Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental and Computational Study

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Supporting Information

ABSTRACT: Pentaerythritol tetranitrate (PETN) finds many uses in the energetic materials community. Due to the recent availability of erythritol, erythritol tetranitrate (ETN) can now be readily synthesized. Accordingly, its complete characterization, especially its stability, is of great interest. This work examines the thermal decomposition of ETN, both through experimental and computational methods. In addition to kinetic parameters, decomposition products were examined to elucidate its decomposition pathway. It is found that ETN begins its decomposition sequence by a unimolecular homolytic cleavage of the internal and external O–NO₂ bonds, while the competing HONO elimination reaction is largely suppressed. The global activation energy for decomposition is found to be 104.3 kJ/mol with a pre-exponential factor



of 3.72×10^9 s⁻¹. Despite the ability to exist in a molten state, ETN has a lower thermal stability than its counterpart PETN.

INTRODUCTION

Although the U.S. has experienced no major bombing in the last 20 years, small bombing events occur on the order of 2000 a year, and these may involve homemade explosives, such as erythritol tetranitrate (ETN).¹ ETN has become a material of concern because the precursors are readily obtained and nitration with mixed acid is relatively straightforward.² ETN was first synthesized in 1849, yet little is known about its stability and decomposition reactions under severe thermal conditions. Thus, there is a prompt need to acquire a thorough understanding of its detonation characteristics and chemistry of decomposition.^{3–5} Because ETN has the same number of nitro groups and better oxygen balance than pentaerythritol tetranitrate (PETN), we have examined it for possible replacement of PETN in formulations.⁶ However, its low melting point (60 °C) requires that its thermal stability be carefully examined. The current study employed both experimental and computational methods to investigate the thermal stability of ETN under thermal decomposition conditions. Isothermal aging was employed to provide an assessment of thermal kinetic parameters. Decomposition products were analyzed using mass spectrometry (MS) to determine if ETN decomposition is similar to PETN. In addition, density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level of theory were used to characterize the decomposition mechanisms of ETN in the gas phase. To

supplement the gas-phase calculations, reactive molecular dynamics simulations with the ReaxFF-*lg* force field augmented with the DFT calculations of the major decomposition routes were conducted to reveal the decomposition mechanisms operating at the reaction zone under simulated detonation conditions.

EXPERIMENTAL SECTION

Materials. ETN was prepared by nitration with acetyl nitrate, a route which results in a high yield of product more completely nitrated than by the mixed acid method.⁷ Glacial acetic acid (16.7 mL) and acetic anhydride (16.7 mL) were added to a round-bottom flask and suspended in an ice bath. White fuming nitric acid (8.4 mL, 99%) was added dropwise, maintaining a reaction temperature below 10 °C. The reaction mixture was allowed to stir for 30 min, and then meso-erythritol (2 g) was added portionwise, keeping the temperature below 10 °C. This mixture was allowed to stir for 2 h at 0 °C before it was removed from the ice bath and stirred another 2 h at room temperature. The reaction mixture was poured into a beaker of ice water, filtered, rinsed with a copious amount of ice water, and allowed to dry. The crude product (4.54 g) was

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Figure 1. Nitration of erythritol to ETN (stepwise nitration of each alcohol).

recrystallized from isopropanol and filtered to give the pure product (3.90 g). Purity was checked by melting point and liquid chromatography/mass spectrometry detector (LC-MS).

Our experiments also required crude, partially nitrated ETN. Since mixed acid nitration generally produces less complete nitration, this method was used with slight modifications.⁸ Sulfuric acid (3.0 mL, 96.5%) was added to a round-bottom flask and cooled to 0 °C. White fuming nitric acid (4.6 mL, 99%) was added dropwise maintaining a reaction temperature below 10 °C. The mixture was allowed to stir for 30 min at 0 °C, and erythritol (1 g) was added portionwise, keeping the temperature below 10 °C. This mixture was allowed to stir 1 h at 0 °C rather than 30 °C. The nitration mixture was also not allowed to stand for an additional half hour; instead it was precipitated in a beaker of ice water and neutralized with sodium bicarbonate. The resultant crude product was filtered, rinsed with ice water, and allowed to dry. It was not recrystallized. Figure 1 shows the nitration of erythritol to ETN.

IR, Raman, and NMR Spectra. IR spectra of solid ETN were obtained on a Thermo Scientific FTIR Nicolet 6700 ATR IR. Raman spectra of solid ETN were obtained using an Ondax 785.4 nm 225 mW laser and an Andor Shamrock 500i-D2-R spectrometer. The "Step and Glue" function was used, allowing the spectrometer to focus on a 2000 pixel portion of the spectrum at a time and then assemble a continuous spectrum. Each spectrum is a summation of ten spectra each with 1 s exposure time. The spectral range was from 755 to 1040 nm. The grating of the spectrometer was set to 1200 lines/mm and a blaze of 850.

One proton NMR sample was prepared by dissolving ETN in deuterated chloroform. The spectrum was collected on a Brüker Ultrashield 300 with a frequency of 300.13 MHz, a sweep width of 6188.199 Hz, and a center of 1853.43 Hz, calibrated on TMS at 0 ppm in deuterated chloroform (CDCl₃) using the pulse program zg30, a 1D pulse program with a 30° flip angle, using 16 scans and 2 dummy scans.

A second proton NMR sample was prepared by dissolving ETN in deuterated acetone. The spectrum was collected on a JEOL Eclipse Fourier transform nuclear magnetic resonance spectrometer equipped with a 400 MHz Oxford liquid refrigerant cooled superconducting magnet with a frequency of 400.13 MHz, a sweep width of 8802.55 Hz, and a center of 513.5938 Hz, calibrated on acetone at 2.09 ppm in deuterated acetone using the pulse program zg30, a 1D pulse program with a 30° flip angle, using 17 scans.

Carbon NMR samples were prepared by dissolving ETN in dimethyl sulfoxide (DMSO). The sample was run on a JEOL Eclipse Fourier transform nuclear magnetic resonance spectrometer equipped with a 400 MHz Oxford liquid refrigerant cooled superconducting magnet, multinuclear tunable probe with temperature control, and gradient shims. Carbon spectra were acquired using a decoupled single pulse and signal averaged over 1000 scans.

Kinetics. Samples were quantified using a liquid chromatograph on a 2.1 \times 50 mm, 3 μ m, 120 Å, Acclaim Polar Advantage II C18 (PA2) column coupled to a Thermo Electron Quantiva triple quadrupole mass spectrometer (LC-MS) with a heated electrospray ionization (HESI) source. Conditions for HESI analysis were: negative ion spray voltage 2800 V; sheath gas 65 AU; auxiliary gas 15 AU; sweep gas 2 AU; ion transfer tube 250 °C; and vaporizer temperature of 220 °C. Data collection and analysis was performed with Thermo Xcalibur software version 2.2, SP 1.48. LC solvent flow was composed of water with 200 μ M ammonium chloride, 200 μ M ammonium acetate, and 0.1% formic acid (A) and acetonitrile (B). The solvent flow rate was 300 μ L/min with the following gradient program (A%-B%): 0 to 1 min isocratic 70%-30%, 1 to 4 min gradient from 70%-30% to 5%-95%, 4 to 5.5 min isocratic 5%-95%, 5.5 to 6 min gradient from 5%-95% to 70%-30%, 6 to 7 min isocratic 70%-30%. Methanol (MeOH), acetonitrile (ACN), and water (H_2O) were used to prepare samples, and all LC-MS work was Optima LC-MS grade.

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ETN (1.000 mg \pm 0.050 mg) was added to melting point capillaries, which were then sealed with a flame sealer. Sealed capillaries were placed in a sand bath in an oven and aged isothermally for various time intervals. The capillaries were broken into vials containing 20.0 mL of methanol. The vials were placed on a shaker for 1 h and sonicated for 1 h. The resulting solution was syringe filtered to remove any glass particles. These samples were diluted (100 μ L of sample, 0.9 mL of ACN:H₂O 50:50 v:v) into LC vials. An internal standard (0.05 mL of 5 μ g/mL 2,4-dichlorophenoxyacetic acid in ACN:H₂O) was added to each LC vial. ETN standards were prepared in ACN:H₂O at concentrations of 1, 2, 3, 4, 5, and 6 μ g/mL. An amount of 1.0 mL of each standard was added to LC vials and spiked with the same quantity of the internal standard as the samples. Standards and samples were run using the LC-MS method described above and quantified based on the area under the chromatogram curves for ETN (retention time = 3.9 min).

For ETN in benzene the thermolysis process described for neat ETN was used with slight alterations in sample preparation. Stock solutions of ETN in benzene were prepared $(100 \pm 10 \ \mu g/mL ETN)$, and ampules were charged with 1.0 mL of stock solution and then sealed. Ampules were cooled in liquid nitrogen to solidify the benzene before being flamesealed using a propane-oxygen torch. Following thermal aging, ampules were broken into empty vials. Since the benzene was not miscible with ACN:H₂O the vials were then placed on an Organomation N-EVAP 116 nitrogen evaporator to remove the benzene. Once the vials were dry 20.0 mL of ACN:H₂O was pipeted into the vials. The vials were placed on a shaker for 1 h and sonicated for 1 h. The resulting solution was syringe filtered to remove any glass particles. An amount of 1.00 mL of the filtered solution was added to LC vials, and no additional dilution was necessary. An internal standard (0.05 mL of 5 μ g/ mL 2,4-dichlorophenoxyacetic acid in ACN: H_2O) was added to

T (°C)	1/RT (mol/kJ)	$k (s^{-1})$	$\max k \ (s^{-1})$	min k (s ⁻¹)	$\ln(k)$	$\max \ln(k)$	min $\ln(k)$
60	0.361	1.48×10^{-07}	2.00×10^{-07}	1.39×10^{-07}	-15.7	-15.4	-15.8
80	0.341	1.47×10^{-06}	2.08×10^{-06}	8.11×10^{-07}	-13.4	-13.1	-14.0
80	in benzene	1.01×10^{-06}	1.25×10^{-06}	6.98×10^{-07}	-13.8	-13.6	-14.2
110	0.314	3.12×10^{-05}	5.44×10^{-05}	2.42×10^{-06}	-10.4	-9.8	-12.9
120	0.306	4.51×10^{-05}	5.04×10^{-05}	4.45×10^{-05}	-10.0	-9.9	-10.0
140	0.291	2.14×10^{-04}	2.72×10^{-04}	1.58×10^{-04}	-8.45	-8.2	-8.8



Figure 2. DSC overlay of ETN and PETN (10 °C/min).

each LC vial. Samples were run using the LC-MS method described above and quantified based on the area under the chromatogram curves for ETN.

Plotting the natural logarithm of fraction ETN remaining versus heating time in seconds (s) allowed determination of the rate constant k (s⁻¹) at each temperature from the slope (Table 1). Plotting natural log of rate constant against -1/RT (where R = 0.00831 kJ/K·mol; and T, temperature in Kelvin) gave a slope with activation energy, E_a (kJ/mol), and *y*-intercept of natural log of the pre-exponential factor, A (s⁻¹).

Product Analysis. To identify potential decomposition products, partially decomposed samples were reexamined by LC-MS under different conditions than were used in the kinetics studies. These partially decomposed samples, representing 10-25% decomposition, produced at various temperatures, were run on the Quantiva LC-MS using a precursor ion scan. The mobile phase gradient, column, and ion source parameters were the same as for the quantification method described in the kinetics experimental section. To scan for decomposition products a precursor ion scan was set to look for precursor ions that fragmented into ions with m/z 62 (NO_3^{-}) and 46 (NO_2) . The first quadrupole was set to allow ions with m/z 80–800 through one m/z at a time. Each ion was then fragmented in the second quadrupole using argon collision gas at 1.5 mTorr with a collision energy ramp from 10 to 20 V. The third quadrupole scanned for anything that created fragments of m/z 62 and 46. The resulting chromatograms showed what parent ions in the decomposition products generated these fragments.

The partially decomposed samples were also run on a Thermo Exactive Orbitrap high-resolution mass spectrometer with an atmospheric pressure chemical ionization (APCI) source coupled to an LC, using the same LC parameters as on the Quantiva. Conditions for APCI analysis were: sheath gas 35 AU; auxiliary gas 17 AU; sweep gas 0 AU; discharge current 10 μ A; capillary temperature 150 °C; capillary voltage -25.00 V; tube lens voltage -100.00 V; skimmer voltage -18.00 V; and vaporizer temperature 200 °C. The Orbitrap MS was set to negative mode, high resolution (50 000), and 50 ms maximum inject time and and looked for ions m/z 100-1000. The resultant data were analyzed by generating extracted ion chromatograms for the exact mass of potential decomposition products ($m/z \pm 5$ ppm) of ETN (Table 3). Decomposition product chromatograms were compared to crude, nonfully nitrated ETN chromatograms to verify some of the products.

COMPUTATIONAL DETAILS

DFT Calculations. The quantum chemical calculations were carried out using the Gaussian 09 package.⁹ The B3LYP hybrid density functional¹⁰ was used in conjunction with the Pople triple ξ (6-311G) basis set. The energetics for local minima and transitions states were recalculated using an augmented diffuse functions (6-311G++(d,p)) basis set. The relative energy of proposed chemical reactions includes the zero-point energy (ZPE) correction of the corresponding species. All the calculated frequencies, the zero-point energies, and the thermal energies correspond to harmonic approximation. The calculations of intrinsic reaction coordinates (IRCs) using internal coordinates were performed in order to examine whether the transition states under consideration connect the expected reactants and products.

ReaxFF-*lg* **Thermal Decomposition Simulations.** The computational cell of crystalline ETN contained 256 molecules (6656 atoms) and was created by multiplying each one of the \vec{a} ,

compound	method	E _a (kJ/mol)	max E _a (kJ/mol)	min <i>E</i> _a (kJ/mol)	$A(s^{-1})$	$\max A \ (s^{-1})$	min A (s^{-1})	$k_{240 \ ^{\circ}\mathrm{C}} \ (\mathrm{s}^{-1})$	$k_{200 \ ^{\circ}\mathrm{C}} \ (\mathrm{s}^{-1})$	$k_{140 \ ^{\circ}\mathrm{C}} \ (\mathrm{s}^{-1})$	ref
ETN	isothermal (LCMS)	104.3	108.4	95.5	3.72×10^{09}	1.39×10^{10}	1.88×10^{08}	8.9×10^{-02}	1.1×10^{-02}	2.4×10^{-04}	this work
ETN	DSC	95.0	N/A	N/A	2.35×10^{10}	N/A	N/A	5.0×10^{00}	7.5×10^{-01}	2.3×10^{-02}	7
PETN	manometric	196.6	N/A	N/A	6.31×10^{19}	N/A	N/A	5.9×10^{-01}	1.2×10^{-02}	8.4×10^{-06}	13
PETN	monometric ^a	165.3	N/A	N/A	1.26×10^{16}	N/A	N/A	1.9×10^{-01}	7.0×10^{-03}	1.6×10^{-05}	13
PETN	weight loss	161.5	N/A	N/A	1.58×10^{15}	N/A	N/A	5.6×10^{-02}	2.3×10^{-03}	5.9×10^{-06}	12
PETN	chemical analysis	132.2	N/A	N/A	2.00×10^{13}	N/A	N/A	6.8×10^{-01}	5.0×10^{-02}	3.8×10^{-04}	12
PETN	DSC	136.5	N/A	N/A	7.47×10^{14}	N/A	N/A	9.4×10^{00}	6.3×10^{-01}	4.0×10^{-03}	7
PETN	manometric	217.4	N/A	N/A	4.70×10^{21}	N/A	N/A	3.4×10^{-01}	4.6×10^{-03}	1.5×10^{-06}	11
^a 5% in dicyclohexyl phthalate.											

Table 3. Decomposition Products Searched for by High-Resolution LCMS



 \vec{b} , and \vec{c} unit cell vectors by 4. The resulting supercell had dimensions 63.8 Å \times 20.8 Å \times 52.9 Å with monoclinic symmetry. Minimization of potential energy was carried out using a conjugate gradient algorithm, followed by temperature (NVT) and pressure (NPT) equilibration steps at ambient conditions (300 K and 1 atm) for 10 ps each. The calculated bulk density of the equilibrated sample was $d_0 = 1.78 \pm 0.01 \text{ g/}$ cm^3 , in excellent agreement with experiment (1.773 g/cm³ at room temperature). Thermal decomposition simulations at simulated detonation conditions (T_{CI} = 4300 K, P_{CI} = 26 GPa) were carried out in the NPT ensemble. During the simulations, bond orders between each pair of atoms were monitored and properly averaged to avoid identification of artificial covalent bonds during possible short-lived, high energy encounters of two atoms. The ReaxFF-lg force field used in the study was further augmented with the reported DFT calculations of unimolecular and bimolecular decomposition energy barriers. The resulting force field accurately reproduced the major decomposition channels of ETN as can be seen in the Supporting Information (SI 1).

RESULTS AND DISCUSSION

Kinetics. We have previously compared the rate of decomposition of ETN and PETN by differential scanning calorimetry (DSC); ETN appeared to decompose more rapidly. Figure 2 illustrates this. To assign reliable values to the ETN



Figure 3. Arrhenius plots for ETN and PETN.

decomposition, isothermal studies were performed on neat ETN over the temperature range 60 to 140 °C. In one set of experiments ETN (100 ug/mL) was heated in benzene at 80 °C; under these conditions ETN decomposed somewhat slower than observed in the condensed phase (Table 1). Percent ETN remaining was assessed from liquid chromatog-

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Figure 4. PETN loss of $\bullet NO_2$



Figure 5. Energetics of PETN decomposition as calculated using B3LYP/6-311++G** level of theory. Energy values are given in kJ/mol.



Figure 6. Energetics of ETN decomposition, calculated by B3LYP/6-311++G^{**} level of theory. Top side of figure shows reactions in which ejection of \cdot NO₂ and HONO proceeds from the internal $-CH-O-NO_2$ group. Bottom side shows the same reactions proceeding from the external $-CH_2-O-NO_2$ group. Energy values are given in kJ/mol.

raphy; only in a few instances did any ETN survive past 70– 75% remaining. Sample decomposition tended to accelerate rapidly from 25 to 30% decomposition to 100% decomposition. This autocatalytic decomposition can be attributed to the reactive nature of ETN as well as that of its decomposition products (discussed in the next section).

Rate constants $(k \text{ in s}^{-1})$ at each temperature were determined and plotted in Arrhenius fashion. The Arrhenius parameters are listed in Table 2. Figure 3 shows the Arrhenius plots generated from our isothermal ETN decomposition data

as well as that of German¹¹ for PETN. The rest of the lines have been generated from reported Arrhenius parameters.^{7,12,13} The isothermal ETN data overlap with Roth's¹² values for PETN, but Roth's reported kinetics are significantly faster than those of both Robertson¹³ and German.¹¹ Robertson reported Arrhenius parameters for the decomposition of neat PETN and in dicyclohexyl phthalate solution. He observed a slight deceleration of the decomposition in solution, and in the present study a similar retarding of decomposition was observed when ETN was heated in benzene. The preponder-

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Figure 7. ETN starting reaction (H atom transfer between two ETN molecules) in intermolecular decomposition routes. Energy values are given in kJ/mol.



Figure 8. Calculated initial decomposition species of bulk ETN during simulated detonation conditions with T = 4300 K and P = 26 GPa. Only the first 10 ps are shown with the major intermediate species. Values are normalized to initial amount of ETN molecules.



Figure 9. Calculated thermodynamically stable decomposition products obtained in decomposition of bulk ETN at simulated detonation conditions, $P_{CJ} = 26$ GPa and $T_{CJ} = 4300$ K. Values are normalized to initial amount of ETN molecules.

ance of data suggests ETN decomposes faster than PETN. This is not surprising since ETN melts at much lower temperature than PETN, and many explosives decompose immediately upon melting. However, from its DSC trace, ETN appears to have a wider temperature stability range than PETN (Figure 2); like TNT, its decomposition does not immediately follow its melt. Elsewhere we have reported our attempts to exploit this feature.⁶

It is generally accepted that "the decomposition of primary and secondary aliphatic nitrate esters involves the initial, reversible, rate-determining scission of the O–NO₂ bond" (Figure 4).^{14–16} This is expected to be the first step in ETN decomposition, as well. However, unlike in PETN, the nitro groups in ETN are not all equivalent. DFT calculations and ReaxFF-*lg* reactive molecular dynamics simulations together with experimental product analysis were performed to probe ETN decomposition routes.

Product Analysis. The LC-MS Quantiva precursor ion scan showed only two parent ions which produced m/zfragments of 62 (NO_3^-) -ETN and erythritol trinitrate $C_4H_7N_3O_{10}$ (EtriN). Under the fragmentation conditions, no parent ions were found to produce fragment m/z of 46 (NO_2^{-}) . The LC-MS Orbitrap found additional evidence of decomposition products erythritol dinitrate $C_4H_8N_2O_8$ (EdiN) and erythritol mononitrate C4H9N1O6 (EmonoN). These may not have been observed in the Quantiva because either they did not produce a m/z fragment of 62 or, more likely, the Orbitrap was simply more sensitive to the mono- and dinitrated species, especially when using an extracted ion chromatogram. The increased resolution of the Orbitrap allowed examination of an extracted ion chromatogram in a mass window of less than 0.005 amu. This reduced the background signal to almost nothing since, for small molecules, the only interfering ions would be those with identical chemical formulas as the analyte. LC-MS extracted ion chromatograms and mass spectra are included in the Supporting Information (SI 2-4).

Density functional theory (DFT) calculations were performed to assess and compare potential first steps in the PETN and ETN decompositions. Two possible unimolecular decompositions were considered (Figures 5 and 6). Breaking the O– NO_2 bond would form two radicals $\bullet NO_2$ and the rest of the molecule. This reaction proceeds via a transition state for which the energy barrier is approximately the same as the energy of reaction. It corresponds to bond dissociation energy. Subsequent reactions would involve ejection of other radicals, and these would proceed via low energy barriers. With free $\bullet NO_2$ in the formulation, autocatalytic decomposition would be expected. The exothermic ejection of HONO was also considered as a potential first step in decomposition. For ETN decomposition, creation of two radicals by elimination of $\bullet NO_2$ proceeds via an energy barrier about 37 (30) kJ/mol lower than



Figure 10. Left panel: Calculated average number of carbon atoms in a molecule colored in blue and percent of carbon atoms in green. Right panel: Calculated elemental ratios in carbonaceous species during decomposition.

Table 4. Decomposition Channels of ETN and PETN^{*a,b*}

decomposition reaction	ETN (lowest)	PETN
	Elimination Reactions	
+NO ₂ (radical) (BDE)	121.3 (109.2)	139.7 (163.2) ^b
+HONO $(\Delta E^{\#})$	158.3 (136.0)	149.8
+HONO $(\Delta E_{\text{react}})$	-164.0 (-130.1)	-92.0
	H Atom Transfer	
H atom shift $(\Delta E^{\#})$	172.4	
H atom shift (ΔE_{react})	12.6	50.6

^{*a*}Energy values in kJ/mol. Method and basis set: B3LYP/6-311++G^{**}. ^{*b*}The quantum chemical calculations used the Gaussian-09 package.⁹ The B3LYP hybrid density functional²⁰ was used with the Pople triple ξ (6-311G) basis set. Numbers in parentheses indicate the energetics for local minima, and transitions states were recalculated using augmented diffuse functions (6-311G⁺⁺(d,p)) basis set M06/6-311G^{**} results from Liu et al.²¹

elimination of HONO, where the elimination of internal groups requires less energy in both reactions. This route is more favored than it is for PETN. In PETN, HONO elimination proceeds via an energy barrier only slightly higher than the decomposition path forming two radicals by about 10 kJ/mol. Unlike PETN, the carbons in ETN are inequivalent. The O-N bond energy in CH₂O-NO₂ (terminal C) and CHO-NO₂ (internal C) differs. Computed energy level diagrams show that •NO₂ elimination is favored from the internal carbon (Figure 6). Computation also reveals that potential bimolecular H atom migration between two PETN or ETN molecules is unfavorable (Figures 5 and 7). The lack of bimolecular ETN decomposition is supported by the observation that the rate of ETN decomposition at 80 °C remained essentially identical whether performed neat or in benzene solution (Table 1). This result also agrees with a recent theoretical study of thermal decomposition of condensed-phase energetic materials.¹⁶

To shed light on the initial steps of thermal decomposition of bulk ETN in a detonation scenario, reactive molecular dynamics simulations were performed on a model single crystal of ETN. The ReaxFF-*lg* force field that was previously trained to accurately reproduce reaction energetics and equations of state of energetic materials,¹⁷ including PETN was used in the simulations. We have augmented the force field with additional DFT data related to ETN, including molecular structures, partial atomic charges, and main decomposition reactions reported in this study, to obtain a high quality force field for ETN chemistry under ambient and extreme conditions. Thermal decomposition simulations were performed in a constant-pressure ensemble (NPT) at 4300 K and 26 GPa simulating the Chapman–Jouguet point. Figure 8 presents the initial steps of ETN decomposition as a function of time under these conditions. The results clearly show that the decomposition sequence begins with the cleavage of the O-NO₂ bond, the weakest bond in the molecule. This leads to increasing concentration of $\bullet NO_2$ radicals in the system, reaching a peak value of 1.2 times that of the initial amount of ETN molecules after about 1.8 ps. Concurrently, the trinitrate (EtiN), dinitrate (EdiN), and mononitrate (EmoN) forms of ETN are observed pertaining for subsequent cleavage reactions. These species were also experimentally observed in the LC-MS Orbitrap measurements and in a recent study of shock-induced decomposition of ETN.³ The \bullet NO₂ radicals quickly (~2 ps) disappear, forming more stable nitro intermediates. A known competing reaction to the O-NO₂ cleavage in nitro esters is the elimination of HONO (nitrous acid) as is observed in the DFT calculations. This reaction requires overcoming a barrier of 136.0 or 158.2 kJ/mol for an internal or external elimination, respectively. Accordingly, the formation of HONO slightly lags behind and is a less favorable route (Figure 8). Nevertheless, contrary to $\bullet NO_2$ elimination which is purely endothermic, the formation of HONO releases 130.1 and 164.0 kJ/mol of energy for the internal and external cleavages, respectively. Hence, this route could lead to an almost self-sustained propagation of decomposition. The •NO is another radical species reaching a significant amount during the initial stages of ETN decomposition. This species appears when ETN relative amount in the system is nearly 40%; hence, it does not seem to be a trigger reaction for decomposition but rather plays the role of a secondary byproduct. A possible route for the production of NO under the assumption of ground-state decomposition is the bimolecular reaction, where RO• is an ETN moiety

$$RO \bullet + \bullet NO_2 \rightarrow ROO \bullet + \bullet NO$$

It should be noted that •NO has been detected experimentally in several thermal decomposition studies of PETN.^{18,19} Formaldehyde is another intermediate observed during secondary product evolution under detonation conditions. It reaches a peak amount (20% relative to ETN) concurrently with HONO but decays faster to negligible amounts. Other less significant intermediates during decomposition involve •NO₃ and NO_xH_y and various carbon moieties of ETN at low amounts; hence, they were not presented in Figure 8 for clarity.

The stable decomposition products of ETN are presented as a function of time in Figure 9. It can be inferred from the figure that a steady state in stable decomposition products concentrations is reached approximately after 10-20 ps. However, there is a clear distinction between the rates of formation of different stable products. The formation rate of H₂O is the highest, and it is also the most abundant species. N₂



Figure 11. Extracted ion chromatograms (291.9825) of partially (a) nitrated and (b) decomposed ETN.

and CO_2 evolve at similar rates and reach practically identical final amounts. Minor products, including $\bullet OH$, H_2O_2 , and trace amounts of H_3O_2 evolve at an intermediate rate. CO is not formed at all since ETN bears a positive oxygen balance of 5.3%. Thus, the net decomposition reaction occurring in the reaction zone of a detonation wave can be summarized as follows:

$$\begin{split} C_4 H_6 O_{12} N_4 &\rightarrow 1.4 CO_2 + 1.5 H_2 O + 1.4 N_2 \\ &+ (0.3 OH + 0.2 H_2 O_2) \end{split}$$

Detailed analysis of the carbon distribution in the system revealed no apparent formation of carbonaceous clusters due to incomplete oxidation reactions. The initial carbon in the system resides solely in the ETN molecules; hence the average number of carbon atoms per molecule is 4, as can be inferred from the left panel in Figure 10. Accordingly, the ratio of carbon atoms out of total number of atoms in the molecules is $4/26 \approx 15.3\%$. During the very first endothermic stage of decomposition, covalent bonds begin to break, and the initial intermediates are highly transient carbonaceous radicals including covalent dimers. Interestingly, the relative amount of carbon atoms in these species grows rapidly during the first 1.7 ps and then gradually decreases to a steady state value of \sim 24%. This trend parallels the instantaneous increase in the average number of carbon atoms in each species and the rapid fall off to an approximate value of 1.5 carbon atoms per species at later times. To understand the underlying mechanisms of carbon transformation in the system, elemental analysis was performed on all carbonaceous species in the system. This is shown in the right panel in Figure 10. The initial elemental ratios correspond to the expected ratios in ETN molecule, and the rapid fall off marks the commencement of the decomposition process. However, unlike the N/C and H/C ratios which continue to gradually decrease, the O/C ratio rises rather quickly to its steady state value. Evidently, the rise in the relative amount of oxygen atoms compared to carbon atoms is due to various oxidation processes. These can be divided into three regimes: instantaneous bond breaking (0 ps until 1.7 ps), fast oxidation (from 1.7 ps until 7.0 ps), and a slow oxidation regime (from 7.0 ps onward). The transition between the first and the second stages coincides with the time of complete decomposition of the initial ETN molecules (Figure 8). Thus, the first stage



Figure 12. IR of ETN, DFT (top) and experimental (bottom). Red: ONO scissoring (calcd: 820–854 cm⁻¹, exptl: 827–874 cm⁻¹). Green: symmetric NO₂ stretching (calcd: 1326–1337 cm⁻¹, exptl: 1259–1277 cm⁻¹). Purple: asymmetric NO₂ stretching (calcd: 1741–1753 cm⁻¹, exptl: 1626–1659 cm⁻¹).

represents the initial degradation mechanisms of parent ETN molecules, mainly via the release of $-NO_2$ and $-ONO_2$ groups. The second, intermediate stage, is governed by the rapid oxidation of unstable intermediates, while the third, slow stage originates from the oxidation of less reactive species coupled to the diffusion mechanisms of free oxygen and other oxidizing agents in the system. At the end of 60 ps of decomposition, approximately \sim 3% of molecular oxygen is still present in the system. Clearly, the simulation duration is not enough for these slow oxidation processes to reach full chemical equilibrium. Nevertheless, the slight gradual increase in O/C ratio indicates that such a state shall indeed be reached. Counterintuitively, the O/C ratio is slightly higher than 2 which would be expected in the state of a complete combustion. This is due to the formation of several overoxidized species, such as CO_3 , C_2O_4 (CO₂ dimer), and C_2O_4 -H radicals. In addition, the final average number of carbon atoms per molecule (Figure 10, left panel) is around 1.5, rather than 1.0, indicative of covalent dimers. However, their amounts in the system are quite low, and these highly unstable species will eventually disintegrate

into the thermodynamically stable CO_2 under isentropic cooling following the expansion of the detonation products on much longer time scales. Table $4^{9,20,21}$ compares the energies involved in various

Table 4^{9,20,21} compares the energies involved in various decomposition routes of PETN and of ETN. The energy differences for the elimination reactions between ETN and PETN are not large; both can access NO₂ or HONO elimination routes. The main difference between the two nitrate esters is in H-interexchange reaction, in which ETN can transfer an internal H at lower energy cost than PETN.^{20,22} However, such a reaction would be expected to form a strong carbonyl bond along with NO₂ ejection. This is not observed under the present experimental conditions.

The decomposition products observed by LC-MS were derivatives of ETN in which, to some extent, $CO-NO_2$ had been replaced by CO-H, reforming the tri-, di-, and mononitrate esters of erythritol. To assess whether H-transfer had formed ketone or aldehyde groups (Figure 7) which had been transformed into alcohol species during the experimental workup, partially nitrated erythritol was prepared as described



Figure 13. Raman of ETN, DFT (top), and experimental (bottom). Red: OCH rocking (calcd: $586-592 \text{ cm}^{-1}$, exptl: 564 cm^{-1}). Green: NO₂ scissoring (calcd: 854 cm^{-1} , exptl: 870 cm^{-1}). Purple: NO₂ symmetric stretching (calcd: 1337 cm^{-1} , exptl: 1296 cm^{-1}).

in the Experimental Section. On the Orbitrap LC-MS, extracted ion chromatogram monitoring of m/z 291.9825 detected three peaks (Figure 11a). The peak at retention time 4.09 min was assigned to ETN and that at 3.54 min to erythritol trinitrate, and the small peak at 3.36 min may also be trinitrate which was nitrated on different carbons. Extracted ion chromatograms were also generated for m/z 246.9975 and m/z 202.0124, looking for evidence of erythritol dinitrate and mononitrate, respectively. Only the tetra- and trinitrates were observed. The 291.9825 m/z extracted ion chromatogram was compared to that of pure ETN which had been partially decomposed (Figure 11b). Two peaks were observed corresponding to the undecomposed ETN (retention time = 4.09) and the trinitrate (retention time = 3.54). The retention time for the erythritol trinitrate matched the largest trinitrate peak in the crude material. Thus, the main decomposition product was erythritol trinitrate, in which an alcohol group replaced one nitrate, and that alcohol was an original decomposition product of ETN,

not a product of subsequent analytical workup. The chromatograms of the partially decomposed ETN were searched for additional products, including the ketone and polymerized ETN. Structures searched are shown in Table 3; no decomposition products other than the lesser nitrates were discovered. In well-sealed and highly decomposed samples, red gas, assumed to be NO₂, was observed. This generation of NO₂ from ETN would explain the autocatalytic decomposition observed in ETN kinetics experiments.

We have previously reported the infrared and Raman spectra of ETN.⁷ Theoretical computations now permit assignment of major features. Figure 12 shows three major IR peaks assigned as ONO scissoring, symmetric NO₂ stretching, and asymmetric NO₂ stretching. In Raman spectra three major peaks are assigned as OCH rocking, NO₂ scissoring, and NO₂ symmetric stretching (Figure 13). The ¹H-decoupled ¹³C NMR in DMSO showed two singlets—terminal C at 68.7 and internal C at 76.5 ppm—which compare well to ETN in CDCl₃ with terminal C

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Figure 14. Carbon NMR of ETN.



Figure 15. Proton NMR of ETN in CDCl₃.

74.9 and internal C 67.4 ppm reported by Matyas²³ (Figure 14). Proton NMR of ETN was performed in acetone and CDCl₃. In CDCl₃ four doublets were observed at 4.65, 4.69, 4.91, and 4.96 ppm representing the four protons on the terminal carbons. A multiplet at 5.51 ppm corresponded to the two protons on the internal carbons. Acetone proton NMR was

similar to four doublets observed at 5.01, 5.05, 5.25, and 5.29 as well as a multiplet at 6.04 (Figure 15).

CONCLUSIONS

Experimental and computational study of ETN stability and reactivity in different thermal regimes was performed.

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Isothermal aging of ETN samples has provided insight into the thermal stability of ETN as well as details on the resulting decomposition products. Despite the ability to exist in a molten state, ETN has a lower thermal stability than its counterpart PETN. However, it was found that ETN was significantly more stable than estimated from DSC data.⁷ Decomposition products identified were exclusively formed by loss of •NO2 which is often the case for nitrate esters. DFT computations indicated that the first step in ETN and PETN decomposition could be NO₂ or HONO ejection, though the former is more energetically favored. After the first step a number of decomposition routes become available. Reactive molecular dynamics revealed the initial steps of the decomposition mechanism at the CJ point of $P_{CJ} = 26$ GPa and $T_{CJ} = 4300$ K. At these conditions, it was observed that bulk ETN begins its decomposition by successively releasing $\bullet NO_2$ groups from parent molecules and that HONO elimination is a secondary reaction. The identified stable decomposition products are H_2O , CO_2 , and N_2 , where H_2O is the most abundant species in the hot and compressed state. No carbonaceous clusters were formed during decomposition since ETN should reach a complete oxidation. Furthermore, oxidation of carbon was observed to proceed in three steps. In the first stage ETN molecules undergo homolysis reactions to release •NO₂ and •ONO₂ groups. The second, intermediate stage, is governed by the rapid oxidation of unstable intermediates, while the third, slow stage originates from the diffusion of molecular oxygen and other oxidizing agents in the system. In experimental tests it was observed that ETN decomposition frequently accelerated rapidly beyond 25-30% to 100% decomposition; this can be explained by the reactive nature of the $\bullet NO_2$ radicals produced.

ASSOCIATED CONTENT

S Supporting Information

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Orbitrap chromatograms and mass spectra (PDF)

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Notes

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