Investigation into the Decomposition Pathways of an Acetal-Based Plasticizer

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ABSTRACT: Until now, it has been assumed that the primary decomposition pathway for the liquid plasticizer bis(2,2-dinitropropyl)acetal and bis(2,2-dinitropropyl)formal (BDNPA/F) was nitrous acid elimination (NAE). An ultrahigh-performance liquid chromatography (UHPLC) coupled to quadrupole time-of-flight mass spectrometry (QTOF) methodology was developed to discover and identify the degradation products of BDNPA/F. No evidence of NAE was found. However, two other degradation pathways were found: (1) hydrolysis of the acetal/formal functional group and (2) radical-based homolysis of the C–N bond, followed by hydrogen atom abstraction. Hydrolysis of BDNPA/F proceeds by the formation of 2,2-dinitropropanol (DNPOH) and 2,2-dinitropropyl hemiacetal/hemiformal, which further decompose into DNPOH and ethanal/methanal, respectively. Hydrolysis is the dominant decomposition pathway in all samples; however, at higher temperatures, C–N homolysis becomes more significant. Also, the solid PBX 9501 has different ratios of decomposition products than the liquid BDNPA/F due to the slower rate of diffusion through solids than liquids.

1. INTRODUCTION

Plastics are found in a variety of applications in modern society, including packaging, household appliances, and electronics, due to their unique physical, mechanical, and electrical properties.1−4 However, there are often unwanted attributes of plastics such as high rigidity that make post synthetic processing of the plastic difficult. To tune the physical properties of a polymer, a plasticizer is often added to improve the rheology of the resulting plastic composite.4−9 However, plasticizers have issues of their own, such as their loss due to evaporation, migration, and/or chemical decomposition, resulting in the degradation of the polymer composite.5−14 It is also possible that plasticizer decomposition products may react with the polymer, causing its chemical decomposition, further degrading the plastic composite.15,16

Polymer-bonded explosives (PBXs) are plastic composites that are used for both civilian and military applications due to their ability to be easily cut and molded for applications such as mining and demolition.17 The polymer and plasticizer binder systems also reduce the vulnerability of the explosive to accidental explosion from insults such as impact, friction, and electrical discharge compared to the raw explosive. One of the most widely used PBXs is PBX 9501, which is composed of 94.9 wt % of the explosive 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 2.5 wt % of a polymeric binder (Pearlstick 5703, formally known as Estane 5703), 0.1 wt % of a radical stabilizer (Irganox 1010), and 2.5 wt % of a plasticizer.17 The plasticizer is a 1:1 eutectic liquid mixture of bis(2,2-dinitropropyl) acetal (1) and bis(2,2-dinitropropyl) formal (2), referred to as BDNPA/F (Figure 1). There are numerous impurities in each component of PBX 9501, including BDNPA/F, that are present from the manufacturing process, some of which have been identified.18 Although decomposition of PBX 9501 and its constituents have been studied in a wide variety of environments,15,19−23 minimal work has been performed evaluating the decomposition of the BDNPA/F. Headspace analysis of aged BDNPA/F at temperatures up to 64 °C revealed the presence of nitrous oxide (N₂O) and nitric oxide (NO), which the authors attributed to the decomposition of nitrous acid (HNO₂).19,24 Based on the resulting data, the authors performed theoretical modeling, predicting that nitrous acid elimination (NAE) from the model compound (3) would yield the 2-nitrovinyl ether (4) and HNO₂.
Scheme 1. Theoretical Calculations of a Model Compound for BDNPA/F for NAE Elimination (Top) and the Formation of Nitrovinyl Ether Compounds for BDNPA/F after NAE Elimination (Bottom)

as the first intermediates in a series of decomposition steps (Scheme 1). However, 4 and HNO$_2$ are calculated to be 3 kcal mol$^{-1}$ higher in energy than 3, with a very high activation energy of 42 kcal mol$^{-1}$, using the B3LYP hybrid density functional and 6-31G(d,p) basis set. Additionally, there is no accepted reaction mechanism under which this intramolecular elimination would proceed.

To experimentally probe the NAE decomposition pathway, accelerated aging studies were performed on BDNPA/F and PBX 9501 at temperatures ranging from 38 to 64 °C for 0 to 60 months. Since the rate of decomposition of a material can be exponentially increased with increasing temperature, accelerated aging studies are useful to determine the long-term stability of a material. Direct injection mass spectrometry (DIMS), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC) have all been used to evaluate BDNPA/F decomposition; however, definitive evidence of the NAE decomposition pathway does not exist.

2. RESULTS AND DISCUSSION

In an effort to provide more evidence for the nitrous acid elimination (NAE) pathway, similarly aged samples of BDNPA/F and PBX 9501 were evaluated using ultrahigh-performance liquid chromatography (UHPLC) coupled to quadrupole time-of-flight mass spectrometry (QTOF) to elicit the degradation products. With UHPLC’s ability to achieve excellent separation of chemically similar compounds and QTOF’s ability to identify unknowns combined with high sensitivity on the part per billion level, we surmised that these techniques coupled would be able to clearly identify the BDNPA/F degradation in samples of aged BDNPA/F as well as in aged PBX 9501. Figure 2 shows the total ion current (TIC) (the sum of all mass channels) for the analyses of a sample of aged BDNPA/F and a sample of aged PBX 9501 (see Figure S1 for unaged samples of BDNPA/F and PBX 9501). The complexity of these samples is noted with numerous overlapping peaks, making it a difficult task to visually identify every compound present. The aged sample of BDNPA/F has been stored at ambient temperature for ~50 years, while the PBX 9501 sample was aged at 70 °C for 18 months. For the aged PBX 9501 sample, 1 significantly degraded and 2 is still largely present, while a minimal decomposition of 1 and 2 was observed in the aged BDNPA/F samples.

A targeted approach can be implemented to evaluate the presence of compounds with a high degree of selectivity and fidelity because high-resolution mass spectrometry (i.e., QTOF) was used, which can further be evaluated with tandem mass spectrometry (MS/MS). We were unable to find QTOF evidence supporting the formation of NAE products (Scheme 1). While a peak at 338.0836 does exist, implying the presence of 5, evaluation of the chromatographic data indicates that this is due to in-source fragmentation of 1 and not evidence of compound 5 (Figure S2). Directly detecting HNO$_2$ may be difficult; however, detection of NAE byproducts is much more viable due to their high $E_a$ (~30 kcal mol$^{-1}$) for decomposition. 2-nitrovinyl ethers similar to compounds 5 and 6 have been shown to be stable materials; therefore, their absence in BDNPA/F samples discussed herein and in prior work is further evidence that NAE does not occur from BDNPA/F. Also, it should be noted that no 2-nitrovinyl ether has ever been synthesized via NAE. Additionally, a total of 24 decomposition products were previously proposed as resulting from NAE (Scheme 1). Not one of these compounds was discovered in any of the aged samples of BDNPA/F or PBX 9501 (Table S1).
Molecular elimination typically proceeds through unimolecular (E1) or bimolecular (E2) mechanisms; however, both of these are unfavorable in the given conditions. For example, the carbocation generated in the rate-determining step of the E1 mechanism would be highly destabilized by the α-NO₂ group, whereas the E2 mechanism requires basic media, but the environment of both BDNPA/F and PBX 9501 is slightly acidic. Therefore, we performed a literature search to unearth any references where NAE occurred under conditions similar to those of the aged BDNPA/F or PBX 9501 samples; however, we were unable to find any reports. It should be noted that NAE has been achieved in other materials with base, at high temperatures, or via C−N photodissociation but not under the relatively mild conditions of the BDNPA/F and PBX 9501 aging studies. Given the lack of experimental evidence and organic mechanistic theory, the formation of NAE probably does not occur.

In an attempt to find statistically significant chemical compounds to elucidate the major decomposition products, Fisher ratio (F-ratio) analysis was applied, comparing the unaged and aged samples of BDNPA/F, as well as unaged and aged samples of PBX 9501. F-ratio analyses revealed numerous statistically significant chemical differences between the unaged BDNPA/F and aged BDNPA/F samples. One of the most significant F-ratio hits in both the aged BDNPA/F and aged PBX 9501 samples was at a retention time (tᵣ) of 3.16 min, with the most significant mass channel being 119.0098. This mass channel was assigned the tentative formula of C₇H₇N₂O₄⁺, which implied the identity as the 1,1-dinitroethane fragment (DNE−). Also, this mass is observed throughout the chromatogram (Figure S4), suggesting that the DNE− fragment has relatively high stability. We initially predicted the identity of this degradation product as 1,1-dinitroethane (DNE). However, to our surprise, UHPLC-QTOF analysis of a DNE standard showed that DNE elutes at a different retention time, supporting that DNE is not present in the aged samples.

We hypothesized that 1 and 2 may undergo hydrolysis, yielding 2,2-dinitropropan-1-ol (7) as a decomposition product. Then, upon ionization in the negative mode of the MS, 7 undergoes a retro-Henry reaction, eliminating methanal, resulting in the DNE− anion fragment (Figure S5). This is supported by a peak at 209.0410 m/z (Figure S6), which corresponds to the adduct of 7 plus acetate. To probe this, a standard of 7 was synthesized and analyzed, eluting at the same retention time as the most significant hit from F-ratio analysis (3.16 min), with the same MS and MS/MS profile, confirming the presence of 7 in the aged BDNPA/F and aged PBX 9501 samples (Figure S7). The most likely way for 7 to form is through the hydrolysis of BDNPA/F, which would yield two equivalents of 7 and one equivalent of ethanal or methanal, for 1 and 2, respectively (Scheme 2). However, hydrolysis previously had been ruled out when hydrolytic decomposition experiments of BDNPA/F failed. To further confirm the decomposition of BDNPA/F, benchtop experiments were performed. A solution of BDNPA/F (60 mM) in a 1:1 mixture of water and tetrahydrofuran (THF) with catalytic hydrochloric acid (HCl) resulted in significant hydrolysis of 1 and minor hydrolysis of 2 after 24 h at room temperature, as determined by NMR and UHPLC-QTOF (Figure S8). Similarly to the thermally aged BDNPA/F and aged PBX 9501 samples, 1 decomposed significantly more than 2. From a mechanistic standpoint, it is expected that the electron donation from the methyl group in 1 would inductively stabilize the transient oxonium ion (8) upon protonation of the acetal more so than the hydrogen atom in the formal group of 2. Although BDNPA/F was hydrolyzed in a laboratory setting, hydrolysis in aged samples requires the presence of water and catalytic acid. Examination of the certificate of analysis of unaged BDNPA/F revealed that it contains a maximum allowed amount of 700 ppm of water and 700 ppm acid. Therefore, hydrolysis of BDNPA/F is possible under the given conditions.

Hydrolitic decomposition of BDNPA/F in aged PBX 9501 is similar to that of aged BDNPA/F; however, there are some differences between their chromatograms, implying that hydrolysis occurs at different rates in these materials. Peaks at 5.61 and 5.25 min with mass channels 253.0672 and 239.0515 were found in aged PBX 9501 using the F-ratio methodology but were not found in the aged BDNPA/F samples. These masses correspond well with the masses of 2,2-dinitropropyl hemiacetal (9) and 2,2-dinitropropyl hemiformal (10). Further confirmation was obtained via MS/MS (Figure S9). Hemiacetals and hemiformals are formed as intermediates both during the synthesis and hydrolysis of acetals and formals, including BDNPA/F; however, in solution, these intermediates are quickly quenched, making their isolation difficult, if not impossible. However, PBX 9501 is a solid, and diffusion is in a solid than in a liquid, making the presence of the hemiacetal and hemiformal in the aged PBX 9501 samples possible.

Although hydrolysis appears to be the major decomposition pathway of BDNPA/F, there are several other significant decomposition products discovered via the F-ratio analysis. The weakest bond in BDNPA/F has been calculated to be the C−N bond, with an activation energy of 42 kcal mol⁻¹, using the B3LYP/6-31G(d,p) level of theory, so we hypothesized that C−N bond homolysis, forming the carbon-based radical (11) and NO₂⁺, could be a possible secondary path for BDNPA/F decomposition (Scheme 3). However, these types of radicals are not stable and will react usually by dimerization or hydrogen...
atom abstraction.\textsuperscript{35} Since the activation energy of C–N bond homolysis is high in energy, the formation and presence of 11 at near-ambient temperatures should be rare, making dimerization unlikely. Therefore, the most likely decomposition product from C–N bond homolysis would be (2,2-dinitropropyl)-(2-nitropropyl) acetal (12) via hydrogen atom abstraction. In numerous aging studies, NO has been measured in the headspace of aged BDNPA/F and PBX 9501, which may be from the hydrolysis of NO\textsubscript{2}\textsuperscript{+}, forming nitric acid (HNO\textsubscript{3}) and NO, further providing evidence for radical-based decomposition.\textsuperscript{19,36}

In both aged BDNPA/F and PBX 9501 samples, a decomposition product elutes at 6.28 min and has a m/z of 340.0992, corresponding well with 12, providing evidence for a radical-based decomposition pathway. This was further confirmed with MS/MS (Figure S10). Moreover, the concentration of the radical-based decomposition product is strongly correlated with the temperature of the samples; higher temperatures resulted in higher concentrations of 12.

3. CONCLUSIONS

In closing, we have provided experimental evidence using UHPLC-QTOF and MS/MS that does not support the decomposition of BDNPA/F via NAE. However, we have demonstrated that BDNPA/F decomposes through two different degradation pathways: (1) acid-catalyzed hydrolysis of the acetal/formal functional group and (2) radical-based homolysis of the C–N bond. Hydrolysis is the dominant decomposition pathway at all temperatures and aging times. However, at higher temperatures, C–N homolysis becomes more significant. Observation of the hemiacetals 9 and 10 in aged PBX 9501 is likely due to its solid state, which results in slow diffusion of the acid catalyst through the material, and therefore slows 9 and 10’s decomposition. Although we determined the identity of four BDNPA/F decomposition products, several more unknown compounds still exist in these samples that have not yet been identified. The synthesis of new standards is an ongoing process, and with these in hand, we hope to identify other BDNPA/F decomposition products and their effect on their local environment. Finally, it should be noted that decomposition processes of organic compounds are no different than other organic reactions; they typically follow known reaction mechanisms that can be predicted based on the conditions to which the material is subjected. NAE had been the only theory of BDNPA/F decomposition for more than 15 years; however, experimental evidence for NAE is weak, and no reasonable NAE mechanism exists for BDNPA/F or other gen-dinitroalkanes under mild conditions. On the contrary, the acetal hydrolysis and C–N homolysis reactions presented herein follow known and predictable mechanisms, and these processes are supported by UHPLC, QTOF, MS/MS, and NMR techniques.

4. EXPERIMENTAL SECTION

4.1. Aging of BDNPA/F. Two samples of naturally aged BDNPA/F were evaluated. Sample 1 was manufactured in ~1966 at the Naval Propellant Plant (Indian Head, Maryland) via the ter Meer process. The history of this sample is unknown.

4.2. Aging of PBX 9501. For the first aging study, 400 g of bulk PBX 9501 molding powder was dried at 60 °C for 4 h under vacuum. It was removed and placed in a desiccant until pressing. The dried bulk PBX 9501 powder was pressed into seventy cylindrical pellets of dimensions 12.7 mm in diameter by 12.7 mm in length. After each pellet was pressed, cooled, weighed, measured, and labeled, it was placed back into the desiccant box. Prior to being sealed inside the test vessels, the PBX 9501 pellets were exposed to four different aging conditions: (1) baked in vacuum oven for 24 h at 60 °C and then placed directly into vessels within a dry nitrogen glove box, referred to as very dry (VD), (2) baked in vacuum oven for 24 h at 60 °C and humidified in 15% RH at 20 °C for 5 days referred to as dry (D), (3) baked in vacuum oven for 24 h at 60 °C and humidified for 7 days in 60% RH chamber at 20 °C referred to as wet (W), and (4) baked in vacuum oven for 24 h at 60 °C and humidified for 7 days in 95% RH chamber referred to as very wet (VVW). For each aging condition, samples were aged at 60 and 80 °C for 0, 12, and 24 months. A total of 6 samples were analyzed via UHPLC-QTOF from this aging study: VD aged at 60 °C for 12 and 18 months, W aged at 60 °C for 12 and 19 months, and VW aged at 60 °C for 12 and 18 months.

For the second aging study, bulk PBX 9501 molding powder was dried at 60 °C for 4 h under vacuum and then uniaxially die-pressed into a cylinder, approximately 4.6 inches long by 3-inches diameter, and placed into stainless steel canisters. The canisters were then back-filled with dry nitrogen and were aged at ambient, 50, and 60 and 80 °C for 0, 6, 16, and 24 months. Five samples were analyzed via UHPLC-QTOF: 16 and 24 months aged at 50 °C and 6, 16, and 24 months aged at 60 °C.

4.3. Chemicals and Sample Preparation. Acetonitrile (HPLC Plus) and dichloroethane (HPLC Plus) were obtained from Sigma-Aldrich. Ammonium acetate was obtained from VWR and was diluted to 10 mM using deionized water (HPLC Plus) obtained from Sigma-Aldrich. The PBX 9501 samples were prepared by dissolving ~150 mg in ~3.75 mL of dichloroethane. The solution was then filtered through a 25 mm diameter Whatman Parafilm 25TF filter (GE Healthcare, Marlborough, MA) containing a 0.45 μm PTFE membrane in a polypropylene housing. The BDNPA/F samples [including those from the hydrolysis experiments (see Section S1.5)] were prepared by dissolving ~2 mg in 2 mL of dichloroethane.

4.4. Instrumental Conditions and Data Analysis. The sample was analyzed via a Shimadzu UHPLC system (Shimadzu, Japan) coupled to a SCIEX X500R QTOF (SCIEX, Framingham, MA). The UHPLC system consisted of two binary pumps (LC30-AD), degasser (DGU-30A), column oven (CTO-30A), autosampler (SIL-30A), and UV–Vis detector (SPD-30A). The UV–Vis detector collected wavelengths from 200 to 700 nm with a slit width of 8 nm at a rate of 6.25 Hz. The QTOF system was equipped with an electrospray ionization (ESI) source that was operated in negative mode. The ESI conditions were as follows: ionspray voltage 5.5 kV, temperature 325 °C, ion source gas #1 3.447 kPa, ion source gas #2 379.2 kPa, declustering potential 50 V, and CAD gas 3 a.u. TOFMS spectra 400–1500 m/z were collected at an accumulation time of 0.25 seconds and a collision energy of ~10 V (minimum value).

Separations were carried out on a Phenomenex (Torrence, CA) Kinetex C\textsubscript{18} column (100 mm × 3.0 mm, 1.7 μm). The injection volume was 1 μL, and the column oven was set to 40
°C with a flow rate of 0.8 mL/min. The mobile phase composition consisted of 10 mM ammonium acetate (A) and acetonitrile (B). The gradient program was: 0 min, isocratic at 0% B; 0–10 min, linear gradient to 100% B; 10–15 min isocratic at 100% B. The UHPLC-UV/Vis-QTOF system was controlled by SCIEX OS 1.6.1 software, and the subsequent data processing was performed using this same software. The relevant data was exported as a text file and then imported into Matlab 2019a for visualization.

For the targeted study of previously proposed BDNPA/F decomposition products, the following thresholds were applied: a peak height of 200 counts, a signal-to-noise ratio (S/N) of 30, m/z error of 0.01 Da, and a peak width <6 s.

The 1H and 13C{1H} NMR spectra were recorded at ambient temperature using a Bruker Ascend 400 MHz spectrometer. Chemical shifts (δ) were referenced to the residual solvent signal. FTIR spectra were measured using a Thermo-Nicolet iS5 FTIR spectrophotometer using OMNIC software.

4.5. Synthesis of Standards. Standards of 1,1-dinitroethane, 2,2-dinitropropan-1-ol, were synthesized using literature procedures.27

4.6. Hydrolysis Experiments. BDNPA/F (0.200 g) was dissolved in a 1:1 mixture of THF/water (10 mL). This solution was cooled with an ice bath to 5 °C, and hydrogen chloride was slowly bubbled through for 1 min, ensuring that the temperature never rose above 20 °C. The resulting solution was sealed with a stopper, and the resulting reaction mixture was stirred for 24 h at 23 °C. The solvent was removed under reduced pressure, resulting in a pale brown oil. An aliquot of this oil was taken up in dimethyl sulfoxide (DMSO), and the 1H, 13C{1H}, and infrared spectra were collected and compared to standards of BDNPA/F, 2,2-dinitropropan-1-ol, and 1,1-dinitroethane. This reaction was run six times, and hydrolysis products were detected every time.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03494.

UHPLC-QTOF analyses of unaged BDNPA/F and PBX (Figure S1); in-source fragmentation of BDNPA (Figure S2); molecular structures of previously proposed NAE products (Figure S3); analytical ion chromatogram for mass channel 119 m/z (Figure S4); retro-Henry reaction of 2,2-dinitropropan-1-ol (Figure S5); mass spectrum from location of most significant F-ratio hit (Figure S6); comparison of 2,2-dinitropropan-1-ol standard to aged BDNPA/F (Figure S7); NMR and UHPLC-QTOF results for benchtop hydrolysis experiments (Figure S8); MS/MS spectra of 2,2-dinitropropyl hemiacetal and hemiformal (Figure S9); MS/MS Spectra of (2,2-dinitropropyl)-(2-dinitropropyl) acetal (Figure S10); and targeted analysis results of the previously proposed NAE products (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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