**ABSTRACT:** In the eutectic mixture of bis(2,2-dinitropropyl) acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF), also known as nitroplasticizer (NP), n-phenyl-β-naphthylamine (PBNA), an antioxidant, is used to improve the long-term storage of NP. PBNA scavenges nitrogen oxides (e.g., NOₓ radicals) that are evolved from NP decomposition, hence slowing down the degradation of NP. Yet, little is known about the associated chemical reaction between NP and PBNA. Herein, using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF), we thoroughly characterize nitrated PBNA derivatives with up to five NO₂ moieties in terms of retention time, mass verification, fragmentation pattern, and correlation with NP degradation. The propagation of PBNA nitration is found to depend on the temperature and acidity of the NP system and can be utilized as an indirect, yet reliable, means of determining the extent of NP degradation. At low temperatures (<55 °C), we find that the scavenging efficiency of PBNA is nullified when three NO₂ moieties are added to PBNA. Hence, the dinitro derivative can be used as a reliable indicator for the onset of hydrolytic NP degradation. At elevated temperatures (≥55 °C) and especially in the dry environment, the trace amount of water in the condensed NP (<700 ppm) is essentially removed, which accelerates the production of reactive species (e.g., HONO, HNO₃, and NOₓ). In return, the increased acidity due to HNO₃ formation catalyzes the hydrolysis of NP and PBNA nitro derivatives into 2,2-dinitropropanol (DNPOH) and nitrophenol/dinitrophenol, respectively.

**INTRODUCTION**

In some energetic materials, the eutectic mixture of bis-2,2-dinitropropyl acetal/formal (BDNPA/F), commonly known as nitroplasticizer (NP), is used to improve shock absorptivity and manufacturability. However, NP inevitably decomposes, which releases reactive species, such as H₂O, NO, NO₂, HONO, and later HNO₃. These species can trigger the catalytic deterioration of both NP and polymeric binders, which directly impacts the properties of these materials. To counter this effect, approximately 0.1 w/w% of n-phenyl-β-naphthylamine (PBNA) is added to NP after production. PBNA is an aromatic amine antioxidant that extends the service life of NP by scavenging the radical species generated from NP decomposition (i.e., NOₓ). In the presence of such reactive species, amine antioxidants can undergo successive nitration (C-NO₂) and/or nitrosation (N-NO), as shown in Scheme 1. However, no conclusion can be made with respect to the reaction mechanism between PBNA and species of nitrogen oxides (HONO, HNO₃, and NOₓ) because the transition states and energy barriers are still in question. However, the reactant at play is likely starting with HONO since NO elimination (+56 kcal mol⁻¹) is more energetically favorable than C-NO₂ homolysis (+66 kcal mol⁻¹) as the first step of NP decomposition. Previous studies on NP aging mostly focused on the products of NP decomposition. Hence, little is known about the activities of PBNA. Herein, leveraging the high spectral resolution and superior mass accuracy of liquid chromatography quadrupole time-of-flight (LC-QTOF) mass spectrometry, for the first time, we conduct a detailed investigation to characterize PBNA derivatives and thus analyze NP decomposition through changes induced in the signal response of PBNA and its derivatives. This study is supported by quantum chemistry simulations.

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Scheme 1. Proposed Primary Consumption Pathway of PBNA by NP Degradation Products (e.g., NO$_2$)

Reference Chemicals. BDNPA and BDNPF reference standards were provided by the Pantex Plant. Deuterated BDNPA-d8, BDNPF-d6, and 2,2-dinitropropanol (DNPOH) were synthesized by David Langlois at Los Alamos National Laboratory.$^{11,22}$ PBNA standard was purchased from Sigma-Aldrich. n-(2,4-Dinitrophenyl) naphthalen-2-amine, a structural isomer of dinitro-PBNA, was purchased from Chempsons (Monmouth Junction, NJ). All chemicals were used as received and/or as synthesized.

Sample and Calibration Preparation. A detailed description of how the aged NP samples were obtained is given in previous works.$^{20,21,23,24}$ Aged NP samples from 0 to 44 months at various temperatures (38, 45, 55, and 64 °C) and headspace environments (W = deionized water, A = air) were prepared as concentrated stock solutions by dissolving 3.0 mg of acetoneitrile (ACN). Prior to LC-QTOF analysis, samples were further diluted by mixing 980 μL of stock solution with 20 μL of aliquot of the internal standards (ISTD). Finally, a method blank of ACN with the added ISTD was utilized as an instrumental control.

The deuterated BDNPA/F was prepared as ISTD and utilized to monitor the abnormality between injections. Nine calibration standards of BDNPA/F, DNPOH, PBNA, and n-(2,4-dinitrophenyl) naphthalen-2-amine were prepared. Based on literature guidelines,$^{25,26}$ the acceptable tolerance of reproducibility in retention time ($T_R$) was adopted at ±0.100 min and evaluated through the known compounds. The resultant $T_R$ drifts are measured at ±0.012 min in ISTDs and ±0.050 min in the DNPOH and BDNPA/F (Tables S1 and S2).

LC-QTOF Parameters. The electrospray ionization (ESI) and information-dependent acquisition (IDA) parameters in positive and negative modes are defined in Table 1. Attributes of precursor ions (e.g., isotopic masses and relative abundances) were extracted from spectra in the first stage of the tandem mass spectrometer (MS$^2$). Fragment ion spectra (MS$^3$) were generated using collisionally activated dissociation (CAD) techniques at low collision energy (CE). The frequency of external calibration was set to every two injections.

Chromatographic separation was achieved on a reversed-phase HPLC column: Phenomenex Kinetex 2.6 μm C8 100 Å, 150 × 2.1 mm. The aqueous and organic mobile phases were 13 mM ammonium acetate at pH 6.0 in water and in 95:5 (v/v) ACN/methanol, respectively. The autosampler was operated at room temperature. The column oven temperature was held at 40 °C. The sample injection volumes were set to 2 μL in ESI− and 4 μL in ESI+. A rinse method was employed with an injection of 10 μL of acetone after every sample injection to prevent carry-over contamination from the needle.$^{27}$ The detailed HPLC programs are given in Table 2.

Computational Details. Electronic structure calculations were performed using the density functional theory (DFT) method with the BP86 functional,$^{28,29}$ the Def2-TZVPP basis set,$^{29}$ the Def2/J auxiliary functions,$^{30}$ and the D3BJ van der Waals correction.$^{31,32}$ All structures were optimized in the gas phase with tight settings and followed by a frequency calculation to ensure that the optimized geometries correspond to minima on the potential energy surface (i.e., no imaginary frequency). Finally, the optimized geometries were used to compute the thermodynamic properties (i.e., Helmholtz free energies) at various temperatures and with solvent effects (e.g., THF and methanol). All simulations were performed using the quantum chemistry package ORCA 5.0.1.$^{33}$

RESULTS AND DISCUSSION

Characterization Overview. Rigorous criteria from the analytical guidance of high-resolution mass spectrometry (e.g., SANTE)$^{25,26}$ were incorporated to improve diagnostic fidelity in data interpretation, including $T_R$, mass accuracy, isotopic pattern, mode of ionization (ESI−/ESI+), and fragmentation rationalization. Through a comprehensive elucidation process, the identification of various PBNA derivatives was achieved unambiguously. The peak intensities of PBNA derivatives, hydroxylized phenols, and DNPOH were examined as functions of aging time. Due to in-source fragmentation, $m/z$ 119.0098 was used as the primary identifier for DNPOH$^{22}$ and its

Table 1. TOF MS$^3$/MS$^2$ Parameters (Sciex X500R)

| source parameters | ESI− | ESI+ |
|-------------------|------|------|
| source gases 1 and 2 (psi) | 50 | 50 |
| curtain gas (psi) | 30 | 30 |
| source temperature (°C) | 275 | 250 |
| spray voltage (V) | −4500 | 5500 |
| CAD gas (psi) | 9 | 9 |
| scan cycle | 1759 | 1759 |

| IDA parameters | IDA, MS$^3$/MS$^2$ (−) | IDA, MS$^3$/MS$^2$ (+) |
|----------------|----------------|----------------|
| $m/z$ range | 80–650/25–580 | 80–650/25–580 |
| declustering potential (V) | −80 ± 5/−50 ± 5 | 80 ± 5/70 ± 5 |
| CE (V) | −10/−20 ± 15 | 10/23 ± 15 |
| accumulation time (sec) | 0.1/0.05 | 0.1/0.05 |
| IDA intensity threshold (cps) | 500 | 500 |
identity was verified through the $T_{3b}$ and fragmentation pattern of the DNP-OH reference standard (2.886 min; Table S1). In collision-induced fragmentations, the competition between kinetic and thermodynamic factors can obscure the elucidation process. Hence, low CE was utilized to minimize the potential fragmentation of the aromatic compounds and in-soruce fragmentations. Unlike aliphatic compounds, the fragmentation of aromatic compounds is more energy-demanding due to the structural stability associated with $\pi$-bonding. A notable distinction of MS$^2$ fragmentation patterns is observed between BDNPA/F and PBNA derivatives (Figures S1–S11). Especially in the MS$^2$ spectra obtained from ESI$^-$ mode, the electronegativity of NO$_2$ groups enhances the signal intensities of PBNA derivatives. Hence, their characteristic ions or stable fragments were easily identified and distinguished from the aliphatic compounds. Based on our assessment of signals at 1 ppb, $n$-(2,4-dinitrophenyl) naphthen-2-amine was detected at 3200 cps$^-$ in ESI$^-$ and only 200 cps$^-$ in ESI+. Due to the lack of NO$_2$ substituents, PBNA was not detected in ESI$^-$ and only detected in ESI+ at 3100 cps$^+$. On the other hand, the protonated adducts ([M + H]$^+$) of tetra- and penta-nitro-PBNA derivatives cannot be detected in the ESI+ mode.

**Identification of 309 Da as Dinitro-PBNA.** Dinitro-PBNA was our prime identification through MS$^2$ interpretation. It first came across as a matching candidate for $m/z$ 308.0672 in the SCIEX OS formula finder (mass tolerance <5 ppm). While common low mass fragments of BDNPA/F such as $m/z$ 131.0096, 119.0098, and 102.0195 (Figures S1 and S2) are absent, strong precursor signals and losses of NO, NO$_2$, and OH radicals are detected in the MS$^2$ spectra of dinitro-PBNA (Figure 1). These small radicals are often signatures of the fragmentation behaviors in nitroaromatic metabolites of explosives. Typically, MS fragmentation is dictated by the even-electron rule, meaning that the formation of even-electron product ions (e.g., M$^+$ or M$^-$) and neutral loss of molecules are energetically favored instead of giving two radicals (e.g., odd-electron product ions, M$^{**}$ or M$^{**}$, and fragment radicals). However, the aromatic compounds are often exceptions to this rule, particularly nitroaromatic compounds, and therefore radical losses of NO, NO$_2$, and OH are common. Furthermore, the losses of NO and the preceding decarbonylation step (e.g., cleavage of the C–CO bond) in the fragmentation reaction are likely associated with the rearrangement of C–NO$_2$ into C–O–NO bonding. Based on the theoretical masses from our proposed fragmentation pathway in Figure 1, the observed fragment masses are in good agreement with mass defects of less than 5 ppm in ESI$^-$ and less than 10 ppm in ESI$^+$ (Table S3), except for the fragments below the mass calibration range (e.g., NO$_2^-$). Using a structural isomer as a reference, dinitro-PBNA was further verified at higher fragmentation order by applying a stronger collision energy of ~30 V (Figure S8). Through rationalization of fragment ions, mass verification, and reference standard, the identity of $m/z$ 308.0672 as dinitro-PBNA is experimentally confirmed.

**Identification of Other PBNA Derivatives.** Based on the finding of dinitro-PBNA, a similar strategy was used to identify the four remaining derivatives: fragmentation behavior, isotopic profile, retention time, and depletion/formation analysis of relative peak intensities.

**Fragmentation Behavior.** MS$^2$ spectra of the ESI$^-$ mode were selected for the fragmentation analyses of the remaining PBNA derivatives to avoid low signal intensity and poor fragment mass accuracy. In the fragmentation reactions of other nitro derivatives, similar losses of NO, NO$_2$, OH, and CO were observed, as shown in Figure 2. However, new leaving groups, including HNO$_3$, CO$_2$, and HNO were found in derivatives with three or more NO$_2$ moieties (e.g., $m/z$ 353.0527, 398.0375, and 443.0220). We reason the following: (1) The elimination of HNO$_3$ (or NO + OH) could be the result of a weakened aromatic C–H bond and intramolecular transfer of hydrogen onto the NO$_2$ substituent. (2) The neutral loss of CO$_2$ could be a consequence of structural rearrangement induced by the fragmentation reaction. (3) Because NO$_2^-$ is a conjugate base that has a net negative charge, the occurrence of the NO$_3$ substituent in an electron-rich compound is very unlikely. Therefore, HNO$_3$ elimination most likely occurs from the combined loss of two radicals: NO$_2$ and OH. When PBNA undergoes serial addition of strong electron-withdrawing groups like NO$_2$, the resonance delocalization of electrons is disrupted, which leads to structural instability and likely promotes structural rearrangement and early cleavage of aromatic carbons.

Among all fragment ions found in tri-, tetra-, and penta-nitro-PBNA derivatives, the strongest signals of the fragment peaks are observed at $m/z$ 277.0620, 322.0465, and 367.0283, respectively (Figure 2, highlighted in blue). This indicates that the most stable ions continue to uphold the aromatic integrity even in highly nitrated products, and expulsion of NO$_2$ and NO is preferred. In less stable and lower mass fragments (e.g., observed $m/z$ 191.0614, 220.0638, and 260.0460), only cleavage of hydrocarbon units (e.g., –CH$_3$, –CH$_2$, etc.) was
observed in m/z 191.0614, which suggests these carbon atoms are aromatic and not aliphatic.

**Analysis of Isotopic Profile.** Unless they are isomers, the isotopic profile is unique to each compound. The isotopic abundance of atoms (e.g., C, N, and O) in a compound generally provides isotopic masses of approximately “M + 1” and “M + 2” at specific abundance or intensity ratios relative to the parent mass (M). Given the low mass errors (≤5 ppm) and low abundance differences (<1.50% in the M + 1 isotopes and <0.10% in the M + 2 isotopes) reported in Table 3, the observed isotopic masses agree well with the exact isotopic masses.

\[ \text{Table 3. Analysis of MS}^1 \text{ Isotopic Masses and Abundances Obtained from the LC-QTOF ESI + and ESI− Modes} \]

| Compound | obs. m/z (Da) | exact m/z (Da) | mass err. (ppm) | obs. abundance (%) | predicted abundance (%) | abundance diff. (%) |
|----------|---------------|----------------|-----------------|--------------------|-------------------------|---------------------|
| PBNA, [M + H]^+ | 220.1118 | 220.1121 | −1.36 | 100.00 | 100.00 | 0.00 |
| | 221.1154 | 221.1153 | 0.45 | 17.86 | 17.83 | 0.03 |
| | 222.1185 | 222.1186 | −0.45 | 1.43 | 1.50 | −0.07 |
| PBNA-NO\(_2\), [M − H]^− | 263.0825 | 263.0826 | −0.38 | 100.00 | 100.00 | 0.00 |
| | 264.0850 | 264.0857 | −2.65 | 18.18 | 18.24 | −0.06 |
| | 265.0885 | 265.0884 | 0.38 | 2.05 | 1.98 | 0.07 |
| PBNA-(NO\(_2\))\(_2\), [M − H]^− | 308.0674 | 308.0677 | −0.97 | 100.00 | 100.00 | 0.00 |
| | 309.0705 | 309.0707 | −0.65 | 19.05 | 18.67 | 0.38 |
| | 310.0728 | 310.0731 | −0.97 | 2.38 | 2.47 | −0.09 |
| PBNA-(NO\(_2\))\(_3\), [M − H]^− | 353.0531 | 353.0528 | 0.85 | 100.00 | 100.00 | 0.00 |
| | 354.0562 | 354.0557 | 1.41 | 17.74 | 19.10 | −1.36 |
| | 355.0582 | 355.0579 | 0.84 | 2.90 | 2.96 | −0.06 |
| PBNA-(NO\(_2\))\(_4\), [M − H]^− | 398.0376 | 398.0378 | −0.50 | 100.00 | 100.00 | 0.00 |
| | 399.0404 | 399.0406 | −0.50 | 19.50 | 19.53 | −0.03 |
| | 400.0433 | 400.0432 | 0.30 | 3.00 | 3.45 | −0.45 |
| PBNA-(NO\(_2\))\(_5\), [M − H]^− | 443.0230 | 443.0229 | 0.23 | 100.00 | 100.00 | 0.00 |
| | 444.0264 | 444.0256 | 3.83 | 20.00 | 19.96 | 0.04 |
| | 445.0284 | 445.0277 | 1.57 | 4.00 | 3.95 | 0.05 |

**Figure 2.** Proposed fragmentation pathways of mono-, tri-, tetra-, and penta-nitro PBNA derivatives based on the MS\(^2\) spectral data in ESI− (detailed mass data in Table S4). The fragment ions highlighted in blue give the strongest signals.
Table 4. Spectral Summary of PBNA and Nitro Derivatives Found in the ESI− and ESI + Modes

| adduct type | PBNA | PBNA-NO2 | PBNA-(NO2)2 | PBNA-(NO2)3 | PBNA-(NO2)4 | PBNA-(NO2)5 |
|-------------|------|----------|-------------|-------------|-------------|-------------|
|              | [M + H]+ | [M – H]− | [M + H]+ | [M – H]− | [M + H]+ | [M – H]− | [M + H]+ | [M – H]− | [M + H]+ | [M – H]− | [M + H]+ | [M – H]− |
| \( T_R \) (min; ± 0.015 min) | 6.420a | 6.062 | 6.086 | 6.086 | 6.034 | 6.057 | 6.212 | 6.033 | 6.048 | 5.701 |
| MS1 mass (Da) | 220.1121 | 263.0826 | 265.0972 | 265.0972 | 308.0676 | 310.0825 | 353.0527 | 355.0677 | 398.0375 | 350.0372 | 443.0220 |
| MS1 ion RMS error (ppm) | ±1.02 | ±1.13 | ±0.54 | ±1.30 | ±0.71 | ±1.13 | ±0.51 | ±0.71 | ±0.51 | ±0.71 |
| accurate mass of MS2 fragment ions (Da) | 143.0726 | 233.0847 | 248.0935 | 277.0619 | 306.0511 | ND | 351.0372 | 351.0372 | 380.0275 | 380.0275 |
| 92.0494 | 216.0840 | 218.0964 | 292.0707 | 290.0574 | 322.0465 | 367.0283 | 351.0372 | 351.0372 | 351.0372 | 351.0372 |

ND, not detected. Examples of mass spectra: Figures S3−S6, S9−S11, and S14. “Secondary or tertiary isomers due to their low intensities.

\( T_R \) Propagation of n-NO2 Additions. The \( T_R \) is dominated by the polarity of the compound and its affinity toward the stationary phase in the column; thus, the elution order typically proceeds from polar to nonpolar compounds in reversed-phase LC.38 Hence, a small polar molecule with high hydridicity such as DNPOH is eluted faster (2.886 min) than the other compounds detected (Tables 4, S1, and S2). Similarly, BDNPF (5.570 min) is eluted 0.3 min earlier than BDNPA (5.891 min) due to a single methyl group difference. Because of the hydrophobic attribute of the unsaturated hydrocarbons, PBNA exhibits even longer \( T_R \) (6.420 min; Table 4) than BDNPA/F. Beside these hydrophobic or hydrophilic differences, the polarity also increases as the number or the strength of electron-withdrawing substituent increases (e.g., NO2). Depending on the location (e.g., ortho-, meta-, or para-) of NO2 substituents, the effect of resonance stabilization can increase the acidity and polarity of nitro derivatives to a different extent. Such enhancement becomes even more complex when considering the naphthalene polycyclic ring. Therefore, the \( T_R \) and the ionic strength of an analyte can be significantly altered by the pH of the mobile phases.38 Since the pKa values of the PBNA derivatives are not known, the measured \( T_R \) cannot draw absolute clarity to the relative behavior of these derivatives. However, besides tri- and tetra-nitro-PBNA derivatives, the resultant elution order of the dominant derivatives closely follows the effect of increasing polarity with decreasing \( T_R \): PBNA (6.420 min) > + 1 NO2 (6.062 min) > + 2 NO2 (6.034 min) > + 5 NO2 (5.701 min).

Table 4 summarizes the spectral features of all identified PBNA nitro derivatives, including mono-, di-, tri-, tetra-, and penta-nitro PBNA derivatives, which are denoted as PBNA-NO2, PBNA-(NO2)2, PBNA-(NO2)3, PBNA-(NO2)4, and PBNA-(NO2)5, respectively. The \( T_R \) drifts were consistently measured at less than 0.05 min. The mass errors of precursor and fragment ions were measured at less than 2 and 10 ppm, respectively.

Formation and Depletion of PBNA Derivatives. Relying on the relative peak intensities, we can infer the relative concentration of PBNA derivatives and thus demonstrate their formation and depletion in a sequential trend (Figure 4). Especially at elevated temperatures (≥ 55 °C), rapid formation of one nitro derivative generally accelerates the formation of the following nitro derivatives and subsequent depletion of the former nitro derivative. Leveraging DFT simulations for the free energies, we can gain additional insight into the preferred position for NO2 addition onto PBNA-NO2 (Figure S16).

In the labeled PBNA structure of Figure 3, the first addition is verified in position #3 based on the previous study.39

Figure 3. Numeric labels of NO2 addition sites that are corresponding to the DFT simulations.

Supported by the free energy calculation, the second addition is more likely in position #9. This is expected, as it is subjected to the least influence of the strong electron-withdrawing from the first NO2 group (Figure S16a). The third addition is found more likely in position #1, which is expected from NO2 being a meta-director (Figure S16b). By the same logic, the fourth addition is found more likely in position #11 (Figure S16c). Although our DFT simulations indicate that the addition of a fifth NO2 group should not be spontaneous (Figure S16d), that derivative is detected experimentally. This result is likely the consequence of our simulation not reproducing exactly the experimental conditions (e.g., small errors inherent in DFT, effective solvent model vs. actual condensed phase).

Interestingly, the dynamic of the reaction changes drastically at higher temperatures and at a longer aging time, as discussed in greater detail below. The propagation of PBNA nitration mainly progresses in three stages and shows an important correlation with the degree of NP degradation, specifically (1) limited efficiency, (2) nullification, and (3) hydrolysis.

Limited Efficiency and Nullification of PBNA. With diminished electron density, mono- and dinitro derivatives are...
considered secondary and tertiary stabilizers to PBNA for the scavenging of radicals. Because nitration can neutralize the basicity of the stabilizer and reduce the resonance energy through further additions, the third, fourth, and fifth additions become increasingly difficult, which is indicated by the low responses of trinitro derivatives and the absence of tetra-nitro and penta-nitro derivatives at 38 °C in Figure 4. This trend is supported by the DFT simulations: as mentioned above, the addition of a fifth NO₂ group is found to be nonspontaneous (Figure S16).

When the dinitro-PBNA derivative is depleted, which is also indicated by the maximum peak intensities of the trinitro derivative (e.g., 28 months of aging at 55 °C or 16 months of aging at 64 °C), the antioxidant activity is effectively nullified. As a result, NP decomposition proceeds at a faster pace and the accumulation of HNOₓ, NOₓ, and water likely dissociates into charged components, which not only create reactive electrophiles (e.g., NO⁺, NO₂⁻, NO₃⁻, H₂NO₂⁺, and HN₂O₄⁺) but also increase the acidity in the aged samples in the later stage of thermal aging. These conditions can catalyze the nitration reaction of polycyclic aromatic hydrocarbons. Hence, the fourth and the fifth NO₂ additions are achievable, especially at elevated temperatures and in the presence of HNO₃ (Figure S18). Accordingly, tetra- and penta-nitro-PBNA derivatives can be deemed less relevant during the early stage of NP aging. The nullification of PBNA at the third NO₂ addition is likely due to the severe reduction of electron density in the aromatic rings. Because PBNA is nullified at the third NO₂ addition, the signal of dinitro-PBNA can be utilized to monitor the onset of NP hydrolysis.

**Scheme 2. Proposed Nitrosation (a) and Protonation Pathways of Hydrolysis (b) and Hydrolyzed (c) Products of PBNA Derivatives**

When the dinitro-PBNA derivative is depleted, which is also indicated by the maximum peak intensities of the trinitro derivative (e.g., 28 months of aging at 55 °C or 16 months of aging at 64 °C), the antioxidant activity is effectively nullified. As a result, NP decomposition proceeds at a faster pace and the accumulation of HNOₓ, NOₓ, and water likely dissociates into charged components, which not only create reactive electrophiles (e.g., NO⁺, NO₂⁻, NO₃⁻, H₂NO₂⁺, and HN₂O₄⁺) but also increase the acidity in the aged samples in the later stage of thermal aging. These conditions can catalyze the nitration reaction of polycyclic aromatic hydrocarbons. Hence, the fourth and the fifth NO₂ additions are achievable, especially at elevated temperatures and in the presence of HNO₃ (Figure S18). Accordingly, tetra- and penta-nitro-PBNA derivatives can be deemed less relevant during the early stage of NP aging. The nullification of PBNA at the third NO₂ addition is likely due to the severe reduction of electron density in the aromatic rings. Because PBNA is nullified at the third NO₂ addition, the signal of dinitro-PBNA can be utilized to monitor the onset of NP hydrolysis.

**PBN Derivatives in Dry versus Wet Environment.**

The difference between the headspace environments can be observed through the relative peak intensities of tri-, tetra-, and penta-nitro derivatives in Figure 4. At low temperatures, the formation rates of trinitro derivative are seemingly higher in the dry environment. At elevated temperatures, while the life span of trinitro derivative is prolonged in the wet environment (>44 months of aging), it is quickly depleted from 28 to 33 months of aging at 55 °C and from 18 to 21 months of aging at 64 °C in the dry environment. The depletion rate of tetra-nitro...
derivative is also faster, and the signal intensity of penta-nitro derivative is significantly stronger in the dry environment than in the wet environment. Since the trinitro derivative is the nullified state of PBNA, a faster formation and depletion rates of tri-, tetra-, and penta-nitro derivatives are suggesting a faster PBNA degradation in the dry environment than in the wet environment. Hence, the degradation of PBNA through nitration is slowed possibly caused by differences in the trace amount of water in this trace water.

**Acid-Catalyzed Hydrolysis.** Even though PBNA primarily degrades through nitration, hydrolysis of PBNA derivatives also contributes to its deficiency process (Scheme 2). Upon protonation or nitrosation, PBNA derivatives will become susceptible to nucleophilic attack from water and potentially form nitrophenol, dinitrophenol, naphthylamine, and naphthol. For example, the dimerization of naphthalene derivatives may form a precipitant and phase separate from the condensed materials. In all aged NP samples, precipitants were observed but could not be identified due to their small quantities and the difficulty of performing an extraction.

At low temperatures (<55 °C), while the changes of peak intensities in DNPOH and nitrophenol are less apparent in the dry environment (Figure 5), their changes reveal a slow linear increasing trend in the wet environment (Figure 5). This phenomenon is possibly caused by differences in the trace amount of water in the NP binders between wet and dry environments.

In the wet environment, the trace amount of water is preserved and provides a greater capacity to dissolve HONO released from initial NP degradation and indicating that DNPOH and nitrophenol can be produced in a weakly acidic environment (pKa of HONO ~ 3.16) but at a slow rate at temperatures below 55 °C. Due to water evaporation in the dry environment, the trace amount of water available to absorb HONO decreases over time and hence limits the amount of DNPOH and nitrophenol being produced. However, considering that the intensities of DNPOH, nitrophenol, and dinitrophenol signals are relatively low at low temperatures in both environments, early-stage hydrolysis of PBNA derivatives is a minor reaction, which is not detrimental to the stability of NP. On the other hand, as indicated by the

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**Table 5. Spectral Analysis of Hydrolyzed Products of PBNA Derivatives, Nitrophenol, and Dinitrophenol**

| Observed m/z (Da) | Proposed Formula [Fragmentation Steps] | Mass Error (ppm) | Abundance Diff. (%) |
|------------------|----------------------------------------|-----------------|--------------------|
| Nitrophenol MS³ ions | C₆H₅NO₃⁻ | −0.72 | 0.00% |
| 138.0196 | “M + 1” isotope | 3.60 | −0.77% |
| 139.0232 | “M + 1” isotope | 0.93 | N/A |
| 108.0216 | C₆H₅O₂⁻ [−NO] | 5.43 | N/A |
| 92.0273 | C₆H₄O⁻ [−NO₂] | 8.70 | N/A |
| 45.9939 | NO₂⁻ | N/A | |
| Dinitrophenol MS³ ions | C₆H₄(NO₂)₂⁻ | 0.55 | 0.00% |
| 183.0048 | “M + 1” isotope | 3.26 | 3.14% |
| 184.0081 | “M + 2” isotope | N/A | |
| ND | ND | N/A | |

“Nitrophenol and dinitrophenol are detected as [M − H]⁻. Examples of mass spectra: Figure S13. Isotopic abundance measurements: Table S5.

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**Figure 5.** Peak intensities of hydrolyzed products in various aging environments and temperatures. The signal intensities of DNPOH are multiplied by 0.30, 0.05, or 0.03 to match the scales of nitrophenol and dinitrophenol (peak intensities = peak area in cps/sample weight in mg). The peak intensities do not reflect the relative concentrations of different measured species.
greatly increased signal and production rates of dinitrophenol and DNPOH in Figure 5 (≥55 °C), acid-catalyzed hydrolysis only aggressively takes off at elevated temperatures when the acidity (i.e., the acid concentration of HNO₃) has increased substantially in the advanced stage of aging experiment.

**CONCLUSIONS**

By closely examining high-resolution LC-QTOF data, nitrated PBNA derivatives were identified and the hypothesis of sequential nitration of PBNA was confirmed for the first time. The correlation between PBNA and NP degradation in the thermal aging study is summarized schematically in Figure 6. In addition to PBNA, mononitro and dinitro-PBNA are identified as the secondary and tertiary stabilizers of NP, respectively. NP degradation will likely start and progress rapidly once a high level of dinitro-PBNA is detected. Hence, dinitro-PBNA can be utilized in monitoring the onset of hydrolytic NP degradation.

The presence of DNPOH, nitrophenol, dinitrophenol, tetra-, and penta-nitro-PBNA derivatives are either absent or stayed at negligible concentrations in normal storage conditions under such the NP hydrolysis is not a primary degradation mechanism. Therefore, these five species are insignificant in the early stage of NP degradation and mere indicators of the advanced degree of degradation when strong signals are observed (e.g., at elevated temperatures). Furthermore, the compounds at 264 Da (detected as [M − H]⁻ or m/z 263) and 385 Da (detected as [M + AcO−H]⁻ or m/z 443.23 at 3.71 min), which were previously incorrectly reported as impurities, are now unambiguously characterized as mono- and penta-nitro PBNA derivatives, respectively.

Compared to the dry environment, the longevity of PBNA derivatives provided by the wet environment may outweigh the drawback of weak hydrolysis. However, in an environment containing an excessive amount of water, the uptake of HONO, generated from the HONO elimination, may increase and hence result in a greater impact of the weak hydrolysis. Further quantitation of the acidity in the aged NP samples will be required to provide a concrete threshold of when NP hydrolysis will occur. As our endeavor in optimizing the LC-QTOF parameters continues to attain high-quality spectral data, future exploration of NP degradation products and investigation of reaction pathways in PBNA nitration may unravel greater details on the mechanism of NP decomposition under various aging conditions.

**ASSOCIATED CONTENT**

- **Supporting Information**

  The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.2c05011](https://pubs.acs.org/doi/10.1021/acsomega.2c05011).

  Spectral analysis: Tables S1−S5; example mass spectra of LC-QTOF: Figures S1−S14; and DFT results: Figures S15−S18 (PDF)

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Notes
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