LX-17 Thermal Decomposition—Characterization of Solid Residues from Cook-Off in a Small-Scale Vessel Under Confinement

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Abstract: Concerns surround whether insensitive (or any) energetic materials are more dangerous to handle when exposed to abnormal thermal environments. This study characterizes the residual material remaining after LX-17 (92.5% 1,3,5-triamino 2,4,6-trinitro benzene (TATB) and 7.5% Kel-F) is exposed to various thermal environments in a sealed small-scale vessel cook-off test reactor (heated at 0.1 to 100 °C/min until the reactor opened at 3000 psi (20.7 MPa)). Previous work has shown no additional sensitivity of these residues as evaluated by small-scale safety analysis, but characterization on the molecular scale indicates the TATB is transformed to more reactive compounds and the residue could be precursors to toxic gases. The solids and chars were characterized by various analytical methods. Heat-flow measurements indicated exothermic release is due to a mixture of residual TATB and related decomposition products (which may be more energetic). The N/C and O/N ratios indicated a material much more degraded than TATB. Primarily, the solids were a network of amorphous C inter-dispersed with N and O. Types of bonding include C—C, C—N, N—H, N=C, N≡C, C—O−, and −OH. Solvent extracts of the solids showed TATB decomposition intermediates benzo-furazans and benzo-furoxans, substituted TATB (mono-nitroso, hydroxyl, and chlorinated) along with several unidentified smaller molecules. These results indicate thermal treatment produces an amorphous carbon residue with heteroatoms incorporated through differing functionality, varying depending upon the thermal severity of exposure. These structures also could further decompose producing toxic light gases (such as cyanide).

Keywords: Explosives safety · TATB · LX-17 · Thermal cook-off · Molecular characterization

1 Introduction

Thermal decomposition of TATB and related materials has been the focus of research for several years. Efforts have been made to understand the decomposition of the bulk material, as well as on a molecular level. Initial work addressed overall kinetics, realizing early the decomposition of a solid-phase material is not well understood kinetically or mechanistically [1–5]. Attempts to characterize volatile decomposition products along with light gases led to the perspective benzo-furazans and benzo-furoxans are potentially stepwise formed and are part of the chain of decomposition reactions [6–15]. The overall mechanism was further developed for thermal modeling purposes showing the first part of the decomposition is the loss of water with the formation of mono-benzo-furazan (F₁), di-benzo-furazan (F₂), tri-benzo-furazan (F₃), and ultimately the ring system falling apart [5,16–19]. This early work has been reviewed recently [20].

Less comprehensively studied has been the char, usually left over from thermal treatment. Figure 1 shows the formula and structure of TATB – fully substituted aromatic ring system with −NH₂ and −NO₂ in alternating positions around the ring. The electron-donating power of the amino group and the electron-withdrawing power of the nitro group gives the molecule unusual stability [21] and electronics [22]. As well, the crystal structure shows a network of planar, graphite-like sheets closely associated due to strong hydrogen bonding [23]. However, TATB is extremely oxygen unbalanced, unusual for many monomolecular explosives,

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such as tri-nitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). As a result, when TATB is thermally treated in a closed system, along with the volatile components evolving, a substantial amount of char can be produced, depending upon the thermal conditions and ambient oxygen available.

Products from thermal treatment of TATB and LX-17 have been studied in some detail recently [24, 25]. The general conclusions from those studies are the residues are not impact, friction, or static (ESD) sensitive as determined by small-scale safety testing; exhibit only slightly enhanced impact, friction, or static (ESD) sensitive as determined by gas analysis mechanisms. The sample exhibits a small exotherm with the $T_{\text{max}}$ approximately 300–400 °C range. The char also produces volatiles, such as HCN and NO, at temperatures well above 400 °C. The residue has also been examined by infrared (IR) and x-ray photoelectron (XPS) spectroscopies and, nuclear magnetic (NMR) and mass (MS) spectrometries. The IR exhibits virtually no detail except for the appearance of a C–N band near CO$_2$. XPS indicates C–C, C–N, and C–O features, indicating C–N and C–O incorporated into a C framework, but the N and O are not from –NO$_2$ as well as some residual C–F features probably from the Kel-F binder decomposing. NMR shows unorganized C structures with sp$^2$ C, sp$^3$ C–N, and nitrile but very little sp$^3$ C. Solvent extraction of the residue, coupled with chromatography and MS detection shows several species also found in LX-17, such as mono-nitroso- (MN-TATB) and hydroxyl-TATB (HO-TATB), as well as thermal reaction products, such as F$_3$ and related structures. The previous conclusions for SSVCT-05 residue are: 1) IR, XPS, and NMR properties indicate amorphous carbon with probable incorporation of N in the C–C structure (these structures include having hydrogen bound likely to heteroatoms); 2) MS evidence suggests that some of the residue still contains TATB-like structures (such as F$_3$) observed in other thermal degradation studies of TATB; 3) calorimetry indicates the residue is energetic but much reduced compared to TATB.

Several residues generated by the thermal treatment of LX-17 by the same method as SSVCT-05, but at differing experimental conditions have been analyzed. The treatment method uses pressed starting materials in a confined reactor, when heated, permanently opens at approximately 3000 psi (20.7 MPa) from self-generated pressure. The residual char materials remaining in the reactor were collected and analyzed. This report compares the properties of these residues with SSVCT-05 residue. This study is part of a bigger effort to understand the amount of care needed for handling TATB-based materials in the event of an abnormal thermal exposure.

2 Experimental Section

Small-Scale Vessel Cook-Off Test (SSVCT) reactions – The technique has been discussed in detail elsewhere [26]. Briefly, a 100- to 125-g sample was heated at 0.1, 1.0, 10, and 100 °C/min heating rates; confined with self-generated pressure to approximately 3000 psi (20.7 MPa); released upon venting. The reaction was considered over when the reactor was permanently opened. Residues were collected and saved in plastic bags for analyses.

Standard Differential Scanning Calorimetry (DSC) – TA Instruments Q2000 DSC; vented (pin hole) and sealed sample holder; 10 °C/min heating rate; room temperature (RT) to 500 °C.

X-ray Photoelectron Spectroscopy (XPS) – PHI Quantum 2000 system using a focused monochromatic Al K$_\alpha$ X-ray (14867 eV) source for excitation and a spherical section analyzer; samples were examined on Indium foil; surface cleaning (sputtering) was 3 kV for 3 min using Ar$^+$ with a 1 X 1 mm raster.

Infrared spectral analysis (IR) – in-house design, Bruker Optics Vector 33 interferometer is used to collect 2 cm$^{-1}$ resolution data between 400 and 5000 cm$^{-1}$.

Nuclear Magnetic Resonance spectroscopy (NMR) – 600 MHz Bruker Avance III spectrometer operating at 150.92 and 600.13 MHz for $^{13}$C and $^1$H, respectively; samples for $^{13}$C analysis were loaded into 2.5 mm (o.d.) rotors and spectra collected at a 20 kHz spinning rate using a Bruker HXY probe; for $^1$H spectra, samples were loaded into 1.3 mm (o.d.) rotors and data were collected at a 50 kHz spinning speed: $^{13}$C spectra chemical shifts were referenced to the –CH$_2$ peak of α-glycine as an external standard (–C–O; $\delta_{C} = 176.5$ ppm and $\delta_{N} = 8.2$ ppm).

High-Pressure Liquid Chromatography with Diode Array and Mass Spectral detection (HPLC-DAD-MS) of solvent extracts – This technique has been discussed in detail elsewhere [27]. Approximately 10 mg of material was placed in
a 2-mL test tube with two 5-mm diameter stainless steel balls and 1.8 mL of solvent; test tube was shaken for 60 min then centrifuged; the supernate was collected and analyzed; a single 130 μL aliquot was collected, and 1.8-mL addition of solvent avoided incomplete solubilization; solvents were DMSO and acetone; for highly degraded samples, extraction was estimated to be less than 50% by wt.

For SSVCT-07, where the majority of the mass was expected to be TATB, the 1.8-mL sample preparation was not used because TATB would saturate the DMSO, and quantitation of TATB would not be possible. Approximately 4 mg of material was placed in 100 mL of DMSO.

An Agilent 1200 series liquid chromatograph was used for the HPLC-DAD analysis to quantify the amount of TATB, T₄A, and mono-benzo-furoxan (Fx₁) in samples. LC-DAD-MS analysis was performed on a Thermo Fisher Vanquish LC with a DAD in line with a QE ion trap or a Velos ion trap mass spectrometer. Two ionization techniques were applied, Atmospheric Pressure Chemical Ionization (APCI) and Heated Electro-Spray Ionization (HESI). Both positive and negative ions were monitored.

**Gas Chromatography Analyses of Samples** – The gas chromatography-mass spectra analysis was performed on an Agilent model 7890A Gas Chromatograph and model 5975C Mass Selective Detector running MassHunter software.

### 3 Results

#### 3.1 Samples

Pressed LX-17 samples at 86 and 98% theoretical maximum density (TMD) were thermally treated in the SSVCT reactor at 0.1, 1.0, 10, and 100 °C/min heating rates. The SSVCT is a cylindrical-type reactor, and the LX-17 is machined to fit closely with approximately 15% head space to accommodate thermal expansion [28, 29]. Figure 2-a shows the typical dimensions of the LX-17. As samples produce gas upon thermal decomposition, the pressure builds until the seal at the top fails due to bolt expansion, at approximately 3000 psi (20.7 MPa). Heating was stopped when the reactor permanently remained open by over-pressurization. In some cases, the reactor vented and re-sealed, but eventually permanently opened.

As a rough metric to compare the experimental performance, Figure 3 shows the pressure as a function of time before explosion (as measured by permanent reactor opening).

Data is time-shifted so reactor opening permanently occurs at 10⁻¹ s. Note these pressure transducers were not designed to measure the exact pressure at the exact time of explosion. The 10 °C/min profile exhibits the most pressure build-up before explosion, as well as early pressure generation. The 1 °C/min profile is similar but shifted. The three 100 °C/min profiles are reasonable similar to each other but exhibit little early pressure generation. The 1 °C/min vented experiment (1 C/min V) was from an experiment with a gas sampling device, so the pressure does not build up (the residue is not discussed here). The 0.1 °C/min profile shows little build up, also. Pressure spikes appear in several experi-

![Figure 2. Photographs of materials in this study: a) LX-17 starting material (pressed part), b-h) reactor product black and yellow chars for SSVCT-01 through -07, respectively.](image_url)

![Figure 3. Time-shifted pressure measured during thermal treatment of LX-17 by SSVCT conditions in Table 1; note time is before the explosion and is logarithmic and explosion time set at 10⁻¹ s; two lines of the same color indicate different pressure transducers to cover pressure range.](image_url)

| Table 1. Sample Information showing density, weights before and after thermal treatment; heating rates. |
|----------------------------------------------------|
| SSVCT[a] | % TMD[b] | Wᵢ[c] g | Wᵢ[d] g | Heating rate |
|---|---|---|---|---|
| -01 (b) | 86 | 108 | 1.1 | 100 °C/min |
| -02 (c) | 98 | 124 | 2.7[3] | 100 °C/min |
| -03 (d) | 98 | 124 | 1.4[3] | 100 °C/min |
| -04 (e) | 98 | 124 | 5.2 | 100 °C/min |
| -05 (f) | 98 | 124 | 0.7 | 0.1 °C/min |
| -06 (g) | 98 | 124 | 0.4 | 1.0 °C/min |
| -07 (h) | 98 | 124 | tr | 10 °C/min |

[a] SSVCT sample (see Figure 2); [b] TMD of LX-17; [c] Initial wt.; [d] Final wt.; [e] Solid sphere, 37.9 g, not included; [f] Solid sphere, 50.7 g, not included.
ments, concurring with Sandia’s Instrumented Thermal Ignition experiments [17] in which cracking was heard. These profiles demonstrate the diverse conditions producing these samples.

3.2 Differential Scanning Calorimetry

DSC was used to screen the samples for energy content. The DSC was operated in standard configuration with a 10 °C/min heating rate from RT to 500 °C with the sample in a vented and sealed sample holder. TATB has a sharp exothermic enthalpy release with a $T_{\text{max}}$ value around 380 °C. The integrated enthalpy value over this release is near 900 J/g. At a 92.5% concentration in the starting LX-17 samples, intact TATB yields an obvious feature in the DSC profiles. TATB in LX-17 shows a sharp increase in heat flow starting around 375 °C, completing shortly after 400 °C.

Figure 4 shows the DSC profiles of SSVCT-01 to -05, indicating heat flow as a function of temperature in the 300 to 500 °C range. The increasing value of the profiles in all cases is due to a sloping baseline varied for display. SSVCT-01 and -03 have no deviation from the baseline flow, just the sloping baselines. SSVCT-02, -04, and -05 have some indication of exothermic flow, but it is extremely low at approximately 100 J/g and has $T_{\text{max}}$ values at approximately 340 °C. These values indicate there may be something exothermic in the material, but, by DSC analysis of the $T_{\text{max}}$ behavior, it is not TATB and is at a very low concentration.

3.3 Vibrational Spectroscopy

Table 2 shows IR features of the SSVCT-01 thru -05 residues. The bands are divided into regions based on previous published assignments. None of the spectra exhibited intense IR features. Band I region shows the presence of some hydrogenated sp$^3$ C chain features, typically two features at approximately 2970 and 2930 cm$^{-1}$. SSVCT-01 exhibits only 1 of these features because of very low concentration of any features. Band II region shows the weak C–N features, possibly assigned as nitrile. Band III shows features associated with G$_{\text{IR}}$ and D$_{\text{IR}}$ features that correlate with similar Raman G and D features when N is incorporated into amorphous carbon. Additional features appear in the fingerprint region. SSVCT-02 thru -05 exhibit similar spectral features in this region. Most of these are absent in SSVCT-01 because of the very low concentration of IR active features.

3.4 X-Ray Photoelectron Spectroscopy

The C 1s, N 1s, and O 1s spectra were measured by XPS on SSVCT-01 to -05. Samples were examined as received (not surface treated) and surface sputtered (cleaned). The elemental composition was determined. The elements detected were primarily C, N, and O. SSVCT-02, -03, and -05 also have minor contributions from F, Si, and Cl (see Figure S1 as an example). Figure 5 shows the N/C and O/C ratios from the atomic elemental compositions (see Table S2). Shown are the as-received and cleaned samples. These ratios indicate the residues are primarily C with some N and O. Note the surface cleaning removes N and O content relative to C, except for SSVCT-05, which also stands out having much higher ratio with the heteroatoms (N/C and O/C ra-
tios are almost 1/1 and 0.30/1) compared to the other samples.

C 1s, N 1s, and O 1s spectra were examined in more detail. Figure 6 shows the C 1s spectra for SSVCT-02. The as-received spectrum shows a broad asymmetric feature. This feature has been deconvoluted (fitted) with 4 peaks of different binding energies: 284.6, 286.1, 288.1, and 290.5 eV (colored lines). The broad feature narrows with surface cleaning (1-min and 3-min sputter) and the contributions at higher binding energies, small already, appear to decrease, particularly with increased cleaning time (discussed below). Spectra for SSVCT-01 through -05 have similar properties (see Table S3 for energy positions) – broad feature that can be fitted into essentially four components. However, the component positions for SSVCT-05 are slightly different than the others, shifted to lower energies. The average values (with relative deviations) for SSVCT-01 through -04 are, in eV: 284.8 ± 0.2 (0.05 %), 286.3 ± 0.1 (0.04 %), 288.3 ± 0.2 (0.07 %), 290.6 ± 0.1 (0.04 %); -05 are, in eV: 283.5, 284.9, 286.5, 289.3. Also, SSVCT-03 has residual evidence of F, Cl, and Si (see Table S5).

Figure 7 shows the N 1s XPS spectra for SSVCT-01 through -05 with Ar+ surface cleaning. The spectra show broad, overlapping maxima, at about equal intensity between 396 and 402 eV with a small maximum between 402 and 404 eV. The fitting of these maxima yields three major components, each with corresponding similar positions for as-received and cleaned samples. Figure 7 shows these maxima align for SSVCT-01 through -04 (see Table S4 for energy positions), except for SSVCT-05. Deconvolution of these maxima indicate positions are very similar, with average values (relative deviation) for SSVCT-01 through -04 are, in eV: 398.4 ± 0.2 (0.06 %), 400.6 ± 0.3 (0.07 %), 403.2 ± 0.5 (0.12 %). The components for SSVCT-05 has the common shape as the others but is shifted slightly to lower energies, in eV, 398.0, 399.8, 402, suggesting a similar N environment but different tertiary environment. SSVCT-05 also had little

Figure 6. XPS spectra of SSVCT-02 showing C 1s behavior with deconvolution into 4 components for as-received, 1-min sputtered and 3-min sputtered samples.

Figure 7. XPS spectra of SSVCT-01 through -05 showing N 1s behavior of surface cleaned samples with deconvolution into 2 and 3 components.
evidence of N–O in either the as-received or cleaned spectra, contrary to SSVC-01 through -04. SSVC-01 also exhibits minor differences. The as-received spectrum (see Figure S1) shows better resolution than the cleaned spectrum (1-min sputter) of the two major features at 398 and 400 eV. All the samples (except -05) exhibited a minor feature in the range of N–O. However, this is not in the position for -NO2 on TATB; the proposed cause is discussed below.

The behavior of O 1s was also examined by XPS. The as-received samples exhibited broad overlapping maxima when deconvoluted produced three distinct features at approximately 531, 533, and 535 eV (Figure S2 shows as-received samples). With surface cleaning, the 531-eV component is substantially reduced in intensity compared to the other components, except for SSVC-05. The 535-eV component also changed likewise but not as consistently (sometimes was not found). The major component remaining after surface cleaning was at 533 eV. As above, SSVC-05 did not follow this behavior (see Table S2 for energy positions and Figure S2) and the spectra were shifted to slightly lower energies than for SSVC-01 through -04.

The average values (relative deviations) for SSVC-01 through -04, in eV, are: 531.4 ± 0.3 (0.06 %), 533.3 ± 0.5 (0.09 %), 535.3 ± 0.8 (0.15 %); -05: 530.3, 532.5, 533.3.

3.5 Nuclear Magnetic Resonance

SSVC-01 through -05 have been examined by 13C and 1H solid-state NMR. Figure 8, left side, shows the solid state 13C NMR spectrum for SSVC-01. The spectrum spans a wide range of several hundred ppm, indicating a complex array of different chemical species. The very broad envelope represents carbon environments likely amorphous carbon, but the sharp components likely represent more ordered carbon species. The deconvolution, shown below the spectrum indicates a broad contribution at 143 ppm overlapping several narrower contributions at 167, 138, 128, 121, and 103 ppm. The positions of these features are less the same for SSVC-02 through -04 (see Table S2).

The 13C solid-state spectrum of SSVC-05 has been published previously [25] (see Figure S3). This sample exhibits additional features indicating a different environment than for SSVC-01 through -04. The principal differences from SSVC-01 spectrum are the very broad envelope is absent, most of the components are broader, and the small contribution at 53 ppm.

Figure 8, right side shows the 1H solid-state NMR of SSVC-01. The spectrum is a broad envelope spanning from approximately −10 to 20 ppm. The deconvolution shows very broad components at 8.65, 4.82, and −2.67 ppm; narrower components at 2.57, 2.44, 1.16, and −1.86 ppm. SSVC-02, -03, and -04 have components at similar positions (see Table S2): -02 and -04 have fewer components; -03 has no downfield components; -03 and -04 have additional components above 10 ppm.

The 1H solid-state spectrum of SSVC-05 has been published previously [25] (see Figure S4). Note the simplicity of the spectrum compared to the 1H NMR spectrum of SSVC-01, with essentially one sharp component at 3.7 ppm and one broad component around 7.5 ppm.

3.6 MS Identification of Intermediates

SSVC-01 through -07 samples were extracted with DMSO and after separation of suspended solids, the components in the extract were separated and analyzed by HPLC-DAD and -MS. These techniques have been developed to quantitatively the amount of TATB as well as identify thermal degradation intermediates with similar structures. Figure 9 shows the concentration of several of these intermediates as well as structures (see Figure S5 for structures and m/z values).

In general, all the species except F X1 are present in some concentration in LX-17, even F1. Other than TATB, these are of very low concentrations (note log scale for concentration). TATB, T 4M, MN-TATB, and HO-TATB are reduced in concentration in the residues; F1 is increased in concentration in the residues; F X1 is produced by the thermal treatment in some of the cases.

Other masses were detected in the DMSO extracts in addition to the species shown in Figure 9. These were reported previously in the analyses of SSVC-05 [25]. Several of these masses have not been fully structurally identified yet, and, as a result, standards have not been made to quantify them. Also, some of the masses have m/z values larger than the value for TATB (m/z 258), indicating adducts, either due to solvent complexation, gas-phase addition, or polymerization. These masses include m/z 220, 221 (F 1 ), 236, 280, 267, 354, 389, and 427.

Acetone extracts followed by GCMS analysis were also performed on the residues. SSVC-03, -05, and -06 were the samples showing any compounds by this method of analysis.
TATB-related structure, m/z 204 (F₃) was detected in SSVCT-03 at low concentration along with several chlorinated aromatic compounds; -05 and -06 exhibited F₃ near the limit of detection. These results will be the subject of future reports when exact mass and isotopically labeling studies have been completed to unequivocally identify the structures.

### 4 Discussion

#### 4.1 Thermal Treatment Conditions

These experiments were designed to determine the thermal response of LX-17 with limited confinement at various heating rates, 0.1 to 100 °C/min. To accomplish the 100 °C/min heating rate, the system employed a custom-designed inductive heating system. This system effectively heated at a rate of approximately 90 °C/min, employing 8 thermocouples to track sample temperatures. The thermal profiles show the center 70 °C cooler than the edge of the sample, at the time the reactor permanently opens (end-cap bolts fail to hold pressure). For 0.1, 1.0, and 10 °C/min heating rates, a traditional heating tape design was employed. In these cases, the system was heated at 10 °C/min to 200 °C, followed by the heating rate profile until end of experiment. The thermal profiles indicated some gradients. For example, the 1 °C/min heating rate experiment exhibited the center to be about 15 °C cooler than the edge of the sample. The reactor was designed to release at approximately 3000 psi (20.7 MPa) to show some measure of violence of explosion. More details on the processing and results are discussed elsewhere [26]. The heating configurations are shown in Figure S₆.

This design can explain the heterogeneous nature of the residues as seen in Figure 2. For the very fastest heating rate with the 98 % TMD samples, the outside of the sample reaches temperatures causing run-away thermal decomposition while the interior of the sample is quite cool. The end products are a mixture of char and essentially unreacted or slightly reacted LX-17. The temperature gradient of the samples shows the inner portion never reaches temperatures above 100 °C, for which TATB is stable. Sample retrieval reveals the large intact mass remaining suggesting the outer edges probably react in a layered fashion, but a substantial portion of material never fully decomposes and remains in the original shape of the pressed part. For the 86 % TMD sample, permeability is much better because the sample is less dense (and more porous), so hot reactive gases probably reach the inner portions of the sample better than in the 98 % TMD cases. For the slow heating rate samples, the heat has time to transfer, so most of the sample reacts. However, Figure 2 shows the residues from the slow heating rates are also heterogeneous exhibiting brown and black with yellow inter dispersed. Figure 3 shows the differing pressure conditions of the experiments depending upon heating rate. This further accentuates the heterogeneity of these samples due to reaction conditions.

#### 4.2 Thermal Properties

In DSC, LX-17 exhibits a sharp exothermic release with a maximum of evolution between 380 and 385 °C (at 10 °C/min heating rate) with enthalpy near 1000 J/g. Figure 4 and Table S₁ show SSVCT-01 through -05 samples have very lit-
tle or no enthalpy, indicating these materials are highly thermally decomposed. The vibrational spectra of these samples show no indication of residual TATB (discussed below); the XPS shows no indication of –NO₂ (discussed below); HPLC-DAD-MS analyses show there is very little TATB in the extract of these residues.

Table S₂ shows SSVCT-06 and -07 samples are energetic and have properties similar to LX-17, indicating less thermal degradation. The Tₚmax values are slightly shifted towards lower temperatures than those observed before in thermal degraded materials [25]. Figure 9 also shows the TATB content of the DMSO extract for SSVCT-07 sample and LX-17 are similar.

4.3 Vibrational Spectra

The IR features of TATB have been assigned in previous studies [30–33], and the thermal decomposition of TATB has been monitored in situ [24,34]. In the decomposition studies, NH₂ (asymmetric) at 3320 cm⁻¹, NH₃ (symmetric) at 3220 cm⁻¹, phenyl at 1450 cm⁻¹, C=NH₂ (stretching) at 1320 cm⁻¹, C-NO₂ (stretching) at 1230 cm⁻¹, phenyl at 1030 cm⁻¹, NO₃ (deformation) at 783 cm⁻¹ and 730 cm⁻¹ were monitored for evidence of reaction. As thermal decomposition proceeds, these bands disappear. SSVCT-01 through -05 end products exhibited similar lack of features. The most prominent feature of these samples is the weak C–N band in 2000 to 2200 cm⁻¹ range. (This was not detected in the previous in-situ studies because of CO₂ production.) This was barely detected in an amorphous C background as evidenced by Gᵣ and Dᵣ features correlating with similar Raman G and D features when N is incorporated into the carbon structures. No evidence of F-type features due to the decomposition of the Kel-F polymer, from LX-17, were observed. These assignments are based on several studies on TATB decomposition [2,35,36], thin film [37–45], amorphous carbon [46–48], and para- and para-iso-cyanogen [49–56].

4.4 X-Ray Photoelectron Spectra

The major components from the XPS data shown indicate the SSVCT-01 through -05 samples are composed of mostly C, N and O. The survey data show C is the primary component. Atomically, it is around 5 times more abundant than N and O in the structures of these residues except for SSVCT-05, having a ratio closer to 1 for N/C and 0.3 for O/C. The survey spectra also exhibit minor concentrations of F in some cases. Surface cleaning removes N, O, F, Cl, and Si except for SSVCT-05.

As with the C environment, the spectra of SSVCT-05 appear shifted to lower energies suggesting a slightly different environment than the other samples.

For the O 1s spectra, two to three components were fitted to the single broad asymmetric profile. The component at approximately 531.4 eV is assigned to COOH functionalization. The component at approximately 533.3 eV is probably due to decomposition products of TATB or secondary oxidation products. This is a minor component in the spectra in all cases and does not change intensity much upon sputtering, so it is not likely to be surface-bound. As with the C environment, the spectra of SSVCT-05 appear shifted to lower energies suggesting a slightly different environment than the other samples.

4.5 Nuclear Magnetic Resonance Spectra

Several of the components in the ₁³C spectra can be identified from the spectra of SSVCT-01 through -05 samples. The broadness of the spectral envelope indicates highly amorphous C with little order. However, the sharp features in the spectra also indicate nano-crystalline or ordered materials along with C–C and amorphous carbon adsorbed on surface. The component at approximately 286.3 eV is assigned to C–O, diamond-like C, and sp² C–N. The component at approximately 288.3 eV is likely due to N incorporated into C structures, such as N=C−N and possibly C–O. The component at approximately 290 eV is probably due to highly oxidized C. Due to the concentrations of these elements in the XPS survey table, the sample appears to have a C structure with N incorporated (preliminary transmission electron microscopy of in-situ prepared residues indicates some graphitic carbon or fullerene-like CN₆ with crystallite size on the order of 50 [57–59], see Figure S₃). O, though present, is not always bound to the C. The C 1s positions of the SSVCT-05 sample stand out as shifted to lower energies compared to SSVCT-01 through -04. As seen in the survey spectra, and how it behaves upon cleaning, this sample appears different. This will be discussed below.
amorphous material. The sharp feature around 115–120 ppm is assigned to sp$^2$-C. The broad feature in this range is probably a collection of amorphous or unorganized graphitic type C environments. These types do not have direct bonding to heteroatoms. The region from 125 to 175 ppm is probably due to sp$^3$C with N incorporation. The sharp features around 160 ppm could be due to triazine ring type N. Those features around 125 to 150 ppm are possibly due to terminal nitrile type C. Those assignments are based on literature on graphite [60, 77, 78], amorphous C–N [42, 66, 79–82], and C–N polymers [71, 83–85].

For the components of the $^1$H spectra, several have standard positions for organic moieties. SSVCT-03 and -04 have features above 10 ppm which reflect carboxylate type molecules possible with N in the structure; SSVCT-01 through -05 have features in the 7 to 9 ppm region indicating H on aromatic positions and amide-type linkages; SSVCT-01, -03 through -05 show features around 4 ppm indicating N- and O-heteroatoms in the structures; all show features in the alkyl range [86–89].

Two unusual features stand out, suggesting interesting atom assemblies. SSVCT-01, -02, and -04 have features around −2.0 ppm. Negative position shifts (with respect to TMS) are not normally observed in standard organic structures. The cause of this upfield shift is possibly due to NICS (nuclear independent chemical shift). This is a feature of molecules interacting with localized electronic effects usually generated by small aromatic domains, as would be found for extended ring systems in weakly organized amorphous carbon. If the moiety is situated close enough to these domains, the electronic effect is to shift the nuclei response upfield of TMS. This type of unusual interaction has been best documented for molecules adsorbed on porous carbon [90–93]. The other unusual feature is the simplicity of the $^1$H spectra of SSVCT-02 and -05 when the corresponding $^{13}$C spectra are as complicated as the other samples.

4.6 Intermediate Formation

DMSO extraction of the residues in the study was examined in more detail by HPLC-DAD-MS, as part of a larger study on detection of thermal degradation intermediates. The results of this effort will be published elsewhere with the details of the separation and identification methods. However, the technique has been developed enough to confidently discuss selected intermediates in these samples.

LX-17 is mostly TATB and TATB is found in all products, but at concentrations less than 10%, except for SSVCT-07. These are concentrations in the residues and do not account for an overall mass balance. Without a mass balance, which is impossible under these experimental conditions, the absolute amount of these species can only be estimated. Assuming the residue in the reactor is the only recoverable solid (not true in all cases), SSVCT-02 and -03 have the largest amount of residue because of solid spheres recovered in the center of the reactors. These spheres appear essentially unreacted, so the TATB has not been degraded. Even though Figure 9 shows very low concentrations in the residue, this mass balance factor puts SSVCT-03 and -04 as the least reacted based on overall TATB content.

Analysis by the DMSO extraction method so far found 14 species linked to TATB thermal degradation intermediates, as reported previously [25, 27]. Nine of these have been identified in the untreated LX-17; the other five are decomposition products only. Figure 9 shows 5 of the 14 species that have been identified. Except for F$_1$, the concentrations of these species, based on their ion chromatograms remains the same or decreases in the residues compared to the LX-17. The other 9 species are at trace levels, including F$_2$, and have been detected in the residues but have not been completely identified structurally yet.

Several ions were detected with m/z values higher than TATB. Based on the severity of thermal treatment, these higher masses could indicate a pathway towards highly condensed materials as detected in the XPS, NMR, and IR data. Alternately, the higher masses could be resulting from reactions with DMSO or the decomposing Kel-F polymer.

The samples were also extracted with acetonitrile and the extracts were analyzed by GCMS looking for F$_3$. Only SSVCT-03 showed any F$_3$, along with several chlorinated aromatics; SSVCT-02 had a few of the chlorinated aromatics, but, along with the rest of the samples, no F$_1$

SSVCT-01 and -04 have the fewest of the intermediates in the extracts. Figure 9 shows of the 5 identified species, only a residual amount of TATB remains in the residue (maybe some F$_1$ for -01). Full analysis reveals SSVCT-04 has a trace amount of F$_2$, also (see Table S8). This suggests these two residues are the most reacted of the set studied here.

4.7 Comparison With Other Thermal Degradation Studies

The behavior of the residues seen in this report has been seen previously in studies of degradation of TATB and other TATB-based explosives. Several studies have observed various spectroscopic markers indicating the potential presence of nitrogen incorporation into the carbon structure as the ultimate insoluble final product.

A recent study on shock compression and shock-induced decomposition of TATB [35] examined the solid products by IR, Raman, and XPS. Although the shock compression products exhibited very complicated XPS spectra, the pyrolyzed product exhibited XPS features similar to the features seen in this study. Based primarily on the C 1s and N 1s results, the pyrolyzed product appears to have sp$^3$ carbon with the nitrogen fully incorporated into the carbon framework. No sp$^2$ carbon was noted. The nitrogen was designated as occupying edges with 5 or 6 membered rings and with interior site of a carbon sheet with three carbon-nitrogen bonds. The IR of the pyrolyzed solid product also
exhibited a band at about 2230 cm\(^{-1}\), assigned based on resembling sputtered \(\alpha\)-CN thin films (possibly C \(\equiv\) N).

In a series of studies focused on hot-spot formation [6,7,94] in TATB insulted by irradiation, thermal, and impact, XPS spectra exhibited nitrogen behavior associated with benzo-furazans and benzo-furoxans. However, thermal samples were generated from conditions implementing only partial damage, as all the thermal product still exhibited \(-NO\), as evidence of remaining TATB.

### 4.8 Discussion on Structure

The spectroscopic evidence presented here indicates a carbon-nitride material having some local order but is not extensively crystalline. Comparison with the spectroscopic properties of para-cyanogen and para-iso-cyanogen show the material is close in structure but is not the same [50,52]. (See Supplementary material for discussion on para- and para-iso-cyanogen.) The full IR spectra of SSVCT-01 through -05 appear similar to para-iso-cyanogen, but the 2200 cm\(^{-1}\) IR band position agrees more with heat treated para-iso-cyanogen. However, the XPS spectra of both the C 1s and N 1s do not match either para-iso-cyanogen. For reference, para-iso-cyanogen, para-cyanogen, and (CN), (theoretical) have C to N ratio of 1:1, 1.4:1, and 1:1, respectively. The residues, by XPS survey (Table S2), discussed here have much more C in the structure relative to N and O. SSVCT-05 residue is the only sample close to those values. Perhaps this is expected because of the probable way TATB decomposes: the outside substitutions, where all the heteroatoms are, react first before the carbon of the ring system breaks apart.

A better fit of the spectroscopic data is presented in the shock and pyrolysis study of TATB [35]. In that study, the pyrolysis residue exhibited IR properties similar to those in this study and also similar to thin film studies on C–N materials. The XPS also exhibited characteristic sp\(^2\) –C–C– and –C–N– positions as well as probable nitrogen in sp\(^2\)-type ring structures with and without carbon. The differences in the C 1s spectra are slight differences in positions (as expected from surface charging) and the potential presence of –C–F– moieties due to the Kel-F in the LX-17, but not in the TATB. The results here agree in most part with those findings with variations no doubt due to the differences in thermal treatment conditions. However, the residues with the least amount of remaining TATB are similar in many respects, indicating the more thermal exposure, the more and more un-functionalized carbon, and less and less mixed heteroatoms in the residues.

The \(^{13}\)C NMR properties indicate little (SSVCT-05) or no sp\(^3\) carbon (SSVCT-01 through -04) and likely sp\(^2\) carbon with nitrogen substitution. The broad background also suggests a large component of unorganized amorphous carbon. Fine structure (sharper features) matches previous reported materials produced in the attempt to prepare carbon-nitride by pyrolysis of high nitrogen content organic compounds [82] and in para-cyanogen synthesis attempts using labeled materials [95] indicating by the spectroscopy the material presented here has sp\(^2\) carbon-nitrogen. Several types of carbon only and carbon-nitride materials show at least some of the features seen in the \(^{13}\)C spectra.

An interesting feature is the high field shift in the \(\text{\textit{H}}\) NMR spectra of SSVCT-01, -02, and -04. This is possibly a result of NICS, and if so, indicates graphitic carbon is weakly organized in high enough concentration to have an effect on other functional groups. Based in XPS, DSC, and HPLC analyses, these samples are the most degraded. A conclusion from this is the thermal degradation process gradually reacts out all the heteroatomic material, leading to essentially un-functionalized carbon. However, the many of the experiments show the residues by the SSVCT preparation method are highly heterogeneous – can be highly re-acted, but still retain TATB.

The results here add to the emerging view of the molecular structural changes occurring with thermal decomposition of TATB based materials. The first step in thermal decomposition has been thought to be the formation of F\(_1\). The compounds found in the DMSO and acetone extracts support the formation of F\(_2\), as well as other derivatives, such as F\(_{X1}\), F\(_{2}\), and F\(_3\) (acetone extract). Species in the same mass range are also detected, possibly related to the furazans and furoxans. From these species, the thermal pathways become less obvious. The residues remaining show evidence of condensing carbon with N and O somehow incorporated. NMR spectra show the remaining residue to have at least some amorphous C structure as well as organized moieties. XPS and NMR spectra verify the binding environments contain some ordered C–N, C–C, and C–O. However, the amount of heteroatom incorporation varies depending upon process conditions, as evidenced by the differences in heteroatom ratios in the samples. NMR of some samples also showed local networks of organized carbon. Monitoring of gas formation during thermal degradation has shown release of light gases, and in these samples, this occurs with the condensation of carbon-based compounds with and without order.

The question remains about what happens between the catastrophic decomposition of the TATB type structure (containing the attendant amino and nitro groups) to the residues examined here. One or possibly two samples show much evidence of anything other than the first step intermediates and the condensed, mostly reacted soot. The solvent extract of these two samples show chlorinated aromatics, but few compounds where the ring has come apart. This would suggest the TATB ring itself does not fall apart but reacts further towards condensing into amorphous or weakly organized carbon networks. This, however, does not account for the formation of CO\(_2\), which is always seen in these reactions, even early on, as well as other oxides of carbon, C\(_2\)N\(_2\), C\(_2\)N\(_3\)O, and other small molecules [2,10,12,24,96]. A key to this can be found in the gas mon-
5 Conclusions

Molecular characterization of the thermal decomposition products is a difficult task because of an apparent multitude of reaction paths. No one species of material dominates the conversion of the TATB to the residue. This is further complicated for LX-17 by the polymer binding component adding to the complexity as well as changing physical and, possibly, chemical properties of the decomposing mixture. The results of using spectroscopic characterization so far indicate at least three levels of reactions. Note, these levels are not to be confused with global kinetic interpretations of the reactivity of TATB and LX-17. 1) Conversion of TATB into benzo-furazan and benzo-furoxan type complexes, as represented by F₁, Fₓ₁, etc., in some of the samples examined here. These types of materials are stable enough to be isolated in solvent extracts and ultimately quantified (when standards are synthesized). 2) Highly reactive intermediates are formed either from the furazans and/or furoxans or directly from TATB. These intermediates are not stable enough to be extracted and detected (as of yet) but appear to be stable enough to be transients in gas evolution, as seen in recent on-line MS studies, and can have structures where the aromatic ring of TATB has been opened up. 3) All these pathways lead to an insoluble residual char, the primary focus of this study. The composition of this char is highly dependent upon the method and condition of thermal treatment and can range from unreactive material (retaining some TATB) to amorphous, almost ordered, carbon. The amount of heteroatom content also varies, probably governed by the extent of degradation. All these cases are accompanied by light-gas formation as the substitutions on the TATB ring react, the remaining ring components further degrade, and the char gradually gasifies away.

The nature of all these intermediate and products is continuing to be examined. These results will help inform safety assessments of these materials as exposed to abnormal thermal environments, particularly with the evolution of light, possibly toxic gases. Characterization is continuing, but the ultimate solution is when reactive network can be integrated into global kinetic models to provide high fidelity results.

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Data Availability Statement

Data available upon request from authors.

References

[1] E. Catalano, P. C. Crawford, An Enthalpic Study of the Thermal Decomposition of Unconfined Triaminotrinobenzeno, Thermochim. Acta 1983, 61, 23–36. doi:10.1016/0040-6031(83)80031-3.
[2] E. Catalano, C. E. Rolon, On the Solid-state Products of the Thermal Decomposition of Confined and Unconfined Triaminotrinobenzeno, Thermochim. Acta 1983, 61, 53–71. doi: 10.1016/0040-6031(83)80302-5.
[3] E. Catalano, R. McGuire, E. Lee, E. Wrenn, D. Ornelias, J. Walton, The Thermal Decomposition and Reaction of Confined Explosives, Proceedings of the 6th Symposium (International) on Detonation (Eds.: D. J. Edwards, S. J. Jacobs), August 24–27, 1976, Coronado CA, Office of Naval Research (CNRAC-221), pages 214–222.
[4] R. N. Rogers, J. L. Janney, M. H. Ebinger, Kinetic-Isotope Effects in Thermal Explosions, Thermochim. Acta 1982, 59, 287–298. doi:10.1016/0040-6031(82)87151-7.
[5] C. M. Tarver, R. R. McGuire, E. L. Lee, E. W. Wrenn, K. R. Brein, The Thermal Decomposition of Explosives with Full Containment in One-Dimensional Geometries, Symposium (International) on Combustion 1979, 17, 1407–1413. doi:10.1016/S0082-0784(79)80132-0.
[6] J. Sharma, W. L. Garrett, F. J. Owens, V. L. Vogel, X-ray Photo-electron Study of the Electronic Structure and Ultraviolet and Isothermal Decomposition of 1,3,5-triamino-2,4,6-trinitrobenzeno, J. Phys. Chem. 1982, 86, 1657–1661. doi:10.1021/j100260a034.
[7] J. Sharma, J. C. Hoffsommer, D. J. Clover, C. S. Coffey, F. Santiago, A. Stolovy, S. Yasuda, Comparative Study of Molecular Fragmentation in Sub-initiated TATB Caused by Impact, UV, Heat and Electron Beam, in: Shock Waves in Condensed Matter (Eds.: J. R. Asay, R. A. Graham, G. K. Straub), Elsevier, Amsterdam 1983, 543–546. doi: 10.1016/B978-0-444-86904-3.50123-8.
[8] T. B. Brill, K. J. James, Kinetics and Mechanisms of Thermal Decomposition of Nitroaromatic Explosives, Chem. Rev. 1993, 93, 2667–92. doi:10.1021/cr00024a005.
[9] T. B. Brill, K. J. James, Thermal Decomposition of Energetic Materials. 61. Perfidy in the Amino-2,4,6-Trinitrobenzene Series of Explosives, J. Phys. Chem. 1993, 97, 8752–8758. doi:10.1021/j100136a017.
[10] T. A. Land, W. J. Siekhaus, M. F. Foltz, R. Behrens Jr., Condensed-Phase Thermal Decomposition of TATB Investigated by Atomic Force Microscopy (AFM) and Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS), Pro-
Thermal Decomposition-Characterization of Solid Residues from Cook-Off in a Small-Scale Vessel Under Confinement

1990
Livermore National Laboratory, Livermore CA, 94550, USA
July
several other references...

Proceedings of the 16th Symposium (International) on Detonation, 2018, ONR-43-5762-19, 2018, 1642–1652, LLNL-PROC-754001.

E. M. Kahl, N. K. Muettterties, A. J. Nelson, H. E. Mason, J. V. Crowhurst, K. R. Coffee, J. S. Moore, J. G. Reynolds, Characterization of Solid Residue Formation in LX-17 Exposed to Abnormal Thermal Environments, AIP Conference Proceedings 2020, 2272, 050010. doi: 10.1063/1.0000948.

E. M. Kahl, G. F. Ellsworth, M. R. De Haven, M. A. Suda, P. C. Hsu, S. A. Strout, M. A. McClelland, R. A. Ryckman, J. S. Moore, K. S. Vandersall, J. G. Reynolds, Fast & Slow Cook-off Experiments of LX-17 Using Induction & Resistance Heating, Presentation from the 16th Symposium (International) on Detonation, Report LLNL-PRES-754699, Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA 94550, USA 2018.

K. R. Coffee, J. A. Olivas, A. F. Panasci, B. J. Steward, E. M. Kahl, J. G. Reynolds, Analysis of Thermally Damaged LX-17 – Methods Development, Report LLNL-TR-820356, Lawrence Livermore National Laboratory, 7000 East Ave., Livermore CA 94550, USA, 2021.

J. R. Kolb, H. F. Risso, Growth of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) I. Anisotropic Thermal Expansion, Propellants, Explos, Pyrotech. 1979, 4, 10–16. doi: 10.1002/prop.19790040104.

J. L. Mainschens, F. Garcia, Thermal Expansion of TATB-based Explosives from 300 to 566 K, Thermochim. Acta 2002, 384, 71–83. doi: 10.1016/S0040-6031(01)00778-X.

T. G. Towns, Vibrational Spectrum of 1,3,5-triamino-2,4,6-trinitrobenzene, Spectrochim. Acta 1983, 39A, 801–804. doi: 10.1016/0039-8533(83)80020-8.

H. Sui, F. Zhong, K. Cheng, X. Liu, X. Ju, IR Vibrational Assignments of 1,3,5-triamine-2,4,6-trinitrobenzene (TATB) Based on Temperature-Dependent Frequency Shifts, Spectrochim. Acta A 2013, 114, 137–143. doi: 10.1016/j.saa.2013.05.067.

B. L. Deopure, V. D. Gupta, Vibration Spectra of 1,3,5-triamino-2,4,6-trinitrobenzene, J. Chem. Phys. 1971, 54, 4013–4019. doi: 10.1063/1.1675458.

H. Li, J. Zhao, G. Ji, D. Wei, Z. Gong, Vibrational Properties of Molecule and Crystal of TATB: A Comparative Density Functional Study, Phys. Lett. A 2006, 358, 63–69. doi: 10.1016/j.physleta.2006.04.096.

P. S. Makashir, E. M. Kurian, Spectroscopic and Thermal Studies on the Decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), J. Therm. Anal. Calorim. 1996, 46, 225–236. doi: 10.1007/BF01979963.

J. A. Carter, J. M. Zaug, A. J. Nelson, M. R. Manaa, Ultra-Fast Shock Compression and Shock-Induced Decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene Subjected to Sub-Nanosecond-Duration Shock: an Analysis of Decomposition Products, J. Phys. Chem. A 2012, 116, 4851–4859. doi: 10.1021/jp301771y.

T. Komatsu, Attempted Preparation of Diamond-like Carbon Nitride by Explosive Shock Compression of Poly (methineimine), J. Mater. Chem. 1998, 8, 2475–2478. doi: 10.1039/a804137g.

J. Bulir, M. Jelinek, J. Lanco, M. Trchova, K. Jurek, Study of CNx Films Deposited using Combined Deposition Method: Pulsed Lased Deposition in the RF Discharged Nitrogen Gas, Proceedings of SPIE 2001, 4430, 261–266.; ROMOPPO 2000: Sixth Conference on Optics, (29 June 2001). doi: 10.1117/12.432850.

J. J. Cuomo, P. A. Leary, D. Yu, W. Reuter, M. Frisch, Reactive Sputtering of Carbon and Carbide Targets in Nitrogen, J. Vac. Sci. Technol. 1979, 16, 299–3023. doi: 10.1116/1.569931.
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