

Laser-Induced Decomposition of TNAZ

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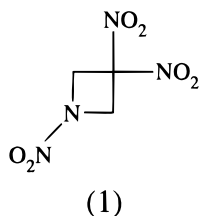
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The initial decomposition products of 1,3,3-trinitroazetidine (TNAZ) are characterized using time-of-flight mass spectrometry. To induce thermal decomposition, solid samples of TNAZ are irradiated with 248 nm laser pulses. Products released to the gas phase are ionized by a pulse of 118 nm light, and the ions are detected using a time-of-flight mass spectrometer. Neutral time-of-arrival scans are used to determine the translational temperature and the relative yields of the products. The translational temperature is found to depend linearly on the decomposition laser fluence, consistent with a photothermal decomposition mechanism. Analysis of the temperature dependence of the relative product yields shows that two reactions are important in the initial decomposition of TNAZ: unimolecular nitro–nitrite rearrangement followed by loss of NO and a bimolecular reaction generating nitrosodinitroazetidine (NDNAZ). Loss of NO₂ appears to be an early, but not initial, decomposition step. Experiments with isotopically labeled TNAZ show that the nitro–nitrite rearrangement occurs on the nitramine group and that NO₂ is lost from both the nitroalkyl and nitramine groups. NDNAZ is generated by replacement of the leaving nitramine nitro group by NO.

Introduction

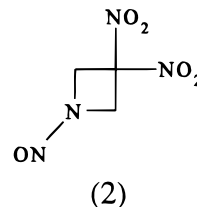
TNAZ (1,3,3-trinitroazetidine) (**1**), a relatively new energetic



material, is the smallest member of a class of cyclic nitramines with *gem*-dinitroalkyl groups. Since TNAZ has a low melting point (374 K) and is thermally stable to greater than 513 K,¹ it is steam-castable and considered a potential replacement for 2,4,6-trinitrotoluene (TNT).² TNAZ is reported to be more powerful and less sensitive than the most powerful military explosive formulation.² TNAZ is also being considered in propellant applications since nitramines such as 1,3,5-trinitrohexahydro-*s*-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are components of propellants.³

Characterization of the thermal decomposition mechanism of energetic materials leads to an increased understanding of the relationship between structure, sensitivity, and performance. Several experimental studies of the thermal decomposition of TNAZ have been reported.^{3–6} Most of these studies examined the pressure and temperature dependence of the product yields, and one determined the global kinetic parameters of TNAZ decomposition.⁶ Information about the thermal stability of TNAZ is derived from slow thermal heating experiments while information about the initial decomposition steps is gained from rapid heating experiments. Results from the slow heating experiments on TNAZ are discussed first.

Behrens and Bulusu used simultaneous thermogravimetric modulated beam mass spectrometry to probe the decomposition of isotopically labeled TNAZ samples.⁵ The major products observed were NO and NO₂, while minor products included H₂O, HCN, CO/N₂, CH₃CN (*m/z* = 41), and nitrosodinitroazetidine NDNAZ (**2**) (*m/z* = 176). Behrens and Bulusu



proposed that the unimolecular decomposition pathways include loss of NO₂ (from the nitramine group initially) and nitro–nitrite rearrangement (probably on the *gem*-dinitro group) followed by loss of NO. They also concluded that NO reacts with TNAZ to generate NDNAZ and NO₂.

After thermal heating of samples of TNAZ, both neat and in solution, Oxley et al. analyzed gas-phase products using a gas chromatograph with either thermal conductivity or mass spectrometric detection, and they analyzed condensed-phase products using NMR and GC/MS.⁶ The observed gas-phase products included CO₂, CO, N₂, and NO, and the most abundant condensed-phase products were NDNAZ (*m/z* = 176), hydrogenated DNAZ (*m/z* = 147), and 1-formyl-3,3-dinitroazetidine (*m/z* = 175). Oxley et al. also concluded that the initial step is loss of NO₂ to produce DNAZ and that N–NO₂ homolysis is slightly favored over C–NO₂ bond cleavage at early reaction time. In contrast to Behrens and Bulusu, Oxley et al. suggest that NO arises from the nitramine nitro group and that NO reacts with DNAZ to generate NDNAZ.

The initial decomposition steps can be elucidated by identifying the products of rapid thermal heating of TNAZ. Brill and co-workers flash-heated a film of TNAZ on a filament wire

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and detected the gas-phase products using FTIR spectroscopy.³ The most abundant products were NO₂ and NO. HCN and H₂-CO were detected, but N₂O was not. In the thermal decomposition of nitramines such as HMX and RDX, the presence of H₂CO and N₂O products together indicates C–N bond cleavage. Because HCN and NO₂ were observed as products of TNAZ decomposition and N₂O was not, Brill and co-workers concluded TNAZ decomposes via N–N bond scission.

Lee and co-workers, using photofragment translational spectroscopy, studied the decomposition mechanism of TNAZ entrained in a molecular beam.⁴ TNAZ was thermally decomposed via infrared multiphoton dissociation, and the products were detected using quadrupole mass spectrometry. Dissociative ionization of decomposition products was a severe complication in these experiments, and much of the mechanistic information was deduced from analysis of the time-of-arrival profiles of fragments. Under gentle heating conditions, the initial decomposition step was proposed to be loss of NO₂ to generate DNAZ. At higher laser fluence conditions, additional products were seen suggesting that the DNAZ ring opens, a second NO₂ group is lost, and subsequently a N–NO₂ group ($m/z = 60$) is ejected.

In addition to their thermal decomposition studies described above, Oxley and co-workers obtained mass spectra of heated TNAZ.⁷ Collision-induced dissociation of the fragment ions was used to help elucidate their structures. In contrast to the thermal decomposition studies, the authors concluded that the C–NO₂ bond breaks first and the N–NO₂ bond breaks second. The observed NO and NO₂ molecules appear to arise from the nitramine nitro group.

Politzer and Seminario used a nonlocal density functional approach to calculate the reaction energetics for TNAZ decomposition.⁸ They report bond strengths of 44.6 and 46.6 kcal mol⁻¹ for the N–NO₂ and C–NO₂ bonds, respectively. The low calculated bond strength for the C–NO₂ is surprising since for cyclic molecules such as 3-nitro-1,2,4-triazol-5-one (NTO), the C–NO₂ bond strength is estimated⁹ to be ~70 kcal mol⁻¹. Possible explanations suggested by the authors include stabilization of the $m/z = 146$ fragment (generated by cleavage of the C–NO₂ bond) by delocalization of the unpaired electron and reduction of the strain introduced by having two NO₂ groups on the same carbon. They predict a primary NO₂ loss followed by a ring-opening step and then secondary loss of NO₂. While ring opening is predicted to be thermoneutral, secondary loss of NO₂ via simple bond scission is calculated to be endothermic by 40–70 kcal mol⁻¹, and secondary loss of NO₂ followed by rearrangement of the $m/z = 100$ fragments is calculated to be exothermic by ~20 kcal mol⁻¹.

In general, there is agreement among the experimental studies that several decomposition steps occur although there is some disagreement about the order of the steps and the identity of the broken bonds. All studies suggest that loss of NO₂ is one of the first steps, and the consensus is that the nitramine nitro group leaves first. NO is proposed to form following nitro–nitrite rearrangement, but there is disagreement about which nitro group undergoes the rearrangement. The mechanism for formation of NDNaz is not clear, i.e., whether NO reacts with TNAZ or DNAZ to make NDNaz.

Information about the initial reaction steps of TNAZ decomposition can be obtained by analyzing relative product yields as a function of temperature. In this paper, we describe a study in which TNAZ is heated photothermally by irradiating solid samples with 248 nm pulses from an excimer laser. The gas-phase neutral products are photoionized with a beam of 118 nm light and detected in a time-of-flight mass spectrometer.

Translational temperatures and relative product yields are determined from analysis of time-of-arrival scans. To obtain additional mechanistic information, experiments on isotopically labeled samples were carried out.

Experimental Section

The experiments were carried out in a time-of-flight mass spectrometer which has been described in detail previously.¹⁰ Briefly, solid samples of TNAZ were placed inside a vacuum chamber. To induce decomposition, the samples were irradiated with 248 nm pulses from an excimer laser. The ejected neutrals including gas-phase decomposition products were photoionized by a beam of 118 nm light, and the ions were detected using time-of-flight mass spectrometry.

The solid samples were placed on the end of the shaft of a rotating motor that was mounted on an XYZ translator attached to the flange of the vacuum chamber. The samples were prepared by pressing ~100 mg of material into 1/2 in. diameter pellets. Unlabeled TNAZ samples were obtained from Thiokol and used as received. Samples of isotopically labeled TNAZ were provided by Smith.^{6,11} The TNAZ pellets initially prepared had a tendency to crumble so a modification of the hot pressing technique¹² was used to compress the powder. The die was wrapped with heating tape and heated to ~50 °C. The temperature was monitored with a thermocouple, and the powder was compressed at a pressure of 12 000 psi for ~10 min. The compressed sample was placed inside a stainless steel tube that had a small mesh screen spot-welded to one end.¹³ An aluminum rod was placed in the tube compressing the pellet against the mesh, and the rod was attached to the end of the rotating shaft.

Preliminary decomposition experiments using 266 nm radiation yielded very low ion signals. Absorption spectra of TNAZ in solution, measured in our laboratory, showed that $\epsilon(248 \text{ nm})$ is 6 times larger than $\epsilon(266 \text{ nm})$, thus the 248 nm output of a KrF excimer laser (Lambda Physik 201MSC) was used to decompose the TNAZ. The pulses (100–250 μJ) were focused normal to the surface of the sample with a spot size of $\sim 2 \times 10^{-3} \text{ cm}^2$, resulting in a fluence between 50 and 125 mJ cm⁻² (5–12.5 MW cm⁻²). The decomposition laser fluence was kept low to ensure that ions were not generated at the surface of the pellet by the decomposition laser.

After traveling to the ionization region, the neutral products are ionized by a beam of 118 nm (10.5 eV) light directed perpendicular to the path of the decomposition laser. At this wavelength, most (but not all) of the gas-phase products will be ionized in a single-photon process. Ionization using low-energy photons minimizes dissociation of the decomposition products; dissociative ionization greatly complicated the interpretation of data taken in experiments employing 70 eV electrons.⁴ The 118 nm light is generated by frequency-tripling the 355 nm output of a Nd:YAG laser (Quantel 581-C) in a cell containing xenon as previously described.¹⁰

The time-of-flight mass spectrometer is of the Wiley-McLaren design (R.M. Jordan Co.). After photoionization, the ions are accelerated through a 0.89 m flight tube and detected with a microchannel plate. The signal from the detector is amplified (SRS SR440) and directed to a digital storage oscilloscope (LeCroy 9400). Mass spectra are obtained at fixed time delays between the decomposition and ionization steps. Timing for the laser triggers is provided by a digital delay generator (SRS DG535) and a personal computer.

Time-of-arrival scans of several decomposition products were taken at various decomposition laser fluences. A time-of-arrival

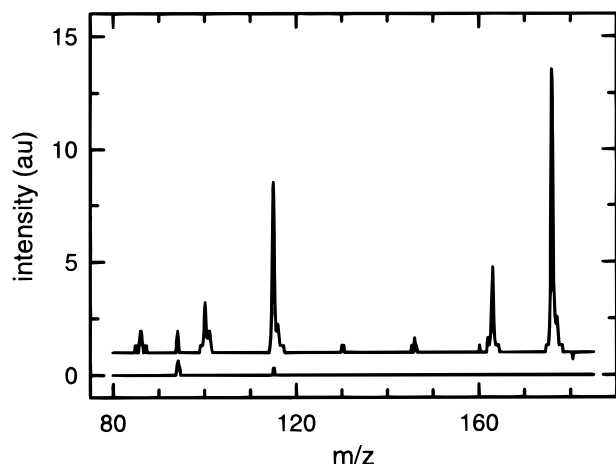


Figure 1. Time-of-flight mass spectra of products from laser-induced decomposition of TNAZ. The lower spectrum is obtained with the decomposition laser off and results from the dissociative ionization of background TNAZ. The upper spectrum was obtained with the decomposition laser on and is slightly offset from the background spectrum.

TABLE 1: Observed Products Following Laser-Induced Decomposition of TNAZ

obsd m/z	proposed product	obsd m/z	proposed product
176	$C_3H_4N_4O_5$	100	$C_3H_4N_2O_2$
163	$C_3H_5N_3O_5$	53, 54	C_3H_xN ; $x = 3, 4$
146	$C_3H_4N_3O_4$	46	NO_2
130	$C_3H_4N_3O_3$	30	NO
115	$C_3H_3N_2O_3$		

scan was acquired by monitoring the ion signal at a particular m/z value (i.e., at a fixed time delay following ionization) and then increasing the time delay between the decomposition and ionization lasers. These time-of-arrival scans were obtained to determine the translational temperature of the products as well as to determine the temperature dependence of the relative product yields.

Experiments were carried out using both isotopically labeled and unlabeled materials. To confirm the purity of these materials, mass spectra of the labeled and unlabeled compounds were obtained in a Fourier transform mass spectrometer (FTMS) using both 70 and 10 ± 2 eV electron impact ionization. The FTMS has been described elsewhere.¹⁴

Results

Figure 1 is a representative mass spectrum taken with a delay of 60 μs between decomposition and ionization lasers and a decomposition laser fluence of 100 $mJ\ cm^{-2}$. The TNAZ molecular ion with $m/z = 192$ was not observed in the TOF spectra using single-photon ionization or in FTMS experiments using electron-impact ionization, and it is presumably not stable. Table 1 is a list of the observed decomposition products and their proposed chemical formulas. The predominant high molecular weight products have $m/z = 176$, 163, and 146, and these fragments correspond to loss of an O atom, loss of NO (with gain of an H atom), and loss of NO_2 from the parent TNAZ molecule. These three pathways have been observed in the thermal decomposition of other compounds with nitro-alkyl^{10,15} and nitramine^{16,17} groups. The fragment corresponding to loss of NO generates a small signal at $m/z = 162$, but H atom transfer is facile in plumes generated by laser desorption of solid samples.¹⁵ Therefore, the product with $m/z = 163$ is considered to arise from nitro-nitrite rearrangement followed

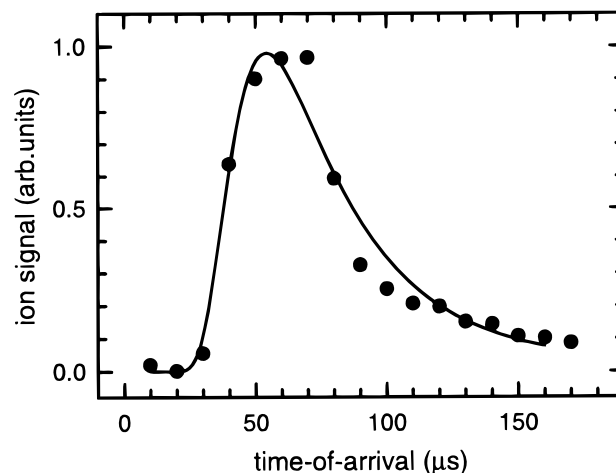


Figure 2. Time-of-arrival scan for the product with $m/z = 176$. The fluence of the decomposition laser is 82 $mJ\ cm^{-2}$. The points are experimental data, and the solid line is a fit to a thermal Maxwellian distribution with a translational temperature of 4000 ± 160 K.

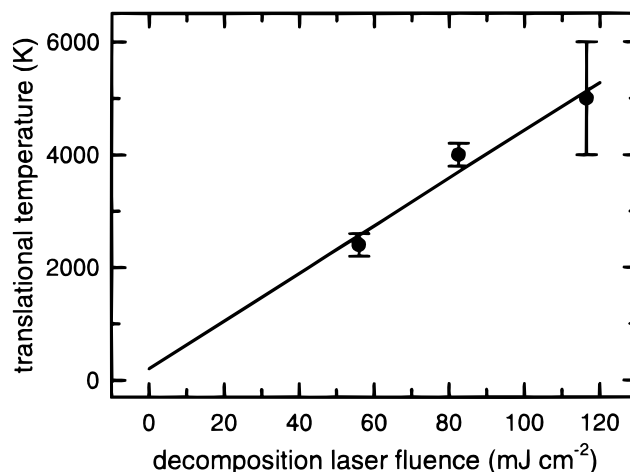


Figure 3. Plot of translational temperature of the $m/z = 176$ product as a function of decomposition laser fluence. The points are obtained from time-of-arrival scans as described in the text, and the solid line is a fit to the data.

by loss of NO, and the H atom addition is a consequence of chemistry in the high-density plume.

TNAZ has a significant vapor pressure at room temperature (0.31 mTorr).¹⁸ Sublimation of TNAZ in the vacuum chamber leads to a very small background signal generated by dissociative ionization of TNAZ including products with $m/z = 146$, 100, 46, and 30 but no products with $m/z > 146$. In addition, the FT mass spectra taken using ~ 10 eV ionization showed no products with m/z between 146 and 192; thus, the products with $m/z = 163$ and 176 are not the result of dissociative ionization of TNAZ in the present experiment.

As mentioned above, time-of-arrival scans of several products were taken to determine the translational temperature and the relative product yields as a function of temperature. Figure 2 is a time-of-arrival scan for the NDNZ product with $m/z = 176$ and a decomposition laser fluence of 82 $mJ\ cm^{-2}$. The points are experimental data, and the solid line is a fit to a thermal Maxwellian distribution with a translational temperature of 4000 ± 160 K. At a given decomposition laser fluence, the translational temperatures of the products with $m/z = 176$, 163, and 146 are the same within experimental error. Figure 3 is a plot of the translational temperature of the NDNZ product as

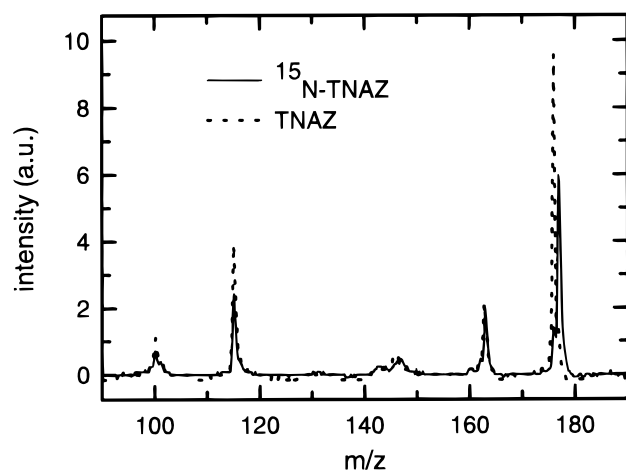


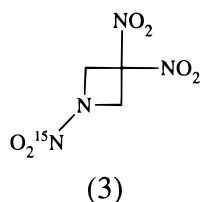
Figure 4. Time-of-flight mass spectrum of products from laser-induced decomposition of TNAZ. The spectrum with the solid line was obtained with a sample of unlabeled TNAZ. The spectrum with the dashed line was obtained with the isotopically labeled sample N-¹⁵N-TNAZ.

a function of decomposition laser fluence. The solid line is a fit to the data.

To characterize the initial decomposition steps of TNAZ decomposition, we obtained relative yields of the products with $m/z = 176$, 163 , and 146 as a function of decomposition laser fluence. The product yields are determined by velocity weighting, i.e., converting measured species density to flux, and then integrating the ion signal from a time-of-arrival scan. At a given decomposition laser fluence, the relative yield for a product is obtained by normalizing the integrated ion signal of the product to the sum of the signals of all the products. In our earlier study on NTO decomposition, the relative product yields showed a discernible dependence on decomposition laser fluence, and these trends were used to distinguish between initial and intermediate decomposition products.¹⁰ For TNAZ decomposition, even though the absolute product yields increased as the laser fluence increased as expected, with the exception discussed below there were no discernible trends in the relative product yields.

Several mass spectra were obtained at very low decomposition laser fluence ($<100 \text{ mJ cm}^{-2}$). While the low signal-to-noise ratio prevented a detailed analysis of the product time-of-arrival scans, at the lowest fluence, the ion signal with $m/z = 146$ is absent, and the ratio of the ion signals at $m/z = 163$ and 176 remains unchanged.

For a molecule like TNAZ, the laser-induced decomposition studies can reveal that a moiety, e.g. an NO_2 group, has departed from the parent. Studies of isotopically labeled samples can reveal mechanistic information including which bond in the molecule is broken. Figure 4 shows the mass spectrum from a TNAZ sample (3) in which the nitramine nitro group is labeled



¹⁵ NO_2 . The time delay between the decomposition and ionization lasers was $70 \mu\text{s}$, and the decomposition laser fluence was 122 mJ cm^{-2} . The spectrum with the solid line was obtained from the isotopically labeled sample while the spectrum with

TABLE 2: Isotopic Distributions (in %) in the High Molecular Weight Products of the Decomposition of N-¹⁵N-TNAZ

decomposition product	contains ¹⁵ N	all ¹⁴ N
TNAZ-O	80	20
TNAZ-NO + H	0	100
TNAZ-NO ₂	55	45

the dashed line was obtained under identical conditions from an unlabeled sample. The observed isotopic distributions for the three high molecular weight products are presented in Table 2.

As noted above, to confirm the purity of the compounds, we obtained mass spectra of the labeled and unlabeled compounds in the FTMS. The purity of the sample was calculated by comparing the intensities of ion signals from the pseudomolecular ion $(M + H)^+$ in each mass spectrum after short reaction time. An isotopic purity of 97–98% was determined by this method.

Discussion

Before describing the formation of the decomposition products, the preparation of hot TNAZ molecules in the present experiment is discussed. In a previous publication,¹⁰ we demonstrated that UV laser-induced decomposition of solid samples of NTO is completely consistent with a photothermal mechanism. Evidence for this conclusion consisted of the following: identical translational temperatures (within experimental error) for products whose mass differed by almost factor of 2, a linear dependence of the product translational temperature on the decomposition laser fluence, and a 1:1 correlation between the experimental translational temperature and the temperature of the surface calculated using the heat conduction equation and assuming that all the laser light energy is converted to heat. As seen in Figure 3, the translational temperature of the NDNAZ product is linearly dependent on decomposition laser fluence, consistent with a photothermal mechanism. In addition, at a given laser fluence, the translational temperatures for the different molecular weight products are the same within experimental error, showing that decomposition occurs at the surface of the sample and not in the source region of the mass spectrometer.

The least ambiguous information about the initial decomposition steps is obtained from characterization of the high molecular weight fragments. Low molecular weight products such as NO and NO_2 can arise from initial unimolecular decomposition as well as from secondary chemical reactions, complicating the interpretation of their behavior.⁴ As seen in Figure 1, among the high molecular weight products, the most abundant initial product is net loss of O atom from TNAZ. Because the ionization potentials and ionization efficiencies of these fragments are not known, care must be taken when attempting quantitative comparisons of the yields of different molecular weight products.

The TNAZ decomposition mechanism appears to be very similar to that of NTO. For TNAZ, the determination of a single initial decomposition step is difficult because the relative yields for the products with $m/z = 176$ and 163 do not change over a wide range of decomposition laser fluences. Since these two products are each the result of a bimolecular reaction, discerning a difference in their relative yields as a function of laser fluence is more difficult than if one of the steps were unimolecular. The initial steps for TNAZ include unimolecular loss of NO and a bimolecular reaction with a net loss of an O atom. Unimolecular loss of NO_2 is probably an early but not initial

reaction. It is surprising that the reaction which is most energetically favorable⁸ (unimolecular loss of NO₂) is the least important at low laser fluences. The other two steps (net loss of O atom and nitro–nitrite rearrangement followed by loss of NO) have been observed in the decomposition of nitroalkyl molecules such as NTO^{10,15,19} and nitramines such as RDX.^{20,21} In those studies, the step corresponding to loss of O atom was considered to be bimolecular because the N–O bond strength (75–85 kcal mol⁻¹) greatly exceeded the activation energy obtained from decomposition rate measurements. The importance of the reactions corresponding to loss of O and loss of NO in the initial decomposition of energetic materials is becoming increasingly apparent.

Mechanistic information about these three reaction steps is obtained from studies using a sample with ¹⁵N labeling on the nitramine nitro group as illustrated in Figure 4. The fragment produced by loss of NO (with addition of a hydrogen atom) does not change mass upon isotopic substitution, showing that the leaving group is isotopically labeled (NO) and that the NO departs from the nitramine group in agreement with the thermal decomposition studies of Oxley et al. The majority of the NDNAZ fragments, corresponding to loss of an O atom from TNAZ, appear at $m/z = 177$ with the labeled compound, but there is still some signal at $m/z = 176$. If NDNAZ were formed by simple addition of an alkyl group to TNAZ followed by loss of the RO group (as suggested by McMillen et al.¹⁵ in the decomposition of NTO), then all NDNAZ products should contain ¹⁵N and there should be no signal with $m/z = 176$ in the mass spectrum of the labeled compound. The FTMS experiments showed that the purity of the labeled compound is >97% so the ion signal at $m/z = 176$ cannot be due to impurity in the sample. Other proposed routes to generate NDNAZ include reaction of NO with TNAZ and addition of NO to DNAZ. In both cases, isotopic scrambling of the NDNAZ product is possible. Our observed isotopic ratio for this product is between that expected for bimolecular abstraction of O (100% ¹⁵N) and reaction of NO with TNAZ or DNAZ (33% ¹⁵N and 67% ¹⁴N). Thus, although most of the observed NDNAZ arises from the direct abstraction of O, 20–30% of the observed product must be due to reaction of NO with TNAZ or DNAZ.

The DNAZ fragment produced by loss of NO₂ from TNAZ has $m/z = 146$. Figure 4 shows that decomposition of labeled TNAZ generates products with $m/z = 146$ and 147 corresponding to NO₂ loss from the nitramine and nitroalkyl groups, respectively. This result is not surprising because the calculated bond strengths are so similar.⁸ The ion signals of both products are of comparable intensity similar to the findings of Behrens and Bulusu.⁵

Experiments in the FTMS confirm that the labeled TNAZ sample is 97–98% pure and, when using 70 eV electrons, reproduce the spectra previously reported by Zheng et al.⁷ Several interesting observations can be made concerning the FT mass spectra recorded using 10 eV electron ionization. First, ion signals from products with $m/z > 150$ were only observed after some reaction time, and they were very weak. This supports the notion that many of these ions are products of secondary reactions. Second, the shift in mass of the DNAZ fragment following isotopic substitution suggests that NO₂ from the nitroalkyl group is lost, but in apparent contradiction, the observed NO₂ arises from the nitramine group. Finally, the NO ion signal at $m/z = 30$ does not change mass upon substitution, suggesting that it arises from the nitroalkyl group in contrast to the conclusions from the TOFMS experiments. This discrepancy illustrates why caution should be exercised in constructing

mechanisms when only low molecular weight products of dissociative ionization are observed in decomposition experiments.

Summary

Solid samples of TNAZ decompose following irradiation with UV laser light. The decomposition products are detected following single-photon ionization in a time-of-flight mass spectrometer. The most abundant high molecular weight products are fragments corresponding to net loss of O atom, NO, and NO₂ from TNAZ. Translational temperatures and relative yields of these products are obtained from analysis of time-of-arrival scans. The translational temperatures show a linear dependence on decomposition laser fluence consistent with a photothermal decomposition mechanism. TNAZ appears to have two initial decomposition channels: the unimolecular loss of NO and bimolecular reaction to generate NDNAZ. The channel corresponding to loss of NO₂ is an early but not initial decomposition step. Experiments with isotopically labeled compounds demonstrate that TNAZ undergoes nitro–nitrite rearrangement on the nitramine group followed by loss of NO and that NO₂ arises from both the nitramine and nitroalkyl groups.

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