105
9-18-92 GS②

MLM--3751

DE92 040816

Spectroscopic Studies of the 110°C Thermal Aging of PETN

Larry R. Dosser and Carl J. Seliskar

July 30, 1992

MOUND

operated by
EG&G MOUND APPLIED TECHNOLOGIES
P.O. Box 3000, Miamisburg, Ohio 45343-3000

for the
U. S. DEPARTMENT OF ENERGY
Contract No. DE-AC04-88DP43495

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (615)576-8401, FTS 626-8401

Available to the public from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.
Springfield, VA 22161

MLM-3751
UC-704

Spectroscopic Studies of the 110°C Thermal Aging of PETN

Larry R. Dosser and Carl J. Seliskar*

Issued: July 30, 1992

*University of Cincinnati

MOUND

operated by
EG&G MOUND APPLIED TECHNOLOGIES
P.O. Box 3000, Miamisburg, Ohio 45343-3000

for the
U. S. DEPARTMENT OF ENERGY
Contract No. DE-AC04-88DP43495

MASTER

Contents

	<u>Page</u>
Abstract	3
Introduction	3
Experimental Details	6
PETN Powders and Detonator Parts	6
Sample Preparation	7
Spectroscopic Characterization of PETN Samples	9
Results and Discussion	10
Analysis of UV Spectroscopic Data	10
Studies of Type 1 Powder Exposed to NO ₂ Vapor	20
Temperature Ramping of PETN to 150°C	22
Experiments on Total Thermolysis of PETN	23
Conclusions	25
Acknowledgments	25
References	26
Distribution	27

Abstract

The 110°C thermal aging parameters, including initial rates of decomposition, of four types of pentaerythritol tetranitrate (PETN) over a period of ten months are presented. Both decomposition products, nitric oxide, NO, and nitrogen dioxide, NO₂, were monitored from multiple, hermetically-sealed, *in vacuo* samples. Nitric oxide appears to be the first nitrogen oxide product evolved. Nitrogen dioxide produced by abrupt thermal aging is more slowly converted to nitric oxide by a 1:1 process. The behavior of samples of RR5K PETN was significantly different from that of other powders studied. Further work is in progress to better define the thermal aging of RR5K PETN.

Introduction

The chemical aging of pentaerythritol tetranitrate (PETN) has significant effects on the lifetime of components that contain this nitrate ester high explosive. The overall chemistry of PETN thermal decomposition has been studied and apparently corresponds to a combustion reaction with the overall proportions [1]:

Inspection of Equation 1 shows that, although the role of nitrogen is nearly accounted for in the detailed balancing, the remaining elements, C, H, and O, are not accounted for. At this time, the elementary chemical reactions which underlie this overall reaction are still not unambiguously known. The recent success of a kinetic model by Pickard* suggests as many as 29 chemical

*J. Pickard, EG&G Mound Applied Technologies, private communication, 1991.

species are involved in the thermal aging of PETN. Assuming that this level of complexity is the case, the underlying reactions will be very difficult to decipher in detail without a comprehensive experimental program aimed at this complex system.

In addition to the complexity of the attendant elementary chemical reactions, an aging PETN sample is at least biphasic, that is, consists of solid and vapor phases. Therefore, chemical aging reactions can occur in each of these phases. As an example of a real system, consider the hermetically sealed PETN system [2]. Prior to aging, a hermetically sealed sample of pure PETN at ambient temperature consists of a solid powder and a vapor phase in the head space of the sample vessel. The chemical composition of the vapor depends, to a significant extent, on the method of preparation. If such a system is hermetically sealed under vacuum, the vapor that develops over solid PETN consists mainly of PETN vapor and any species contributed by crystal-included solvent or tightly adsorbed gases. Chemical aging reactions then contribute species to both the solid and vapor phases of the sample. Thermally induced, that is, thermally accelerated, aging of such a sample potentially increases the phase complexity as well as the chemical complexity of the sample. For example, if such a sample is aged at temperatures approaching the melting point, a new solid phase [3] and/or the liquid phase of PETN appears.

In time, aging products appear in the vapor as well as the condensed phases. The incursion of air into such a system biases the aging process by including additional reactive species, such as O_2 , H_2O , and, possibly, even N_2 . The presence of O_2 drives the nitrogen oxide chemistry toward more oxidized species at least temporarily. Therefore, in air-contaminated systems, it is necessary to carefully distinguish between chemistry native to PETN and that peculiar to air/PETN.

Several vapor species have been identified [1-2, 4-6] in aging PETN systems. They include NO_2 , NO , CO_2 , CO , H_2O , H_2CO , N_2 , and N_2O . Since these species have not been identified in every aging study, one can only speculate

about the relative importance of each in the underlying chemistry. Suffice it to say that the aging PETN system is a multidimensional chemical system that needs to be studied by multidimensional methods. Since this chemistry develops over time, the studies must also be implemented systematically over time. Therefore, chemical aging studies on well-defined PETN samples, which focus on identification and quantitation of the wide variety of chemical products released with aging, are still sorely needed.

Several general conclusions from the experimental work reported to date can be made concerning the aging chemistry of PETN. First, the nitrogen oxides are very important intermediates in aging systems. Second, little is known about the specific reactions of carbon in the aging process, although formaldehyde has been identified in several studies. The overall carbon scheme produces oxidized carbon at the expense of reduced nitrogen. Third, nitrate nitrogen in PETN experiences chemical reduction in the aging process, perhaps ultimately ending up as N_2 [2]. Fourth, water has not been adequately quantified in aging systems. Nonetheless, the presence of water tremendously increases the complexity of the chemical reactions possible in an aging sample. Fifth, there appears to be a distinct gas phase aging chemistry that does not rely on the presence of PETN solid and is not well understood. In fact, little or nothing is known about the fundamental chemistry of considerably simpler four-component vapor systems related to aging and consisting of NO , NO_2 , CO and CO_2 . Finally, it is clear that the lack of basic knowledge about the chemistry of aging PETN prevents the reliable prediction of the long-term stability and associated corrosion characteristics of any PETN powder.

In an effort to further study the aging chemistry of PETN under well-defined conditions, additional spectroscopic studies have been done *in situ*, on selected PETN samples. This paper presents data on the thermal aging of four types of PETN: ER-17125C, Type 1, UHP, and RR5K. The present studies were done at $110^\circ C$, with appropriate ambient standards, for ~10 months. Both NO and NO_2 were monitored during thermal aging for multiple, hermetically sealed (*in vacuo*) samples of each powder. In one case,

test parts of a weapon component were included in aging samples to probe the relationship between metal inclusions and PETN chemistry.

Experimental Details

PETN Powders and Detonator Parts

Four types of PETN powders were used in this series of measurements. All powders were used as supplied without further modification. Each sample vessel was coded with a metal band that was colored to identify the type of powder and numbered to identify the sample. The powders, and their identification color code, are summarized in Table 1. In our ongoing effort to study the aging of PETN, numerous samples of PETN have been examined. This report focuses on selected results for four powders of interest.

Table 1 - PHYSICAL PROPERTIES OF PETN POWDERS

<u>Powder Type</u>	<u>Band Color</u>
ER-17125C	Red (RB6, RB7 ^a , RB14 ^a)
Type 1	Blue (BB3, BB8 ^a , BB10 ^a)
RR5K	Yellow (YB1, YB3, YB4)
UHP(ER-17010)	Green (GB1)

^aalso contained detonator sleeves or closure discs

PETN samples RB6, BB3, GB1, YB2, YB3, and YB4 each contained 0.1 g of powder only. Some sample vessels were prepared with either ER-17125C

(samples RB7, RB14) or Type 1 (samples BB8, BB10) powder along with parts from a detonator test vehicle. The parts (Hastelloy alloy B-2) added to the powder were either a sleeve or three closure discs. The parts were cleaned by soaking them in three separate washes of spectral grade methanol and then air-drying them at ambient temperature. Sample RB7 contained 0.1 g of ER-17125C and three closure discs, and sample RB14 contained 0.1 g of ER-17125C and a sleeve. Similarly, sample BB8 contained 0.1 g of Type 1 and a sleeve, and Sample BB10 contained 0.1 g of Type 1 and three closure discs.

Sample Preparation

All samples were prepared by quantitatively adding PETN powder to the bottom of a vessel of the type shown in Figure 1. The main body of the vessel was constructed of Pyrex. A 10-mm square cross-section, suprasil

Figure 1 - A typical sample vessel prior to evacuation and seal-off.

quartz, optical cell, ~5 cm long, was attached to the vessel body by a 4-mm bore graded seal. Approximately 100 mg of the selected PETN was transferred to the bottom of the vessel with a micro-funnel using a 600 micron quartz fiber to assist in pushing the powder down the funnel stem. The final mass of powder for each sample was recorded to the nearest 0.0001 g.

After the powder had been transferred to a vessel, the vessel was black-waxed onto a glass, greaseless, manifold attached to a high vacuum line, which was pumped with a turbomolecular pump. The air above the powder was carefully expanded into the isolated evacuated glass portion of the manifold by slowly opening the stopcock to the vessel. This stopcock was then closed and the sample manifold pumped out to forepump pressure. This procedure was repeated two more times, and then the powder was pumped down with the turbomolecular pump until a pressure of 2.0×10^{-5} torr was achieved.

When the first samples for this study were prepared, after the sample had been pumped with the turbomolecular pump, the portion of the vessel containing the powder was immediately cooled in liquid nitrogen and the vessel sealed off with a glassblower's torch. However, after evaluating the effects of this procedure, it was found that some of the samples prepared in this manner contained NO or NO₂ when their baseline spectra were recorded only moments after seal-off.

After the experimental procedure had been analyzed, it was concluded that NO and NO₂ were produced from the decomposition of minute amounts of PETN, which adhered to the vessel walls during the weighing procedure. The sample preparation procedure was correspondingly modified to eliminate this problem. In the modified procedure, the vessel was evacuated with the turbomolecular pump to 2×10^{-5} torr and the vessel walls in the seal-off region were flamed with a glassblower's torch without cooling the powder in liquid nitrogen. It is important to note that the powder in the vessel bottom did not experience elevated temperature during the flaming procedure. This

amended procedure prevented any thermal decomposition products produced by the torch from condensing onto the powder. During this flaming procedure, the pressure in the manifold was monitored carefully with an ion gauge to follow the off-gassing from the thermal decomposition of PETN in the vessel seal-off region. The glass in this region was heated hot enough to observe the characteristic yellow sodium flame from the Pyrex, and nearly to the flowing point of the glass. When a significant amount of gas was observed to evolve, the heating was discontinued and the vessel was evacuated again to about 2×10^{-5} torr. This flame/pump procedure was continued until no significant pressure increase was observed with further flaming of the seal-off region. This usually took three cycles, but sometimes as many as five were required. After the final heating, the vessel neck was allowed to cool while evacuating to 2×10^{-5} torr.

The portion of the vessel containing the powder was then placed in liquid nitrogen and the seal-off was performed while actively pumping on the vessel with the turbomolecular pump. The baseline UV spectra taken of the samples prepared in this manner routinely exhibited no NO or NO₂, and this procedure was adopted for all of the samples discussed in this paper. Samples prepared in this manner and kept at ambient temperature for the duration of this study, approximately one year, showed no measurable amounts of NO or NO₂ by absorption spectroscopy.

Spectroscopic Characterization of PETN Samples

All optical measurements were made on a Shimadzu UV-260 spectrophotometer. For the purposes of NO analysis, the spectrum of each sample vessel was recorded periodically from 250 nm to 190 nm against an air reference. There were significant differences in the baseline spectra of the optical cells of the sample vessels and this had to be taken into account in the quantitative analyses. This was accomplished by "zeroing" the spectrometer at 250 nm before recording the spectrum of NO in a given vessel. The spectral features of NO were then recorded against this background level and referenced to the spectrum of a known amount of NO.

The estimated limit of detection of NO by UV spectroscopy was 1.0 torr. In the case of the analysis of NO₂, a strong sharp absorption maximum at 488 nm was used to quantify the amount present by a procedure similar to that described above for NO. The estimated limit of detection realized in this case was also 1.0 torr.

Results and Discussion

Analysis of UV Spectroscopic Data

Ultraviolet data were collected on numerous samples of different powders aged at 110°C. The discussion that follows has been divided into sections for clarity. After a short discussion of the general characteristics of the thermal aging data, the results are discussed for groups of samples by powder type.

General Characteristics

The curves for NO evolution at 110°C for a typical sample showed that this gas was produced in a nonlinear way. An illustration of this behavior is shown in Figure 2. For the sake of comparison we differentiate between the initial rate and the long-term behavior of NO production. The initial rate for the NO evolution is considerably faster than the rate at longer times. As shown in Figure 2, the initial rate was computed by linear regression analysis for the first 10 to 20 points. The baseline point at zero days was excluded from the linear regression. A minor day-to-day variation, sometimes even indicating a decrease in NO pressure, was typically observed. A summary of the initial rate data for the PETN powders examined is given in Table 2. As a measure of the long term behavior of NO production, the pressure of NO at Aging Day 240 was selected as an additional powder characteristic. These values are also listed in Table 2. Samples of each powder prepared and aged at ambient exhibited no measurable amount of NO or NO₂ by either UV spectroscopy or laser induced fluorescence (LIF) spectroscopy [7] during this study (10 months).

Figure 2 - A typical thermal aging curve, representing the partial pressure of NO versus the thermal aging time. The points represent actual data for a representative PETN sample; the solid line denotes a linear regression fit to the points taken between days 4 and 24. The slope of the linear regression line is taken to be the initial rate parameter as discussed in the text.

Table 2 - RATE PARAMETERS FOR PETN POWDERS

Sample	Initial Rate (torr/day/100.0 mg)	R ²	P(NO) at Day 240 (torr)
RB6	0.302	0.97	36
BB3	0.245	0.98	36
GB1	0.298	0.97	38
RB7	0.275	0.98	38
RB14	0.258	0.96	36
BB8	0.289	0.99	33
BB10	0.732	0.90	36
			avg 36
YB1	4.00	0.99	49
YB3	2.96	0.93	43
YB4	27.5	0.92	83

Samples RB6(ER-17125C), BB3(Type 1), and GB1(UHP)

The three PETN powders, ER-17125C, Type 1, and UHP, all behaved in a similar manner and the NO evolution from these samples for a period of several months is shown in Figure 3. The initial rates for these three powders are similar (see Table 2) and, given sample-to-sample variation, are all essentially the same with a mean value of 0.28 torr/day/100 mg. All three powders reached approximately the same final pressure of NO (average value 36 torr) at Aging Day 240. It is interesting to note that in the case of sample GB1 (UHP powder), as shown in Figure 3, the aging rate increases unusually at day 40. Nonetheless, the long term behavior of this sample is very similar to the other two samples. It is our current opinion that this variation in the rate is sample variation, and not a characteristic of the powder. This conclusion is further emphasized in the following section. Samples RB6 and

Figure 3 - The 110°C thermal aging curves for PETN samples RB6 (ER-17125C), BB3 (Type 1), and GB1 (UHP).

BB3 had a final pressure of 36 torr at day 240, and sample GB1 obtained a pressure of 38 torr. It is believed that the pressure difference of 2 torr between these samples is not significant. PETN itself has a significant vapor pressure at 110°C and is readily measured in the UV region at 195 nm. In this regard, note that the UHP powder showed the highest vapor pressure of PETN, and samples of this powder even showed crystal growth on the optical cell walls.

RB(ER-17125C) and BB(Type 1) Samples with Detonator Parts

Plots of the NO evolution from ER-17125C and Type 1 powders and detonator parts are shown in Figures 4 and 5, respectively, along with the appropriate reference. Refer to Table 2 for the sample parameters. The overriding conclusion to be drawn from our data is that detonator parts have no significant, observable effect. The average initial rate is 0.28 torr/day/100 mg for RB6, RB7, and RB14. The consistency of the initial rates for these three samples, two of which contained detonator parts, shows that no effect was observed by including the parts. This was further emphasized by noting that all three samples reached an average NO pressure of 37 torr at Aging Day 240. In the case of the Type 1 powder, a similar result is tempered by the unusual behavior of BB10 (Figure 5). Samples BB3 and BB7 had an average initial rate of 0.27 torr/day/100 mg and an average NO pressure of 34 torr at Aging Day 240. Sample BB10 had a similar pressure (36 torr) on Aging Day 240. However, the initial rate of NO evolution for sample BB10, being 2.7 times the average value of BB3 and BB8, is unusually high. Our experience to date indicates that this is sample-to-sample variation as discussed in the previous section for sample GB1(UHP).

YB1, YB2, YB3, YB4 (RR5K)

The procedure for recrystallizing RR5K PETN is significantly different from that for the other powders discussed above. An example of this difference is the use of the high boiling point solvents, diacetone alcohol and gamma-butyrolactone (168° and 204°C, respectively).

Figure 4 - The 110°C thermal aging curves for ER-17125C PETN samples RB6 (powder only), RB7 (three closure discs), and RB14 (sleeve).

Figure 5 - The 110°C thermal aging curves for Type 1 PETN samples BB3 (powder only), BB8 (sleeve), and BB10 (three closure discs).

A behavior common to all of the samples, with the exception of the ambient reference YB2, was the evolution of solvent within the first few minutes of aging at 110°C. When the RR5K samples were initially placed in the 110°C oven, a large, broad absorption band was observed in the UV spectrum in less than 30 min. The broad absorption band was readily identified as diacetone alcohol from its UV spectrum. The growth of the residual solvent band in the RR5K sample YB3 was recorded by measuring the absorbance at the band maximum, 222 nm. The data for the first 34 days are displayed graphically in the bottom half of Figure 6. The solvent initially evolved very rapidly in the first 24 hours, and then began to decrease for the next 10 days. By Day 13 the solvent vapor pressure appeared to have reached nearly a constant value. However, at this point the contribution to the absorbance at 222 nm from NO background was significant. It is also possible that there are some contributions from the background from NO₂. NO was recorded by UV absorption in vessel YB3 two days after it was placed in the 110°C oven. A plot of NO pressure for the first 34 days is shown in the top half of Figure 6.

A composite plot of the NO evolution from samples YB1, YB3, and YB4 for the entire aging period is shown in Figure 7. The associated initial rates of NO evolution may be found in Table 2. Turning attention to samples YB1 and YB3 shows that the initial rates of NO evolution are comparable, but an order of magnitude larger than the initial rates for ER-17125C and Type 1. Samples YB1 and YB3 develop comparable NO pressures at Day 240 (average value 46 torr), but this pressure is significantly higher than the corresponding pressure recorded for the other samples of PETN in this study. At Aging Day 10, samples YB1 and YB3 change significantly. At this time, we are uncertain of the origin of this difference. All samples were prepared in an identical manner, and thus the difference does not appear to be technique-related. The difference observed may represent sample-to-sample variation. Our continuing studies with RR5K are designed, in part, to resolve such issues.

NO FORMATION AT 110°C

Solvent Absorbance at 222 nm

Figure 6 - The thermal aging behavior for RR5K PETN sample YB3 during the first days of aging at 110°C. The top curve represents the evolution of NO, as measured by UV absorbance spectroscopy; the bottom curve represents the evolution of the solvent, diacetone alcohol.

Figure 7 - The 110°C thermal aging curves for RR5K PETN samples YB1, YB3, and YB4. The corresponding ambient temperature reference, YB2, showed no measurable NO evolution during the same time period.

Sample YB4 was found to behave strikingly differently from either YB1 or YB3. In YB4 there was a very rapid rise in the NO evolution to a peak value of 148 torr on Day 8. This is in contrast to a NO pressure of 28 torr after Day 8 for Sample YB1, and 22 torr after Day 8 for sample YB3. The initial rate of NO evolution for YB4 was eight times greater than the average initial rate of YB1 and YB3 and roughly 100 times that of the ER-17125C and Type 1 powders. Sample YB4 also had visible amounts of NO₂ present during the first four days, and this may have catalyzed the production of NO [8,9]. By all of our measurement techniques, YB4 appears to be anomalous.

Studies of Type 1 Powder Exposed to NO₂ Vapor

Since there is some evidence that NO₂ is autocatalytic in nitrate ester, high-explosive, decomposition reactions [8,9], measurements were taken on a PETN sample that was intentionally subjected to an excess of NO₂ vapor. A Type 1 powder sample was over-filled with ~50 torr of NO₂. As a suitable reference, an identical vessel without powder was filled with roughly the same pressure of NO₂ and aged identically at ambient temperature (~23°C). Spectroscopic analyses of these vessels were made over the period of ten months and continue to be made. The results are summarized in Table 3.

Inspection of the table enables the following conclusions to be drawn. First, both the Type 1 powder/NO₂ and the NO₂ vessel showed a small, systematic decrease in NO₂ content over the period of ten months. This decrease amounted to a loss of NO₂ of ~7%. No evidence for any NO was found in either vessel, although it would be difficult to detect a small amount by UV absorption in the presence of a high concentration of NO₂, which also absorbs in the UV region. Therefore, a small but significant decrease occurred in both vessels and can logically be attributed to processes indigenous to the NO₂/vessel system.

Table 3 - NO₂ EFFECTS ON AMBIENT AGING OF TYPE 1 POWDER

Ambient Aging Time (Days)	NO ₂ Pressure (Torr)		P(NO ₂)/P(REF)	% Deviation (from mean)
	BB12	REF		
0	47.3	45.6	1.039	+0.15
1	45.8	44.8	1.023	-1.35
2	45.8	44.5	1.029	-0.77
5	45.7	44.5	1.027	-0.98
7	46.1	44.2	1.043	+0.56
5	45.9	44.8	1.024	-1.21
29	45.0	43.8	1.029	-0.79
70	45.6	43.2	1.054	+1.69
181	44.4	42.1	1.054	+1.67
300	44.4	42.4	1.048	+1.03
			mean: 1.037	mean: 0.00

Second, it was surprising to find, as shown in the table, that the presence of powder made no apparent difference in the loss or gain of NO₂. This is shown by inspection of the ratio of NO₂ in the sample containing the powder to that of the vessel containing NO₂ only (column 4, Table 3). The ratio stays approximately constant with a mean value of 1.037. Computation of the deviations from the mean value over the 300-day aging period (column 5) shows, furthermore, that the deviation is random (sums to zero). Therefore, it appears that no measurable effect has been exerted by the presence of the powder at ambient temperature for 300 days. Third, the coloration of the powder remained pristine white, even after exposure to NO₂ for this extended period of time.

Temperature Ramping of PETN to 150°C

Previous studies [2] on the thermal aging of PETN have shown that nitrogen oxides are rapidly produced at temperatures approaching the melting point of the solid (141°C). Temperature ramping experiments were performed using a new Thermally Stabilized Aging Chamber (TSAC), which will be described in a forthcoming paper. A ramping experiment was conducted on a Type 1 powder sample (100 mg) between ambient and 150°C. During this experiment the LIF of NO₂ was monitored continuously as the temperature increased at the rate of about +4°C per minute. The appearance of the NO₂ LIF signal came at roughly the melting point of PETN (140°C) and plateaued at a nominally small value. Indeed, the sample was visibly brown with NO₂ after reaching 150°C and yet showed relatively little fluorescence. The lack of a strong, laser-induced fluorescence signal from NO₂ suggests that the fluorescence was largely quenched by other gases that were generated in the decomposition. Further analysis of the vessel after cool-down showed that NO was present in an amount of several tens of torr pressure. The liquid phase of PETN in the ramped sample persisted at room temperature for days after the ramping. During this same time period, NO₂ was converted exclusively to NO by what appeared to be a 1:1 process, as indicated by the maintenance of a nearly constant partial pressure sum of P(NO) + P(NO₂).

The results of the ramping experiments show several things. First, the gases NO and NO₂ appear quickly at the melting point of PETN under hermetically sealed vacuum conditions. Second, the liquid phase of PETN is metastable and can exist for days at ambient temperature following melting. Third, NO₂ is converted to NO in what appears to be a 1:1 process of chemical reduction following melting. Our present measurements do not allow us to stipulate the nature of the associated reducing agent responsible for this conversion. Clearly, the identification of this reducing agent is crucial to an understanding of the aging process for PETN.

Experiments on Total Thermolysis of PETN

In several experiments, it had been observed that NO_2 was produced during the temperature ramping of a sample to the melting point of PETN. After such an experiment, further monitoring the presence of NO_2 showed that it was converted to NO in time. Since no means of knowing what fraction of the PETN was converted to NO_2 or NO were available to us, it was decided to specifically design an experiment in which the relationship among NO, NO_2 , and PETN decomposition could be better defined. Pursuant to this goal, we calculated the amount of PETN required to give, on complete conversion of all PETN nitrogen to NO_2 , a partial pressure of NO_2 , leaving the vessel intact on complete conversion of the remainder of the molecules to CO_2 and H_2O . On this basis, it was decided to place 2.6×10^{-3} g of PETN (Type 1) in a vessel that would then to be subjected to the standard seal-off procedure. For 2.6×10^{-3} g of material, it was calculated that complete thermolysis, as defined above, would cause the sample maximally to develop ~125 torr of NO_2 .

A conventional oven was set for $\sim 165^\circ\text{C}$ and the sample was placed in the oven until all PETN solid and liquid had disappeared from view. During this process the liquid phase of PETN was observed even as the temperature fell to ambient for spectral measurements. The spectrum of the extensively thermolysed sample is shown in Figure 8. From analysis of the spectrum, it can be verified that all the spectral features present are due to NO, and none to NO_2 or PETN. The gas yield of NO was found to be 65.2 torr and this represents ~50% yield in comparison to that possible if all nitrogen were converted to NO_2 or NO. In addition, note that there was a slight brown residue in the bottom of the vessel after the thermolysis was complete. Unfortunately, there is presently no way to quantify the amounts of other gases, such as CO and CO_2 , that are known to be produced in this experiment. However, it is clear that ~50% of the nitrogen ends up in something other than NO and NO_2 . Likely candidates are N_2 , N_2O , and N-oxyacids, all of which have ill-defined UV-VIS spectra.

Figure 8 - The ultraviolet absorbance spectrum of a sample subjected to high temperature (165°C) for an extended period of time until no solid PETN remained. The solid curve represents the resultant NO vapor from the thermolysis of PETN; the dashed curve represents the absorbance of the sample before thermolysis. All the spectral features observed can be assigned to NO vapor.

Reference to the GAMS reports [2] suggests that N_2 and N_2O are the likely other sources of nitrogen. Clearly, a more comprehensive spectroscopic study of the decomposition products of aging PETN is needed. In the present situation, infrared spectroscopic analysis of the samples that are prepared will be necessary to identify several other decomposition products and the associated kinetics.

Conclusions

Several conclusions can be drawn from the thermal aging experiments on PETN described above. First, NO appears to be the first nitrogen oxide product from thermally aged PETN observed in hermetically sealed vessels by our technique. Second, NO_2 produced by abrupt thermal aging of PETN is more slowly converted to NO by an apparently 1:1 process. Third, NO_2 in the presence of Type 1 PETN powder aged at ambient temperature is stable at least over the period of ten months. Fourth, the laser-induced fluorescence of NO_2 in temperature-ramped samples of PETN near 140°C is apparently quenched by excess gas pressure in the vessel. Fifth, the samples of RR5K PETN studied behaved significantly differently from the other powders, and also exhibited considerable sample-to-sample variation. Further work is in progress to better define the thermal aging of this powder.

Acknowledgments

The authors thank Bethel Abernathy for his skillful construction of the many sample vessels crucial to our studies.

Tim Valentine carefully weighed out the numerous samples of PETN and assisted in apparatus construction; David Landis assisted in the final graphical representation of the thermal aging data. We thank them both for their help.

References

1. W. L. Ng, J. E. Field, and H. M. Hauser, *J. Chem. Soc., Perkin Trans.*, 637 (1976).
2. *C-4 Trident Missile Body Ordnance Aging GAMS Program Annual Report for November 1982-October 1983*, W. Andrzejewski, (ed.), SAND84-0871, June 1984, pp 12-23, 67-75.
3. *LASL Explosive Property Data*, T. R. Gibbs and A. Popolato (eds.), University of California Press, Berkeley, CA (1980), pp 130-140.
4. H. N. Volltrauer, *J. Hazard. Mater.* 5, 353 (1982).
5. H. M. Hauser, J. E. Field, and V. Krishna Mohan, *Chem. Phys. Letters* 99, 66 (1983).
6. G. D. Miller, L. D. Haws, and R. H. Dinegar, *Kinetics of the Thermal Decomposition of Solid PETN*, LA-UR-81-3416, Los Alamos National Laboratory (1982).
7. L. R. Dosser and C. J. Seliskar, *Investigation of Ambient and High Temperature Aging of PETN by Laser Induced Fluorescence and Ultraviolet Absorption Spectroscopies*, MLM-3590, EG&G Mound Applied Technologies (June 1989), 19 pp.
8. L. Druet and M. Asselin, *J. Energetic Mater.* 6, 27 (1988).
9. A. J. B. Robertson, *J. S. C. I.* 67, 221 (1948).

Distribution

External

OSTI, UC-704 (106)

G. Bambikidis, Wright State University, Department of Physics

J. Clark, Wright State University, Department of Physics

D. Dolson, Wright State University, Department of Chemistry

A. M. Frank, Lawrence Livermore National Laboratory

C. J. Kerschner, Femto-Tech, Carlisle, Ohio

J. A. Morley, DOE/DAO

C. J. Seliskar, University of Cincinnati, Department of Chemistry (5)

C. M. Tarver, Lawrence Livermore National Laboratory

W. G. VonHolle, Lawrence Livermore National Laboratory

Los Alamos National Laboratory

G. Buntain

J. C. Dallman

J. Kennedy

D. Paisley

T. Rivera

Sandia National Laboratories, Albuquerque

W. J. Andrzejewski

S. G. Barnhart

J. G. Harlan

D. E. Hoke

D. Ingersoll

R. Jungst

D. E. Mitchell

A. M. Renlund

S. St. Clair

W. M. Trott

Internal

P. Back

G. L. Ball

B. D. Barton

D. C. Bradley

R. J. DeSando

L. R. Dosser (5)

D. W. Firsich

J. T. Gill

J. A. Holy

J. Lavoie

C. Love

D. E. Michel

G. D. Miller

J. Pickard

S. A. Siwecki

R. Thorpe

R. E. Vallee

M. D. Vannet

H. A. Woltermann

C. M. Woods

Publications

Library (10)

P. A. Fitzharris, Editor
Technical Publications