Identification of liquid-phase decomposition species and reactions for guanidinium azotetrazolate

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The objective of this work is to analyze the decomposition of guanidinium azotetrazolate (GzT) in the liquid phase by using a combined experimental and computational approach. The experimental part involves the use of Fourier transform infrared (FTIR) spectroscopy to acquire the spectral transmittance of the evolved gas-phase species from rapid molysis, as well as to acquire spectral transmittance of the condensate and residue formed from the decomposition. Time-of-flight mass spectrometry (ToFMS) is also used to acquire mass spectra of the evolved gas-phase species. Sub-milligram samples of GzT were heated at rates of about 2000 K/s to a set temperature (553–573 K) where decomposition occurred under isothermal conditions. N2, NH3, HCN, guanidine and melamine were identified as products of decomposition. The computational approach is based on using quantum mechanics for confirming the identity of the species observed in experiments and for identifying elementary chemical reactions that formed these species. In these ab initio techniques, various levels of theory and basis sets were used. Based on the calculated enthalpy and free energy values of various molecular structures, important reaction pathways were identified. Initiation of decomposition of GzT occurs via ring opening to release N2.

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Nomenclature

Symbols
γ out-of-plane bending vibration
δ in-plane bending vibration
ν stretching vibration
Subscripts
a asymmetric
s symmetric

1. Introduction

Recently, research on nitrogen-rich energetic materials has received significant attention because of their high positive heats of formation which provide the potential for releasing a large amount of heat on combustion as well as reducing the emission of harmful pollutants [1]. These materials produce molecular nitrogen as one of the primary decomposition products, achieving a high specific impulse without undesirable smoke or soot. Tetrazoles with their heterocyclic ring structure fall within this class of compounds [2]. Within tetrazoles, compounds such as triminouguanidinium azotetrazolate (TAGzT) [3] and guanidinium azotetrazolate (GzT) [4] which contain an ion pair are of great interest due to their potential application as gas generators and burn rate modifiers for propellants. The nitrogen-rich compound GzT shown in Fig. 1, which is the focus of this work, is a yellow-colored salt with cotton fiber-like appearance. It leaves behind a thermally stable residue on burning.

In addition, it is remarkably insensitive to impact and melts roughly around 513 K. GzT has been explored as a replacement for sodium azide in safety equipment [5]. It has also been suggested as an additive to propellant charges for improving performance and reducing gun-barrel erosion [6,7].

The process to synthesize GzT was patented by Bucerus et al. [8]. The nature of the hydrogen bonding in the GzT molecule was discussed in detail by Chen et al. [9]. Using thermal analysis techniques such as thermogravimetry (TG), differential thermal analysis (DTA), thermogravimetry–Fourier transform infrared spectrometry (TG–FTIR) and pyrolyser–gas chromatography–mass spectrometry (py-GC–MS), Damse et al. investigated the

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decomposition of GzT [4]. According to these investigators, the first stage of GzT decomposition corresponds to an exothermic reaction involving abstraction of protons available at the guanidinium cation (G+) by the azotetrazolate ring. They further state that proton transfer leads to the formation of a highly unstable product which then decomposes to release molecular nitrogen and cyanamide via ring-opening reactions. Hammerl et al. studied the structure of several GzT based salts [10]. Based on vibrational spectroscopy, they identified several important absorption bands. They also investigated the thermal behavior of GzT using DSC. The products were analyzed using infrared (IR) spectroscopy and mass spectrometry. The major decomposition products were found to be molecular nitrogen (N2), ammonia (NH3), and hydrogen cyanide (HCN); carbodiimide (HNCN) was also detected as a gaseous product. It was suggested that decomposition of azotetrazolate dianion (Azt−2) was initiated via the protonated species. The same products were observed by Sivabalan et al. in their work on GzT [11]. Decomposition pathways for GzT were investigated using computational methods by Liu et al. [12]. Quantum chemical ab initio methods were used to suggest a decomposition mechanism. The computational analysis was based on the assumption that decomposition occurred in the gas phase. The first decomposition step was identified as a “cracking” process to form two guanidinium cations and the azotetrazolate dianion. Very recently, Ting et al. proposed a reaction scheme for the decomposition of GzT based on their TG, differential scanning calorimetry (DSC), condensed-phase thermolysis using Fourier-transform infrared spectroscopy (FTIR) and mass spectrometry experiments [13]. Their reaction scheme is very similar the ones discussed previously [4,10].

The literature survey on GzT decomposition presented here indicates that most of these studies are experimental and involve some degree of speculation concerning the chemical reactions that take place during the decomposition based on the observed products. It is essential, however, to explore other approaches to interpret the experimental information. Here we adopt recently developed methods based on the use of quantum mechanics. As described in several works, quantum mechanics techniques have been used to analyze the decomposition of guanidinium 5-aminoazotetrazole as well as hypergolic reactions between mono-methyl hydrazine and nitrogen dioxide [14,15]. These results can subsequently be used to formulate comprehensive chemical reaction mechanisms that are needed to simulate ignition and combustion of energetic materials. However, comprehensive chemical reaction mechanisms are available only for the gas phase. In the solid or liquid phase, global reactions are most frequently used to simulate the ignition and combustion of energetic materials [16,17]. Current understanding of liquid-phase reactions is very limited regarding several aspects: (i) identities of the intermediate decomposition products, (ii) reaction pathways, and (iii) rates of elementary reactions. Much additional work is needed regarding the development of liquid-phase decomposition and reaction models of energetic materials, which should improve the predictive capability of propellant ignition and combustion models. The present work on GzT is an attempt in this direction. FTIR spectroscopy and time-of-flight mass spectrometry (ToFMS) experiments have been performed on GzT to analyze its decomposition in the liquid phase, and formation of the observed products has been explained by formulating elementary chemical reactions based on quantum mechanics based calculations.

2. Experimental

2.1. Materials

The chemicals guanidinium chloride (GCl) and guanidinium nitrate (GN) used in this work were purchased from Sigma-Aldrich. The GzT material used in our studies was synthesized at Los Alamos National Laboratory. All the materials were used without further purification.

2.2. Fourier transform infrared (FTIR) spectroscopy

Confined rapid thermolysis (CRT)/FTIR technique used here has been discussed in previous works [18,19]. The technique is very sensitive to decomposition processes occurring in the liquid phase, compared to the gas phase, as the molecules are quenched by the relatively cooler atmosphere into which they evolve. A brief summary of the technique is provided here. A small amount of the sample, approximately 0.5 mg, was confined between two heated, parallel surfaces within a constant pressure CRT chamber. The surfaces belong to a stationary top heater and a mobile bottom heater, made of copper; they are maintained at isothermal conditions by cartridge heaters controlled by PID controllers. After the thermolysis chamber is purged by an inert gas, the sample is rapidly heated to the set temperature at heating rates of 2000 K/s as it is confined between the two parallel surfaces of the top and bottom heaters; the heater surfaces are separated by a thin aluminum foil. The gaseous products evolving from the condensed phase are sampled by a modulated FTIR beam from the spectrometer passing through two ZnSe windows. Thus, the spectra are obtained in near real-time with a spectral resolution of 2 cm−1 and a temporal resolution of 50 ms. As the two heaters come in contact, one notes a slight base-line shift in the spectral transmittance that serves as the indicator for the beginning of heating.

Three different types of tests were conducted using FTIR spectroscopy as described below.

i) About 0.5–1 mg of GzT sample was subjected to preset temperatures (563–593 K) in the CRT chamber and the corresponding FTIR spectra were obtained by passing the infrared beam through the FTIR probe volume. The goal is to subject the sample to decomposition under isothermal conditions. The total measurement time is about 10 s, and the time required for achieving isothermal conditions is about 0.2–0.3 s.

ii) About 0.5 mg of GzT sample was subjected to preset temperatures (563–593 K) in the CRT chamber and the evolved gases were allowed to condense on a glass slide. The condensate on the slide was then mixed with 150 mg of potassium bromide (KBr) and pressed into a pellet. The CRT chamber in the path of infrared beam from the spectrometer was replaced by a specially designed fixture. The pressed pellet was then placed
inside this fixture and its IR spectrum was obtained with a pure KBr pellet as background. The fixture is designed such that it can hold both the sample and the background KBr pellets, and either of them can be aligned in the path of the infrared beam by operating a slider. This was done with an objective to capture and detect the heavier molecules resulting from decomposition of the sample which are expected to condense out easily from the gas phase.

iii) About 0.5 mg of GzT sample in the CRT chamber was heated to 553 K and was held at this temperature for a fixed time interval. This time the residue left behind on the aluminum foil of the sample holder was pressed into a KBr pellet and analyzed similarly by FTIR spectroscopy. The aim here was to identify reaction products that did not evaporate but stayed in the liquid phase.

All these tests provided valuable information about the initial decomposition pathways of GzT.

2.3. Time of flight mass spectrometry (ToFMS)

Reference [19] contains the details of the setup and procedure used to conduct ToFMS tests. The decomposition products were sampled by a ToFMS system equipped with a 1 m flight tube and a 44 mm microchannel plate detector. In this system, molecular beam sampling is done by directing the evolved gases towards a 100 μm orifice, which separates the first stage of the vacuum system of the ToF mass spectrometer from the thermolysis chamber. The ToFMS system has a much better time resolution than the FTIR system, but it is nonetheless set to examine the behavior over the same time period and same temperature. The amount of GzT sample used in a test varied between 0.5 and 1 mg.

3. Molecular modeling

Quantum mechanics calculations provide an avenue for corroborating experimentally measured data and providing information otherwise unavailable experimentally. The Gaussian 09 [20] suite of programs was utilized to this end. Molecular structures of species involved in the decomposition of GzT were identified from ground-state and transition-state optimization calculations. The search for transition states was in most cases performed by using the B3LYP/6-31G(d) level of theory [21,22]. The optimized structures served as an initial guess to the B3LYP/6-311+ +G(d,p) level of theory which employs a triple split valence basis set with additional polarized functions and accounts for the significant charge delocalization in the ions present [23]. All the molecular structures were also optimized using the CBS-QB3 compound method developed by Montgomery et al. [24]. This method was chosen because it gives a good balance between accuracy and computational effort. For cases in which large discrepancies were observed in the enthalpy and free energy values of the structures between B3LYP and CBS-QB3 methods, the MP2 perturbation theory [25] along with 6-311++G(d,p) basis set and the compound G4(MP2) theory [26] were additionally used. It was observed that in most cases, with the exception of B3LYP/6-311+ +G(d,p), reaction parameters predicted by various methods were in close agreement, and the values obtained by the CBS-QB3 method are presented for all the reactions considered in this work. Vibrational frequency calculations were performed on all the optimized structures thus obtained to ensure that local energy minima (in case of reactants and products) and saddle points (in case of transition states) were achieved. Structures for reactants and products correspond to local energy minima having no negative vibrational frequencies whereas those for transition states correspond to saddle points on the potential energy surface and have only one negative or imaginary frequency. Transition-state optimizations corresponding to all the proposed reactions were also subjected to IRC (intrinsic reaction coordinate) calculations [27,28] using B3LYP/6-31G(d) method to ascertain that the transition state indeed connected the reactants to the products. Because our focus is on chemical reactions in the liquid phase, the polarizable continuum model (PCM), using the integral equation formalism variant (IEFPCM) [29,30] was used to reflect the assumption that the liquid-phase reactions can be treated as occurring in a solution phase. This model accounts for the continuum solvation effects. The UFF (universal force field) radius, which is the default option in Gaussian 09, was used to build the cavity in PCM. Acetonitrile (CH$_3$CN) was specified as the solvent in all the optimization, frequency and IRC calculations to represent the solution-phase medium. Ramos et al. reported that the solvent can significantly affect rates of some reactions [31]. Hence, we used other solvents to ascertain the effect of solvent type on the computed thermodynamic properties. By using acetonitrile, methanol, nitromethane and water as the solvent, the differences in heats of reaction and activation enthalpies in most cases did not exceed by more than 1.05 kJ/mol compared to the results obtained by using acetonitrile. This finding is similar to the conclusion reached by other investigators [15,32].

4. Results and discussion

4.1. Experimental results

In order to interpret the acquired spectral transmittance data for GzT, it is useful to examine other guanidinium salts. Here we include guanidinium chloride (GCl) and guanidinium nitrate (GN). First, we focus on the band assignments to the guanidinium cation. Figs. 2 and 3 show the transmittance spectra of GCl, GN and GzT obtained from the use of pressed KBr pellets, as well as unscaled predicted spectra from the use of the Gaussian 09 program package [20] using the B3LYP method [21] and the 6-31++G(d,p) basis set [22].

The guanidinium cation produces several important features [33,34]. First, as shown in Fig. 2, the symmetric nature of the guanidinium cation reveals strong bands from ν(C−N) stretching near 1650 cm$^{-1}$ and the asymmetric scissoring deformation bands (in-plane bending) of the NH$_2$ groups near 1580 cm$^{-1}$. The predicted wavenumbers for vibrations are at 1702 and 1588 cm$^{-1}$, suggesting a scale factor of about 0.969, which is excellent agreement with scaling factors for a wide variety of molecules [35]. Second, as shown in Fig. 3, we observe a very broad band with several peaks in the region 3450–3200 cm$^{-1}$. It is attributed to an uneven distribution of the positive charge on the atoms in the CN$_3$ skeleton. Third, bands corresponding to the symmetric and asymmetric ν(N−H) stretching can be observed in the region near 3500 cm$^{-1}$. The difference between measured and predicted ν(N−H) frequencies in this region is much larger and is attributed to hydrogen bonding effects. The generally accepted experimental band centers for the asymmetric and symmetric stretching frequencies are 3400 and 3320 cm$^{-1}$, respectively. There are two weak bands at 3235 and 3150 cm$^{-1}$ listed by Bonner and Jordan [36]. It should be noted that the data shown in Figs. 2 and 3 were acquired by using a relatively large amount of sample so these two latter bands appear as strong. Nonetheless, the scale factor for these asymmetric and symmetric ν(N−H) bands should be about 0.92 for the guanidinium compounds [37], with increased difference for the GCl, which has a relatively small anion and thus produce a larger role of intermolecular interactions among the neighbouring H atoms. Additionally, the guanidinium ion is generally free from experimentally detected IR-active bands below 1537 cm$^{-1}$. In the molecular modeling case, however, two very
Fig. 2. Comparison of measured spectra for guanidinium chloride, guanidinium nitrate, guanidinium azotetrazolate with the predicted spectrum of the guanidinium cation covering the wavenumber range from 600 to 2000 cm$^{-1}$.

Fig. 3. Comparison of measured spectra for guanidinium chloride, guanidinium nitrate, guanidinium azotetrazolate with the predicted spectrum of the guanidinium cation covering the wavenumber range from 2000 to 3750 cm$^{-1}$. 
weak bands are listed at 1112 and 1049 cm\(^{-1}\); perhaps they are not detected experimentally.

Fig. 4 shows the spectral transmittance of GzT, as well as the predicted band locations and intensity of the azobistetrazolate dianion AzT\(^2^-\). It is quite clear that the predicted spectra of the dianion is quite accurate without any significant scaling. This is largely attributed to the lack of H atoms on the tetratozole ring, which otherwise produces anharmonicity in the motion of the atoms. Such anharmonic effects are not considered in the molecular modeling calculations. It is also noted that some vibrational bands lack a permanent dipole moment and are thus invisible. The bands at 1438 and 735 cm\(^{-1}\) involve motion of the N\(_2\)-azo molecule and thus are of particular interest. In general, vibrational motions are complex and involve many atoms simultaneously. Here an attempt has been made to account for what appears to be the major atoms involved in the vibrational motion. We should note that the band at 1571 cm\(^{-1}\) for GzT is likely a combination between bands at 1019 and 557 cm\(^{-1}\) (not shown) or caused by association effects within the condensed phase; combination bands or overtones were not considered within the molecular modeling calculations. The band at 557 cm\(^{-1}\) is otherwise important as it describes the in-plane-bending (i.p.b.) mode of the N\(_2\)-azo group. The predicted strong band at 1019 cm\(^{-1}\) is very weak for GzT.

IR spectrum obtained from test (i) as described in Section 2 for GzT is shown in Fig. 5. It was observed that GzT decomposes first slowly and then rapidly at 563 K, leaving behind a white residue on the foil. In this test, although the decomposition products are detected in the gas phase, they are assumed to have been formed in the liquid phase for the following reasons. First, the low molecular weight species of the decomposition products rapidly vaporize at these relatively high temperatures, but no further gas-phase...
reactions are assumed to occur since the products evolve into a “cool” environment. Second, evaporation rates of high molecular weight species within the temperature range studied are considered to be very slow. Fig. 5 shows two selected FTIR spectra obtained at 573 K. The top spectrum was acquired during the relatively slow phase of its decomposition, whereas the bottom spectrum was acquired after a rapid decomposition occurred. The bands at 1440, 1600, 3455 and 3575 cm⁻¹ are exactly the same as those obtained by Wang et al. for melamine (C₆H₆N₆) [38]. Hence, in this case, they are also attributed to gas-phase melamine, the formation of which will be explained in Section 4.2.3.

During the early decomposition phase, only NH₃ and melamine evolve as IR-detectable quantities in the gas-phase region. However, in the later spectra, we observe several decomposition products of GzT. The band near 1650 cm⁻¹ and 1560 cm⁻¹ indicate the presence of guanidine. The band at 1650 cm⁻¹ belongs to the C= N stretch and the band at 1560 cm⁻¹ belongs to NH₂ deformation. This conclusion is based in part on analyzing the solid-phase IR spectra of GC1, GN and GzT discussed previously. There are small amounts of species containing C = N or NCN or both in the region near 2100–2300 cm⁻¹. A small amount of HCN at 712 cm⁻¹ is also detected. Most of the condensed phase is melamine or melamine-like compounds, which are very stable. To confirm this, the residue obtained was heated to 673 K. It did not produce any IR-active gases suggesting the presence of a very stable compound.

From the ToFMS spectra of GzT, as shown in Fig. 6, mass to charge (m/z) ratios are observed corresponding to the above decomposition products. In addition, a significant quantity of N₂ is detected, which is IR inactive and thus absent in the FTIR spectra. The presence of strong peaks at m/z = 60, m/z = 59 and m/z = 43, indicate the presence of guanidine, and protonation of guanidine that occurred within the ionization region of the ToFMS. Several peaks corresponding to heavier molecules, m/z = 96, 111 and 126 are also observed in the ToFMS spectra. The peak at m/z = 96 and 111 indicates either the loss of one or two NH groups from melamine which is detected at m/z = 126, or that the reactions produced 1,3,5-triazine-2,4-diamine which has a six membered heterocyclic ring with two amine (−NH₂) groups attached to it.

The condensate spectrum obtained for GzT decomposition by performing test (ii) as described in Section 2.1 did not provide any useful data. However, test (iii) which analyses the residue after decomposition proved useful in obtaining additional information. The IR spectra of GzT residue taken at 4, 12 and 16 s are shown in Fig. 7. The GzT sample subjected to thermolysis for the duration of 16 s possesses an IR spectrum that is exceedingly different from the IR spectra of samples corresponding to 4 and 12 s. These studies were performed at 553 K. The bands belonging to the guanidine cation are labeled in Fig. 7(a). Strong N−H stretch bands are observed from 3000–3500 cm⁻¹ whereas NH₂ deformation is seen at 1560 cm⁻¹. Stretching of C−N bond of guanidine cation is observed as a strong band at 1650 cm⁻¹. Several of these bands are also observed in Fig. 5, indicating the evolution of guanidine during the decomposition of GzT.

Hammerl et al. studied the vibrational spectra of several azotetrazole salts [39]. According to the study, C−N stretch vibrations belonging to azotetrazole ring are located near 1390 and 735 cm⁻¹. These bands were identified and labeled in Fig. 7. However, vibrations from N=N(N₁,N₂) N=N(N₁,N₂) and C−N(N₂) could not be identified easily. According to Hammerl et al., these vibrations are absent in IR spectra but present as strong bands in Raman spectra. Since N=N bond in the ring possesses a partial single-bond character, IR active bands are likely to be present in the N=N vibrational region. A study performed by Bugalho et al. on

![Fig. 6. Mass spectrum showing gas-phase species evolved during the decomposition of GzT at 573 K and 1 atm Ar & He.](image)
vibrational assignment of tetrazoles was used to identify such bands in Fig. 7 [40]. Our studies on GCl and GN were also useful in identifying the bands for azotetrazole. One peculiar feature of Fig. 7(d) is the presence of weak bands at 2190, 2147 and 2040 cm⁻¹ which are not visible in Fig. 5. According to the discussion of IR data by Socrates [41], it is known that in the region from 2000 to 2200 cm⁻¹, one of the following structures shows a distinct peak: N≡C, C≡N, N≡N, C≡C and X = X = X where X could be either N or C. Using FTIR, we studied various compounds such as azides, nitriles, and isonitriles having the above structures in order to identify these two absorption bands. We also performed frequency calculations on the optimized structures of several compounds containing the above stated functional groups. Based on these studies and the detailed analysis of the CN⁻ anion by Klapotke and Stierstorfer [42] we conclude that the band at 2147 cm⁻¹ corresponds to the asymmetric stretching vibrations of an azide group (−N≡N≡N⁻). The corresponding symmetric stretching vibration should be much weaker in intensity and present near 1250 cm⁻¹; this region has some small peaks but a definite assignment is difficult due to large absorbance in this region. The azide group is most probably attached to either a tetrazole or a triazole ring. The band at 2190 cm⁻¹ confirms the presence of a molecule that contains the −N≡C≡N—functional group. It should be noted that for the frequency calculations mentioned above, high-level methods such as CCSD(T)/aug-cc-pVTZ [43–45] were also attempted but the computational time requirements were too large. Thus, IR frequencies for the various molecules were calculated using B3LYP/6-311+G(d,p). Typically, frequencies calculated using this level of theory differ with experiment by about 50 cm⁻¹ even after scaling.

**4.2. Molecular modeling results**

In this work, we aim to analyze the overall decomposition behavior of GzT by explaining the formation of product species: N₂, HCN, NH₃, guanidine and melamine. A chemical mechanism for liquid-phase decomposition of GzT was derived by using the ab initio computational methods described in Section 3. Reactions in the mechanism presented here were formulated by using our experimental results as a guide, and they include unimolecular decompositions, bimolecular and ion recombinations, as well as proton transfers and isomeric rearrangements. It should be noted that a transition state for proton transfer within the liquid phase from the guanidinium cation to the azotetrazolate dianion as described by others [4,10,13] could not be identified in our calculations. These ions prefer to stay separated in the liquid phase due to solvation effect. Same has been reported for the ions in ammonium perchlorate (AP) by Zhu and Lin [46]. Their calculation results suggest that a strong solvent effect exists on the dissociation kinetics in solution.

Ab initio calculations are helpful in deciding which reactions to exclude from the mechanism based on thermodynamic arguments. If a reaction is found to be highly endothermic, or considerably more endothermic than a competing pathway, then that reaction may be safely omitted from the mechanism in most cases. Transition state theory estimates of the rate constants can be used for making similar arguments. Thus, thermodynamic parameters and rate coefficient values were used to eliminate certain reactions from this mechanism. The computational approach adopted for developing the chemical reaction mechanism in this work is similar to that of Kumbhakarna and Thynell [14] and Liu et al. [15]. Based on this methodology, the liquid-phase decomposition of GzT can be explained as follows.

**4.2.1. Formation of N₂**

Based on the quantum chemical calculations, important chemical reactions in the decomposition of GzT that result in the production of molecular nitrogen are listed in Table 1 with their corresponding thermodynamic parameters. For all the reactions discussed in this paper, Gibbs free energy changes between
transition states and reactants or products are given because they are convenient for estimating the reaction rate constant using the conventional transition state theory. In addition the difference between enthalpies of the products and reactants, which is the enthalpy of reaction, is also given for every reaction. This parameter tells us whether the reaction is endothermic or exothermic. Optimized structures of transition states that are labeled for each of the reactions in Table 1 are shown in Fig. 8. Contrary to the commonly held belief, our calculations show that proton transfer is not the initial step in GzT decomposition. Instead, one of the two five-membered rings in AzT$^{2-}$ opens to release N$_2$ and to form an ionic intermediate INT4 as seen in reaction R1. This reaction is entropically favored and takes place when GzT is heated to a temperature of about 523 K in our fast thermolysis experiments. Enough energy is provided by heating to cause one C—N and one N—N bond of the tetrazole ring to break. Since the N$_2$ molecule readily escapes the sample during thermolysis and does not accumulate in any significant amount, the reverse of reaction R1 plays a lesser role although its barrier is about 34 kJ/mol lower than the forward barrier. An alternate pathway for AzT$^{2-}$ is the release of azide (N$_3^-$) ion as shown in reaction R2. But R1 is clearly preferred over this pathway because

Table 1

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>$\Delta G_f^a$</th>
<th>$\Delta G_f^b$</th>
<th>$\Delta H_r^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>AzT$^{2-}$ $\rightarrow$ INT4 $\rightarrow$ N$_2$ + INT4</td>
<td>156.9</td>
<td>122.6</td>
<td>84.5</td>
</tr>
<tr>
<td>R2</td>
<td>AzT$^{2-}$ $\rightarrow$ TS9 $\rightarrow$ INT9</td>
<td>212.9</td>
<td>106.6</td>
<td>154.8</td>
</tr>
<tr>
<td>R3</td>
<td>INT4 $\rightarrow$ Gu$^+$ $\rightarrow$ INT4a $\rightarrow$ Guanidine</td>
<td>No barrier</td>
<td>88.2</td>
<td>$-96.2$</td>
</tr>
<tr>
<td>R4</td>
<td>INT4a $\rightarrow$ TS4a1 $\rightarrow$ INT4a1</td>
<td>103.3</td>
<td>251.4</td>
<td>$-104.1$</td>
</tr>
<tr>
<td>R5</td>
<td>INT4a1 $\rightarrow$ Gu$^+$ $\rightarrow$ INT4a1d $\rightarrow$ Guanidine</td>
<td>211.7</td>
<td>223.8</td>
<td>32.6</td>
</tr>
<tr>
<td>R6</td>
<td>INT4a1 $\rightarrow$ Gu$^+$ $\rightarrow$ INT4a1i $\rightarrow$ Guanidine</td>
<td>96.2</td>
<td>17.5</td>
<td>73.2</td>
</tr>
<tr>
<td>R7</td>
<td>INT4a1i $\rightarrow$ TS4a1i1 $\rightarrow$ isocyanoethenes</td>
<td>$-7.9$</td>
<td>407.1</td>
<td>$-322.1$</td>
</tr>
</tbody>
</table>

* Gibbs free energy of activation in the forward direction (kJ/mol).
*b Gibbs free energy of activation in the backward direction (kJ/mol).
*c Enthalpy of reaction (kJ/mol).
R2 is more endothermic and has much higher forward Gibbs free energy change barrier as compared to R1. The resulting intermediate INT4 dianion in R1 is unstable and can easily accept a proton from Gu+. Proton transfer occurs at this stage. The carbon atom in INT4, which is no longer a part of the ring, acts as a nucleophile with the highest partial negative charge and easily accepts the proton resulting in the formation of INT4a and guanidine. This reaction (R3) is exothermic and very rapid having no energy barrier. It also results in weakening of the C—N bond in INT4a which easily breaks with a small energy addition releasing another N2 molecule and forming INT4a1 in the exothermic reaction R4. INT4a1 can react with Gu+ in numerous ways. One of these ways is through reaction R5 which is an endothermic proton-transfer reaction having relatively high barrier. Hence formation of the neutral intermediate INT4a1d via this reaction is unlikely but it is also formed through another pathway as will be explained in Section 4.2.4. Reaction R6 is an alternate pathway for reaction between INT4a1 and Gu+. Reaction R6 has low activation energy as compared R5 and results in the formation of INT4a1i. The ring in INT4a1i becomes unstable and readily comes apart in reaction R7 to produce isocyanoethene and nitrogen. As shown in Table 1 reaction R7 is highly exothermic and has no energy barrier.

R1 is an important reaction because decomposition of G2T is initiated with this ring-opening step. Thus, enthalpy and free energy changes for reaction R1 calculated using various levels of theory are presented in Table 2. The variation in these values due to change in the method and basis set is very large or more than 40 kJ/mol; thus, a great deal of uncertainty is introduced in the kinetic rate parameters which suggests that much additional work is needed for the determination of the kinetic rate parameters. Examining the values, however, a forward barrier of 146 kJ/mol rather than 156.9 kJ/mol would closer represent the experimentally detected N2 evolution. This reduction by 10.9 kJ/mol is probably within the uncertainty of the two compound methods CBS-QB3 and G4(MP2). It should be noted that release of N2 from ring-opening of the second tetroazole ring in a unimolecular manner of INT4a1 has large barrier, and this reaction is not included. Ring-opening essentially occurs via R6, since the barrier for R7 is effectively zero.

### 4.2.2. Formation of HCN

Evolution of HCN was observed in our experiments as mentioned earlier. HCN formation pathways revealed by molecular modeling calculations are listed in Table 3, and the corresponding transition state structures are shown in Fig. 9. Reactions R8 and R9 are additional ways in which INT4a1 and Gu+ react. In R8, the carbon in Gu+ attaches itself the non-ring N atom of INT4a1 adjacent to the carbon. INT4a1h is formed along with HCN and N2.

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**Table 2**
Thermodynamic parameters for reaction R1 calculated using various levels of theory.

<table>
<thead>
<tr>
<th>Reaction R1: AzT2 → INT4 + N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory and basis set</td>
</tr>
<tr>
<td>B3LYP/6-311++G(d,p) [21]</td>
</tr>
<tr>
<td>CBS-QB3 [24]</td>
</tr>
<tr>
<td>MP2/6-311++G(d,p) [25]</td>
</tr>
<tr>
<td>M062X/6-311++G(d,p) [47]</td>
</tr>
<tr>
<td>G4(MP2) [26]</td>
</tr>
</tbody>
</table>

<sup>a</sup> Activation enthalpy in the forward direction (kJ/mol).

<sup>b</sup> Activation enthalpy in the backward direction (kJ/mol).

<sup>c</sup> Enthalpy of reaction (kJ/mol).

<sup>d</sup> Gibbs free energy of activation in the forward direction (kJ/mol).

<sup>e</sup> Gibbs free energy of activation in the backward direction (kJ/mol).

<sup>f</sup> Gibbs free energy of reaction (kJ/mol).
In R9 a proton from Gu⁺ is transferred to the non-ring N atom of INT4a1. This proton transfer alters the C—N bond and destabilizes the ring, resulting in the formation of guanidine, HNC, HCN, and N₂. Reaction R10 shows another HCN formation pathway in which INT4a1d that was formed earlier comes apart in a low barrier reaction forming additional N₂ and HCN. INT4a1h, which was formed in R8, releases the cyanide (CN⁻) anion as shown in reaction R11. The CN⁻ anion is also formed in reaction R12 from isocynoethene. This anion accepts a proton and forms HCN in reaction R13. It should be noted that some of the reactions in Table 3 are highly exothermic. Such high exothermicity is expected for these reactions because C≡N and N≡N bonds are formed.

Formation of N₂ in this manner with the release of large amount of energy is the process that makes high-nitrogen compounds like GzT attractive as propellant ingredients.

### 4.2.3. Formation of NH₃

NH₃ is seen to evolve very early in the GzT decomposition process. Table 4 gives details of the reactions that result in NH₃ generation, and Fig. 10 shows the optimized transition state structures for these reactions. After proton transfer has taken place, we have both Gu⁺ and guanidine in close vicinity of each other in the liquid phase. These recombine to form a charged intermediate INT1. The Gibbs free energy of activation for this...
reaction, R14 is low and the reaction is exothermic. In guanidine, the most preferred site for bond formation is the N atom carrying a single H atom. Our calculations showed that an alternate pathway for \( \text{NH}_3 \) formation via the combination of two guanidine molecules has very high activation energy (~250 kJ/mol). Hence reaction R14 is preferred over this alternate pathway. Once INT1 is formed, it easily releases \( \text{NH}_3 \) in reaction R15 forming INT1d1. This intermediate further combines with another guanidine molecule

**Table 4**

Important reactions in the decomposition of GzT resulting in the formation of \( \text{NH}_3 \) along with thermodynamic parameters calculated at the CBS-QB3 level of theory.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>( \Delta G^H )</th>
<th>( \Delta G^S )</th>
<th>( \Delta H^S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R14</td>
<td>( \text{Gu}^+ + \text{Gu}^+ \rightarrow \text{INT1} )</td>
<td>106.6</td>
<td>53.9</td>
<td>-5.8</td>
</tr>
<tr>
<td>R15</td>
<td>( \text{INT1d1} \rightarrow \text{INT1d1} + \text{NH}_3 )</td>
<td>77.4</td>
<td>117.5</td>
<td>10.8</td>
</tr>
<tr>
<td>R16</td>
<td>( \text{INT1d1} + \text{Gu}^+ \rightarrow \text{INT1d1a} )</td>
<td>232.2</td>
<td>239.7</td>
<td>-9.6</td>
</tr>
</tbody>
</table>

*Fig. 9.* Transition state structures for reactions producing HCN during GzT decomposition optimized using the CBS-QB3 level of theory.
in a bimolecular reaction and simultaneously releases additional NH₃. This bimolecular reaction can either be R16 or R17 depending on the location of H atom on INT1d1 that is removed to form NH₃. Both these reactions have comparable activation energies but R16 is slightly exothermic whereas R17 is endothermic. The activation energies are somewhat high but alternative pathways that were explored for NH₃ formation were not found to be thermodynamically feasible. Reaction R18 is an additional way in which NH₃ can be formed by unimolecular decomposition of guanidine. Although this reaction has relatively low rate constants, it is assumed to occur because HNCNH/NH₂CN is observed in our mass spectrum at m/z = 42 (Fig. 6).

**4.2.4. Formation of melamine**

Table 5 elaborates the chemical processes involved in the formation of melamine which is one of the main products of GzT decomposition. The corresponding transition state structures are shown in Fig. 11. The positively charged intermediates INT1d1a and INT1d1c produced in reactions R16 and R17, respectively, are unstable structures and tend to stabilize by releasing energy through molecular rearrangement and ring closure followed by release of NH₃. Reactions R19 through R21 show this process for INT1d1a whereas reactions R22 through R24 show it for INT1d1c. It can be seen in R21 and R24 that the product obtained from these series of chemical reactions is a melamine-like structure with a

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>ΔG&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ΔG&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ΔH&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>R17</td>
<td></td>
<td>251.8</td>
<td>201.6</td>
<td>47.6</td>
</tr>
<tr>
<td>R18</td>
<td></td>
<td>202.5</td>
<td>172.8</td>
<td>79.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Gibbs free energy of activation in the forward direction (kJ/mol).

<sup>b</sup> Gibbs free energy of activation in the backward direction (kJ/mol).

<sup>c</sup> Enthalpy of reaction (kJ/mol).

---

Fig. 10. Transition state structures for reactions producing NH₃ during GzT decomposition optimized using the CBS-QB3 level of theory.
Table 5
Important reactions in the decomposition of GzT resulting in the formation of melamine along with thermodynamic parameters calculated at the CBS-QB3 level of theory.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>( \Delta G_f^a )</th>
<th>( \Delta G_b^b )</th>
<th>( \Delta H_f^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R19</td>
<td>INT1d1a</td>
<td>21.75</td>
<td>19.6</td>
<td>−18.4</td>
</tr>
<tr>
<td>R20</td>
<td>INT1d1a</td>
<td>56.0</td>
<td>54.3</td>
<td>2.1</td>
</tr>
<tr>
<td>R21</td>
<td>INT1d1a1a</td>
<td>127.1</td>
<td>233.0</td>
<td>−66.9</td>
</tr>
<tr>
<td></td>
<td>INT1d1a1a</td>
<td>66.9</td>
<td>53.5</td>
<td>2.1</td>
</tr>
<tr>
<td>R22</td>
<td>INT1d1c</td>
<td>33.6</td>
<td>53.5</td>
<td>−27.6</td>
</tr>
<tr>
<td>R23</td>
<td>INT1d1c</td>
<td>117.9</td>
<td>209.2</td>
<td>−43.0</td>
</tr>
<tr>
<td>R24</td>
<td>INT1d1c1a</td>
<td>154.8</td>
<td>202.9</td>
<td>−46.0</td>
</tr>
<tr>
<td>R25</td>
<td>INT1d1c1a</td>
<td>151.4</td>
<td>236.3</td>
<td>−33.4</td>
</tr>
</tbody>
</table>

\( a \) Gibbs free energy of activation in the forward direction (kJ/mol).
\( b \) Gibbs free energy of activation in the backward direction (kJ/mol).
\( c \) Enthalpy of reaction (kJ/mol).
single positive charge carrying an extra proton. It is labeled as melamine−. This melamine− needs to lose the proton, most likely to a negatively charged species in order to form melamine. Proton transfer to the C atom of INT4a1 was found to be thermodynamically most favorable. INT4a1 was produced from AzT2− earlier in reaction R4. On receiving the proton INT4a1 becomes unstable and N2 separates from it as shown in reaction R25. It was explained earlier that INT4a1d readily undergoes unimolecular decomposition to produce HCN and N2 (reaction R10). The reaction pathway described here for formation of melamine is more favorable as compared to an alternate one in which the intermediate INT1d1 donates a proton and forms a neutral complex before ring closure. It was found that for closing the ring in the neutral complex a considerably large energy barrier (∼230 kJ/mol) needs to be overcome hence formation of melamine via this alternate pathway is unlikely.

5. Conclusions

Liquid-phase decomposition of G2T was studied using FTIR spectroscopy and ToF mass spectrometry. The formation of chemical species observed in these studies was explained by using quantum mechanics based calculations. Major reaction pathways were identified based on these calculations and on thermodynamic considerations. Within the framework of experiments and calculations in the present work, the following conclusions can be drawn.

i) When subjected to rapid heating to isothermal conditions, G2T decomposes to form N2, NH3, HCN, melamine and guanidine as the final products.

ii) Decomposition is initiated within the AzT2− dianion, because IR active spectral bands belonging to the dianion disappear quickly and molecular nitrogen is detected in large quantities early in the decomposition event.

iii) Proton transfer takes place only after ring opening has occurred, and it is a very rapid, barrier-less reaction.

iv) The initial ring-opening reaction is endothermic, and most of the subsequent reactions are highly exothermic.

v) Principal mechanisms of NH3 and melamine formations are the reaction between Gu+ and guanidine followed by many subsequent steps.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tca.2014.06.005.

References
