Liquid-phase Decomposition Mechanism of Triaminoguanidinium Azotetrazolate

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Abstract

The objective of this work is to analyze the decomposition of triaminoguanidinium azotetrazolate (TAGzT) in the liquid phase by using a combined experimental and computational approach. The experimental part involves the use of Fourier transform infrared (FTIR) spectroscopy and Time-of-flight mass spectrometry (ToFMS) analysis of TAGzT decomposition. N₂, NH₃, HCN, N₂H₄, and the 3-azido-1,2,4-triazol-4-ide anion 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 form these species.

Keywords: Triaminoguanidinium azotetrazolate, liquid-phase decomposition.

1 Introduction

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 or both [1]. Traditional energetic materials such as RDX 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 [2]. 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 [2]. These properties of high-nitrogen materials make them suitable for numerous applications such as airbags and gun propellants.

The recently synthesized triaminoguanidinium azotetrazolate (TAGzT) has the potential to act as a burn-rate enhancer when used with traditional energetic materials such as RDX [3, 4]. However, with the current knowledge available for this compound, predicting the combustion behavior of propellant mixtures containing TAGzT 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 in the mixture. There are numerous works describing the thermal decomposition and combustion behavior of conventional propellants such as RDX [5]. 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 TAGzT. A review of available decomposition studies on TAGzT is presented next.

TAGzT is a bright yellow crystalline solid with a distinct melting temperature at 195°C. The structure of TAGzT is shown in Figure 1. Vibrational and NMR spectroscopy, elemental analysis and safety testing were performed by Hammerl et al. [6] on TAGzT. Burning rate experiments, T-Jump/FTIR spectroscopy measurements, and laser-ignition studies of TAGzT were performed by Tappan et al. [7]. It was found that TAGzT had extremely high low-pressure burn rates compared to conventional explosives, such as HMX. The authors concluded that ignition and decomposition behavior of TAGzT
was controlled by condensed-phase reactions. The condensed-phase thermal decomposition chemistry of TAGzT was studied by Chowdhury et al. [8] by Fourier transform infrared (FTIR) and time-of-flight mass spectroscopy (ToFMS). It was suggested that deprotonation from the triaminoguanidinium cations initiated the decomposition. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), FTIR spectrometry and mass spectrometry experiments were performed on TAGzT by Damse et al. [9]. They stated that rapid initial exothermic decomposition of the nitrogen-rich TAGzT is responsible for its high burn rate. More recently, decomposition of TAGzT was studied by Hayden [10]. She investigated the underlying chemical and physical processes that control the thermal decomposition behavior of TAGzT alone and in the presence of RDX.

**Figure 1**: Molecular structure of TAGzT.

The literature survey on TAGzT decomposition presented here indicates that most of these studies are experimental and that attempts to explain the major reaction pathways have been made. However, it is our experience that identification of the major reaction pathways using experimental data alone is quite challenging. Thus it is essential to explore other approaches to interpret the experimental information. Here we adopt recently developed methods based on the use of quantum mechanics. In the present work, FTIR spectroscopy and time-of-flight mass spectrometry (ToFMS) experiments have been performed on TAGzT to analyse its decomposition in the liquid phase and formation of the observed products has been explained by formulating elementary chemical reactions based on calculations involving molecular modelling ab initio methods.

### 2 Experimental setup and procedure

**Fourier Transform Infrared (FTIR) Spectroscopy**

Confined rapid thermolysis (CRT)/FTIR technique used here has been discussed in previous works [11, 12]. 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. When TAGzT is heated in the CRT chamber it forms gaseous products some of which condense out. It also leaves behind some residue. All three, (i) the gaseous products, (ii) the condensate and (iii) the residue were analyzed using FTIR to detect the decomposition products of TAGzT.

**Time of Flight Mass Spectrometry (ToFMS)**

Reference [12] contains the details of the setup and procedure used to conduct ToFMS tests on TAGzT. These tests provided additional results which were complimentary to FTIR data.

### 3 Molecular Modeling

Quantum mechanics calculations provide an avenue for corroborating experimentally measured data and providing information otherwise unavailable experimentally. The Gaussian 09 [13] suite of programs was utilized to this end. Molecular structures of species involved in the decomposition of TAGzT were identified from ground-state and transition-state optimization calculations. 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 obtained. Transition-state optimizations corresponding to all the proposed reactions were also subjected to IRC (intrinsic reaction coordinate) calculations. Various levels of theory available in Gaussian 09
were used for all these calculations taking care that a good balance is maintained between computational effort and accuracy. Because our focus is on chemical reactions in the liquid phase, for all the calculations, the polarizable continuum model (PCM), using the integral equation formalism variant (IEFPCM) 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.

4 Results and Discussion

Experimental results

Figure 2 is just one representative result which shows an IR spectrum of gaseous products containing prominent bands that appear when TAGzT decomposes at 250 °C under atmospheric pressure. After obtaining a number of IR spectra of undecomposed TAGzT and structurally similar compounds as well as those of gaseous products, condensate and residue from the rapid thermolysis of TAGzT, a thorough analysis of the experimental results was carried out. Mass spectra for TAGzT decomposition were also obtained which complemented the FTIR results. From solid reasoning based on both FTIR and ToFMS data it was concluded that the important products of TAGzT decomposition are molecular nitrogen (N₂), hydrogen cyanide (HCN), hydrazine (N₂H₄), ammonia (NH₃) and 3-azido-1,2,4-triazol-4-ide anion.

Figure 2: FTIR spectra showing the gas-phase species evolved during the decomposition of TAGzT at 250 °C and 1 atm N₂
Molecular modeling results

In this work we aim to analyze the overall decomposition behavior of TAGzT by explaining the formation of the product species observed in our experiments. A chemical mechanism for liquid-phase decomposition of TAGzT consisting of 28 reactions was derived through ab initio calculations described earlier. 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. Some of these important reactions are shown in Table 1. It should be noted that a transition state for proton transfer within the liquid phase from the triaminoguanidinium cation to the azotetrazolate dianion as described by others [6, 9] for similar compounds could not be identified in our calculations. These ions prefer to stay separated in the liquid phase due to solvation effect. Out of the multiple pathways identified for formation of each product species from TAGzT, reactions for a few selected ones are given in Table 1. As shown in the table, decomposition sequence is initiated by unimolecular decomposition of azotetrazolate (AzT\(^{2-}\)) dianion releasing N\(_2\) through reaction R1. Reactions R1-R4 are N\(_2\) formation reactions. HCN is formed in reactions R4 and R5. R4 is a bimolecular reaction between the intermediate that comes from AzT\(^{2-}\) and the triaminoguanidinium (TAG\(^+\)) cation whereas R5 is a proton transfer reaction. N\(_2\)H\(_4\) is formed when triaminoguanidine (TAG) and TAG\(^+\) interact (reactions R6-R8). NH\(_3\) results from the neutral TAG molecule attacking another TAG. The 3-azido-1,2,4-triazol-4-ide anion is formed because of ring closing and subsequent opening in one of the intermediates. Optimized structures of transition states corresponding to selected reactions from Table 1 are shown in Figure 3. These structures were obtained using the CBS-QB3 method.

Table 1: Important reactions in the liquid-phase decomposition mechanism of TAGzT

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>(\Delta G^f)</th>
<th>(\Delta G^b)</th>
<th>(\Delta H^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>(\text{AzT}\text{C}_3\text{N}_3\text{O}_3\text{H}_2) (\xrightarrow{\text{TS4}}) (\text{INT4}) (\xrightarrow{\text{INT4}}) (\text{N}_2)</td>
<td>37.5</td>
<td>29.3</td>
<td>20.2</td>
</tr>
<tr>
<td>R2</td>
<td>(\text{INT4}) (\xrightarrow{\text{TS4a}}) (\text{TAG}^+) (\xrightarrow{\text{INT4a}}) (\text{TAG})</td>
<td>-3.2</td>
<td>15.1</td>
<td>-18.5</td>
</tr>
<tr>
<td>R3</td>
<td>(\text{INT4a}) (\xrightarrow{\text{TS4a1}}) (\text{INT4a1}) (\xrightarrow{\text{INT4a1}}) (\text{N}_2)</td>
<td>24.7</td>
<td>60.1</td>
<td>-24.9</td>
</tr>
<tr>
<td>R4</td>
<td>(\text{INT4a1}) (\xrightarrow{\text{TS4a1}}) (\text{TAG}^+) (\xrightarrow{\text{TAG}^+}) (\text{TAG})</td>
<td>37.5</td>
<td>166.5</td>
<td>-97.1</td>
</tr>
<tr>
<td>R5</td>
<td>(\text{TAG}^+) (\xrightarrow{\text{TS7}}) (\text{TAG})</td>
<td>3.3</td>
<td>2.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Reaction</td>
<td>Gibbs free energy of activation in the forward direction (kcal/mol)</td>
<td>Gibbs free energy of activation in the backward direction (kcal/mol)</td>
<td>Enthalpy of reaction (kcal/mol)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>R6</td>
<td>$31.2$</td>
<td>$13.6$</td>
<td>$3.1$</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>$5.9$</td>
<td>$1.2$</td>
<td>$4.0$</td>
<td></td>
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<tr>
<td>R8</td>
<td>$12.2$</td>
<td>$17.9$</td>
<td>$8.6$</td>
<td></td>
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<td>$20.8$</td>
<td>$26.2$</td>
<td>$-3.5$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Gibbs free energy of activation in the forward direction (kcal/mol).

$^b$Gibbs free energy of activation in the backward direction (kcal/mol).

$^c$Enthalpy of reaction (kcal/mol).
5 Conclusions

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

i) When subjected to thermolysis, TAGzT decomposes rapidly at temperatures above 230 °C in the liquid phase and the major decomposition products are N₂, N₂H₄, NH₃, HCN and the of 3-azido-1,2,4-triazol-4-ide anion.

ii) TAGzT decomposition is initiated within the AzT²⁻ dianion.

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

iv) The energetic material characteristics of TAGzT are a result of the HCN and N₂ producing reactions which are revealed by molecular modeling calculations to be highly exothermic.

v) CRT tests show that decomposition of TAGzT is more rapid as compared GzT. This is confirmed from the values of thermodynamic parameters calculated for reactions involved in the decomposition mechanism of these compounds.

References


