Thermal Stability of Eutectic Mixture of Bis(2,2-dinitropropyl)acetal and Bis(2,2-dinitropropyl)formal: Part A. Degradation Mechanisms in Air and under Nitrogen Atmosphere

Dali Yang^{1)*}, Robin Pacheco¹⁾, Stephanie Edwards¹⁾, Kevin Henderson¹⁾, Ruilian Wu²⁾

Andrea Labouriau³⁾ and Peter Stark³⁾

¹⁾ Materials Science and Technology,

²⁾ Biosciences and

³⁾ Chemistry Divisions

Los Alamos National Laboratory, Los Alamos, New Mexico, 87545

Abstract: We investigated the chemical and thermal stability of a eutectic mixture of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF) (referred to as NP) in various environments at temperatures below 70 °C. Changes in the chemical composition of aged samples were characterized using TGA, FTIR, GPC, ESI-MS, and ¹H NMR spectroscopies over a period of two years. The results show that the initial signs of NP degradation can be detected as early as 12 months at 70 °C in air. The initial step in the degradation is the elimination of HONO molecules, followed by the formation of nitroso-alcohol isomers. While the temperature plays a key role in determining the degradation kinetics of the initial stages, the absence or presence of oxygen determines the types and rates of formations of various isomers and intermediates during the thermal decomposition processes. In addition, oxygen accelerates the decomposition of the isomers and intermediates, whereas nitrogen has a stabilizing effect. BDNPA shows higher reactivity than BDNPF regardless of the aging conditions, which is attributed to the presence of an extra methyl group in its structure.

Key words: Nitroplasticizer, BDNPA, BDNPF, Stability, Degradation, Condensed phase

1. Introduction

Binders are frequently added to energetic materials to lower their sensitivity and improve manufacturability through increases in their flexibility and tensile strength. The

* Corresponding author: D. Yang (dyang@lanl.gov), phone: 1-505-665-4054.

binders typically comprise of a mixture of a plasticizer and a polymer. The plasticizers can be either inert or energetic. The energetic ones are usually used to improve the compatibility between the polymer and explosive crystals, and to add energy to the formulation.[1, 2] Since the energetic plasticizers often contain nitro and/or nitrate groups, they are commonly referred to as nitroplasticizers. One nitroplasticizer widely used in plastic-bonded explosive (PBX) formulations is a eutectic mixture of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF). The molecular structures of BDNPA/F are shown in Figure 1a. The BDNPA/F mixture is a key component of the binder used in PBX 9501 formula, which nominally consists of 94.9 wt% HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), 5.0 wt% binder, and 0.1 wt% stabilizers. The binder consists of 50 wt% Estane[®] 5703 [Estane – a poly(ester urethane)] and 50 wt% BDNPA/F mixture with a 50 wt% to 50 wt% ratio (hereafter referred to as NP).[3-5] The detailed composition of the PBX 9501 formula is schematically summarized in Figure 1b as well.

Like many other plasticizers, NP comprises low molecular weight components, which have tendency to diffuse out of the binder domain and can decompose to reactive byproducts at elevated temperatures ($>40\text{ }^{\circ}\text{C}$).[3, 6-10] Therefore, the thermal stability of NP can directly determine the shelf life of explosive charges and nearby components in munitions. Although thermal stabilities were investigated for various classes of polynitro compounds, relatively few studies focused on the understanding of the decomposition pathways of BDNPA/F[11-14] and the effects of their aging at temperatures below $70\text{ }^{\circ}\text{C}$. [15-18] Of those studies, the most extensive one is a constituent aging study (CAS) of over 1100 samples comprised of various combinations of the components used in the PBX 9501 formula, performed at temperatures below $64\text{ }^{\circ}\text{C}$. [15] One of the goals of that work was to study the correlation between the chemical degradation of PBX 9501 and the amount and type of gases evolved in the aging process of PBX 9501. For the samples containing no NP, which showed high stability, the GC-mass spectroscopy analysis revealed low concentration of the evolved gases. On the other hand, the samples containing NP released significant quantities of various gaseous products, such as N_2O , NO , CO , and CO_2 . Those samples were found to degrade even under Argon atmosphere as indicated by significant decreases in the molecular weight of Estane. Together with

other studies, it has concluded that it is the oxidizing gas species from the NP degradation that react with the other components in PBX 9501 and are primarily responsible for the degradation of Estane. The degradation of Estane directly impacts the chemical and mechanical properties of PBX 9501 materials.[4, 15-22]

One of the limitations of the CAS study was that the changes in the compositions of the condensed phase materials were not evaluated.[15] Furthermore, the CAS study and similar aging experiments focused on global properties of the composite, rather than its components, making it difficult to evaluate the stability, mechanism, and kinetics of decomposition of the NP itself. Other studies investigated the thermal stability of BDNPA/F mixture, but were conducted at relative high temperatures ($>150\text{ }^{\circ}\text{C}$).[14, 23, 24] In 2008, Pauler *et al.* used density functional theory electronic structure calculations to identify plausible degradation mechanisms for BDNPA and BNDPF.[25] Their work predicted possible reaction pathways for the NP decomposition at the moderate temperatures using the experimental results of the CAS study as a supporting evidence. Their results suggested that a set of reactions involved in the decomposition of a model compound representing NP can yield reactive intermediates such as methyl formate, nitro-oximes, aliphatic esters, ketones, and nitric/nitrous acids. Because of their reactivity, these intermediates are expected to degrade neighboring polymers and other components.

At moderate temperatures ($<70\text{ }^{\circ}\text{C}$), the degradation of NP is expected to proceed at a slow rate. Some small gas molecules are produced at the initial stages of the decomposition process. In a closed system, these small molecules would co-exist with other intermediates in the binder for an extensive period of time and create a reactive environment. However, because of their high mobility, they quickly diffuse out of the composite. As a result, the concentration of the gas molecules within the composite remains low and their contribution to the polymer degradation is minor. In contrast, the nongaseous intermediates, due to their lower volatility, are likely to play a much more significant role in the polymer degradation. Therefore, understanding the mechanism and rate of the formation of these intermediates from the NP degradation is a critical prerequisite for preserving the long-term stability of polymer binders used in the munitions. To address this need, we conducted a systematic thermal aging study of neat

NP under various environmental conditions with temperatures ranging from room temperature (RT) to 90 °C. The products of degradation in the condensed phase were characterized using TGA, FTIR, GPC, ESI-MS, and ¹H NMR. In Part A of this series, we discuss the aging study conducted in air and under nitrogen atmosphere. In Part B, we will discuss the aging study conducted in water and high humidity conditions within the same temperature range.

2. Experimental

2.1. Liquid NP

NP was manufactured at the Naval Propellant Plant (Indian Head, Maryland) using an oxidative nitration process.[26]. NP used in this study was synthesized in 1992 with a lot number of OCP-A/F-XB 8/8. Typically, 0.1 wt% of N-phenyl-β-naphthylamine (PBNA, aka Neozone D), serving as an anti-oxidant, was added for long-term storage. The chemical structure of PBNA is also shown in Figure 1b. The melting points of BDNPA and BDNPF are 31 and 34 °C, respectively, and the melting point of NP is -15 °C.[14] In closed-drum storage at ambient temperature, the chemical purity of BDNPA/F has been tested periodically to ensure it remained within material specifications.[14, 15, 27, 28] Once received, the NP container was stored in a refrigerator at 4 °C. Since this NP sample was used as a starting material, we designate it as a baseline sample, but recognize its age.

BDNPA and BDNPF were synthesized at the Naval Propellant Plant in late 1990. Both chemicals were stored under nitrogen and kept in a freezer for long-term usage. We designate these samples as the reference samples of BDNPA and BDNPF, but recognize their age.

2.2. Sample Preparation and Aging

Small fraction of the baseline NP was transferred into two sets of glass vials, which were placed inside PTFE containers. To create a nitrogen environment, one set of the PTFE containers with NP was first evacuated and then back filled with nitrogen. The other set of containers was sealed at ambient conditions. To simplify the later discussion, the first set of samples will be referred to as N₂ samples, and the second, as Air samples.

To study the effects of temperature, the containers were heated at 38, 55, 70, and 90 °C in an oven. The TGA and FTIR spectra of these samples were recorded multiple times over a period of two years. To collect N₂ samples, the samples were transferred into a sealed glass vial inside a nitrogen glove box. At the end of the aging study (24 months), the samples were further characterized using GPC, ESI-MS, and ¹H NMR.

2.3. Characterizations

Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q500. To fully cover the bottom of a sample pan (aluminum), 20 - 30 mg of the liquid sample was typically used. The sample was heated from RT to 300 °C at a rate of 5 °C/min under a nitrogen purge (10 ml/min).

Fourier Transform Infrared (FTIR) spectra were recorded using a Bruker Vertex 80v FTIR bench operating in Attenuated Total Reflectance (ATR) mode. The ATR accessory was equipped with a diamond crystal allowing for probing the sample with a single bounce of the IR beam. A small drop of liquid sample was placed on the crystal, and the spectrum was collected at RT. Data were collected using Bruker DigiTech™ data acquisition software. All data were collected with a 4 cm⁻¹ resolution and represent an average of 100 scans.

Gel Permeation Chromatography (GPC) analysis was performed with a Waters® GPC system, consisting of an Alliance 2690 pump, a Waters® 996 photodiode array (PDA) detector, and a PLgel mixed E column (3.6 x 250 mm in diameter x length, Agilent). The column temperature was 40 °C. The injection volume was 30 µL, and the effluent flow rate was 0.3 ml/min. The typical concentrations of aged NP solutions were 1.0 mg/ml in anhydrous tetrahydrofuran (THF) (Aldrich, HPLC grade, without BHT). The concentration of PBNA (Aldrich) was 0.05 mg/ml in the anhydrous THF. The monitoring range of the PDA detector was set to 190-500 nm. One polystyrene standard tap containing 5 narrow polystyrene (PS) standards (Agilent, EasiCal PS2B), with a molecular weight ranging from 580 to 210K g/mol, was used to calibrate the detector. Empower 2 software was used to retrieve the GPC results and UV-Vis spectra.

ElectroSpray Ionization (ESI) mass spectra were acquired with a Waters® Micromass® ZQ™ single quadrupole mass spectrometer equipped with a direct injection

ESCi® multimode ESI probe. Prior to the injection, samples were first dissolved in acetonitrile (Fisher Scientific Optima® □ □ containing 0.1% formic acid (Waters® □ ERA) used as an aid to enhance the ionization. Samples were introduced into the ESI probe and subsequently into the mass analyzer using a syringe pump at a rate of 40 $\mu\text{L}/\text{min}$ and with a N_2 desolvation of 400 L/hr. Spectra were collected using MassLynx® (ver. 4.1) control software for one minute duration, in a positive ion mode and a scan time of 0.5 seconds. Source and analyzer settings are listed in Table 1.

For ^1H Nuclear Magnetic Resonance (NMR) spectroscopy, samples were dissolved in deuterated chloroform (CDCl_3 , 99.6% Acros Organics) prior to the measurement. The ^1H NMR signals were referenced to the tetramethylsilane internal standard. Experiments were carried out using a Bruker Avance NMR spectrometer operating at 500.13 MHz.

3. Results and Discussion

3.1 Visual Observation

Figure 2 shows the color changes of samples exposed to air at various aging conditions. After 12-month aging, the color of the sample changes from light brown to dark brown, orange, or yellow as the temperature increases from room temperature to 55, 70, and 90 $^\circ\text{C}$, respectively. The 90 $^\circ\text{C}$ sample gives a strong acidic odor and has a distinctly lower viscosity than the baseline sample. After heating for 18 months at 90 $^\circ\text{C}$, the liquid NP turns to a black-paste like material. In contrast, when the NP is heated at the temperatures below 90 $^\circ\text{C}$, its color changes, but it remains liquid for 24 months. After 24 months, the color of the 70 $^\circ\text{C}$ sample turns a faint yellow, exhibits a strong acidic odor, and possesses poor solubility in water. Its physical properties are similar to the 12-month aged 90 $^\circ\text{C}$ sample. Clearly, temperature plays a critical role in determining the physical properties of the aged samples. Since we are primarily interested in the moderate temperature range, in the following discussion, we will focus on data collected at the temperatures ≤ 70 $^\circ\text{C}$.

Figure 3 shows the color changes in the samples exposed to nitrogen at various temperatures for 24 months. As temperature increases, the color of these samples changes from light brown (baseline color) to brown, dark brown, and then light brown. Overall, the color change in N_2 samples is less dramatic than that in Air samples.

Although all of the samples have some acidic odor, they are not nearly as strong as Air samples aged under the same conditions.

3.2. Thermal Properties of BDNPA/F, NP, Aged samples

Figure 4 presents the TGA results of the baseline NP compared with its two components – BDNPA and BDNPF. The decomposition temperatures (DTs) of BDNPA, NP, and BDNPF are 231.7, 234.1, and 237.2 °C, respectively. The thermal stability of BDNPA is slightly lower than that of BDNPF. The thermal stability of NP, the 50%/50% mixture of BDNPA/F, sits between those of BDNPA and BDNPF.

Figure 5 shows the effect of temperature on the TGA results of Air samples aged for 24 months. Aging at 38 and 55 °C slightly decreases the stability of the samples. As the temperature increases to 70 °C, a new peak is detected at 154 °C, which suggests the formation of new compounds with much lower DT compared to the baseline NP (234 °C). Accordingly, the main peak shifts toward a slightly higher DT at 236 °C.

To better understand the aging effects, Figure 6 compares the TGA results of Air samples aged at 70 °C for different time periods. After 12-month aging, the aged sample decomposes at a lower temperature (230.5 °C) than the baseline sample (234.1 °C). After 18-month aging, new compound(s) with a DT of 163 °C is detectable. The main peak shifts from 230.5 to 234.0 °C. After 24-month aging, the amount of the new compound(s) increases with decreasing DT (154 °C), but the main peak shifts toward a slightly higher DT compared to the 12- and 18-month aged samples. In contrast, aging under nitrogen does not significantly change the TGA results of the aged samples, shown in Figure 7. The results suggest that NP is fairly stable under the nitrogen environment at 70 °C over the period of two years.

3.3. FTIR Spectra of BDNPA, BDNPF, Baseline NP, and Aged NPs

To better understand the changes in the FTIR spectra observed during the aging, we first discuss the spectra of BDNPA, BDNPF, and baseline NP, shown in Figure 8, and summarize the tentative assignments of their most prominent peaks in Table 2.[10, 12, 29, 30] Since most of the major peaks are observed in the two spectral regions (2600-3600 cm^{-1} and 700–1800 cm^{-1}), and the overall absorbance in high wavenumber region is

relatively weak, we present the results separated into these two regions, hereafter referred to as H-region and L-region respectively. All spectra were normalized to the maximum of the asymmetric -NO_2 peak at 1560 cm^{-1} . In the H-region, the spectra were multiplied 10 times to better illustrate the spectral changes. The same methodology is applied to all FTIR spectra in Part A and B of this series. In the H-region, the dominant peaks at $3020 - 2800\text{ cm}^{-1}$ are associated with $\nu_{\text{as}}(\text{-CH}_3)$, $\nu_{\text{as}}(\text{-CH}_2)$, $\nu_{\text{s}}(\text{-CH}_3)$, and $\nu_{\text{s}}(\text{-CH}_2)$ respectively. Due to the extra -methyl group (-CH_3) in BDNPA, two peaks associated with $\nu(\text{-CH}_3)$ at 3038 and 2949 cm^{-1} are stronger in BDNPA than in BDNPF. On the other hand, the $\nu(\text{-CH}_2)$ peaks at 2976 and 2909 cm^{-1} in BDNPF are stronger than these in BDNPA. The weak peaks between 2600 and 2700 cm^{-1} are assigned as the overtone peaks of $\nu_{\text{s}}(\text{-NO}_2)$. In the L-region, due to the structural similarity, the major peaks of BDNPA/F, such as those associated with -NO_2 , -CCOC- , -CNO- , and -CH_n , overlap in the NP spectrum, though the extra -CH_3 in BDNPA causes some minor shifts of these peaks. This structural difference also results in unique peaks in the spectra of the individual molecules – BDNPA and BDNPF. For example, the spectrum of BDNPF is dominated by $\nu_{\text{as}}(\text{-NO}_2)$, $\nu(\text{-COC-})$, $\delta(\text{-NO-})$, and $\nu(\text{-CNO}_2)$ peaks at 1544 , 1179 , 945 , and 877 cm^{-1} , respectively. Without the -CH_3 group, the two $\text{-CH}_2\text{-CO-}$ (at 1440 and 1400 cm^{-1}), and two -COCC- (1118 and 1060 cm^{-1}) peaks in BDNPF have much higher absorbances than those in BDNPA. Conversely, in BDNPA, the peaks associated with $\delta_{\text{as}}(\text{CH-CH}_3)$ (1464 cm^{-1}), $\nu(\text{-COC-})$ (at 1093 and 1014 cm^{-1}) and $\delta(\text{N-O})$ (at 910 cm^{-1}) are not observed in BDNPF. Interestingly, BDNPF also gives a distinct peak at 1593 cm^{-1} while BDNPA shows only a weak shoulder at 1591 cm^{-1} , but there is no absorbance found in NP in this spectral range. All these characteristic peaks can be used to track the presence of BDNPA/F in the aged samples.

3.3.1. Temperature effects on the 24-month aged samples

Figure 9 summarizes the effect of temperature on the FTIR spectra of N_2 samples aged for 24 months. Changes in the spectra are observed for temperatures as low as 38°C . In the H-region, the absorbances of all $\nu(\text{-CH}_n)$ peaks increase. At 38 and 55°C , the overall intensities of all peaks almost triple in size and a broad band grows at $\sim 3258\text{ cm}^{-1}$, which suggests the formation of poly-OH compounds. The shoulder at 3400 cm^{-1} and

3600 cm^{-1} are associated with liquid water and $-\text{OH}$ group free of H-bonding (called free-OH), respectively. The absorbance of a peak at 2670 cm^{-1} increases, which is attributed to the formation of $-\text{OH}$ groups and/or the overtone of $\nu_s(-\text{NO}_2)$. At 70 $^{\circ}\text{C}$, the absorbances of these peaks increase further. Simultaneously, two $-\text{CH}_n$ peaks are replaced with one large peak at 2979 cm^{-1} with a shoulder at 2972 cm^{-1} . This large peak is a characteristic peak of BDNPF, which suggests that more BDNPF is present in the aged sample than in the baseline NP. The increased intensities of all peaks suggest that the functional groups in the aged samples are able to vibrate more freely than in NP due to the reduced viscosity of the aged samples. In the L-region, very weak absorptions grow between 1800-1600 cm^{-1} for the 70 $^{\circ}\text{C}$ sample, which suggests the formation of various free-OH, alkenes, and imines with a characteristic vibration of $\text{C}=\text{N}$ at $\sim 1650 \text{ cm}^{-1}$. Compared to $\nu_{\text{as}}(-\text{NO}_2)$ intensity, all $-\text{COC}-$, $-\text{CNO}-$, and $-\text{C}-\text{NO}_2$ peak intensities slightly decrease. However, the intensities of peaks at $\delta_{\text{as}}(\text{CH}-\text{CH}_3)$ (1464 cm^{-1}) scissoring (1464 cm^{-1}), $\nu(-\text{COC}-)$ (1090 cm^{-1}), and N-O bending (910 cm^{-1}) decrease more noticeably than the rest of peaks. Since all of these peaks are associated with BDNPA, the spectral changes suggest a decrease in the concentration of BDNPA in the N_2 sample aged at 70 $^{\circ}\text{C}$ for 24 months.

Figure 10 summarizes the effect of temperature on the FTIR spectra of Air samples aged for 24 months. Compared to N_2 samples, the spectral changes in Air samples are more complex. For the 38 $^{\circ}\text{C}$ sample, the growth of the broad band at $\sim 3258 \text{ cm}^{-1}$ is more pronounced, which suggests that more poly-OH compounds form in Air samples than in N_2 samples. The intensity at 3600 cm^{-1} grows significantly, which is partially associated with free-OH vibrations. Accordingly, the intensity of the 2670 cm^{-1} peak increases, which is partially due to the newly formed $-\text{OH}$ groups. Although the original $-\text{CH}_n$ peaks between 3050 and 2800 cm^{-1} are preserved, their intensities are more than triple. Additionally, the $\nu_{\text{as}}(-\text{CH}_3)$ peak at 3034 cm^{-1} becomes detectable. In the L-region, very weak absorptions grow between 1800-1600 cm^{-1} , which suggests the formation of various $-\text{OH}$, alkenes, and imines. While the intensities of $-\text{COC}-$ and $-\text{CNO}-$ peaks decrease compared to $\nu_{\text{as}}(-\text{NO}_2)$ intensity, the intensities of $\delta_{\text{as}}(\text{CH}-\text{CH}_3)$ (1464 cm^{-1}), $-\text{COC}-$ (1090 cm^{-1}), N-O bending (910 cm^{-1}) peaks decrease more appreciably than the rest of peaks. Again, since all of these peaks are associated with

BDNPA, the results suggest that the structural changes preferentially occur in BDNPA even at the temperature as low as 38 °C. At 55 °C, the intensity of the band at $\sim 3258\text{ cm}^{-1}$ slightly increases while the intensity of a shoulder at 3400 cm^{-1} increases, which suggest the presence of different forms of --OH structure and is directly related to water molecules. Simultaneously, two --CH_n peaks are replaced with one large peak at 2979 cm^{-1} with a shoulder at 2972 cm^{-1} , which suggests that more BDNPF is found in the 55 °C sample. In the L-region, the changes are similar to those in the 38 °C samples. Due to the major changes occurring in BDNPA, the concentration of BDNPA is appreciably lower than that in the baseline NP. As the temperature further increases to 70 °C, the intensities of the broad band at 3258 cm^{-1} and the peak at 2979 cm^{-1} decrease, which suggest the decreased concentrations of poly-OHs and BDNPF, respectively. Accordingly, the intensity of the shoulder at 3400 cm^{-1} continuously grows, suggesting an appreciable amount of water in the sample. The peak at 2900 cm^{-1} becomes broader, which suggests a newly formed --CH_2 group. In the L-region, very weak absorptions grow between $1800\text{--}1600\text{ cm}^{-1}$ at 38 and 55 °C, which are associated various --OH , alkenes, and imines. At 70 °C, a peak associated with --OC=O at 1750 cm^{-1} is clearly detected. Another peak associated with --COC-- at 1220 cm^{-1} emerges. These spectral changes suggest the formation of an ester group, which is distinct from ketones ($>\text{C=O}$). Accordingly, the characteristic peaks of BDNPA at CH--CH_3 (1464 cm^{-1}), --COC-- (1090 and 1014 cm^{-1}), and N–O bending (910 cm^{-1}) almost disappear. These spectral changes suggest that the molecular structure of this 70 °C sample has changed. Although most changes are related to BDNPA, the decreased intensity of the peak at 2979 cm^{-1} and the newly formed poly-OH and --CH_2 groups indicate that some changes are related to BDNPF as well. Therefore, we conclude that both BDNPA and BDNPF degrade after 24 month aging at 70 °C in air, with BDNPF degrading at a slower rate than BDNPA.

3.3.2. Aging effects at 70 °C

Figure 11 shows the FTIR spectra of N_2 samples aged at 70 °C for different periods of time. After 15 months of aging, the intensity at $\sim 3600\text{ cm}^{-1}$ increases, which suggests the presence of free-OH groups, associated with the formation of water molecules. A broad band at $\sim 3258\text{ cm}^{-1}$ is detected. The peaks between 3040 and 2940 cm^{-1} ,

associated with the $-\text{CH}_n$ groups, change significantly. Their intensities increase accordingly. After 18 months, the $-\text{CH}_n$ peaks are replaced with a large peak at 2979 cm^{-1} with two shoulders at 3001 and 2972 cm^{-1} . The $\nu_{\text{as}}(-\text{CH}_3)$ peak at 3034 cm^{-1} becomes detectable. After 24 months, the shoulder at 3001 cm^{-1} , associated with BDNPA, almost disappears. The intensity of the broad band at $\sim 3258\text{ cm}^{-1}$ decreases while a shoulder grows more at 3400 cm^{-1} , suggesting presence of H-bonded $-\text{OH}$ groups from liquid water molecules. The peaks associated with $-\text{OH}$ groups at 3600 and 2670 cm^{-1} gradually grow with increasing aging. In the L-region, the effect of aging on the spectra is insignificant though very weak absorptions grow between $1800\text{--}1600\text{ cm}^{-1}$, which is associated with $-\text{OH}$ groups. Noticeable decrease in intensity occurs for the characteristic peaks of BDNPA; *i.e.*, $\text{CH}-\text{CH}_3$ scissoring (1464 cm^{-1}), $-\text{COC}-$ stretching (1090 and 1014 cm^{-1}), and N-O bending (910 cm^{-1}). While the peak intensity at 910 cm^{-1} decreases, the shoulder at 945 cm^{-1} ($>\text{C}=\text{N}-\text{O}-$) grows. Together with the peak at $\sim 3600\text{ cm}^{-1}$ (partially due to $=\text{N}-\text{O}-\text{H}$), the spectral changes suggest the presence of oxime.[31] Since the TGA results, shown in Figure 7, suggest that their overall thermal stabilities do not change significantly, we believe that the main structural changes in these N_2 samples are due to structural rearrangement, for example, the formation of isomers of BDNPA/F with minor degradation of BDNPA.

Figure 12 shows the FTIR spectra of Air samples aged at 70°C over indicated periods of time. Since we anticipated that the change would occur faster in air, we started collecting the spectra as early as 3 months. Initial 6 month aging does not noticeably change the properties of NP. After 12 months of aging, the peak at 3580 cm^{-1} is detected. A tiny peak at 3120 cm^{-1} , due to the H-bonding interaction of $-\text{OH}\cdots\text{O}=\text{C}$ groups, is detectable. A detectable peak at 3070 cm^{-1} suggests the presence of $>\text{C}=\text{C}<$ functional groups. Accordingly, a broad band between 1800 and 1700 cm^{-1} with a peak at 1715 cm^{-1} suggests the presence of various $>\text{C}=\text{O}$ groups, such as aliphatic ester ($\sim 1740\text{ cm}^{-1}$) and ketone ($\sim 1715\text{ cm}^{-1}$). [12, 29] Additionally, the characteristic peaks of BDNPA decrease in the L-region, suggesting that the structural changes are associated with the BDNPA molecules. While the peak intensity at 910 cm^{-1} decreases, the shoulder at 948 cm^{-1} ($>\text{C}=\text{N}-\text{O}-$) grows. Together with the peak at 3580 cm^{-1} ($=\text{N}-\text{O}-\text{H}$), these spectral changes suggest the presence of oximes in this Air sample.[31] The TGA result of the

12-month Air sample, shown in Figure 6, suggests that the aged sample becomes less thermally stable than the baseline sample. However, the overall changes in the thermal stability of the 12-month sample are insignificant. After 18 months, new peaks around $\sim 3600\text{ cm}^{-1}$ grow, suggesting that in addition to oximes, free-OH groups are found in this aged sample. The intensities associated with $-\text{CH}_n$ groups at 3001 , 2976 , and 2960 cm^{-1} increase, so does the shoulder at 3030 cm^{-1} . Interestingly, the poly-OHs, dominant in the N_2 samples, are barely detected in these Air samples. Instead, the $>\text{C}=\text{O}$ from an aliphatic ester ($-\text{COO}-$) becomes a dominant peak at 1760 cm^{-1} together with a growing peak at 1230 cm^{-1} . The original ketone peak at 1715 cm^{-1} becomes a shoulder. Between 1700 and 1600 cm^{-1} , many small peaks are detectable, which are attributed to the formation of various $-\text{OH}$, alkenes, and imines with a characteristic vibration of $\text{C}=\text{N}$ at $\sim 1650\text{ cm}^{-1}$. Between 1540 and 1500 cm^{-1} , small peaks are detected, which suggest the presence of newly formed $-\text{NO}$ groups. Correspondingly, all characteristic peaks of BDNPA further decrease. The TGA result of the 18-month Air sample, shown in Figure 6, suggests that the compounds with a low thermal stability are formed, which we attribute to newly formed aliphatic esters and/or ketones. After 24 months, the FTIR spectrum changes in both H- and L-regions. In the H-region, in addition to the spectral changes occurring in the 18-month sample, the large poly-OH band at 3250 cm^{-1} and H-bonded $-\text{OH}$ band at 3400 cm^{-1} form together with the formation of the characteristic peaks of BDNPF at 2976 and 2960 cm^{-1} . The small peak at 3002 cm^{-1} from BDNPA disappears while the peak at 2947 cm^{-1} from BDNPA becomes a shoulder. The grown peak at 2850 cm^{-1} suggests the newly formed $-\text{CH}_3$ and/or $-\text{CH}_2$ groups. The peaks at 3600 and 2670 cm^{-1} grow, suggesting increased concentrations of the $-\text{OH}$ and oxime in this aged sample. In the L-region, the characteristic peaks of BDNPA almost disappear. The intensities of the bands at 1440 and 1400 cm^{-1} from BDNPF are reduced as well. Together with a growing peak at 1230 cm^{-1} , the $>\text{C}=\text{O}$ from an aliphatic ester ($-\text{COO}-$) peak at 1760 cm^{-1} further grows, and the ketone peak at 1715 cm^{-1} becomes a shoulder. All of these spectral changes suggest that both BDNPA and BDNPF degrade after they are exposed to Air at 70°C for 24 months. Accordingly, the color of the aged NP, as shown in Figure 2, changes from light brown to faint yellow over the aging course.

3.4 GPC Characterization

Figure 13 shows the GPC results of BDNPA ($M_w = 326$), NP ($M_w \sim 319$), and BDNPF ($M_w = 312$). Since PBNA ($M_w = 219$) was typically added into NP for the long-term storage, its GPC result is also included in Figure 13. Among the four samples, BDNPA has the highest molecular weight and gives the shortest retention time whereas PBNA has the smallest molecular weight and gives the longest retention time.

Figure 14(a) shows the effect of temperature on Air samples aged for 24 months. The intensity of the main peak decreases even though the solution concentrations are the same, which suggests a reduced NP concentration in the aged samples. Both 38 and 55 °C aged samples have a slightly longer retention time compared to NP, which suggests that the two aged samples contain more BDNPF than BDNPA. When the temperature increases to 55 °C, PBNA is barely detectable. At 70 °C, the GPC result is distinctly different. The sample gives a bimodal distribution with a tail at both high and low molecular weight ends. The observation of the long tail at the high molecular weight end, as shown in an inset, is unexpected, and suggests that the degradation of NP yields products with the molecular weight higher than 5000 g/mol. This may explain the slight increase in the DT of the main peak in the TGA result of the 24-month sample, as shown in Figure 5. On the other hand, the 2nd large peak confirms the presence of the significant amount of degraded products with a molecular weight less than 319 g/mol. The tail at the low molecular weight end also suggests some fragments in the condensed phase are broken down into small molecules with M_w less than 219 g/mol.

Figure 14(b) presents the GPC results of N₂ samples aged at different temperatures for 24 months. In contrast to the Air samples, the overall changes in the GPC results of N₂ samples are small and monotonic. As the temperature increases, the intensity of the main peak slightly decreases with slightly increasing retention time. This result agrees with the FTIR results, and confirms the decreased concentration of BDNPA in the N₂ samples. Also, the concentration of PBNA decreases with increasing temperature, which suggests the decomposition of PBNA even under the nitrogen environment. At the low molecular weight end, the signal decreases as the temperature increases, which suggests that the intermediates and degraded fragments are preserved better at 38 °C than at 70 °C, due to their poor thermal stability.

In summary, the GPC results show that NP degrades when it is exposed to 70 °C in air for an extensive amount of time, yielding a variety of small molecular weight products. In the presence of oxygen, some of the fragments react to form oligomers with the molecular weight up to 5000 g/mol. Comparatively, NP is more stable under nitrogen. All of these observations are consistent with the TGA and FTIR results discussed above.

3.5. ESI Mass Spectrometry (ESI-MS)

To identify the degraded fragments, we analyzed the aged samples using ESI-MS. The reason why ESI-MS was chosen is its soft ionization process. During the measurement, very little fragmentation is induced, which allows for the molecular ions (or more accurately pseudo molecular ions) resulting from the degradation to be detected. However, since there are often multiple coupling peaks associated with the main peak, the results of ESI-MS are difficult to interpret.[32]

Figure 15 presents the ESI-MS spectra for the baseline NP and the samples aged at 70 °C for 24 months under different atmospheres. For the baseline NP, we detect the distinct peaks at $m/z = 65, 77, 105, 118, 218, 256-260, 270-274, \sim 317$, and ~ 322 . We assign the ESI⁺ ion mass (m/z) of ~ 317 and ~ 322 to BDNPF and NP, respectively. Due to the different ionizations, these peaks are actually shifted and give the m/z ratios of 317.5-319.5 and 320.5-323.5. The zoom-in regions of BDNPF and NP are shown as insets. The zoom-in on PBNA ($M_w = 219$) peaks, as shown in the left-hand inset, confirms the presence of anti-oxidant in the baseline NP after being stored at the ambient conditions for more than 18 years. The clusters at 218 and 256-260 are associated with the NP isomers and intermediates from the structure rearrangement between BDNPA/F and their isomers.[25] In addition to these major peaks, there are several peaks at the m/z values smaller than 150, which can be attributed to clusters and/or even by-products produced by the degradation. Among these peaks, $m/z = 77$ is assigned to the cluster of water and acetonitrile while $m/z = 105$ is the cluster of water and HNO_3 . The spectrum of N_2 sample is more or less the same as one of the baseline NP, though N_2 sample contains less PBNA than the baseline NP. However, the intensity of the BDNPF peak in N_2 sample is higher than that in NP, which suggests a higher concentration of BDNPF in

the former sample, which agrees with the FTIR results as shown in Figures 9 and 11.

For the Air sample, PBNA is barely detectable. The concentrations of both BDNPA/F are greatly decreased. Furthermore, many fragments with m/z less than 200 are detected, which confirms the degradation of this sample. Many new peaks are detected with the m/z values at 30, 42, 57, 87, 95, 134, 138-139, 141, 150-154, 168, 181-183, 196, 224-226, 238-240, 252-254, and 301. Accordingly, most peaks found in NP and N_2 sample are reduced or disappear. These significant changes suggest that Air sample is not only degraded, but degraded through the reaction pathways different from those occurring under the nitrogen atmosphere. $M/z = 30$ is likely a formaldehyde while $m/z = 57$ is a water cluster. This result is consistent with the FTIR results as shown in Figure 10, and confirms the presence of an appreciable amount of water molecules in the Air sample. The pronounced peak at $m/z = 42$ could be simply assigned to acetonitrile – the solvent used in the analysis. However, since three samples were analyzed identically, and this solvent peak is weak in both the baseline NP and N_2 sample, the large peak in the Air sample suggests the presence of species other than acetonitrile (e.g., ethenimine[14]) found in this air sample. In Table 3, we summarize the ESI^+ ion masses (m/z) of the major peaks observed in these three samples and the likely compounds from which they originate. As for these postulated compounds, more detailed discussion will be given in Section 3.7.

3.6. 1H NMR Spectroscopy

Figure 16 shows the 1H NMR spectra of the baseline NP and the samples aged at 70 °C for 24 months under different atmospheres. Table 4 summarizes the chemical shifts of possible functional groups possibly present in these samples. For the baseline NP, a trace amount of PBNA at ~3.7 ppm is detected. While PBNA is detected in N_2 sample, it is barely detected in Air sample. For the baseline NP, other than expected chemical shifts corresponding to the $-CH_n$ groups from BDNPA/F molecules, two chemical shifts at 4.86 and 3.79 ppm are attributed to $-CH$ and $-OH$ from $>CH-OH$ group. The baseline NP and N_2 sample give similar spectra though the relative intensities of these peaks are different. Furthermore, two noticeable peaks are detected at 4.36 and 2.64 ppm. The peak at 4.36 ppm might be associated with R-OH group while the small peak at 2.65 ppm is

characteristic of $-\text{CH}_3$ from ethylnitrolic acid (1-nitro-oxime ethanone) (also called oxime).[33] These results suggest that more chemical compounds are found in the N_2 sample than in the baseline NP.

For the Air sample, the intensities of all peaks associated with BDNPA decrease. Accordingly, many new peaks are detected. The major changes occur at 5.30–5.22, 4.95, 4.87, 4.36, 2.15, 2.09/2.07, and 1.58 ppm. The observation of a peak at 4.36 ppm suggests the formation of $-\text{C}-\text{OH}$ group. The peaks at 2.15, and 2.09/2.07 ppm are likely associated with the newly formed $-\text{CH}$ and $-\text{CH}_2$ groups, respectively. Small peaks between 4.7 and 4.5 ppm together with a group of low intensity peaks at 5.30–5.22 ppm are associated with different methylene ($-\text{HC}=\text{C}<$) in *cis*- and *trans*-conformations. Interestingly, the Air sample is lacking the signal at 2.64 ppm, suggesting that it does not contain a detectable amount of oxime (molecular mass = 104), and explaining the weak peak at $m/z = 105$, shown in Figure 15. Overall, the ^1H NMR spectra are consistent with the other characterizations and confirm the degradation taking place in Air samples.

3.7 Proposed Reaction Pathways under Various Environments

In 2001, Melius *et al.* proposed the initial reaction steps in the condensed-phase decomposition of propellants using quantum chemical calculations.[34] Using nitroethane as a prototype for $\text{C}-\text{NO}_2$ nitro compounds, they proposed that HONO elimination is the first step of the nitroethane decomposition when the compound is thermally treated at low temperatures. In 2007, Pauler *et al.* extended this hypothesis to 2,2-dinitro-1-methoxypropane as a model compound for BDNPA/F in the density functional theory electronic structure calculations, and postulated possible decomposition pathways at the low temperatures. Both of these theoretical works emphasize the importance of the cage effect in the decomposition of these nitro compounds, and suggest that the trapped HONO can react with and bind back to the energetic molecules before diffusing out of the liquid. This cage effect can cause the formations of nitrite and/or nitroso alcohol isomers, as illustrated in Scheme A.1. There are two possible reaction pathways for the conversion of BDNPA and BDNPF into *trans/cis* products by the elimination of HONO. Two types of isomers – nitroso alcohol ($\text{HO}-\text{R}-\text{R}'-\text{NO}$) and nitrite ($\text{R}-\text{ONO}$) can be formed.[25, 34] However, the strong poly-OH peak in the FTIR spectra

and the R-OH peak in the ^1H NMR spectra suggest that the rearrangements of BDNPA/F most likely proceed through reactions (a and a.1/a.1') and (c and c.1/c.1') to form two types of trans-products, nitroso alcohol isomers, but not the cis-products - nitrite isomers through reactions (b/b.1) and (d/d.1). In the ESI-MS spectrum of the baseline NP, in addition to the expected BDNPF and NP peaks, we also detect a series of compounds with m/z values from 65 to 270-274. It is known that HONO molecules are reactive and can react with each other to form HNO_3 , H_2O and NO_x . [25] Thus $m/z = 65$ may be associated with an ion cluster of $\{\text{HCOOH} + \text{H}_2\text{O}\}$, formed from acetic acid added into the solution during the ESI-MS analysis. The $m/z = 77$ can be assigned to the cluster of $\{\text{acetonitrile} + 2\text{H}_2\text{O}\}$. The $m/z = 105$ can be associated with the small molecular fragments formed from one type of nitroso-alcohol isomers through reactions (a.2/a.3) and (c.2/c.3) in Scheme A.2, [25] where both 1-nitro-oxime ethanone ($M_w = 104$) and 1,1-diformate methanediol ($M_w = 104$) can give a peak of $m/z = 105$. However, since there are no detectable $-\text{OCO}-$ and oxime peaks in the FTIR and NMR spectra of the baseline NP, these reactions likely do not take place. Therefore, the 105 peak is assigned to the cluster of $\{\text{acetonitrile} + \text{HNO}_3\}$, and the 118 peak is assigned to the cluster of $\{\text{HNO}_3 + 3\text{H}_2\text{O}\}$. Using similar reasoning, $m/z = \sim 218$ is attributed to bis-2,2-nitro-propylene formal (BNPeF) – an intermediate from the BDNPF structural rearrangement, and $m/z = \sim 230$ is attributed to bis-2,2-nitro-propylene acetal (BNPeA) – an intermediate from the BDNPA structural rearrangement. The $m/z = 256-260$ can be assigned to the ion cluster of $\{\text{BNPeF} + 2\text{H}_2\text{O}\}$ while $m/z = 270-274$ can be due to the cluster of $\{\text{BNPeA} + 2\text{H}_2\text{O}\}$. Interestingly, the intensities of 218 and 256-260 cluster are noticeably higher than these of 230 and 270-274 cluster, which suggests that the stability of BNPeF is higher than BNPeA. As a result, a significant amount of BNPeF can coexist with BDNPF in NP, which may explain why the concentration of BDNPF is typically less than BDNPA in the baseline NP even though the same amount of BDNPA and BDNPF were added to formulate the NP mixture. [7] On the other hand, due to the lack of stability, the formed BNPeA tends to react with HONO yielding nitroso alcohol isomers of BDNPA. However, water may stabilize BNPeA so that its water clusters ($m/z = 270-274$) give a concentration higher than BNPeA ($m/z = 230$) in the ESI-MS spectrum of NP. These observations are consistent with the FTIR spectra of BDNPA/F, shown in

Figure 8. Close inspection of the spectra reveals broader and slightly more intense R-OH band around 3258 cm^{-1} in BDNPA than in BDNPF. In the L-region, BDNPA gives rise to a broad band at $1670\text{-}1600\text{ cm}^{-1}$ whereas BDNPF shows a clear shoulder peak at 1600 cm^{-1} . These absorbances might be attributed to the $>\text{C}=\text{C}<$ bonds in BDNPA/F, and confirm that the concentration of BNPeF in BDNPF is higher than that of BNPeA in BDNPA. When BDNPA and BDNPF are mixed together, the stability of BNPeF allows some of free HONO in the mixture to react and to form HNO_3 and H_2O . Therefore, after more than 18 years storage at ambient temperature, some small molecules, such as HNO_3 and H_2O , co-exist in the condensed phase of the baseline NP. At ambient conditions, in the presence of an anti-oxidant such as PBNA, some trans-nitroso alcohol isomers and the BNPeA/F intermediates form and coexist with the native forms of BNDPA/F in the condensed phase, but do not noticeably decompose into the smaller molecules as depicted in Scheme A.2. The formation of BNPeA/F is likely responsible for darkening the color of the long-term stored NP.

However, when NP is aged either in air or under nitrogen, the intensity of the poly-OH peak significantly increases with increasing temperature (see FTIR spectra in Figures 9 and 10). These results suggest that temperature accelerates the formation of the trans-isomers, and confirm the endothermic characteristics of the overall reactions (a/a.1/a.1') and (c/c.1/c.1') in Scheme A.1.[25]

We will now discuss possible decomposition pathways for NP aged under the nitrogen atmosphere. The FTIR and ^1H NMR results suggest the formation of 1-nitro-oxime ethanone (called oxime) in the N_2 sample aged at $70\text{ }^\circ\text{C}$ for 24 months. Based on this observation and the results from the ESI-MS study, we conclude that the decompositions of the trans-isomers of BDNPA/F under nitrogen mainly follow reactions (a.2/a.3) and (c.2/c.3), but not reactions (a.2'/a.3') and (c.2'/c.3'), as shown in Schemes A.2 and A.3, respectively. In these Schemes, the unstable molecules are shown in grey color. Compared to the ESI-MS spectrum of NP, the intensities of all peaks are different in the spectrum of the N_2 sample. Furthermore, some new peaks are detected. The peak of water cluster at $m/z = 57$ slightly increases. With disappearance of the peak at $m/z = 65$, a peak at 68 grows, which might be due to the formation of the $\{\text{HNO} + 2\text{H}_2\text{O}\}$ cluster. Interestingly, the intensities of the peaks at 77, 105, and 118 decrease, which

suggests a decrease in the concentrations of the water clusters formed with acetonitrile and HNO_3 in the N_2 sample. Since both the FTIR and ESI-MS spectra suggest that BDNPA degrades more than BDNPF, the stability of the trans-isomers of BDNPF is likely higher than those of BDNPA. If the trans-isomers of BDNPA decompose through reactions (a.2/a.3), the compounds with $-\text{COO}-$ would have formed. However, a trace amount of $-\text{COO}-$ in the FTIR spectrum and small peak at $m/z = \sim 118$ suggest two alternative possibilities: 1) reaction (a.3) does not occur, or 2) 1,1-diformate, 1,1-ethanediol, formed from Reaction (a.3) (a very unstable compound with a boiling point of $46\text{ }^\circ\text{C}$), quickly decomposes into CO_2 and C_2H_6 at $70\text{ }^\circ\text{C}$, which accelerates the degradation of BDPNA. The second scenario is more likely because the presence of CO_2 is commonly reported in the PBX 9501 aging studies.[4, 15, 25] Three new peaks at $m/z = 230, 244,$ and 303 may be attributed to the radicals of BNPeA, cluster of {product of reaction (a.2) + H_2O }, and cluster of {product of reaction (a.2) + H_2O + HNO_3 }. One important question is whether the trans-isomers of BDNPF will follow reactions (c.2/c.3) to degrade, as shown in Scheme A.3. If the degradation proceeds by these pathways, the final products should contain the oxime and 1,1-diformate methanediol with two $-\text{COO}-$ groups. This methanediol ($m/z = 104$) has a boiling point of $127\text{ }^\circ\text{C}$ and is relatively stable. The absences of the $-\text{COO}-$ feature in its FTIR spectrum and the peak at $m/z = \sim 208$ in the ESI-MS spectrum suggest only the minimal degradation of BDNPF. Furthermore, the thermal energy seemingly drives the conversion of BNPeF into BDNPF, which explains the decreased amount of BNPeF and increased intensity of the peak at 317 – including both BDNPF and its isomers in the N_2 sample after being aged at $70\text{ }^\circ\text{C}$ for 24 months. In summary, when BDNPA/F is heated at $70\text{ }^\circ\text{C}$ under nitrogen, the thermal energy accelerates the structural rearrangements into their trans-nitroso alcohol isomers, which are less stable than their native forms. In the case of BDNPA, its isomers will further degrade into small molecules – oxime, CO_2 , and C_2H_6 . However, in a closed system under the nitrogen atmosphere, this decomposition process is rather slow. After two years of aging, only a small amount of BDNPA is completely degraded whereas BDNPF is more likely converted into a mixture of its native, intermediate, and isomer forms. The color of nitro-oximes is often light yellow,[35] which may explain the lighter color of the $70\text{ }^\circ\text{C}$ sample compared to that of the baseline NP, as shown in Figure 3.

When NP is heated in air, the presence of oxygen significantly changes the thermodynamics and kinetics of the NP degradation. The changes in the FTIR spectrum suggest the presence of poly-OHs, $>C=O$ groups (from aliphatic esters and ketones), $-CH$, $-CH_2$, and various alkenes. As PBNA is depleted, so are BDNPA and some of BDNPF. While many new peaks are detected in the ESI-MS spectrum of the Air sample aged at 70 °C for 24 months, all peaks found in the baseline NP and N_2 sample are either greatly reduced or completely absent. These results suggest that oxygen significantly degrades NP and generates more small fragments than those found in the N_2 samples aged at the same conditions. The largest peak in its ESI spectrum is the peak at $m/z = 42$. We attribute this peak to ethenimine,[14] which can form from the oxime decomposition through reaction (a.5) in Scheme A.2. This result may explain the detachable oxime in the 12-month sample, but not much in the 18- and 24-month samples. However, the absence of 1,1-diformate methanediol ($m/z = 105-106$) suggests that BDNPF, unlike BDNPA, does not degrade into small molecules through reactions (c.3/c.4/c.5). Interestingly, the presence of aliphatic ester and ketone suggests that reactions (a.2'/a.3') and (c.2'/c.3') in Schemes A.2 and A.3, not occurring under the nitrogen atmosphere, take place in air. The newly formed peak at $m/z = 93$ in its ESI-MS spectrum may be attributed to 1-nitro-acetaldehyde – a product of reaction (a.2') and (c.2'). The weak peaks at $m/z = 134$ and 148 may be associated with one of the final products from reactions (c.3') and (a.3'), respectively. These two products are unstable, with the one from BDNPA more so than the one from BDNPF, which explains the lower intensity at $m/z = 148$ than that at $m/z = 134$. Both products may further decompose into small molecules, such as methanimine ($H_2C=NH$), acetaldehyde, formaldehyde, HNO_x , etc.[25] Their poor stability accelerates the degradations of BDNPA/F. The weak peaks at $m/z = 225$ and 239 are associated with the products from reactions (c.2') and (a.2'), respectively, and suggest their low concentrations in the Air sample. Additionally, many peaks with $m/z < 100$ are formed, which are attributed to the clusters of small molecules, water, and/or HNO_3 , and degraded fragments. The strong peak at $m/z = 95$ may be the cluster of $\{HNO_3 + HNO\}$ and/or $2HONO$. The noticeably enhanced peak at $m/z = 57$ is most likely due to the water cluster. We hypothesize that due to the presence of oxygen, some hydro-peroxide forms through the reactions proposed in Scheme A.4, where the

unstable molecules are also shown in the grey color. Additionally, HOOH can also form in the reaction with PBNA. Because of its instability, HOOH can only exist in cluster forms with other molecules. Two small peaks at $m/z = 52$ and 86 may be the clusters of $\{\text{HOOH} + \text{H}_2\text{O}\}$ and $\{2\text{HOOH} + \text{H}_2\text{O}\}$, and the peak at $m/z = 141$ might be a cluster of $\{1\text{-nitro-acetaldehyde (Mw} = 89) + \text{HOOH} + \text{H}_2\text{O}\}$. If the decompositions follow reactions (a.7') and (c.7') in Scheme A.4, acetaldehyde and formaldehyde will also form. The peaks between $m/z = 152\text{-}154$ and 196 are unique for the Air sample. They might be associated with the products from reactions (a.3'/a.8') and (a.6'), correspondingly. The reaction (a.3') produces another kind of oxime, which is unstable and can rearrange into its ketone isomer. Furthermore, in air, the intermediates from reactions (a) and (c) may be also degraded through the reactions proposed in Scheme A.5. We propose that the temperature increases the conversion of HONO into $\text{HNO} + \text{HNO}_3$, and results in more BNPeA/F formation. In the presence of oxygen, the formed BNPeA/F can be oxidized under the acidic conditions into 1,1-diformate ethanediol and 1,1-diformate methanediol (at $m/z = \sim 108$), respectively. The former one is less stable and can further decompose into formaldehyde and acetaldehyde through a dehydration process, which accelerates the decomposition of BDNPA more than that of BDNPF. As the molecules break down, the color of Air samples gets lighter, as shown in Figure 2. Accordingly, the viscosity of the sample decreases. Finally, the GPC results suggest that in addition to the small molecules, high molecular weight materials are also formed in air. We suspect that both the temperature and the oxygen contribute to the formation of some radicals from the degraded fragments. In Scheme A.6, we postulate a few possible oxidative pathways to form cross-linked oligomers from various fragments. Depending on the temperature and time, they can further react to form the highly cross-linked materials, which are responsible for 1) the high molecular weight materials in the GPC result in Figure 14(a); 2) the newly detected alkenes in the FTIR spectra of the 18- and 24-month samples in Figure 12; and 3) the slightly increased DT of the second peak in the TGA result of the 24-month sample, as shown in Figure 6.

4. Summary and Future Work

In this work, we experimentally confirmed that the HONO molecule elimination is an

initial step of the NP thermal decomposition at temperatures below 70 °C. When the temperature is below 55 °C, this process is slow. However, an elevated temperature will accelerate the HONO elimination and structural rearrangement, which results in the formation of the BNDPA/F isomers. During these rearrangements, the steric constraint favors the formation of the trans-nitroso alcohol isomers over the cis-nitrite isomers for both BDNPA and BDNPF. Under confined conditions, the cage effect helps the formation of the BDNPA/F isomers. Therefore, the isomers, intermediates, and small molecules such as H₂O, HONO, and HNO_x often coexist with NP in its condensed phase. This is especially true when NP is stored in the facility where the temperature is greatly influenced by seasonal changes. We also find that BDNPF has a greater tendency to form HONO and BNPeF than BDNPA. This may explain why we often find slightly higher concentration of BDNPA than BDNPF in the aged NP even though their initial concentrations were the same. Nonetheless, due to the extra –CH₃ group in BDNPA, the intermediates, isomers, and degraded compounds from BDNPA are less thermally stable than those from BDNPF. Therefore, regardless of the environmental condition, BDNPA is more reactive than BDNPF.

In addition to temperature, the composition of the surrounding atmosphere also plays a critical role in the BDNPA/F degradation. It determines not only the fate of the intermediates and isomers of BDNPA/F, but also the reaction pathways by which these compounds further thermally degrade. Oxygen significantly accelerates the NP degradation into many small organic molecules. In addition, oxygen seems to facilitate the formation of radical fragments, which can form cross-linked products as well. In contrast, NP is relatively stable under nitrogen below room temperature though the structural rearrangement does occur to generate HONO and BNPeA/F. Therefore, to minimize its degradation, NP should be stored at low temperatures and under an inert atmosphere. Furthermore, the anti-oxidant, added at the beginning of the storage, is gradually consumed during a long-term of storage. Therefore, the anti-oxidant concentration should be monitored over the storage period.

Traditionally, NP has been considered to be a stable additive and was not expected to degrade significantly at the temperatures below 70 °C. This study demonstrates that NP does degrade at the moderated temperatures. This is especially true when oxygen is

present in the storage environment. The degradation products, such as water, N_xO , and organic molecules, will serve as catalysts to accelerate the degradation of Estane in the PBX 9501 formula. The degradation of Estane will directly impact the mechanical properties of the PBX 9501. Furthermore, in the applications, NP also migrates into other polymeric materials nearby the PBX 9501. NP will degrade inside these materials, which will trigger the degradation of these polymeric materials as well.[10][27] To completely resolve the NP migration and degradation, more stable nitro-plasticizers with less mobility and high chemical stability should be evaluated and/or developed as replacements for BDNPA/F.

In addition to the air and nitrogen environments, we are also interested in the NP aging behavior under water or high humidity environment. This will be discussed in Part B of this series.

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Figure 1. Components in PBX 9501 formula and the molecular structures of BDNPA, BDNPF, and PBNA. All percentages are based on the mass of the components.

Figure 2. Color changes in Air samples aged at different conditions.

Baseline 38 °C 55 °C 70 °C

Figure 3. Color changes in N₂ samples aged at different temperatures for 24 months.

Figure 4. TGA results of BDNPA, BDNPF, and NP.

Figure 5. TGA results of Air samples aged at different temperatures for 24 months.

Figure 6. TGA results of Air samples aged at 70 °C for different times.

Figure 7. TGA results of N_2 samples aged at 70 °C for different times.

Figure 8. FTIR spectra of BDNPA, BDNPF, and NP (as-: asymmetric-stretching and s-symmetric stretching). In the H-region, the spectra were multiplied 10 times to better illustrate the spectral changes. The same methodology is applied to all FTIR spectra in entire paper.

Figure 9. FTIR spectra of N₂ samples aged at different temperatures for 24 months.

Figure 10. FTIR spectra of Air samples aged at different temperatures for 24 months.

Figure 11. FTIR spectra of N₂ samples aged at 70 °C for different times.

Figure 12. FTIR spectra of Air samples aged at 70 °C for different times.

Figure 13. GPC results of BDNPA, NP, BDNPF, and PBNA in THF solutions.

Figure 14. GPC results of (a) Air samples and (b) N₂ samples aged at different temperatures for 24 months.

Figure 15. ESI mass spectra of baseline NP, and N₂ and Air samples aged at 70 °C for 24 months.

Figure 16. ^1H NMR spectra of baseline NP, and N_2 and Air samples aged at 70 °C for 24 months.

Scheme A.1. The possible structural rearrangements of BDNPA and BDNPF at $\leq 70^\circ\text{C}$.

trans-nitroso alcohol isomers of BDNPA

Scheme A.2. Possible decomposition pathways of the nitroso isomers of BDNPA under the acidic environment at $\leq 70^\circ\text{C}$ (shaded chemicals are barely or not detected using ESI-MS).

trans-nitroso alcohol isomer of BDNPF

Scheme A.3. Possible decomposition pathways of the nitroso isomers of BDNPF under the acidic environment at $\leq 70^\circ\text{C}$ (shaded chemicals are barely or not detected using ESI-MS).

Scheme A.4. Possible decomposition pathways of the nitroso isomers from the reactions of (a.1') and (c.1) under air environment at ≤ 70 °C (shaded chemicals are barely or not detected using ESI-MS).

Scheme A.5. Possible decomposition pathways of the intermediates from the reactions of (a) and (c) under air environment at $\leq 70^\circ\text{C}$ (shaded chemicals are barely or not detected in ESI-MS).

Scheme A.6. Possible oxidative pathways of between the BNPeA/F radicals and BDNPA/F in air.

Table 1. Experimental parameters for ESI mass spectrometer.

Instrumentation	Setting
Capillary (KV)	3.0
Cone (V)	55.0
Extractor (V)	3.0
RF lens (V)	0.4
Source T (°C)	100
Desolvation T (°C)	250
Multiplier (V)	650

Table 2. FTIR spectra (3600 – 700 cm⁻¹) of BDNPA and BDNPF, and pristine NP¹⁾.

BDNPA	BDNPF	NP	Tentative Assignment
3038 vw	3034 vw		$\nu_{as}(\text{CH}_3)$
3002 w	3001 vw	3001 vw	$\nu_{as}(\text{CH}_2)$
2975 w - sh	2976 m		$\nu_{as}(\text{CH}_2)$
2947 m	2960 m	2949 w	$\nu_s(\text{CH}_3)$
2897 m	2909 m	2903 m	$\nu_s(\text{CH}_2)$
2860 w			$\nu_{as}(\text{-CH-CH}_3)$
2680 w	2684 w	2680 vw	$2\{\nu_s\text{NO}_2\}$
2650 w	2664, 2641 vw	2650 vw, sh	$2\{\nu_s\text{NO}_2\} + \nu(\text{OH})$
	1593 m, sh	1591 vw, sh	$\nu(>\text{C}=\text{C}<)$
1565 vs	1555 vs	1560 s	$\nu_{as}(\text{NO}_2)$
1464 w	1468 w	1464 w, sh	$\delta_{as}(\text{CH}_3)$ scissoring
1449 w	1444 s	1444 w	$\nu(\text{CO-CH}_2)$
1410 w	1410 vw, sh	1410 vw, sh	$\delta_{as}(\text{CH}_3)$ scissoring
1395 vw	1401 s	1395 w	$\delta_s(\text{CH}_3)$ scissoring
1383 w			$\nu(\text{CO-CH}_2) + \delta_s(\text{CH}_3)$
1373 vw	1374 w	1378 w, broad	$\nu(\text{CO-CH}_2) + \delta(\text{CH}_2)$
1359 vw	1356 w	1357 vw	$\nu(\text{CO-CH}_2) + \delta(\text{CH}_2)$
1342 vw, sh			$\delta(>\text{CH-CH}_3)$
1332 s	1324 s	1326 s	$\nu_s(\text{NO}_2)$
1278 w	1266 w	1278 vw	$\nu_s(\text{NO}_2)$
1238 w	1225 w	1233 vw	$\nu_{as}(\text{-COC-})$
	1179 w	1178 vw	$\nu_{as}(\text{-COC-}) \{\text{O}(\text{CH}_2)_2\}$
	1152 w, sh		$\nu_{as}(\text{-COC-})$
1137 s		1137 w, sh	$\nu_{as}(\text{-COC-}) \{\text{-CH}_2\text{OCH-}\}$
1114 w	1118 vs	1118 s	$\nu_s(\text{-COC-})$
1093 s		1093 s	$\nu_s(\text{-COC-}) \{\text{-CH}_2\text{OCH-}\}$
1064 vs	1060 vs	1050 vs	$\nu_s(\text{-COC-})$
1014w		1014 vw	$\nu_s(\text{-COC-})$
975 w	978 s	977 w	$\delta(\text{-CNO-})$
	959 vw		$\delta(\text{N-O})$
948 vw	945 w	948 vw, sh	$\delta(\text{N-O})$
910 s		910 w	$\delta(\text{N-O})$
863 s ²⁾	877 s ²⁾	862 s	$\nu(\text{C-NO}_2) + \text{C}=\text{C-H}$
847 s ²⁾	849 s ²⁾	847 vs	$\nu(\text{C-N}) + \text{C}=\text{C-H}$
773 s	772 s	774 w	$\delta(\text{O-N=O})$
733 w	729 w	732 vw	(CH_2) rocking

¹⁾: vw – very weak; w – weak; m – moderate; s – strong; vs – very strong; sh- shoulder.

²⁾: These peaks were only labeled as -CH_n bending in our previous paper.[10]

Table 3. Summary of ESI⁺ ion found in the pristine and aged-NPs and the tentative compounds and clusters in these samples (age conditions: 70 °C for 24 months).¹⁾

ESI ⁺ Ion (m/z)	Pristine NP	N ₂ -aged NP	Air-aged NP	Tentative ionized compound and cluster
30			w	H ₂ CO (formaldehyde) or C ₂ H ₆ (ethane) (???)
38	vw	vw	m	2H ₂ O
42	w	w	vs	Acetonitrile or H ₂ C=C=NH
51	vw			HNO + H ₂ O
52-55			w	HOOH + H ₂ O
57	vw	w	m	3H ₂ O cluster
64	vw	w	vw	HNO ₃
65	w	vw	vw	HCOOH + H ₂ O
68			m	H ₂ CO + 2H ₂ O
69	w	w		HNO + 2H ₂ O
77	vs	s	w	acetonitrile + 2H ₂ O
83	vw	w	m	HNO ₃ + H ₂ O
87			w	2HOOH + H ₂ O
92	w	vw		5H ₂ O cluster
93	vw	vw	m	2HCOOH cluster or O ₂ NC(O)CH ₃ or 3HNO
95			m	HNO ₃ + HNO or 2HONO cluster
105	w	m	vw	acetonitrile + HNO ₃ (for NP) or O ₂ N-C(=N-OH)CH ₃ (oxime) (from a.2/a.3)
110	vw	vw	m	OHCH ₂ OCH ₂ OCH ₂ OH (from c.9')
118	w	w	vw	HNO ₃ + 3H ₂ O (for NP)
124	vw	vw	w	OHCH ₂ OCH(CH ₃)OCH ₂ OH (from a.9')
134			w	(HC(NO)H)O ₂ CH ₂ (from c.2'/c.3')
137	vw	vw		O ₂ N-C(=N-OH)CH ₃ (oxime) (from a.2/a.3) + HNO
139			w	O ₂ NC(O)CH ₃ + HNO + H ₂ O
141			m	O ₂ NC(O)CH ₃ + HOOH + H ₂ O
149	vw	vw	w	(HC(NO)H)O ₂ CH(CH ₃) (from a.2'/a.3')
150	w	w	vw	2 {acetonitrile + H ₂ O} + HNO
152	vw	vw	m	O ₂ N(OH)CHCH(CH ₃)NO ₂ (from a.3'/a.8' and c.3'/c.8')
168			m	(NO ₂)(OH)CHCH(CH ₃)(OH) (from a.6'/c.6')
181-183 ²⁾			m	RC(O)H (from c.6')
195-197 ²⁾			m	RC(O)CH ₃ (from a.6')
208-210			w	5 {HOOH + H ₂ O} or {H ₂ CO + 2O ₂ NC(O)CH ₃ }
217-218	m	m	vw	((NO ₂)(CH ₃)C=C(H)O) ₂ CH ₂ (from c) (BNPeF)
219	m	w	vw	PBNA (anti-oxidant)
225 ²⁾			w	RCH ₂ OC(NO)H (from c.2')
230	w	w	vw	((NO ₂)(CH ₃)C=C(H)O) ₂ CH(CH ₃) radical (from a) (BNPeA)
231 ³⁾	vw	w		R'CH ₂ OC(O)H (from a.2) + H ₂ O
239 ²⁾			w	RCH(CH ₃)OC(NO)H (from a.2')
244		w		RCH(CH ₃)OC(O)H (from a.2) + H ₂ O
252-254 ²⁾			w	RCH ₂ OC(NO)H (from c.2') + H ₂ O
256-260	w	w		((O ₂ N)(CH ₃)C=C(H)O) ₂ CH ₂ (from c) + 2H ₂ O
266-268 ²⁾			vw	RCH(CH ₃)OC(NO)H (from a.2') + H ₂ O
270-274	w	w	vw	((O ₂ N)(CH ₃)C=C(H)O) ₂ CH(CH ₃) (from a) + 2H ₂ O
293	vw	vw		{3HONO+2HNO+5H ₂ O}
301 ²⁾			w	RCH(CH ₃)OC(NO)H (from a.2') + HNO ₃
303 ³⁾		w		R'CH(CH ₃)OC(O)H (from a.2) + HNO ₃ + H ₂ O
317	m	m	w	BDNPF
322.5	vs	vs	m	BDNPA/F cluster

¹⁾: vw – very weak; w – weak; m – moderate; s – strong; vs – very strong.

²⁾ R = (O₂N)(OH)(CH₃)-CH(NO)-O- (Mw = 149).

³⁾ R' = (O₂N)(NO)(CH₃)-CH(OH)-O- (Mw = 149).

Table 4. Summary of main chemical shifts in ¹H NMR spectra of pristine, N₂ aged, and Air aged NPs at 70 °C for 24 months¹⁾.

Species	Chemical shifts (ppm)		
	NP	N2-aged NP	Air-aged NP
-HC=CH-			5.22 – 5.30 vw
(H(O)CO) ₂ CH ₂ (degraded from BDNPF)			5.2 w
(H(O)CO) ₂ CH(CH ₃) (degraded from BDNPA)			4.95 w
>CH-OH			4.87 s
>CH-OH	4.86 m	4.86 s	
-CH ₂ - (BDNPF)	4.78 s	4.78 s	4.78 s
-CH ₂ - (BDNPA)	4.68, 4.75 w, vs	4.68, 4.75 w, vs	4.68, 4.75 vw, s
(H(O)CO) ₂ -CH(CH ₃) (degraded from BDNPA)	4.46 vw	4.46 vw	4.46 w
R-OH	4.36 vw	4.36 m	4.36 s
(NO ₂) ₂ C-CH ₃	4.28, 4.32 vs, vs	4.28, 4.32 vs, vs	4.28, 4.32 s, m
>C(CH ₃)-R (BDNPA)	4.21, 4.24 vs, vs	4.21, 4.24 vs, vs	4.21, 4.24 m, m
>CH-OH	3.79 w	3.79 w	3.79 vw
HON=C(NO ₂)-CH ₃ (oxime)		2.64 vw	
-CH ₂ -	2.2 vs	2.2 vs	2.2 vs
(H(O)CO) ₂ CH(CH ₃) or R-OH (degraded from BDNPA)			2.15 w
R''-CH-R'''			2.09 s, 2.07 m
>C(H)CH ₃ (BDNPA)	1.58 m	1.58 m	1.58 m
-C(NO ₂) ₂ CH ₃ group	1.2 – 1.4 vs	1.2 – 1.4 vs	1.2 – 1.4 s

¹⁾: vw – very weak; w – weak; m – moderate; s – strong; vs – very strong.