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Decomposition of Aminotetrazole Based Energetic Materials under High Heating Rate Conditions

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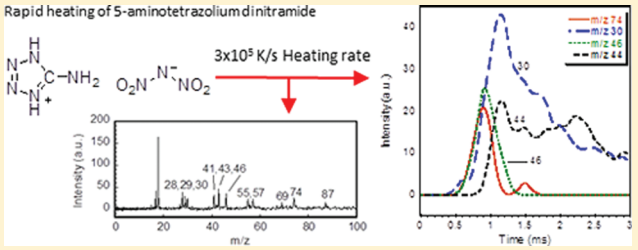
ABSTRACT: A T-jump/time-of-flight mass spectrometer (T-Jump/TOFMS) is used to probe the decomposition of several aminotetrazole containing energetic materials under very high heating rates of 10^5−10^6 K/s. The materials investigated are 5-amino-1-methyl-1*H*-tetrazolium dinitramide (MeHAT_DN), 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide (MeDAT_DN), 1,5-diamino-1*H*-tetrazolium nitrate (DAT_N), 1,5-diamino-4-methyl-1*H*-tetrazolium azide (MeDAT_N3), and 5-aminotetrazolium dinitramide (HAT_DN). Subtle differences between materials in functional group placement and anion composition allow for further understanding of the decomposition pathway of the tetrazole structure and various anions. Two decomposition pathways for the tetrazole ring are observed, which result in the primary formation of HN_3 or N_2. The N_2 formation pathway occurs when functional groups are placed symmetrically around the tetrazole ring, whereas asymmetric placement results in HN_3 production. The differing anion compositions also show effects on thermal stability of the salts, as is demonstrated by a lower decomposition temperature for the azide containing salt compared to the similar dinitramide containing material. For the decomposition of the dinitramide molecule, high temperature (N_2O forming) and low temperature (NO_2 forming) decomposition pathways are observed, as has been previously suggested.



INTRODUCTION

Recently, a shift has been made to create energetic materials (EMs) that are not only efficient performers but also meet up to date safety and environmental standards. Current EMs such as RDX and HMX meet performance needs but are sensitive to impact and friction and possess an unwanted level of toxicity. These materials also produce environmentally harmful product species, which are largely due to carbon containing nitro groups.[1] So called "green energetic materials" (GEMs) are produced with concern toward environmental impact throughout the lifetime of a material. Many of these compounds contain a high-nitrogen content tetrazole substructure, which is paired with a functional anionic molecule to form stable energetic salts. These materials are unique in that their energy release comes primarily from the high heats of formation from their many nitrogen containing bonds.[2] The high-nitrogen content materials generally produce more environmentally friendly combustion products due to the diminished carbon containing product species. However, these materials are relatively new and have not been as extensively studied as more traditional EMs. As such, the decomposition products and reaction pathways are, for the most part, still unknown.

Several groups have performed experimental and theoretical work to help understand the thermal decomposition of aminotetrazole containing materials.[2−10] Tools ranging from thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and FTIR/TOF mass spectrometry have been used, but traditionally these experiments are performed under low heating rates (10−100 K/min). Under rapid-heating conditions closer to that of a real-time combustion event, there will typically be a different set of dominant chemical processes. As a common substructure of many high-nitrogen content materials, 5-amino-1*H*-tetrazole and the breaking of the tetrazole ring, has been the focus of many studies. A temperature-jump/FTIR spectroscopy system with a heating rate of 2000 K/s was used by Brill et al. to investigate the reaction pathways of aminotetrazole and a few of its related salts.[8] They identify two possible reaction pathways that vary with temperature; one that is dominant at low temperatures and consists of the breakdown of the ionic tetrazole structure, and one that is dominant at high temperatures and treats the aminotetrazole as a neutral. The main identifying products of these two pathways are HN_3 for the high temperature pathway and N_2 for the low temperature pathway. Theoretical work has been performed by Paul et al. on unimolecular 5-aminotetrazole decomposition.[5] Their studies also reveal two possible decomposition pathways for the tetrazole structure, which differs for aminotetrazole and its tautomer iminotetrazole. They predict that the main aminotetrazole reaction pathway will be that of N_2 extraction, whereas the main iminotetrazole pathway will produce HN_3.

Due to an extensive amount of relatively new high-nitrogen content energetic salts, few studies have examined the decomposition of these energetics, especially under rapid-

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heating conditions. Chowdhury et al. used a confined rapid thermolysis technique to investigate the reactions of tetrazole based ionic liquids at heating rates of up to 2000 K/s. The main diagnostic tools for this study were FTIR spectroscopy and TOF spectrometry, which obtained temporal resolutions of 50 and 1 ms, respectively.[6] They showed that positions of functional groups on the tetrazole ring play a significant role on the thermal stability and decomposition pathway of the tetrazole structure. Despite some rapid heating rate studies on tetrazole containing materials, to our knowledge none exist for the materials of this study. Slow heating rate DSC, mass spectrometry, and IR spectroscopy have been performed by Fischer and co-workers for MeDAT_DN and MeDAT_N3.[10] Their decomposition analysis for these materials will be used for comparison and breakdown of the reaction products in this investigation.

In general, it has been shown that the decomposition of the tetrazole molecule can differ due to the placement and composition of its attached functional groups.[6,11] It is also predicted that heating rate has an effect on the decomposition. In a complementary study our group tested several energetic salts in a high heating rate μ-DSC experiment.[12] This study showed a significant decrease in activation energy for energetic materials at rapid heating rates, suggesting that different mechanistic processes are at play. To investigate the intermediate processes of a reaction, an experiment with very high heating and sampling rates is required. In this paper we employ a temperature-jump/time-of-flight mass spectrometer to characterize the decomposition pathways of several amino-tetrazole containing energetic salts. The uniqueness of this instrument is its ability to heat samples at very high heating rates of 10^5-10^6 K/s while simultaneously sampling the reaction products at a temporal resolution of 100 μs, which can allow for probing of the early stages of reaction.

EXPERIMENTAL SETUP

The primary experimental device is a temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS), which has been described in detail elsewhere.[13] The core of this instrument is a fine platinum filament that is ~76 μm in diameter and 1−2 cm in length. This filament can be heated at a rate of up to 10^6 K/s using a tunable current pulse. Samples are received in a solution of ethanol or methanol and are placed onto the sample probe by manually applying a drop of the solution to the platinum wire. This procedure allows for a quick coating of the sample but typically results in a sparse, nonuniform coating. We have previously taken scanning electron microscope (SEM) images of filaments coated with nitrocellulose or RDX. These two materials were studied as their coatings under this process vary significantly. Nitrocellulose can be thickly coated onto the wire, whereas RDX is sparse and nonuniform, more in-line with a typical sample. After a volume estimation and assuming the density of MeDAT_DN of 1.719 g/cm^3,[10] we predict larger samples to be ~10 μg and a typical sample ~1 μg.

Sample heating is performed under high vacuum (10^{-7} Torr) to minimize gas phase chemical reactions, in an attempt to probe the intrinsic chemistry occurring within the condensed matrix. However, sampling of organic energetic materials under such conditions raises concern about evaporation prior to decomposition and we thus limit our characterization to energetic salts that have negligible vapor pressures. All samples used in this experiment are provided by T. M. Klapötke of Ludwig-Maximilians University in Munich, Germany, and consist of 5-amino-1-methyl-1*H*-tetrazolium dinitramide (MeHAT_DN), 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide (MeDAT_DN), 1,5-diamino-1*H*-tetrazolium nitrate (DAT_N), 1,5-diamino-4-methyl-1*H*-tetrazolium azide (MeDAT_N3), and 5-aminotetrazolium dinitramide (HAT_DN), and the synthesis of each material is documented elsewhere.[2,7,14,15] For sampling purposes, the filament is inserted into the high vacuum sampling region of the TOFMS within close proximity (~2 cm) to the ionization source, a 70 eV electron impact beam. This allows for reaction products to reach the MCP detector of the mass spectrometer at a fast time scale well below the characteristic time of the experiment. A typical heating run consists of a ~3 ms heating pulse that heats the filament to ~1270 K or a rate of ~326 000 K/s. Throughout the heating of the sample, a mass spectrum is taken every 100 μs, and the current and voltage are simultaneously recorded to determine the temperature of the filament. Reported temperatures are that of the filament, determined from the variance of platinum resistivity with temperature.[16] Though there are inconsistencies in the sample coating thickness, which presumably could lead to temperature gradients within the sample, heat transfer calculations suggest that the near surface portion of the sample follows the temperature of the filament closely.

RESULTS AND DISCUSSION

The investigation of rapid condensed phase reactions is a difficult task. Part of the motivation for conducting the chemistry in high vacuum was to eliminate secondary gas phase reactions, so as to simplify interpretation. However, the condensed phase reactions themselves could be very intricate. Upon the initial decomposition of a reactive molecule, the product could undergo thousands of collisions and numerous other reactive processes before exiting the condensed state. Thus any investigation of condensed state reactive systems are necessarily tracking global processes from which microscopic interpretation is being inferred. Thus the mechanistic interpretation inferred by us in this work, should be placed in the context of the difficulty in truly isolating microscopic pathways in the condensed state.

Decomposition temperatures and reaction times for the six compounds were determined from mass spectrometer results at a heating rate of ~326 000 K/s and are listed in Table 1. The decomposition temperatures were taken from the onset of product species, and the reaction times were determined from the full-width half-max of the detected product species concentration. Previously reported temperatures of the onset of decomposition during slow heating rate (~10 °C/min) DSC

Table 1. Measured Onset Decomposition Temperature and Reaction Time

compound	onset decomposition temp (°C)	reaction time (ms)	reported decomposition temp (°C)
MeHAT_DN	201 ± 10	0.3	145[2]
MeDAT_DN	303 ± 7	0.2	150[10]
DAT_N	193 ± 14	0.5	168[a,7]
MeDAT_N3	184 ± 7	0.4	137[10]
HAT_DN	251 ± 7	0.7	117[14]

[a]Temperature taken from the peak of a DSC trace.

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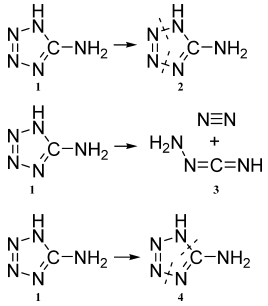
experiments are also reported in Table 1. When subjected to very high heating rates, each material exhibits a higher decomposition temperature. This may be indicative of different reaction processes under these high heating rate conditions. In the following we explore the decomposition behavior of each compound. For reference, the two predicted reaction pathways for tetrazole ring decomposition are shown in **1** → **2** and **1** → **4**. The main reaction products that are representative of these two pathways are NH_2NCNH for **1** → **2** and HN_3 for **1** → **4**. Due to complex spectrometric analysis, each material will be discussed separately.



5-Aminotetrazolium Dinitramide. The cation of 5-aminotetrazolium dinitramide (HAT_DN), **5**, contains the basic aminotetrazole structure and is paired with the dinitramide ($N_3O_4^-$) anion. Of the materials studied, this has the slowest reaction time (Table 1), which allows for the capture of multiple steps within the reaction that may not be detectable for other materials. Figure 1 is a single detailed

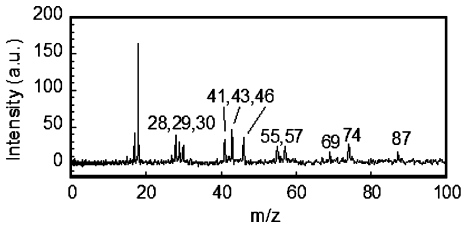
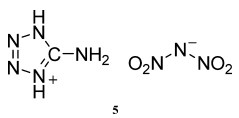
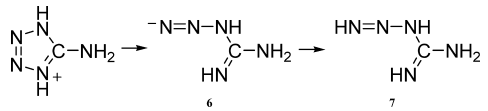


Figure 1. Detailed mass spectrum of the reaction products from heating for HAT_DN, **5**.

spectrum of the reaction products for **5**. With the significant amount of reaction products for HAT_DN it would be difficult, even with a complementary species identification study, to accurately identify each species and its origin, whether from fragmentation or decomposition. Therefore, we will only assume the identity of peaks for which we can provide ample evidence of their origin and will note the uncertainty of other assignments. Table 2 lists the detected mass peaks for each decomposition experiment and also provides the possible methods of formation for each species. During peak assignment we also assume that, because this study is performed at rapid heating rates under high vacuum, there are not substantial secondary reactions or recombination within the condensed phase. This thought process, combined with comparison to previous studies in the literature allows for identification of critical reaction products unique to certain mechanisms.



As an example we consider the largest mass observed for HAT_DN, m/z 87, and we note that the cation of **5** has a molecular mass of 86. This m/z was not reported for the decomposition of tetrazole or dinitramide containing materials in the literature. Paul et al. suggests that there is an intermediate step in the reaction of the tetrazole structure where the ring first splits before N_2 is released, as shown by **6**.[5] This work by Paul is a theoretical unimolecular decomposition study, so it is unable to predict intermolecular hydrogen exchange. We assume that with the ionic nature of this material there is some exchange of hydrogen atoms between molecules. As the tetrazole ring splits apart by breaking an N−N bond, it is reasonable to assume that protonation of the open ring could occur to form a structure similar to **7** with m/z 87, which is consistent with our observation. This large and presumably unstable molecule would undergo significant fragmentation during ionization, which may account for many of the detected spectral peaks. However, there is a significant amount of uncertainty in assigning ion fragment peaks to this molecule. Therefore, focus will be lent to assigning values to peaks that presumably come from other sources. There are other possible molecular structures with m/z 87 such as CHN_3O_2, CH_3N_4O, and C_2HNO_3. Each of these structures would require significant decomposition and recombination in the condensed state. We assume m/z 87 is due to the open ring tetrazole structure, shown in **7** due to the simplicity of its formation.



The other large molecule detected by our system, m/z 74, has not been previously reported in the literature as a decomposition product of tetrazole or dinitramide reactions and may represent an intermediate step in the initial reaction process. This peak is not from fragmentation of **7**, as this would require removal of a mass of 13 amu, which is not feasible given the molecular structure. It is difficult to create m/z 74 from the tetrazole containing cation as it again requires significant recombination and intermixing with the anion or the addition of several hydrogen atoms. With a molecular mass of 106 the dinitramide molecule can form m/z 74 through the loss of two oxygen atoms. Examining the dinitramide structure **8** proposed by Bottaro et al.,[17] we predict a loss of $2O^-$ to form N_3O_2. N_3O_2 has been experimentally observed in positive[18,19] and negative[20] ionic forms, but to our knowledge, not as a neutral molecule. Although the neutral molecule has not been experimentally observed, theoretical work has shown that this formation is possible, but thermodynamically unstable.[21] Regardless of overall charge, there is evidence that N_3O_2 will decompose to NO and N_2O.[22−24] Figure 2 shows the temporal evolution of select product species pertaining to the decomposition of the dinitramide structure. The earliest species observed are m/z 74 and m/z 46, where m/z 46 represents NO_2, a common decomposition product of N_3O_4 containing compounds,[17,25] and later in the decomposition N_2O is observed. For HAT_DN decomposition, the formation of N_2O consistently forms at a higher temperature and later time than NO_2 and m/z 74. As a measure of consistency, analysis of five experimental runs gives an average time difference from the formation of NO_2 to the formation of N_2O of 0.3 ± 0.1 ms.

The presence of these different reaction products suggests that there may be competing mechanisms for decomposition.

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Table 2. Detected Spectral Peaks during Decomposition Experiments[a]

name	abbreviation	detected product species	species identification	species origin
5-aminotetrazolium dinitramide	HAT_DN	28	N_2	EI
		29	HN_2, CH_3N	EI
		30	NO	dinitramide decomp/EI (NO_2)
		41	CHN_2	EI (m/z 87)
		43	HN_3	tetrazole fracture
		46	NO_2	dinitramide decomp
		55	CHN_3	EI (m/z 87)
		57	NH_2NCNH	tetrazole fracture/EI (m/z 87)
		69	*na*	EI (m/z 87)
		74	N_3O_2	dinitramide decomp
		87	$HN_3HCN_2H_3$	partial tetrazole ring split
5-amino-1-methyl-1*H*-tetrazolium dinitramide	MeHAT_DN	14	N	EI
		15	CH_3	methyl group
		28	N_2	EI
		30	NO	dinitramide decomp/EI (NO_2)
		42	N_3	tetrazole fracture
		43	HN_3, $HNCNH_2$	tetrazole fracture
		46	NO_2	dinitramide decomp
1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide	MeDAT_DN	14	N	EI
		15	CH_3	methyl group
		16	CH_4	methane
		28	N_2	tetrazole fracture/EI
		29	HN_2, CH_3N	EI
		30	NO	dinitramide decomp/EI (NO_2)
		44	N_2O	dinitramide decomp
		46	NO_2	dinitramide decomp
		55	CHN_3	tetrazole decomp/EI
		57	NH_2NCNH	tetrazole fracture
1,5-diamino-4-methyl-1*H*-tetrazolium azide	MeDAT_N3	15	CH_3	methyl group
		28	N_2	tetrazole fracture/EI
		30		
		43	HN_3	azide protonation
		57	NH_2NCNH	tetrazole fracture
1,5-diamino-1*H*-tetrazolium nitrate	DAT_N	28	N_2	EI
		29	HN_2, CH_3N	EI
		30	NO	dinitramide decomp/EI (NO_2)
		43	HN_3, $HNCNH_2$	tetrazole fracture
		46	NO_2	dinitramide decomp

[a]For each mass peak the origin of formation for the peak is denoted.

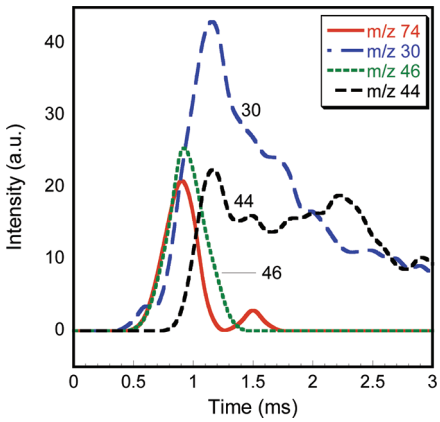
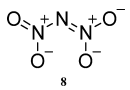


Figure 2. Detected product species during heating of HAT_DN, **5**.



8

There have been previous reports of two mechanistic pathways for dinitramide breakdown in an ammonium dinitramide compound.[25−27] The two pathways consist of a low temperature NO_2 forming pathway, and a high temperature N_2O forming pathway. These two mechanisms are consistent with what we observe, as NO_2 is present at a lower temperature, followed by the appearance of N_2O (m/z = 44) at a higher temperature. Analysis of these two pathways is a much more complex problem. Though previous studies attribute N_2O formation as a single step process, we consider that there could be more processes at play. Whereas m/z 46, 44, and 30 can all be attributed to the dinitramide breakdown, m/z 30 also has contributions from fragmentation of other species. There are three main contributing sources to the detected NO concentration in HAT_DN decomposition, production of NO from the reaction itself as well as from fragmentation of N_2O and NO_2. There may also be a minor contribution to m/z 30 from fragmentation of m/z 57 via H_2N_2. On the basis of fragmentation patterns obtained using neat NO_2 and N_2O gas, we conclude that at low temperatures the majority of the NO is

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produced from NO_2 fragmentation, whereas at higher temperatures NO is also directly formed from the decomposition process. Because NO and N_2O are both produced at higher temperatures, it is possible that this is due to N_3O_2 decomposition. It is also possible that N_2O is not produced directly from the dinitramide, but rather from decomposition of a reaction product from the NO_2 formation process. Because NO_2 is produced early in the reaction process, a condensed state decomposition product of this step could be formed and further decomposed to produce N_2O. In the MeHAT_DN analysis below, we observe NO_2 as a primary decomposition product, but only occasionally observe N_2O. This suggests that N_2O is a result of a higher temperature reaction mechanism or secondary condensed phase mechanism, rather than the decomposition of a primary reaction product from the NO_2 reaction step.

As with the dinitramide structure, there are multiple reaction pathways for the tetrazole molecule. The m/z ratios 43 and 57 represent the two different tetrazole breakdown mechanisms[4] and are noted as both being present in the spectrum for decomposition. However, due to the presence of larger molecules and fragmentation of these molecules, a decisive conclusion cannot be made as to how the tetrazole ring breaks down during HAT_DN decomposition.

1,5-Diamino-4-methyl-1*H*-tetrazolium Dinitramide. The structure for MeDAT_DN is given in **11**. This structure is similar to HAT_DN in that it is a tetrazole containing cation paired with a dinitramide anion. The cation does have some slight variations as it has two functional groups, an amino and methyl group, symmetrically placed on the tetrazole ring. These small differences have a significant impact on the decomposition of the tetrazole ring as seen in Figure 3. This

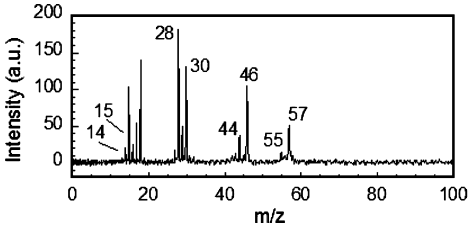
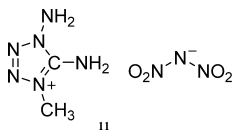


Figure 3. Detailed mass spectrum of the reaction products from heating of MeDAT_DN, **11**.

decomposition follows that of the tetrazole ring as demonstrated in **2**, and is consistent with the N_2 extraction mechanism seen in previous studies. As noted, this mechanism will produce a peak at m/z 57 and an intense peak at m/z 28. For MeDAT_DN this involves the removal of the functional groups from the tetrazole structure, which can be confirmed from the presence of m/z 15 (CH_3), whereas the amino group may be further protonated to form ammonia (NH_3, m/z 17). With the loss of both functional groups, the remaining structure would have a net negative charge and would likely undergo protonation before splitting to m/z 28 and 57.



11

For the dinitramide anion we see the production of both N_2O and NO_2, suggesting a decomposition mechanism similar to that of HAT_DN. One main difference in the decomposition between this molecule and the HAT_DN molecule is that this reaction occurs much faster. If we take the full-width at half-maximum of the detected product species as a representative reaction time for both reactions, **11** reacts 2−3 times faster than **5**. For the decomposition of **5** we were able to observe multiple steps in the reaction as NO_2 appears prior to N_2O. In the decomposition of **11** the reaction happens at a much faster rate and NO_2 and N_2O appear simultaneously and relatively early. However, it can be seen in Figure 4 that N_2O

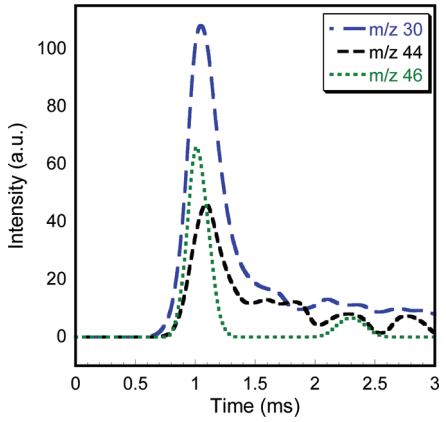


Figure 4. Detected product species during heating of MeDAT_DN, **11**.

production does peak later than NO_2. If we compare the decomposition temperature of the three dinitramide containing materials in Table 1 with their reaction products, we observe that N_2O is observed in MeDAT_DN, and HAT_DN, with decomposition temperatures 303 and 251 °C, respectively. However, N_2O is not typically observed in the decomposition of MeHAT_DN, which has the lowest decomposition temperature of 201 °C. This evidence further confirms the previous assumptions of a high and low temperature decomposition mechanism for the dinitramide molecule.

Although we have assigned species to each spectral peak, there is still some vagueness as to whether these peaks are directly due to decomposition, or whether they are from fragmentation of a larger molecule. Typically, additional experiments are needed for comparison, in this case a slow heating rate experiment using mass spectrometry with 70 eV electron impact source and FT-IR spectroscopy has been previously performed for MeDAT_DN by Fischer and coworkers.[10] The gas phase decomposition products were investigated at a 4 °C/min heating rate, and from the reaction products they predict that the tetrazole ring decomposes to form HN_3 as in **4**, rather than forming N_2 as our results suggest. More importantly, this previous experiment allows us to determine whether some of the reaction products of this study are due to fragmentation or decomposition. The Fischer work does observe some larger molecules that undergo significant fragmentation during ionization. The main decomposition products are N_2O (m/z 44), MeN_3 (m/z 57), $MeONO_2$ (m/z 75, mass peak not observed, authors assume fragmentation), $(HCN)_3$ (m/z 81), HCN (m/z 27), NH_3 (m/z 17), and H_2O (m/z 18). Comparing our study to these results, we conclude that m/z 57 is due to NH_2NCNH, not MeN_3. In the Fischer study they confirm the presence of MeN_3 with FT-IR spectroscopy and observe a m/z 57 peak with their mass

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spectrometer. However, they do not observe a peak at m/z 15 for the methyl group as we do. Because both studies use a 70 eV electron impact source, this confirms that our CH_3 peak is not due to fragmentation of MeN_3 and further suggests that m/z 57 is not due to MeN_3 as the methyl group is occupied elsewhere. The Fischer study also detects $MeONO_2$ with FT-IR spectroscopy; however, this does not fragment to produce an NO_2 (m/z 46) peak, which we do detect. This clearly demonstrates that NO_2 is a result from a different breakdown mechanism that does not produce $MeONO_2$. Our study also does not identify any of the larger product species that are detected in the previous study. Due to this evidence it is highly unlikely that the primary reaction products in the current study are due to fragmentation of larger molecules.

5-Amino-1-methyl-1*H*-tetrazolium Dinitramide. The structure for MeHAT_DN is shown in **9** and a decomposition spectrum is shown in Figure 5. This structure is very similar to

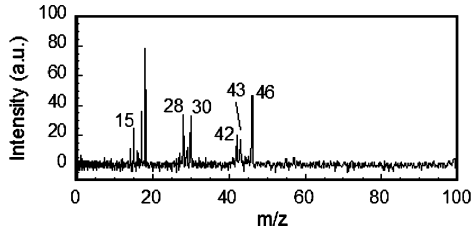
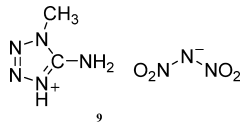


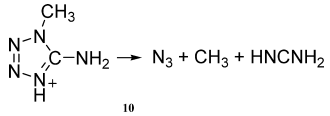
Figure 5. Detailed mass spectrum of the reaction products from heating of MeHAT_DN, **9**.

5 except one hydrogen atom on the tetrazole ring is replaced with a methyl group. Comparison of this decomposition with that of HAT_DN, and MeDAT_DN shows there is no peak at m/z 57. This suggests that the addition of the methyl group has a significant impact on the decomposition of the tetrazole ring and implies some other reaction pathway. With the presence of m/z 43 we consider the pathway in **4**, which should lead to $HNCNH_2$ and CH_3N_3. CH_3N_3 has a m/z of 57; however, we have already demonstrated the tendency of the methyl group to break off during decomposition, which leaves a remaining N_3 molecule with a net negative charge that can be further protonated to form HN_3. We again observe m/z 15 corresponding to CH_3, but there is no study on MeHAT_DN for direct comparison. However, from the above discussion on MeDAT_DN, it can safely be concluded that the CH_3 molecule is a direct result of the reaction.



9

The products due to the reaction of the tetrazole structure following this mechanism are given in **10**. As mentioned previously, for both the dinitramide and tetrazole structures, there are at least two possible breakdown mechanisms. The addition of the methyl group to the tetrazole ring changes the breakdown mechanism to form HN_3 rather than the N_2 and NH_2NCNH as is seen for MeDAT_DN. For the dinitramide decomposition in HAT_DN and MeDAT_DN, we assumed a high temperature N_2O forming route, and a low temperature NO_2 forming route. In a typical experimental run, N_2O is not observed as a decomposition product, as MeHAT_DN starts to decompose at a lower temperature than either HAT_DN or MeDAT_DN and is likely complete before the high temperature reaction begins. In a few instances N_2O was observed late in the reaction of MeHAT_DN. These cases were for larger sample sizes, which allows for either longer residence times on the wire, allowing for heating at higher temperatures, or secondary condensed phase reactions. We attribute the presence of N_2O to the longer residence time on the wire, which allows for the sample to remain on the wire at higher temperatures. This evidence should eliminate the theory that N_2O is the result of decomposition of a secondary product of NO_2 production as previously suggested. Because we are able to observe NO_2 in all cases, if a product of this reaction yields N_2O, it would also happen in all cases.



10

1,5-Diamino-4-methyl-1*H*-tetrazolium Azide. Aside from dinitramide containing salts, we also investigated the tetrazole containing cations with various other anions. The spectrum for MeDAT_N3, **12**, is shown in Figure 6. The

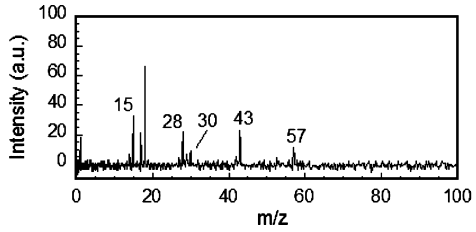
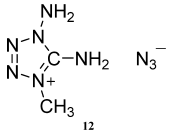


Figure 6. Detailed mass spectrum of the reaction products from heating of MeDAT_N3, **12**.

decomposition for this material is similar to what was seen for **11**. We see the evidence of the nitrogen expulsion mechanism with peaks at m/z 57 and 28. Peak 43 in this case can be attributed to the protonated azide structure HN_3. When comparing this material with MeDAT_DN, we would expect MeDAT_N3 to show a lower thermal stability.[7] This is the case as we see decomposition temperatures of 303 and 184 °C for MeDAT_DN and MeDAT_N3, respectively. The work by Fischer also examined the gas phase decomposition products of MeDAT_N3. The main reaction products detected in their study are HN_3 (m/z 43), HCN (m/z 27), CH_3N_3 (m/z 57), NH_4N_3 (m/z 60), and N_2 (m/z 28).[10] Although we observe most of these m/z's in our spectra, we attribute the products to different processes. They believe that HN_3 is produced from the breaking of the tetrazole ring as in **4** rather than from the azide anion. As is the case for MeDAT_DN, we do not believe that CH_3N_3 is present for MeDAT_N3 due to the large presence of CH_3 in our spectra. It appears that CH_3 breaks off of the tetrazole ring easily and relatively early. We attribute the peak at m/z 57 to NH_2NCNH following the mechanisms for other materials in this study. Fischer also notes the presence of some larger molecules, $(H_2NCN)_3$ (m/z 126) and 1,2,4-triazole (m/z 69), neither of which is present in our study.



12

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1,5-Diamino-1*H*-tetrazolium Nitrate. The structure for DAT_N is shown in **13**. This material is slightly different from the other tetrazoles examined, as it is a diaminotetrazolium cation without a methyl group and is also paired with a nitrate anion. From examination of the breakdown mechanisms of each of the other materials, there appears to be a trend in how the tetrazole molecule will break apart on the basis of the placement of the functional groups around the outside of the tetrazole ring. Molecules **11** and **12** both have functional groups symmetrically placed around the tetrazole structure, whereas **9** has the methyl group on one side of the ring. The decomposition of the tetrazole ring for **11** and **12** follow the same pattern of N_2 expulsion, and molecule **9** produces HN_3. Following this logic, DAT_N will decompose in a similar fashion as structure **9** to produce HN_3. From Figure 7 this

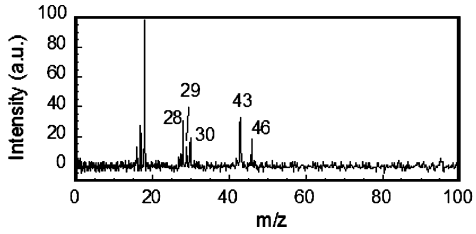
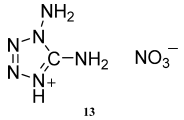


Figure 7. Detailed mass spectrum of the reaction products from heating of DAT_N, **13**.

mechanism is confirmed as there is a large peak at *m/z* 43 representing HN_3, and the absence of species representative of the N_2 expulsion mechanism, mainly peak 57. We also observe peaks at *m/z* 46 and 30 that can be attributed to NO_2 formation from the nitrate anion. A slow heating rate DSC study was previously performed on a similar material, 5-aminotetrazolium nitrate.[3] Using FT-IR spectroscopy, the authors suggest that the material protonizes the NO_3 anion to form HNO_3 and this decomposes to form H_2O and NO_2 gas, whereas the tetrazole decomposes via the HN_3 mechanism. This is very consistent with our results for DAT_N at high heating rates. The correlation of these two experiments suggests that protonation of the anion may occur before decomposition. This, combined with other instances of protonation for the previous materials, strongly suggests that proton transfer readily occurs during heating of ionic salts.



13

CONCLUSIONS

Using a T-Jump/TOFMS, we have studied the thermal decomposition of several tetrazole containing energetic salts under conditions that minimize secondary gas phase reaction. By examining several different variations to the cation structure, we were able to draw some conclusions about the decomposition pathways of the tetrazole ring. Despite some uncertainty in the origin of every detected spectral peak, whether it comes from fragmentation or decomposition, we identify reaction products that are representative of different mechanistic pathways of tetrazole decomposition. It is clear that there are two different reaction pathways demonstrated for the tetrazole ring. Both pathways decompose through a breaking of the tetrazole ring, one with the expulsion of molecular nitrogen, the other producing HN_3. There is not significant evidence in this study to suggest that the reaction pathways played a major role in the decomposition temperature of the materials; however, there is correlation between the placement of functional groups and the breakdown of the tetrazole ring. Symmetrically placed functional groups such as the MeDAT containing salts decomposed via the N_2 decomposition, whereas the others showed characteristics of the HN_3 mode. A high and low temperature decomposition pathway is observed for the dinitramide anion, as dinitramide containing materials that exhibited higher decomposition temperatures, produced N_2O at these high temperatures. Although there are limited studies on these energetic salts available for direct comparison, we did observe differences from previous work under slow heating rates for MeDAT_DN and MeDAT_N3. These differences at slow heating rates, mainly the presence of larger molecules in the reaction products, are likely due to a large amount of secondary reactions, which are not present in the current study.

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