353-357.
- ⁴Dosser, L. R.; Seliskar, C. J. Technical Report by EG&G Mound Applied Technologies MLM-3751, July, 1992.
- ⁵Ng, W. L.; Rield, J. E.; Hauser, H. M. J. C. S. *Perkin II*, 1976, 637-639.
- ⁶Hiskey, M. A.; Brower, K. R.; Oxley, J. C. J. *Phys. Chem.* 1991, 95, 3955-3960.

Degradation Chemistry of PETN and its Homologues*

Timothy Shepodd
Sandia National Laboratories MS 9403
PO Box 969
Livermore, CA 94550-0969
Phone: 510-294-2791
Fax: 510-294-3231
tjshepo@sandia.gov

Deon Anex
Sandia National Laboratories MS 9671
PO Box 969
Livermore, CA 94550-0969
Phone: 510-294-3644
Fax: 510-294-1489
dsanex@sandia.gov

Kraig Anderson
Sandia National Laboratories MS 9052
PO Box 969
Livermore, CA 94550-0969
Phone: 510-294-2583
Fax: 510-294-1004
kkander@sandia.gov

Rich Behrens
Sandia National Laboratories MS 9052
PO Box 969
Livermore, CA 94550-0969
Phone: 510-294-2170
Fax: 510-294-1004
rbehren@sandia.gov

Daniel Miller
Sandia National Laboratories MS 9403
PO Box 969
Livermore, CA 94550-0969
Phone: 612-825-4876
Fax: 612-825-4876
mill1011@tc.umn.edu

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

Type of Presentation: 20 min. Oral

The submitted manuscript has been authored by a contractor of the United States Government under contract. Accordingly the United States Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for United States Government purposes.

M98050608

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

Publ. Date (11) 199711

Sponsor Code (18) DOE/DP, XF

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

DOE