THERMOLYSIS OF HIGH-NITROGEN ENERGETIC COMPOUNDS
USING FTIR SPECTROSCOPY AND TIME OF FLIGHT MASS SPECTROMETRY

A Thesis in
Mechanical Engineering

by
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ABSTRACT

Thermal decomposition of high-nitrogen energetic materials was studied using Fourier transform infrared spectroscopy (FTIR) and time-of-flight mass spectrometry (ToFMS) at high heating rates. The information obtained from these studies will be used in formulating detailed chemical reaction mechanisms for further use in predicting the burn rate of solid propellants from comprehensive modeling tools. The decomposition studies were conducted using an existing confined rapid thermolysis chamber, to which the FTIR and ToFMS systems were interfaced to allow in situ measurements of the evolved gas-phase species. The evolved gas-phase species were also allowed to condense on a glass plate. This residue, as well as the residue that remained on the foil in the confined region, were pressed into KBr pellets and examined ex situ using FTIR transmission spectroscopy. The experiments were conducted in an inert environment at atmospheric pressure. Small quantities of the sample were subjected to heating rates of 2000 K/s. The energetic material of interest is triaminoguanidinium azotetrazolate (TAGzT). To understand its behavior, guanidinium azotetrazolate (GzT) was also examined. The decomposition of GzT and TAGzT begins within the azotetrazolate dianion, releasing nitrogen. GzT decomposition produces chain-branching reactions resulting in a nearly explosive event. Once the explosive event has occurred, the remaining products continue to release gaseous ammonia via secondary reactions. Decomposition of TAGzT on the other hand, occurs at a much slower rate than GzT and at lower temperatures. The early phase of TAGzT decomposition involves release of hydrazine, but it ends when the AzT dianion is completely consumed. The TAGzT
decomposition produces the 5-azido-tetrazole as one of the major decomposition products, in addition to NH$_3$ and N$_2$. Small amounts of HCN are also released.
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NOMENCLATURE

Symbols

$A$ Absorbance
$\delta$ In-plane bending vibration
$\gamma$ Out-of-plane bending vibration
$\nu$ Stretching vibration
$\omega$ Out-of-plane wagging vibration

Abbreviations

DSC Differential scanning calorimeter
DTA Differential thermal analyzer
FTIR Fourier transform infrared spectroscopy
HITRAN High-resolution transmission molecular absorption database
IR Infrared
TG Thermo-gravimetric
ToFMS Time of flight mass spectrometry

Chemical Abbreviations

AGN Aminoguanidinium nitrate
AzT Azotetrazolate
GCl Guanidinium hydrochloride
GN Guanidinium nitrate
GzT Guanidinium azotetrazolate
HCN Hydrogen cyanide
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
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<tbody>
<tr>
<td>HNCNH</td>
<td>Carbodiimide</td>
</tr>
<tr>
<td>HNNCH</td>
<td>Nitrileimine</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Molecular nitrogen</td>
</tr>
<tr>
<td>NCG</td>
<td>N-cyanoguanidine</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>Hydrazine</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>Ammonium cation</td>
</tr>
<tr>
<td>NH$_4^+$Cl$^-$</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>NH$_2$CN</td>
<td>Cyanamide</td>
</tr>
<tr>
<td>TAG</td>
<td>Triaminoguanidine</td>
</tr>
<tr>
<td>TAGN</td>
<td>Triaminoguanidinium nitrate</td>
</tr>
<tr>
<td>TAGzT</td>
<td>Triaminoguanidinium azotetrazolate</td>
</tr>
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</table>
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Chapter 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Background

Propellants have high-energy content that undergo combustion and sustain it in the absence of an external heat source. Propellants are used in space propulsion systems, guns, automobile air bags and ejection seats of airplanes where generation of high pressure within a very short time is required [1-4]. The combustion is complex and involves many different processes such as, decomposition, oxidation, phase conversion, species diffusion, etc. Hence, a significant research effort has been expended to investigate combustion of propellants.

Recently, research in the area of high-nitrogen energetic materials has received attention due to the many benefits of the low carbon content, namely, reduced emission of greenhouse gases, reduced barrel erosion, fast burning behavior and lower adiabatic flame temperatures compared to conventional double-base propellant ingredients. Research has been directed towards understanding their decomposition and combustion behavior at different heating rates and pressure. In order to improve the predictive capability of numerical simulation of combustion processes, analysis of the early decomposition chemistry of these novel energetic materials in detail is important.
1.2 High-Nitrogen Energetic Materials and Their Application

Propellants derive their energy either from the very high positive heat of formation due to the presence of N-N and C-N bonds or oxidation of the long carbon backbone [5] or both. Traditional energetic materials such as 2,4,6-trinitrotoulene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), contain nitro groups which oxidize the carbon and hydrogen in the backbone to form water and oxides of carbon.

High-nitrogen materials produce large amounts of molecular nitrogen and have high positive heats of formation [6]. However, the adiabatic flame temperatures are often lower compared to nitro-cellulose-based propellants, and high-nitrogen materials have the potential of forming less smoke or soot. In addition, some of the high-nitrogen materials are remarkably stable towards friction, heat and impact, hence easy to store and transport [6].

The combustion properties of high-nitrogen materials make them suitable for numerous applications. First, high-nitrogen compounds produce a large amount of gaseous products per gram making them suitable as gas generators in airbags [6]. Second, the cooler combustion products formed due to the presence of copious amount of nitrogen make them suitable for use in low-signature propellants and gun propellants [6]. Third, as gun propellants, the produced nitrogen re-nitrides the bore surface inhibiting surface corrosion [7]. Fourth and finally, lower hydrogen concentration from high-nitrogen compounds minimizes hydrogen-assisted cracking of the bore surface [8].
1.3 Motivation

The recently synthesized triaminoguanidinium azotetrazolate (TAGzT) has the potential to act as burn-rate enhancer when used with traditional energetic materials such as RDX. However, with the current knowledge available on this compound, predicting the combustion behavior of RDX and TAGzT mixtures is very difficult. In order to understand mixture compatibility issues, thermal stability and combustion behavior, one must have a thorough knowledge of the thermolysis of individual components. There are numerous works describing the thermal decomposition and combustion behavior of RDX [9-11]. On the other hand, the thermal decomposition behavior of azotetrazolates has been the subject of relatively few studies. Hence, this work is directed towards understanding the condensed-phase decomposition reactions of this new class of compounds. In addition to TAGzT, results from decomposition studies of GzT are also included. A review of available decomposition studies on these two compounds is presented next.

1.4 Decomposition Studies on Guanidinium Azotetrazolate

Guanidinium azotetrazolate is a yellow-colored salt with cotton fiber-like appearance. GzT on burning generates smoke and leaves behind some thermally stable residue. In addition it is remarkably insensitive to impact. This is attributed to lower molar heat of formation per unit atom and presence of hydrogen bonding between guanidinium cation and the nitrogen in the azo-linkage. Guanidinium azotetrazolate melts
roughly around 240°C. Due to its excellent thermal and impact stability, GzT has been explored as a replacement for sodium azide in safety equipments [6].

To prepare GzT, 5 g of sodium azotetrazolate pentahydrate is dissolved in 70 ml of water at 80 to 90°C with constant stirring. To this solution 3.18g of guanidine hydrochloride is added which results in instantaneous precipitation of a yellow solid. The precipitate is digested by boiling the suspension for two minutes and then allowing it to cool to room temperature. The solid is then filtered, washed and dried to give 4.15 g of guanidinium azotetrazolate [12].

Using thermal analysis techniques such as DTA, TGA, TG-FTIR and pyrolysis-GC-MS, Damse and his co-workers investigated the decomposition of GzT [2]. From the TG data, they observed that the decomposition of GzT occurs in two stages. The first stage corresponds to an exothermic reaction in the temperature range of 200 to 256°C with 59% weight loss. The first stage denotes abstraction of acidic protons available at the guanidinium cation by the azotetrazolate ring. The proton transfer lead to the formation of a highly unstable products which then decomposed to release molecular nitrogen and cyanamide via ring-opening reactions. The theoretical weight fraction of 3 times N₂ and NH₂CN was found to be 0.5881, which is close to the experimentally observed weight loss of 59%. The second stage is a slow endothermic reaction observed beyond 256°C. This stage indicates cleavage of relatively strong C-N bonds of the cation.

Hammerl et al. studied the spectra, structure and thermal behavior of several guanidinium azotetrazolate based salts [1]. Based on vibrational spectroscopy, they identified several important absorption bands: 3400-3000 cm⁻¹ belonging to ν(NH₂) and ν(NH), 1680-1550 cm⁻¹ to δ(NH) and δ(NH₂), 1550-1350 cm⁻¹ to ν of tetrazolate ring
and $\delta$(NH), 1350-700 cm$^{-1}$ to $\nu$(NCN), $\nu$(NN), $\omega$(NNH2), $\gamma$(CN) and $\delta$ of tetrazolate ring, <700 cm$^{-1}$ to $\delta$, out of plane bend (N-H) and $\omega$ (NH$_2$). The thermal behavior of GzT was investigated using DSC with heating rate of 10°C/min. Approximately 2 mg of the sample was heated up to 450°C. The products were analyzed using IR spectroscopy and mass spectrometry. The DSC curve revealed a distinct exothermic step at 262°C. The major decomposition product is molecular N$_2$ which was identified by mass
spectrometry. Using IR spectra, NH₃, HCN and carbodiimide (HNCNH) were also detected as gaseous products from the explosion study. The presence of these products is confirmed by their corresponding m/z ratios from mass spectra. Based on these experimental results as shown in Fig. 1.3, it was concluded that decomposition of azotetrazolate anion is initiated via the protonated species. Thus, protonation reduces the stability of the ring. The ring then decomposes to nitrile via release of hydrogen azide or nitrile imines under release of molecular nitrogen [13]. Since hydrogen azide is not detected in the IR spectra, it was concluded that the azotetrazolate anion decompose via the latter pathway. The decomposition of guanidinium cation is initiated by elimination of NH₃ to form carbodiimide. Carbodiimide being unstable as high temperatures decomposed further to form gaseous products such as N₂, NH₃ and HCN.

Decomposition pathways for GzT were investigated using computational methods by Liu et al. [14]. Density functional theory (DFT) with B3LYP/6-31G(d,p), and ab initio MP2/6-31G(d,p) and HF/6-31G(d,p) basis sets available in Gaussian 98 were used to model the decomposition mechanism. Thus the analysis is assumed to occur in the gas phase. The first decomposition step was identified as a “cracking” process to form two guanidinium cations and the azotetrazolate dianion. The decomposition of guanidinium cation then proceeds via three different pathways depending on the initial step to form C⁺≡N and two NH₃ molecules. The initial step could be either elimination of H⁺, H• radical or NH₂ radical. The decomposition of azotetrazolate anion is initiated by ring opening with simultaneous elimination of nitrogen by cleavage of N-N bonds outside the ring.
1.5 Decomposition Studies on Triaminoguanidinium Azotetrazolate

Triaminoguanidinium azotetrazolate being the compound of interest is analyzed in detail. TAGzT is a bright yellow crystalline solid with a distinct melt temperature at 195°C. The structure and physical properties of TAGzT are shown in Fig. 1.3 and Table 1.1, respectively. TAGzT is synthesized from ammonium azotetrazolate. 5 g of
ammonium azotetraolate is dissolved in 60 ml water at 80 to 90°C. To this solution, 7 g of triaminoguanidinium chloride is added with constant stirring. A yellow solution is formed which is allowed to cool to room temperature. Upon cooling a yellow crystalline solid is formed which is filtered and air dried to yield 7.7g of TAGzT [6]. TAGzT has been considered to replace TAGN as a burn-rate enhancer with RDX. TAGN is incompatible with nitrate esters because TAGN being a salt of a weak base and strong acid hydrolyzes in the presence of water or a strong base to form nitric acid. However, TAGzT on hydrolysis forms azotetrazolic acid, which is weaker than nitric acid and hence does not act as a strong oxidizing agent [15]. Bracuti and Marchak performed X-ray diffraction studies to determine the crystal and molecular structure of TAGzT [15].

<table>
<thead>
<tr>
<th>Property</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Appearance</td>
<td>Bright yellow thin crystalline solid</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.602</td>
</tr>
<tr>
<td>Heat of Formation (kcal/mol)</td>
<td>+257</td>
</tr>
<tr>
<td>Impact Sensitivity (cm, Type 12) (HMX=26)</td>
<td>25</td>
</tr>
<tr>
<td>Vacuum Stability (ml/g for 48h at 100°C)</td>
<td>0.25</td>
</tr>
<tr>
<td>Friction Sensitivity (BAM, kg)</td>
<td>8.4</td>
</tr>
<tr>
<td>DTA Exotherm</td>
<td>195</td>
</tr>
<tr>
<td>Detonation Velocity (km/s)</td>
<td>9.05</td>
</tr>
<tr>
<td>Detonation Pressure (GPa)</td>
<td>292</td>
</tr>
</tbody>
</table>
the TAG cation, the carbon and nitrogen atoms as well as the three imino hydrogen atoms are co-planar. The C-N bonds are shorter than the accepted C-N single bond length suggesting a partial double-bond character. The N-N bonds are the weakest in the TAG cation. Two out of the three imino H atoms form intra-molecular hydrogen bonds with nitrogen from the neighboring amino group. The divalent azotetrazolate (AzT) anion is composed of two identical co-planar five-member rings. Within each tetrazole ring, there are two partial C-N double bonds. Also the N-N bonds within the ring show a double-bond character. This suggests delocalization of $\pi$-electrons within the ring. As a result of the electron delocalization, the C-N$_{azo}$ bond is the weakest in the AzT anion. The crystal packing of TAGzT reveals that each cation is surrounded by three anions which are held together by an intermolecular hydrogen bond in the same plane. Several of these planes are stacked on top of one another to form the TAGzT crystal. It is this infinite three-dimensional network of inter-molecular hydrogen bonds that enhance the stability of TAGzT.

Hammerl et al. was the first group to investigate the vibrational spectra and decomposition of TAGzT [1]. The decomposition pathways are similar to that summarized in Fig. 1.2. The major difference with respect to decomposition of GzT is the temperature at which TAGzT starts to decompose and the decomposition pathway of the TAG cation, as shown in Fig. 1.4. TAGzT shows a distinct exothermic step at 209°C. The decomposition temperature being lower than GzT is due to the presence of weak N-N bonds in the TAG cation. According to Hammerl et al., the TAG cation decomposes via elimination of hydrazine to yield carbodiimide [1]. The presence of hydrazine is confirmed by observing $m/z = 32$ in the mass spectra. Hydrazine being unstable at these
reaction conditions decomposes to form N_2, H_2 and a meager amount of NH_3. Carbodiimide decomposes to form NH_3, HCN and N_2.

Tappan et al. performed burn-rate experiments, T-Jump/FTIR spectroscopy and laser-ignition studies on TAGzT [16]. Burn-rate studies were performed using 6.3mm×6.4mm pure TAGzT pellets. The pellets were ignited using resistive chromium wire in a 2L stainless-steel vessel pressurized from 0.2 to 7 MPa. The combustion event was filmed using a 30 fps (frames per second) video camera. The authors observed that TAGzT has a higher burn-rate and lower ignition temperature compared to traditional explosives, such as HMX. They concluded that due to absence of oxygen, the extent of gas-phase reactions is limited and hence most of the decomposition occurs in the condensed phase. Due to these condensed-phase reactions, TAGzT has a lower pressure dependence compared to other propellants. The T-Jump/FTIR spectroscopy experiment was performed by taking 200 µg of the sample and heating it at a rate of 2000°C/s in the center of a thin platinum ribbon. The gases evolved were sampled by the IR beam which passed a few millimeters above the sample. The acquired spectra indicated the presence of NH_3, HCN, NH_2CN (cyanamide) and its dimer N-cyanoguanidine [(NH_2)_2CNCN] as the main IR-active decomposition products.
Damse et al. also studied the decomposition of TAGzT [2] and suggested the decomposition pathways shown in Fig. 1.5. The instruments used were similar to those mentioned in Sec. 1.4. From the TG data, the authors observed a four-stage weight-loss pattern. The first stage corresponds to the rapid exothermic reaction observed in the DTA between 141 to 159°C, corresponding to an 8% weight loss. This weight loss is approximately equal to the theoretical mass fraction of $N_{azo}=N_{azo}$ atoms. By comparing to

\[
\text{Gas-phase reactions}
\]

\[
6 \text{NH}_2 \rightarrow 4 \text{NH}_3 + \text{N}_2
\]

1st stage: Exothermic $N=N$ release

\[
\begin{align*}
\text{H}_2\text{N} \equiv \text{NH}_2 & \rightarrow N = N \\
\text{H}_2\text{N} \equiv \text{NH}_2 & \rightarrow 2 \left( \text{NH}_2 \text{N} \equiv \text{NH} \right)
\end{align*}
\]

2nd stage: Exothermic $\text{NH}_2$ homolysis

\[
\begin{align*}
2 \left( \text{NH}_2 \text{N} \equiv \text{NH} \right) & \rightarrow -6 \text{H}_2 \\
2 \left( \text{NH}_2 \text{N} \equiv \text{NH} \right) & \rightarrow 2 \left( \text{HN} \equiv \text{NH}^{+} \right)
\end{align*}
\]

3rd stage: Ring opening

\[
\begin{align*}
2 \left( \text{HN} \equiv \text{NH}^{+} \right) & \rightarrow 2 \text{N} \equiv \text{NH}^{+} + 3\text{N}_2 + 2\text{HCN}
\end{align*}
\]

4th stage: Endothermic C-N bond cleavage

\[
\begin{align*}
2 \text{N} \equiv \text{NH}^{+} & \rightarrow \text{N}_2 + 2\text{HCN}
\end{align*}
\]

Figure 1.5: Decomposition pathway for TAGzT according to Damse et al. [2].
the initiation of GzT decomposition, it is believed that the AzT anion is not able to extract the acidic proton due to steric hindrance caused by the three amino groups attached to the TAG cation. The second stage corresponds to a rapid exothermic reaction between 173 and 183°C, producing 26% weight loss. This weight loss corresponds to the mass fraction of (NH$_2$)$_3$. The third stage corresponds to the exothermic decomposition between 183 and 198°C, resulting in 35% weight loss due to formation of HCN. Finally, the fourth stage corresponds to a very slow endothermic reaction between 198 and 279°C, corresponding to a 20% weight loss. This latter process is thought to occur from cleavage of strong C-N bonds in the TAG cation. The presence of various species evolved during the slow decomposition is confirmed by data acquired from TG-FTIR and GC-MS experiments.
Chapter 2
EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1 Experimental Setup

The technique utilized to study the products formed under rapid decomposition of a material is referred to as confined rapid thermolysis (CRT)/FTIR/ToFMS. Using this technique, the thermal decomposition is limited to a volume confined between two heated, parallel surfaces. The setup is composed of a constant pressure chamber, a Bruker IFS 66/S FTIR spectrometer and a ToF mass spectrometer. A three-dimensional view of the chamber used with the FTIR setup, including a cut that exposes the sample holder, is shown in Fig. 2.1. The sample holder is designed to be lifted by the bottom heater to enclose the sample between the two heaters. Two ports are provided on the chamber, one serves as an inlet to the purge gas and the other exhausts decomposition products and the purge gas stream. The constant pressure chamber, resting on a rigid frame, has a height of 27.5 cm and an inner diameter of 5 cm approximately. The CRT/FTIR/ToFMS technique has been described in detail in a previous work [17].

The rapid heating is achieved by using two heaters: a stationary top heater and a mobile bottom heater. In both heaters, isothermal conditions are established by using high-watt density cartridge heaters and controlled by proportional-integral-derivative controllers. Both heaters are embedded in copper rods, 53 mm in height and 15.6 mm in diameter. There are two auxiliary systems, a pneumatic piston-cylinder for lifting the
bottom heater and a purge gas system. The purge system uses an inert gas and serves a dual purpose. One, it purges the chamber of the decomposition products and prevents recirculation of products into the path of the modulated FTIR beam, and two, it prevents oxidation of the copper rods at elevated temperatures. The temperature of the cartridge heaters is monitored and controlled by two 75 μm K-type thermocouples, embedded in the copper rods.

To achieve rapid thermolysis, defined as an event that occurs within 5 seconds, high temperatures are used. The experimental procedure is as follows: the heaters are

![Figure 2.1: Three-dimensional view of the high-pressure thermolysis chamber, exposing the sample holder, upper and lower heater, and the ZnSe windows through which the modulated beam of the FTIR propagates.](image-url)
brought up to the pre-set temperature. Approximately 0.5 mg of the energetic material is placed on the sample holder. As shown in Fig. 2.1, the sample holder is a hollow cylindrical ring with a thin foil attached on top. Though it is possible to utilize different types of foils, an 11 μm thick aluminum foil is used to minimize conductive heat transfer resistance. The sample holder is then placed over the guiding tube for the bottom heater and the bottom heater is raised by the pneumatic piston-cylinder. The sample holder is brought in contact with the ring retaining an aluminum foil over the top heater. This ring also defines and seals a gap of approximately 300 μm between the two heaters. The final position of the sample holder and the two heaters is shown in Fig. 2.2. A rectangular slit, 8.25 mm by 300 μm, is left open in the gap for gases generated during decomposition of the sample to gain access to the FTIR beam or to the orifice port on the vacuum chamber.

2.1.1 FTIR Spectroscopy

The gaseous products evolve into the FTIR beam passing through two ZnSe (or KRS-5) windows, which are offset by 0.313 inches from the center of the chamber, offering a spectral coverage of 500-10,000 cm⁻¹. This wide range is truncated using a germanium coated KBr beamsplitter and a mercury-cadmium-telluride detector to the mid-IR range of 600-5,000 cm⁻¹. The gases evolved during the thermolysis are detected, identified and quantified using FTIR transmission spectroscopy. The spectra are acquired with a spectral resolution of 2 cm⁻¹ and a temporal resolution of 50 ms.
2.1.2 ToF Mass Spectrometry

A low-pressure chamber with identical heater configurations is utilized for acquiring the ToF mass information at a high temporal resolution. The ToF MS system is equipped with a 1m flight tube and a 44 mm microchannel plate detector. Here, the recharging of the microchannel plate detector limits the temporal resolution to about 0.01 ms. The vacuum system is differentially pumped using a Leybold DIP8000 diffusion pump in the first stage, a Leybold TW700 turbomolecular pump in the second stage, and
a Leybold TMP151 turbomolecular pump as well as two Varian Starcell 75 ionpumps in the third stage; four backing pumps are also used. Typical pressures are $10^{-4}$ torr in the first stage, $10^{-6}$ torr in the second stage and $10^{-7}$ torr in the third stage. Molecular beam sampling from atmospheric pressure gases is performed using a 100 µm orifice plate attached to the first stage, a 1mm diameter Ni skimmer (manufactured in-house by electroplating) attached to the second stage and a vertically translatable 0.5×12mm$^2$ slit attached to the entrance of the third stage. A schematic is shown in Fig. 2.3. The distance between the orifice plate and the electron beam in the flight tube is 0.279m. Electron impact ionization is set at 70eV, resulting fragmentation of molecules, but allowing comparison with mass spectral and related data bases [17]. The electron beam interacts
with the molecular beam during a period of 3 µs, after which extraction of positive ions occurs as a 250V voltage difference is applied between the grid plates; the overall potential is normally set at 2.5kV. Data acquisition at 1GHz is PC-based using the 8-bit PDA1000 PCI-board (www.Signatec.com), which has 256MB of on-board memory and a 3-dB bandwidth of 0.5GHz. The MCP output signal is inverted and amplified 3.5× using a THS3201 amplifier from Texas Instruments. Time-to-mass scaling is sufficient using the expressions $m = a(t-t_0)^2$, where the two constants for each mass spectrum are obtained from known positions of helium and argon.

### 2.2 Data Reduction in FTIR Spectroscopy

A non-linear, least-squares method is utilized to extract the species concentrations of the evolved gases by comparison with theoretical transmittance [18]. The radiative properties, such as partition function, half-width of spectral lines, and its temperature exponent, are obtained from the HITRAN data base [19]. The measured gas-phase temperature serves as an input to the data-reduction technique. The computational procedure involves specifying the total pressure, measured gas-temperature profile, and assumed path length. The algorithm computes the partial pressures, and coefficients for linear base-line shifts. Iterations are continued until a change in the sum of the errors between successive guesses is less than 0.01%. After completion of the iterations, the relative concentrations of various species are obtained for each spectrum.
Isothermal conditions are sought for the decomposition, spanning a time interval of about 10 seconds during which time 220 spectra are collected by the FTIR spectrometer. During these approximately 10 seconds, the decomposition should be largely unaffected by the transient initial heating period. The transient initial heating period usually lasts about 0.2 to 0.3 seconds. For most materials, the decomposition is examined at five different temperatures over a 40°C temperature interval; however, new condensed-phase species may be formed requiring thermal decomposition of the residue at a higher temperature. Since variations occur in the species evolution from one experiment to the next, tests are repeated at least three times. The ToFMS system has a much better time resolution, but it is nonetheless set to examine the behavior over the same time period and same temperature. However, due to clogging of the orifice through which the thermolysis products enter the first stage of the vacuum chamber, fewer tests are usually conducted compared to the use of the FTIR spectrometer. The sample amount used depends on its thermal decomposition behavior. If a large amount of residue is formed, then a larger amount of the sample is required, and vice versa. Usually, the amount of sample used varies from about 0.5 to 1 mg. Additional experiments are performed at lower decomposition rates to probe further into the condensed-phase reactions. Compounds are decomposed at temperatures lower by 10°C for a fixed period of time. The IR spectra of the residue, which is mixed with KBr and pressed into a pellet,
is obtained after each period and compared with the original virgin material. Small changes in the vibration modes may provide useful information regarding the initial decomposition pathways. The gas-phase species departing from the confined region of the sample holder are collected on a glass plate via condensation. The condensate is the pressed in a KBr pellet. The glass plate is placed in close vicinity of the sample holder. Only large molecular weight species condense on the glass plate. Smaller molecular weight species such as N$_2$H$_4$, NH$_3$ and HCN do not condense and thus simplify the analysis of the acquired spectra.

3.1 Spectral Identification of Bands in GzT and TAGzT

In order to interpret the acquired spectral transmittance data of both gas and condensed phases for GzT and TAGzT, it is useful to examine other guanidine salts. Here we include guanidinium chloride, guanidinium nitrate and triaminoguanidinum nitrate. First, we focus the band assignments to the guanidinium cation.

Figures 3.1 and 3.2 show the transmittance spectra of GCl, GN and GzT obtained from the use of pressed KBr pellets, as well as the predicted spectra from the use of the Gaussian 03 program package using the B3LYP method and the 6-311++g(d,p) basis set [20]. The protonation of the guanidine group produces several important features [21, 22]. First, the classical C=Н absorption band may disappear due to resonance, and if it completely disappears, it usually produces two bands in the region 1700-1580 cm$^{-1}$ caused by one symmetric and another asymmetric stretching frequency of the C-N bond. For GCl and GzT, this effect is quite clear as there are two bands near 1653 cm$^{-1}$. Second,
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, hydrogen bonding is known to decrease the \(\nu\)(NH) stretching frequencies; it is not clear if the hydrogen bonding produces the two bands at 3235/3150 cm\(^{-1}\) for GCl, 3340/3200 cm\(^{-1}\) for GN and 3200/3093 cm\(^{-1}\) for GzT related to the asymmetric and symmetric stretching of the amino groups. As a result, in case of deprotonation, an effect should be seen on the bands at 1663/1640 cm\(^{-1}\) for GCl, and 1697/1653 cm\(^{-1}\) for GzT. It is not apparent from these spectra, if a resonance-stabilized structure is formed for GN during protonation.
In Fig. 3.1, the symmetric nature of the guanidium cation reveals strong bands from $\nu$(C-N) 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 gas-phase data for a wide variety of molecules [23].

However, as we examine Fig. 3.2 for the region near 3500 cm$^{-1}$, the difference between measured and predicted $\nu$(N-H) frequencies is much larger. The generally accepted experimental band centers for the asymmetric and symmetric stretching frequencies are, respectively, 3400 and 3320 cm$^{-1}$. There are two weaks bands at 3235 and 3150 cm$^{-1}$ listed by Bonner and Jordan [24]. It should noted also that the data shown in Figs. 3.1 and
3.2 were acquired by using too much of the sample, as these two latter bands appear as strong. Nonetheless, the scale factor for these asymmetric and symmetric \( \nu(N-H) \) bands should be about 0.918 to 0.931 for the guanidinium compounds, with increased difference for the GCl, which has a relatively small anion and thus produce a larger role of intermolecular interactions among the H atoms. The band near 2400 cm\(^{-1} \) for GN is most likely a combination band from the cation. Two bands for the nitrate ion is also apparent: one at 1384 cm\(^{-1} \) for an asymmetric \( \nu(NO) \) stretch and another band at 824 cm\(^{-1} \). Additionally, the guanidinum ion is free from experimentally detected IR-active bands below 1537 cm\(^{-1} \), except for a weak band at 1240 cm\(^{-1} \); this band does not appear in our spectra. In the molecular modeling case, however, two very weak bands are listed at 1112 and 1049 cm\(^{-1} \); perhaps they are not detected experimentally.

Figures 3.3 and 3.4 show the spectral transmittances of TAGN, GzT, TAGzT, as well as the predicted band locations and intensity of the \( \text{TAG}^+ \) cation and the azobistetrazolate dianion \( \text{AzT}^{2-} \). It is quite clear that the predicted spectra of the dianion is highly accurate without any significant scaling. This is attributed to the lack of H-atoms on the tetrazole ring, which otherwise produces anharmonicity in the motion of the atoms. Such anharmonic effects are not considered in the Gaussian 03 program package, but they are accounted for in the Gaussian 09 program package. It is also noted that some vibrational bands lack a permanent dipole moment and are thus invisible. A few bands are also nearly lacking a permanent dipole moment. The bands at 1438 and 735 cm\(^{-1} \) involve motion of the \( N_2_{azo} \) molecule and thus are of particular interest. In general, definition of the 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 for GzT is likely a combination between band of 1019 and 557 cm\(^{-1}\) (not shown) or caused by association effects within the condensed phase; combination bands or overtones are not considered within the Gaussian 03 program package. 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 strong band at near 1,000 cm\(^{-1}\) is very weak for GzT. In addition, the location for some AzT\(^{-2}\) bands differs by about 8-20 cm\(^{-1}\) between GzT and TAGzT. The GzT bands are

Figure 3.3: Comparison of measured spectra for triaminoguanidinium nitrate, guanidinium azotetrazolate and triaminoguanidinium azotetrazolate with the predicted spectrum of the triaminoguanidinium cation and azotetrazolate dianion covering the wavenumber range from 600 to 2000 cm\(^{-1}\).
located at higher wavenumbers, suggesting perhaps a stronger attraction between the ions and perhaps a more stable dianion.

Regarding the TAG\(^+\) cation, the split in the symmetric and asymmetric stretching of the CN group is not visible in the spectra near 1686 cm\(^{-1}\). Similarly, the predicted bands near 1643 cm\(^{-1}\) appears to be more associated with either symmetric and asymmetric stretching of the CN and NCN groups but coupled with motion of the NH\(_2\) groups. In general, however, it is possible to assign the various bands to TAG\(^+\) and similarly to AzT\(^-\).

Figure 3.4: Comparison of measured spectra for triaminoguanidinium nitrate, guanidinium azotetrazolate and triaminoguanidinium azotetrazole with the predicted spectrum of the triaminoguanidinium cation and azotetrazolate dianion covering the wavenumber range from 2000 to 3750 cm\(^{-1}\).
3.2 High-temperature Thermolysis Products of Cyanamide and N-cyanoguanidine

To guide the spectral interpretation of the acquired gas- and condensed-phase spectra of both GzT and TAGzT, several molecular species similar to guanidine were subjected to high temperature conditions. They include cyanamide and \textit{N}-cyanoguanidine. These compounds were acquired from Sigma-Aldrich and used without further purification.

Figure 3.5 shows gas-phase spectral transmittance data of the compounds obtained from the use of the confined rapid thermolysis apparatus, as well as data from the use of the Gaussian 03 program package. The compound labeled cyanamide largely contains NH$_2$CN; this compound also contains a small amount of carbodiimide

![Figure 3.5: Comparison of measured spectra for cyanamide early and later in the decomposition, \textit{N}-cyanoguanidine with the predicted spectrum of melamine.](image)
(HNCNH), which is also detected in file number 2 near 2180 cm\(^{-1}\). The \(N\)-cyanoguanidine contains two isomers: 1-cyanoguanidine and 2-cyanoguanidine [25]. If subjected to a high temperature of 340°C, these molecules rearrange themselves to form the 1,3,5-triazine-2,4,6-triamine, which is referred to here as melamine. The acquired experimental spectral transmittance data agree exactly with data published by Wang et al. [26]. Some bands near 1,000 cm\(^{-1}\) are quite weak and are difficult to identify. Using the B3LYP/6-311++g(d,p) program and a scaling factor of about 0.96, then there is excellent agreement between experimental data and theory for our detected 4 bands. The band near 1550 cm\(^{-1}\) is quite weak and overwhelmed by the strength of the neighboring band. In addition, during the reactions of cyanamide and \(N\)-cyanoguanidine, it is observed that a small amount of ammonia is also detected. The release of ammonia is attributed to the formation of larger cyclic structures involving the 1,3,5-triazine backbone.

### 3.3 Decomposition of Guanidinium Azotetrazolate

To study the effects of temperature, experiments were performed between 290 to 320°C. Approximately 0.5 mg of the sample was heated in the rapid confined thermolysis chamber. The products were analyzed using both FTIR spectroscopy and ToFMS. In addition, condensed-phase spectra of virgin and residue of thermolyzed GzT samples were also acquired and examined.

GzT decomposes first slowly and then rapidly at 290°C, leaving behind a white residue on the foil. Figure 3.6 shows two selected FTIR spectra obtained at 300°C. 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\(^{-1}\) belong to gas-phase melamine as discussed previously. During the early decomposition phase, only ammonia and melamine evolve in detectable quantities into 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 and the band at 1560 cm\(^{-1}\) belongs to NH\(_2\) def. This conclusion is based in part on analyzing the solid-phase IR spectra of GCl, GN and GzT described 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 400°C. It did not produce any IR-active gases suggesting the presence of a very stable compound.

From the ToFMS spectra, as shown in Fig. 3.7, m/z charge ratios are observed corresponding to the above decomposition products. In addition, significant quantities of molecular nitrogen is detected, which is IR inactive and thus absent in Fig. 3.6. Most

![Mass spectrum showing gas-phase species evolved during the decomposition of GzT at 300°C and 1 atm Ar & He.](image)

Figure 3.7: Mass spectrum showing gas-phase species evolved during the decomposition of GzT at 300°C and 1 atm Ar & He.
probably, the large quantity of nitrogen released arises from azo-N₂ release, ring-opening and secondary reactions of azotetrazoles [1]. 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. The presence of guanidine clearly signifies that proton transfer may have occurred, since ionic compounds are not likely to exist as a single ion pair in the gas-phase region. However, proton transfer could be a secondary pathway. 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 the loss of one or two NH from melamine, detected at m/z=126.

Figures 3.8 and 3.9 show the species evolution calculated using data-reduction algorithm and integrated band absorbance, respectively. The evolution of NH₃ and melamine is slow. However, a significant acceleration in the species formation is observed. This significant rise in concentration and reaction rates (indicated by the slope) is most probably due to chain-branching reactions, although enhanced charge transfer by a strong acid or a base could also play a limited role. Since the decomposition of GzT does not produce a strong acid, the enhanced charge transfer, must be either due to NH₃ or guanidine, which are strong bases. As the temperature increases, we observe that the time taken to reach critical concentration is reduced drastically. This is because with rise in temperature, the initial rate of production of species responsible for the acceleratory effect increases proportionally. In addition, at higher temperatures, the evolution of NH₃ continues after the acceleratory decomposition event, as a result of secondary reactions among guanidine and melamine. The presence of HCN is only detected during the autocatalytic event.
Figure 3.10 shows the temporal variation of intensity of m/z ratio acquired from the ToFMS data. Since the ionization cross section of various species is different, the intensity is therefore an approximate measure for species concentration. Once again, an acceleratory effect is observed for NH$_3$ and N$_2$. Therefore, based on Fig. 3.6, 3.7 and 3.8, it is suggested that the production of N$_2$, NH$_3$ and melamine are largely linked to a one significant pathway, since all three follow the same trend. The other species begin to evolve once the acceleratory point has been reached. Once again, analogous to the observation made in the previous paragraph, the other decomposition products are
observed for a short time interval at the autocatalytic point. This clearly indicates that the pathway producing melamine, ammonia and nitrogen create a pool of radicals which on reaching a critical concentration lead to rapid depletion of GzT.

The condensed-phase IR spectra of GzT and its residue also reveal the rapid decomposition behavior. The IR spectra of GzT residue taken at 4, 8 and 12 seconds are nearly identical except for some minor variations in band intensity. However, the GzT sample subjected to thermolysis for the duration of 16 sec possesses an IR spectrum that is exceedingly different from the IR spectra of samples subjected to 4, 8 and 12 sec. This
Figure 3.10: Comparison of species evolution from the decomposition of GzT at different temperatures using data obtained from ToFMS.

clearly indicates occurrence of an autocatalytic event during which GzT is rapidly consumed leaving behind a residue seen in Fig 3.11 (d). KBr studies of GzT were performed at 280°C. The bands belonging to the guanidine cation are labeled in Fig 3.11 (a). Strong N-H stretch bands are observed from 3000-3500 cm\(^{-1}\) whereas NH\(_2\) deformation is seen at 1560 cm\(^{-1}\). Stretching of C-N bond of guanidine cation is observed as a strong band at 1650 cm\(^{-1}\). Few of these bands are also observed in Fig. 3.6, indicating the evolution of guanidine during the decomposition of GzT. Hammerl et al. studied the vibrational spectra of several azotetrazolate salts [27]. According to the study, C-N
stretch vibrations belonging to azo-tetrazole ring are located near 1390 and 735 cm\(^{-1}\). These bands were identified and labeled in Fig. 3.11. However, vibrations from N=N\(_{\text{ring}}\), N\(_{\text{azo}}\)N\(_{\text{azo}}\) and C-N\(_{\text{azo}}\) 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 vibrational assignment of tetrazoles was used to identify such bands in Fig. 3.11 [28]. An autocatalytic effect is very likely to be present based on the results shown in Fig. 3.11. There is no major change in the vibrational structure of the GzT. Only small variations in the transmittance bands attributed to ring vibrations are observed until 12 seconds.

Figure 3.11: FTIR spectra of GzT and its residue obtained after fixed time intervals at 280°C.
Based on the observations from FTIR and ToFMS studies, GzT decomposes in two distinct phases. The initial phase involves reactions that result in slow evolution of ammonia, melamine and nitrogen as seen in Fig. 3.8 to Fig. 3.10. The nitrogen evolves in quite significant quantities. Following the slow decomposition is the autocatalytic event resulting in rapid decomposition of GzT, in particular the AzT portion. Since the weakest bond in the GzT molecule is the C-N$_{2,\text{azo}}$ bond, initiation of the decomposition occurs in this part of AzT by N$_2$ release. The carbon atoms on each tetrazole ring may form a new C-C bond due to a cage effect; however, the role of the negative charge on each tetrazole ring is not clear. The role of these electrostatic effects will depend on the resulting electronic structure, which is not known. Studies have been conducted on azobisamidines to suggest the electrostatic effects are limited [29]. Since copious amounts of N$_2$ are detected, the tetrazole rings further decompose to release nitrogen due to ring opening. The release of the nitrogen in these two events probably occur very quickly. As a result, we write the initiation step as

\[
2 \begin{array}{c}
\text{H}_2\text{N}^+ \\
\text{N} = \text{N} \\
\text{N} = \text{N} \\
\text{N} = \text{N} \\
\text{H}_2\text{N}
\end{array} \rightarrow \text{N}_2 + 2 \begin{array}{c}
\text{H}_2\text{N}^+ \\
\text{N} = \text{N} \\
\text{N} = \text{N} \\
\text{N} = \text{N} \\
\text{H}_2\text{N}
\end{array}
\]

followed quickly by

\[
\begin{array}{c}
\text{N} = \text{N} \\
\text{C} \end{array} \rightarrow \text{N}_2 + \begin{array}{c}
\text{N} \\
\equiv \text{N}
\end{array}
\]

The two cyanogen radicals subsequently attacks the guanidinium cations, resulting in charge transfer, the formation of melamine, release of additional nitrogen and ammonia, as well as the formation of a aminoguanidine.
The aminoguanidine is unstable at these high temperatures and is the potential source to subsequent chain-branching reactions, by attacking other guanidinium cations. It is not understood how that occurs but those reactions are driven in directions where melamine and NH₃ are formed. Thermodynamically, the formation of these species is favored. In addition, the release of NH₃ from decomposition of the guanidine radical has a slight positive heat of reaction (+15 kcal/mol) and is thus not a major pathway to NH₃ formation [30].

Ring opening via proton transfer is not considered as an initiation step. This is because GzT keeps the proton tightly bound to the guanidine cation. Therefore, at the temperatures considered, sufficient energy is unavailable to overcome the barrier for its transfer to the anion, which initiates ring opening [6].

### 3.4 Decomposition of Triaminoguanidinium Azotetrazolate

The experiments with TAGzT were performed from 230 to 270°C due to the fact that previous DSC studies showed that the decomposition temperature of TAGzT was roughly 50°C lower than that of GzT. Approximately 0.5 mg of the sample was heated at a rate of 2000 K/sec in the rapid thermolysis chamber. The decomposition products were analyzed using IR spectroscopy and ToFMS. On completion of the decomposition process, a white residue remained on the aluminum foil, which turned deep red on
exposure to atmospheric conditions. In addition, condensed-phase spectra of virgin and residue of thermolyzed TAGzT samples were also acquired and examined to determine the initiation step.

Figures 3.12, 3.13 and 3.14 show the spectral transmittance changes of the condensed phase for the temperatures of 230, 240 and 250°C, respectively. A close inspection reveals significant changes in bands belonging to the azobistetrazolium dianion, and to some of the ν(NH) vibrations for the triaminoguanidinium cation. Some of the results in the range from 600 to 1,100 cm\(^{-1}\) may be affected by noise referred to as channel spectra and need to be redone. This type of noise may occur as a result of internal reflection within the sample holder. Nonetheless, at a temperature of 230°C, the gradual

![Figure 3.12: FTIR spectra of the residue remaining on the foil after thermolysis of TAGzT for a period of 4, 8, and 12 s at 230°C.](image)
disappearance of the AzT bands are very clear, whereas the bands associated with CN₃ skeleton are changing quite slowly. The results for this temperature may even suggest that bands associated with vibrations of the carbon atom within AzT²⁻ gradually disappear slower than the other bands, which may suggest that N₂ release from the ring occurs first. Furthermore, at this low temperature of 230°C, a few new bands appear and a very slight shift in a few bands from AzT²⁻ is noticed as well. The shift is probably caused by the release of N₂ from the cation, which affects the intermolecular bonding to the anion. Such similar shifts in band locations were observed previously when comparing the bands for AzT²⁻ in GzT versus TAGzT. As the temperature is increased to 250°C, the disappearance of the AzT²⁻ is very rapid. In fact, after 4 sec at 250°C the

Figure 3.13: FTIR spectra of the residue remaining on the foil after thermolysis of TAGzT for a period of 4, 8, and 12 s at 240°C.
AzT$^{2-}$ has completely decomposed. Reactions with the decomposition products from AzT$^{2-}$ and decomposition of the cation produces many new bands and thus represent new products that remain in the condensed-phase region.

Regarding the disappearance of two $\nu$(NH) stretches near 3300 cm$^{-1}$, it can be caused by either proton transfer or by increased intermolecular or intramolecular hydrogen bonding as the dianion disappears. Since the bands, in the range 1700 – 900 cm$^{-1}$ attributed to the triaminoguanidinium cation, are not changing significantly at the temperature of 230°C, it is likely that intermolecular bonding increases due to reduced effects of a steric hindrance as the dianion decomposes. As a result, the sharp band at 3315 cm$^{-1}$ is then likely a stretch from the imino hydrogen. The bands attributed to the

![Figure 3.14: FTIR spectra of the residue remaining on the foil after thermolysis of TAGzT for a period of 4, 8, and 12 s at 250°C.](image-url)
TAG cation changes otherwise in a very limited fashion at 230°C whereas much larger changes are observed at 250°C. The small change may not be surprising, because proton transfer would be a reversible process. In fact, since the guanidine-based molecules have very large $pK_a$ values, it is highly likely that new anions may be formed and present in the condensed phase.

Figure 3.15 shows the spectral transmittance of the residue collected by a glass plate placed in close vicinity of the opening of the exit hole of the confined region in the thermolysis chamber. The high-molecular weight species condense on the glass plate, whereas small molecular weight species do not. Thus ammonia and HCN are absent. It is clear that some triaminoguanidine evaporates from the confined region, and as it collects

![Figure 3.15: FTIR spectra of products from thermolysis of TAGzT and condensed on a glass plate placed outside the confined thermolysis region over a 20s time interval at temperatures of 240, 250 and 260°C.](image-url)
on the glass plate. Proton transfer also occurs in the condensed phase on glass plate and many bands matches with the previously presented information. However, at the high temperature of 260°C, much of the collected triaminoguanidine remains neutral, as the amount of proton-donating species collected on the glass plate is significantly reduced. A strong band at 2147 cm\(^{-1}\) appears prominently, whereas this band was barely seen in the residue spectra from the condensed phase. Since this band appear prominently at all temperatures, it is likely not a proton-donating species. When comparing band appearances in Fig. 3.14 with those of Fig. 3.15, it is clear that only a few bands are identical. However, the region between 1,100 and 600 cm\(^{-1}\) is difficult to interpret as noise from channel spectra is significant.

Figure 3.16 shows FTIR spectra of gas-phase species evolving into the modulated beam of the FTIR spectrometer from the decomposition of TAGzT at 250°C. Here, six spectra are averaged near \(t = 2.8\) sec and at 4.8 sec to reduce the effects from random noise. Bands belonging to hydrazine overlapped with ammonia evolve early and gradually. Simultaneous to the evolution of hydrazine, the band at 2147 cm\(^{-1}\) is observed. Hydrazine is clearly a product from TAG, and it could be formed via cleavage of weak N-N bonds whereas azide is a ring-opening product of AzT. As these products evolve, small amount of HCN is also observed, most likely indicating the decomposition of the azotetrazolate ring. The band at 3510 cm\(^{-1}\) is strikingly similar in shape and position to a band caused by a stretching vibration from an ‘H’ atom attached to an ‘N’ on a ring as indicated in Fig. 3.16. Billes et al. [31] show the vibrational frequencies from both measurements and prediction of \(1H\)-1,2,4-triazole, \(1H\)-tetrazole and \(2H\)-tetrazole. Their condensed-phase experimental data reveal the \(\nu(NH)\) stretch position at 3447 cm\(^{-1}\) for all
three molecules. However, they reveal a band at 1520 cm$^{-1}$ that does not arise from fundamental vibrational effects. Instead, it arises from intermolecular effects referred to as association.

In our gas-phase measurements, the $\nu$(NH) stretch is located at 3512 cm$^{-1}$ for the 1H-1,2,4-triazole. Thus, there is a difference of about 70 cm$^{-1}$ for this particular band between gas and condensed phases. The $\nu$(CH) stretch, however, is at 3119 cm$^{-1}$ for both our gas-phase measurements and the condensed-phase spectra by Billes et al. [31]. In a
recent paper on the synthesis of 5-azido-1H-tetrazole [32], condensed-spectra indicate the \( v(\text{NH}) \) stretch to be at 3343 cm\(^{-1}\) with a weak intensity; even if this spectral location is shifted by 70 cm\(^{-1}\), the band coincides with similar stretches for both hydrazine and ammonia and thus is difficult to distinguish. However, it is likely that the band at 3519 cm\(^{-1}\) for our gas-phase measurements arise from the 1\( H \)-tetrazole based structure. As a result of this \( v(\text{NH}) \), the proton transfer must have occurred at some point during the decomposition of TAGzT. The proton most probably migrates to the AzT dianion and attaches itself to either atom N1 (next to the carbon) or N2 on the ring.

There are several additional important aspects regarding the gas-phase spectra, and these are described without showing additional figures. First, one notices that the \( v(\text{NH}) \) band appears strong and subsequently decreases in intensity as the number of acquired spectra increases. Second, if one closely monitors the peak position of the band at 2147 cm\(^{-1}\), it actually is centered at 2148 cm\(^{-1}\) in the first two spectra, but then it gradually moves to near 2144 cm\(^{-1}\). Third, similarly the band at 1532 cm\(^{-1}\) appears initially at 1536 but then gradually moves to 1520 cm\(^{-1}\). Fourth, the baseline is initially flat but then gradually begins to show a definite slope, indicating small particulate formation. These processes are associated with two molecules initially forming a complex. Then as the complex grows, proton transfer occurs, causing the disappearance of the band at 3512 cm\(^{-1}\), slight shifts in the bands at 2148 and 1536 cm\(^{-1}\), and a slope in the baseline. Such particulate formation in the gas-phase region and proton transfer has been observed for other ionic compounds, such as ammonium nitrate.

Figure 3.17 shows the data obtained from ToFMS. Peaks corresponding to products seen in the FTIR spectra are identified in Fig. 3.17. The peak at m/z=26 could
either indicate CN radical formed during the decomposition process or a fragment of HCN. Copious amount of N$_2$ (m/z=28) is produced, similar to GzT due to the decomposition of the azotetrazolate ring. The strong peak at m/z=32 indicates the presence of hydrazine. Since the intensity of hydrazine is large in the ToFMS data, one must be able to identify it in the IR spectra as well. However, due to overlapping of bands from NH$_3$ and HCN, the presence of hydrazine could not be detected easily. In order to confirm its presence, hydrazine obtained from Sigma Aldrich, was vaporized at 140°C and its FTIR spectrum acquired. The FTIR spectrum of hydrazine was plotted alongside

Figure 3.17: Mass spectrum showing species evolved during the decomposition of TAGzT at 260°C and 1 atm Ar & He.
the decomposition spectrum of TAGzT, as shown in Fig. 3.18. It is observed that hydrazine is present during the initial stages of decomposition. Comparing Fig. 3.16 (b) and Fig. 3.18, it is clear that hydrazine is present only during the initial phase of decomposition, and its formation rate decreases as the decomposition proceeds, as it is absent in the later spectra. Bands corresponding to heavier fragments are also observed.

From the FTIR spectra of TAGzT, vibrational bands belonging to many species are not listed in the HITRAN database. Instead of using the data reduction algorithm to determine evolution trends, normalized integrated band absorbance was used. Figure 3.19 shows the evolution trends of certain identified species or bands. We clearly see that N$_2$H$_4$ and –N$_3$ at 2147 cm$^{-1}$ evolve first. As the temperature is increased, N$_2$H$_4$ peaks first and then decreases rapidly. Meanwhile, –N$_3$ evolution still continues, but at a much smaller rate. The gradual evolution of the band at 3500 cm$^{-1}$ signifies proton transfer. Once this band reaches its peak, we observe an increase in the rate of evolution of NH$_3$ and HCN. The concentration of NH$_3$ and HCN is small compared to the other products.

Figure 3.18: Spectrum showing the presence of hydrazine as the decomposition product of TAGzT during the initial phase.
Using the data obtained from ToFMS experiments, the temporal evolution of certain identified m/z ratios were plotted as shown in Fig. 3.20. It is observed that the initial rate of evolution of N$_2$H$_4$ and N$_2$ is the same. Therefore, the evolution of these two species is linked to a common reaction pathway. However, hydrazine evolution profile peaks much earlier during the decomposition process. This indicates that while other products are being formed, hydrazine formation is no longer favored.

The residue formed in the condensed phase contains largely neutral or ionic forms of triaminoguanidine-like and tetrazole-based species. To confirm this, the residue was
decomposed at 350°C. The main products observed were HN₃ and NH₃ as shown in Fig. 3.21. The formation of HN₃ from thermolysis of the residue suggests the presence of a tetrazole containing compound, such as 1H-tetrazole [33, 34]. NH₃ mostly evolves from the decomposition and reactions among the guanidine-like species that remained after the low-temperature thermolysis.

The major question that arises from studying the FTIR spectrum is identification of the strong peak at 2147 cm⁻¹. Tappan et al. [16] identified cyanamide as a major species of decomposition of TAGzT. The absorption bands corresponding to cyanamide
were shown previously and are not present in our data, most likely due to the sample confinement. However, cyanamide is a very reactive species, and, as a pure compound, it cannot be stored at room temperature. In fact, cyanamide was purchased several years ago and stored at room temperature; recent spectral transmittance tests in a KBr pellet showed that it completely was converted to its dimer \( \text{N-cyanoguanidine} \).

According to discussion of IR data by Socrates [35], it is known that in the region from 2000 to 2200 cm\(^{-1}\), one of the following structures shows a distinct peak: \( \text{N}≡\text{C} \), \( \text{C}≡\text{N} \), \( \text{N}≡\text{N} \), \( \text{C}≡\text{C} \) and \( X=X=X \) where \( X \) could be either \( \text{N} \) or \( \text{C} \). Using the information available from the mass spectra shown in Fig. 3.17, various compounds (based on m/z ratio) were studied having any of the above structures and summarized in Table 3.1. Three classes of compounds were studied in order to identify the absorption band at 2147 cm\(^{-1}\): azides, nitriles, and isonitriles. In general, azides exhibit a strong band around 2100 cm\(^{-1}\) corresponding to \( \text{N}=\text{N}^+=\text{N}^- \) asymmetric stretch, whereas the symmetric stretch appears in the range 1300-1100 cm\(^{-1}\). However, in crystalline or complex form, the

Figure 3.21: FTIR spectra showing the species evolved into the gas-phase region during the decomposition of TAGzT residue at 350°C and 1 atm \( \text{N}_2 \).
symmetric band may be of much weaker intensity. By comparing several nitriles and
isonitriles, it was inferred that the stretching frequency for isonitrile was lower by
approximately 100 cm\(^{-1}\) than a nitrile [36]. Based on the above information, the band at
2147 cm\(^{-1}\) could belong to either an azide or isocyanamide (NH\(_2\)NC). Isocyanamide is
eliminated for several reasons. First, C≡N stretching posses a \(P\) and \(R\) branch character,
as shown by cyanamide in Fig. 3.5. This feature is absent in Fig. 3.16. Secondly,
isocyanamide is unstable and should rearrange itself to form the more stable isomers
cyanamide or carbodiimide, none of which were observed in the FTIR data. Therefore,
after studying several azides, nitriles and isonitriles, it is concluded that the band at 2147
cm\(^{-1}\) belongs to an azide.

Since the spectra contains contributions from amino groups, strong effects from
C=N stretches, it is assumed that the molecule has the formula C\(_3\)H\(_5\)N\(_5\). Since
characteristic methyl group stretching frequencies are absent in the spectra, in particular
those acquired for the gas phase, the number of potential isomers is quite limited. From
the gas-spectra, a likely assignment is the 5-azido-tetrazole, due in large part on the band
at 3510 cm\(^{-1}\), a molecular weight of 111 and data in the literature on this and related
compounds [4, 32]. It was actually identified in the earlier work by Chowdhury et al.
[37], although the grounds for such an assignment was not entirely clear.

However, due to the complexity of both the gas-phase and condensed-phase
spectra of species from residue on glass plate, further support from this hypothesis comes
from using the G03 program package. In Table 3.2, data from the measurements and the
G03 program package are presented. A close inspection reveals that all bands can be
identified with a high degree of certainty associated with the neutral 5-azido-tetrazole, or
the 5-azido-tetrazolium ion. Actually, the agreement is remarkable. The obtained frequencies from the G03 program package were scaled by 0.96. For the gas-phase spectra, however, assignment of bands in 1,100 – 700 cm\(^{-1}\) range is impossible due to the very strong bands of ammonia and hydrazine in that region. In addition, the agreement

<table>
<thead>
<tr>
<th>m/z ratio</th>
<th>Compound</th>
<th>Structure</th>
<th>Reason for elimination</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Acetylene</td>
<td>H-C≡C-H</td>
<td>No strong peak observed at 2100 cm(^{-1}) [38].</td>
</tr>
<tr>
<td>30</td>
<td>Isodiazene</td>
<td>H(_2)N≡N</td>
<td>No strong peak in the region of 2100cm(^{-1}) [39].</td>
</tr>
<tr>
<td>40</td>
<td>1,2 Propadiene</td>
<td>H(_2)C=C=CH(_2)</td>
<td>No strong band at 1970cm(^{-1}) observed in data [38].</td>
</tr>
<tr>
<td>40</td>
<td>Propyne</td>
<td>H(_3)C≡C-H</td>
<td>No strong band present in the region of 2950cm-1 in our data [38].</td>
</tr>
<tr>
<td>41</td>
<td>Acetonitrile</td>
<td>H(_3)C≡N</td>
<td>Peak occurring at 2250 cm(^{-1}) not observed in spectrum 40.</td>
</tr>
<tr>
<td>41</td>
<td>Isocyanomethane</td>
<td>H(_3)C=N≡C</td>
<td>Peak occurring at 2161 cm(^{-1}) not observed in spectrum 40.</td>
</tr>
<tr>
<td>42</td>
<td>Cyanamide</td>
<td>H(_2)N-C≡N</td>
<td>Peak occurring at 2260 cm(^{-1}) not observed in spectrum [41].</td>
</tr>
<tr>
<td>42</td>
<td>Diazomethane</td>
<td>H(_2)C=N≡N</td>
<td>Peak occurring at 2102 cm(^{-1}) not observed in spectrum [42].</td>
</tr>
<tr>
<td>42</td>
<td>Carbodiimide</td>
<td>H-N=C≡N-H</td>
<td>Peak occurring at 2097 cm(^{-1}) not observed in spectrum [43].</td>
</tr>
<tr>
<td>43</td>
<td>Hydrogen Azide</td>
<td>H-N=N≡N</td>
<td>No strong peak occurring at 1150 cm(^{-1}).</td>
</tr>
<tr>
<td>44</td>
<td>Ammonium Cyanide</td>
<td>[NH(_4)](^+)[CN](^-)</td>
<td>Peak occurring at 2094cm(^{-1}) not observed in the spectrum [44].</td>
</tr>
<tr>
<td>60</td>
<td>Ammonium Azide</td>
<td>[NH(_4)](^+)[N(_3)](^-)</td>
<td>Peak occurring at 2030cm(^{-1}) is observed in the spectrum, but an accompanying peak at 1672cm(^{-1}) is not observed [45].</td>
</tr>
<tr>
<td>75</td>
<td>Hydrazinium Azide</td>
<td>[N(_2)H(_5)](^+) [N(_3)](^-)</td>
<td>Peak occurring at 2033cm(^{-1}) is observed in the spectrum, but an accompanying peak at 1347cm(^{-1}) is not observed [46].</td>
</tr>
</tbody>
</table>

Table 3.1: Compounds with strong absorption bands in the region 2000-2300 cm\(^{-1}\).
between measurements and predictions for triaminoguanidinium cation is far worse due to the hydrogen bonding that occurs in the region 3300 to 3400 cm\(^{-1}\).

Based on the acquired data and detailed analysis, the decomposition of TAGzT clearly involves ring opening of the azobistetrazolium dianion. Since the 5-azido-1\(H\)-tetrazole evolves into the gas-phase, proton transfer must have occurred at some point. However, it is not clear if the proton transfer is a reaction that occurs within the condensed-phase; instead, it is more likely that it occurs as the 5-azido-tetrazolium anion and triaminoguanidinium cation depart at the interface between the gas and condensed phase.

Table 3.2: Comparison of measured and calculated frequencies of various products from TAGzT decomposition.

<table>
<thead>
<tr>
<th>Exp. TAGzT Data: TAG(^+)</th>
<th>Exp. TAGzT Data: AzT(^2)</th>
<th>Data of residue collected on Glass Plate</th>
<th>5-azidotetrazolium anion 6-311++ g(d,p) MW=110</th>
<th>Intensity</th>
<th>Gas-phase Data at 260(^\circ)C</th>
<th>5-azido-1(H)-tetrazole 6-311++ g(d,p) MW=111</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1688 3424 2147 1688 1520 1488 1455 1388</td>
<td>3424 2147 1688 1520 1488 1455 1388 1365</td>
<td>2142</td>
<td>896</td>
<td>3510 2147 1680 1536 1495 1465 1364 1364</td>
<td>3492 2172 1520</td>
<td>356</td>
<td>83 664</td>
</tr>
<tr>
<td>1362 1330 1270 1212 1140 1090 1038 1000 975</td>
<td>1362 1330 1270 1212 1140 1090 1038 1000 975</td>
<td>1369 1256 1154 1096 1042 1015 985 985 985</td>
<td>43 19 5 8 2 9 4</td>
<td>1364 1327 1258 1205</td>
<td>1369 1344 1239 1197</td>
<td>22 70 19 18</td>
<td></td>
</tr>
<tr>
<td>950 732 705</td>
<td>950 732 705</td>
<td>735 711 708</td>
<td>25 3 1</td>
<td>1021 982 959</td>
<td>14 13 6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
phases. As these two species enter the cool atmosphere, where detection occurs by the FTIR spectrometer, they again form a complex that grows, and at some point proton transfer occurs again. The 5-azido-1H-tetrazole is however rather unstable. In slow heating studies, the decomposition begins to occur around 165°C [32], compared to TAGzT which begins to decompose near 203°C [1]. Ionic compounds based on 5-azido-tetrazolium anion begin to decompose at similar temperatures, e.g., 159°C with the aminoguanidinium cation [4]. This suggests that the formed 5-azido-tetrazolium anion either departs from the confined thermolysis region, or further decomposes as very small quantities are detected in the residue remaining on the foil.

Regarding initiation, it is also possible that cleavage of C-N$_{2,azo}$ bond occurs, for two reasons: first, there is a significant amount of N$_2$ entering the gas phase, and its difficult to attribute this significant amount of nitrogen to ring-opening reactions alone. Second, the additional decomposition of the residue on the foil at higher temperatures revealed the emergence of HN$_3$, without any 5-azido-tetrazolium present initially. The hydrazoic acid is common product from the decomposition of 1$H$-tetrazole. Thus, the additional nitrogen must arise from further decomposition of the 5-azido-tetrazolium anion.

The hydrazine formation occurs until the azobistetrazolium dianion is completely consumed, as seen in the time evolution of the condensed-phase spectra and matched with the time-evolution of the hydrazine in the gas-phase spectra. As the 5-azido-tetrazolium anion is formed, the CN$^-$ anion is also formed. What product(s) besides hydrazine that are formed from a reaction between the CN$^-$ anion and the tri-
aminoguanidinium cation is not clear; it seems that a neutral compound must be formed without a C≡N bond, which is not detected in the condensed phase. Additionally, the extent of the formation of HCN is very limited, suggesting that much of the CN\(^-\) anion is consumed in reactions with the cation forming the observed ammonia.

The formation of the ammonia proceeds at a rapid rate once the azobistetrazolium dianion is completely consumed. Such formation is the likely result of an excess triaminoguanidine in the condensed phase and reactions with CN\(^-\) anion, although some of the azobistetrazolium dianion was protonated, entered the gas phase and was collected of the glass plate. At these temperatures of 230-270°C, reactions among the triaminoguanididine molecules should proceed at a reasonably fast rate, but the applied temperatures are too low to allow the formation of the previously mentioned melamine compounds.
Chapter 4

CONCLUSION

The energetic materials were examined in fast-heating or fast-cooling experiments using a confined rapid thermolysis test rig. FTIR spectroscopy was used to examine species entering the gas-phase region during thermolysis, and to examine the residues obtained after the thermolysis had been completed. Two kinds of residues were examined: first, the residue that remained on the foil after a selected time interval of thermolysis, and second, the residue that condensed on a glass plate outside the thermolysis region. The residues were mixed and pressed into a KBr pellet, and spectra were acquired using the FTIR spectrometer. ToF mass spectrometry was used to examine gas-phase species that evolved into the gas-phase region during the thermolysis. The FTIR spectra obtained from the experiments were compared with model predictions using the Gaussian 03 program package using the B3LYP method, the 6-311++g(d,p) basis set and a scaling factor of 0.96.

4.1 Guanidinium Azotetrazolate

The decomposition of the GzT occurs in two stages, with the second one represented by an almost explosion-like behavior, which makes it quite challenging to examine using any diagnostic tool. However, condensed-phase experiments with KBr reveal that the decomposition is initiated within the azobistetrazolium dianion, as a result
of bands belonging to the dianion disappearing most quickly and the copious amount of nitrogen is released. Since the N$_2$azo bond is the weakest, release of N$_2$ from this part of the molecule appears to be most probable. The remaining tetrazolium radicals further decompose to release additional N$_2$, but also react with the guanidinium cations to form ammonia. The remaining radicals then take part in chain-branching reactions that produce the explosive-like event. The melamine-based compounds in fairly slow reactions releasing some ammonia. The decomposition of GzT terminates via the formation of melamine and larger similar molecules, as the guanidine recombines to release additional ammonia. In addition, the temperatures considered for these studies of GzT are too high to allow any formation of the 5-azido-tetrazolium anion.

### 4.2 Triaminoguanidinium Azotetrazolate

The fast thermolysis behavior of TAGzT begins at temperatures of 230°C, and it is very rapid at temperatures of 270°C. Some of the traminoguanidinium loses its proton and enter the gas-phase region, whereas very small quantities of the azobistetrazolium dianion gains two protons and enters the gas-phase region. In general, when examining room temperature condensed-phase residues, ion pairs are present. At high temperatures much of the azobistetrazolium dianion is consumed and most of the residue contains a neutral guanidine-like species. In general, the comparison of results obtained from pressed KBr pellets with gas-phase results is complicated by the fact that single ion-pairs are not initially present in the gas-phase region, whereas the formation of ion pairs in the condensed phase is highly favorable from and thermodynamic point of view. However,
particulates are formed in the gas-phase region, and these contain ion pairs from the triaminoguanidinium cation and the azido-tetrazolium anion. Thus, if one examines the gas-phase region alone, the assumption is automatic that proton transfer has occurred and such a process may even initiate the decomposition. Regarding the decomposition process, the following steps are identified:

1. Initiation of decomposition occurs within the azobistetrazolium dianion. The major identified species from the decomposition of the dianion is the 5-azido-tetrazolium anion.

2. Initiation of decomposition via release of the N\textsubscript{azo} group cannot be ruled out. In fact, the presence of hydrazoic acid as part of decomposition of the residue suggests that a tetrazole is also formed. The likely molecule is 1\textsubscript{H}-tetrazole.

3. The hydrazine is formed early and continues until the azobistetrazolium dianion is consumed.

4. The formation of hydrazine is likely to occur in reactions between the triaminoguanidinium cation and the CN\textsuperscript{-} anion, which is a likely product from ring-opening reactions forming the 5-azido-tetrazolium anion, which is protonated and departs from the condensed-phase region.

5. Ammonia formation increases substantially once the azobistetrazolium dianion is consumed, as a result of increased concentrations of and reactions between the triaminoguanidine, triaminoguanidinium cation and radicals from decomposition of the azobistetrazolium dianion.


