Numerical validation of the liquid-phase decomposition mechanism of guanidinium azotetrazolate

Hardik Panchal, Neeraj Kumbhakarna

Indian Institute of Technology Bombay, Powai, Mumbai, India

**Abstract**

The objective of this work is to numerically validate a previously formulated detailed chemical kinetics mechanism for the liquid phase decomposition of guanidinium azotetrazolate (GzT). GzT is of keen interest to researchers because of its energetic properties therefore it is critical to thoroughly understand the chemistry involved in its decomposition. The present work is a step in this direction. The reaction mechanism used in the present model, which consists of 76 species and 107 elementary reactions along with their kinetic parameters, was compiled from two previously published works. Simulations of the mass loss in thermogravimetric analysis and heat flow in differential scanning calorimetry were carried out using a numerical model. Results of the simulations were found to match satisfactorily with those from the experiments. Critical pathways in the GzT reaction mechanism were also identified by carrying out a sensitivity analysis.

1. Introduction

Nitrogen-rich energetic materials have received significant attention in the past few years for their high positive heats of formation which result in the release of a large amount of heat on combustion [1]. Compounds such as guanidinium azotetrazolate (GzT) have a significant scope for use in gas generators and burn rate modifiers for propellants.

Molecular structure the compound of interest, GzT, is shown in Fig. 1. It is a yellow colored salt with cotton fibre-like appearance. GzT was synthesized using GN and was patented by Bucerius et al. [2]. The detailed synthesis process was given by An et al. [3]. Kumbhakarna et al. [4] justified in their work the need for developing a detailed chemical reaction mechanism for GzT in the condensed phase by presenting a detailed literature survey on GzT. In their attempt to fulfill this need, they studied the decomposition of GzT by using Fourier transform infrared spectroscopy (FTIR) and time-of-flight mass spectrometry (ToFMS) techniques. Based on the results of their experiments, they formulated a reaction mechanism with the help of ab-initio molecular modelling calculations. An et al. [3] also studied the decomposition of GzT and presented its decomposition mechanism. Sivabalan et al. [5] studied the decomposition and combustion of a series of azotetrazolate salts including GzT and established the potential of such materials as energetic additives in rocket propellant formulations. Sinditskii et al. [6] also examined decomposition and combustion of GzT and proposed a detailed combustion mechanism for it. Han et al. [7] designed six types of gas generators having different oxidants based on GzT to investigate in terms of gas production, combustion temperatures and non-toxic gaseous emissions. The formulation GzT – LiNO₃ has the most potential for gas production among other formulations.

It can be concluded by reviewing the literature on GzT that substantial experimental analysis of this compound has been done and detailed chemical kinetics mechanism of its decomposition has also been proposed by computational analysis. The present work aims to build on the previously available data and validate the mechanism proposed by Kumbhakarna et al. [4] by simulating thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments numerically. It also intends to identify the critical reactions in the mechanism through a sensitivity analysis.

2. Numerical simulation

In TGA and DSC experiments few milligrams of the sample, in the present case that of GzT, is used in the instrument crucible as shown in Fig. 2. The sample is heated at a predetermined rate and its mass (TGA) and heat release with respect to a reference (DSC) are recorded with temperature. As the experiment progresses, the sample decomposes to form products which evaporate and mass of the sample diminishes with time. To simulate the mass loss in TGA, a control volume analysis of the sample was done and equations derived by Kumbhakarna and Thynell [8] were used. They have been reproduced below.
The governing equations, in their final form, are:

\[
\frac{d}{dt} \text{li} \sigma = \dot{\omega}_{\text{li,i}} - y_{\text{li,i}}\dot{k}_{\text{evap,i}} + Y_{\text{li}} \sum_{j=1}^{N} Y_{\text{li,j}}k_{\text{evap,j}} 
\]

\[
\frac{d}{dt} \text{f} \sigma = m_{\text{f}}y_{\text{f,i}}k_{\text{evap,i}} 
\]

\[
\frac{d}{dt} \text{l} \sigma = -m_{\text{l}} \sum_{i=1}^{N} y_{\text{l,i}}k_{\text{evap,i}} 
\]

Where \( k_{\text{evap,i}} \) is the evaporation rate parameter for species \( i \).

The equation for heat release rate for simulating DSC, after applying energy conservation, can be written as:

\[
\dot{Q} = m_{\text{f}} \sum k_{\text{evap,i}}Y_{\text{f,i}}h_{\text{f,i}} + \frac{m_{\text{f}}}{c_{\text{p}}_{\text{f}}} \sum y_{\text{f,i}}h_{\text{f,i}} + m_{\text{l}} \sum y_{\text{l,i}}c_{\text{p}}_{\text{l,i}} \frac{dT}{dt} + m_{\text{l}} \sum \frac{dy_{\text{l,i}}}{dt}h_{\text{l,i}} \]

All species are assumed to have finite evaporation rates. Values of evaporation rate parameters were calculated from experimental evaporation data if available and reasonable assumptions were made for rest of the species. As per these values N₂ evaporates most rapidly and melamine, being the heaviest species among those present in the gas phase, evaporates the slowest.

The Governing equations discussed above were solved with the DVODE stiff solver developed by Brown et al. [9], which employs Gears method for integrating stiff ordinary differential equations. The initial conditions for the \( p \) are: at \( t = 0 \), 1 g of GzT is present at \( T = 290 \) K.

Simulations were carried out with heating rates matching those adopted in the experiments. We assume that only 7 species depart the liquid phase out of the 76 species present in the mechanism. These are N\textsubscript{3}H\textsubscript{4}, HN\textsubscript{3}, guanidine, HCN, N\textsubscript{2}, melamine and NH\textsubscript{2}CN. The complete mechanism of Kumbhakarna et al. [4] is given in the supplementary data.

3. Results and discussion

The TGA measurements of An et al. [3] for GzT for a heating rate of 2.5 K/min showed first stage of mass loss at about 510 K and the second stage at around 720 K. The mass spectra showed N\textsubscript{2} (\( m/z = 28 \)), HCN (\( m/z = 27 \)), NH\textsubscript{3} (\( m/z = 17 \)), guanidine (\( m/z = 43 \)) and melamine (\( m/z = 96, 112, 126 \)) as the pre-exponential constant, the activation energy.

Sensitivity coefficients were calculated for the product species which appear in the gas phase. The results from sensitivity analysis are displayed in Fig. 3. The chosen temperature coincides with first mass loss step at around 518 K. Based on the sensitivity analysis results, out of the 107 reactions, those which play a major role in the overall GzT decomposition process are listed in Table 1. The pathway that proceeds through intermediate INT4 and guanidium\textsuperscript{+} is found to be the most dominant, as mass fractions of NH\textsubscript{3}, N\textsubscript{2}, HCN and melamine are most sensitive to R3 as seen in Fig. 3. Reaction R1, in which ring opening of Azt\textsuperscript{2-} occurs, plays a major role in production of N\textsubscript{2}. The less favorable pathway for ring opening of Azt\textsuperscript{2-}, Reaction R2, does not affect any

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**Fig. 1.** Molecular structure of GzT.

**Fig. 2.** Liquid sample of GzT heated in a pan (figure Reproduced with permission from reference [8]).

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**Nomenclature**

**Symbols**

- \( A \): Pre-Exponential factor
- \( \epsilon \): Specific heat at constant pressure
- \( e \): Charge on the electron
- \( E_{A} \): Activation energy
- \( G \): Gibbs free energy
- \( H \): Enthalpy
- \( h \): Mass specific enthalpy
- \( h_{p} \): Planck constant
- \( k \): Reaction rate constant
- \( k_{B} \): Boltzmann constant
- \( m \): Mass
- \( R_{0} \): Universal gas constant
- \( S \): Entropy

**Subscripts**

- \( b \): Backward
- \( evap \): Evaporation
- \( f \): Forward
- \( g \): Gas phase
- \( i,j \): Subscripts denoting species \( i \) and \( j \) respectively
- \( l \): Liquid phase

**Subscripts denoting species**

- \( \text{li} \)
- \( \text{f} \)
- \( \text{l} \)

**Nomenclature**

- \( T \): Temperature
- \( t \): Time
- \( y \): Mass fraction
- \( Z \): Atomic number
- \( \kappa \): Transmission coefficient
- \( \sigma \): Sensitivity coefficient
- \( \omega \): Species generation rate in terms of mass fraction (unit: 1/s)

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**Fig. 1.** Molecular structure of GzT.

**Fig. 2.** Liquid sample of GzT heated in a pan (figure Reproduced with permission from reference [8]).
species other than HN₃. Guanidine is most sensitive to Reaction R15, in which unimolecular decomposition of intermediate INT1 occurs producing NH₃. Reaction R18, which is one of the steps in the formation of melamine, does not affect any species other than N₂ and NH₃. Regarding the initiation of GzT decomposition, Kumbhakarna et al. [4] have stated that in their work the transition state for proton transfer within the liquid phase from the guanidinium cation to the azetrazolate dianion as described by other researchers could not be identified.

![Fig. 3. Sensitivity of species mass fractions to reaction rates (heating rate = 2.5 K/min).](image)

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>ΔHₑ⁰</th>
<th>ΔGᵢᶠ</th>
<th>ΔGᵦᶠ</th>
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<tr>
<td>R1</td>
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<tr>
<td>R2</td>
<td></td>
<td>154.8</td>
<td>212.9</td>
<td>106.6</td>
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<tr>
<td>R3</td>
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<td>−96.2</td>
<td>No barrier</td>
<td>88.2</td>
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<tr>
<td>R15</td>
<td></td>
<td>10.8</td>
<td>77.4</td>
<td>117.5</td>
</tr>
<tr>
<td>R18</td>
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<td>19.6</td>
</tr>
<tr>
<td>R94</td>
<td></td>
<td>79.0</td>
<td>202.5</td>
<td>172.8</td>
</tr>
</tbody>
</table>

a Enthalpy of reaction (kJ/mol).

b Gibbs free energy of activation in the forward direction (kJ/mol).

c Gibbs free energy of activation in the backward direction (kJ/mol).

‡ Gibbs free energy of activation.

![Fig. 4. Comparison of mass loss profile obtained from simulation to that obtained from experiments of An et al. [3] for a heating rate of 2.5 K/min.](image)
was identified to be a key reaction, is reduced by 2 kcal, the agreement between simulation and experiments is observed to improve. Further reducing the activation enthalpy of reaction R3 by 4 kcal shows an even better agreement between the numerical model and experiments. This is because guanidine is formed rapidly and evaporation rate also increases, which causes mass loss more rapidly. Activation enthalpy of reaction R3 was reduced by 2 kcal and then by 4 kcal keeping in mind that this variation falls within margin of uncertainty associated with the level of theory used for ab-initio calculations in the work of Kumbhakarna and Thynell [8].

Fig. 5 shows liquid species mole fractions with temperature and Fig. 6 shows gas species masses with temperature. It should be noted that species profiles in these figures correspond to modified reaction mechanism in which activation enthalpy of reaction R3 is reduced by 4 kcal. In the mass loss profile, 60% mass loss occurs in the first step and the species profiles show that this is mainly because of evaporation of N2, HCN and NH3. The second step in mass loss occurs at higher temperatures melamine starts to evaporate as can be seen from Figs. 5 and 6.

An et al. [3] also conducted DSC experiments on GzT samples. In the present model, heat release rate was computed with Eq (5) and 1 g of pure GzT was used as reference to calculate differential heat release rate. Comparison of the heat release rate from the present model and DSC data is presented in Fig. 7 for the modified reaction mechanism in which activation enthalpy of reaction R3 is reduced by 4 kcal. The prominent exothermic peak occurring in the DSC profile at about 530 K is also shown by the model although not as sharp. The model is unable to reproduce the weak endothermic peak, observed in the DSC data at about 530 K. In order to gain more insight in the heat release behavior during decomposition of GzT, the total heat release was split into its three components as shown in Fig. 8: (i) heat interaction due to evaporation of species, (ii) net heat generation due to chemical reactions, (iii) sensible heat required to raise the temperature of the sample. Fig. 8 reveals that heat from chemical generation dominates the other two components of the total heat release rate. Thus, the exothermic reactions R3 and R18 provide the heat causing the evaporation and are mainly responsible for the mass loss.
4. Conclusion

Numerical simulation of the GzT decomposition process was carried out by solving a system of ordinary differential equations representing the mass loss, reversible reactions and evaporation of stable species. The detailed reaction mechanism for the decomposition of GzT consisting of 76 species and 107 elementary chemical reactions proposed by Kumbhakarna et al. [4] was validated. Simulation results were found to satisfactorily match the experimental data of An et al. [3]. Important reaction pathways were discussed and critical reactions were identified that could be the subject of further studies. The following major conclusions were obtained, within the present modelling framework and assumptions:

1. Decomposition of GzT begins with the ring opening of AzT₂⁻ to release \( \text{N}_2 \), forming the intermediate INT4.
2. Pathway in which the intermediate species INT4a and guanidine are formed is the most critical, as all the major product species are sensitive to this pathway.
3. The first step observed in mass loss is caused by formation and evaporation of \( \text{NH}_3 \), \( \text{N}_2 \) and \( \text{HCN} \) whereas melamine evaporation results in the second step.
4. Decomposition proceeds through exothermic reactions throughout, producing the \( \text{N}_2 \), \( \text{NH}_3 \), and \( \text{HCN} \).

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.2017.10.009.

References