



# Development of a reaction mechanism for liquid-phase decomposition of guanidinium 5-amino tetrazolate

N. Kumbhakarna, S.T. Thynell\*

Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, United States



## ARTICLE INFO

### Article history:

Received 19 December 2013

Received in revised form 12 February 2014

Accepted 17 February 2014

Available online 25 February 2014

### Keywords:

Guanidinium 5-amino tetrazolate

Reaction mechanism

Liquid phase

Continuum-based model

Sensitivity analysis

## ABSTRACT

The objective of this work is to formulate a detailed reaction mechanism of the decomposition of guanidinium 5-amino tetrazolate (GA) in the liquid phase using a combined experimental and computational approach. The experimental information comes from data published in the literature. The computational approach is based on using quantum mechanics for identifying species and determining the kinetic rates, resulting in 55 species and 85 elementary reactions. In these ab initio techniques, various levels of theory and basis sets were used. A continuum-based model for predicting species formation and mass loss of a TGA experiment was also developed and solved numerically, accounting for reversible chemical reactions and mass transfer in simulations of the GA decomposition process. The model accounts for reactions within the liquid phase and evaporation of several of the observed experimentally measured products. Simulation results for species concentrations and heat release were obtained, and these results were found to satisfactorily match the temporal experimental results previously published in literature for the decomposition of GA. Important reaction pathways in the proposed reaction scheme were identified based on a sensitivity analysis.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, research on nitrogen-rich energetic materials has received significant attention for a variety of reasons. First, their high positive heats of formation may release a large amount of heat on combustion as dinitrogen ( $N_2$ ) is one of the major products [1]. Second, the formed molecular nitrogen may achieve a high specific impulse without undesirable smoke or soot. Third, the molecular nitrogen is an environmentally friendly final product. Tetrazoles, with their heterocyclic ring structure, fall within this class of high-nitrogen compounds [2]. Within tetrazole family of compounds, the triaminoguanidinium azotetrazolate (TAGzT) [3] and guanidinium azotetrazolate (GzT) [4], are of interest due to their potential applications as gas generators and burn rate modifiers for propellants. Similarly, the guanidinium 5-aminotetrazolate (GA), shown in Fig. 1, is also of interest and possesses a much simpler molecular structure.

The molecular and electronic structures of GA were reported by Paoloni et al. [5]. Tao et al. characterized GA and several compounds containing the amino-tetrazolate ( $ATz^-$ ) anion based on infrared

(IR), nuclear magnetic resonance (NMR), elemental analysis, thermal stability, phase behavior, and density [6]. Their conclusion was that these compounds have good thermal and hydrolytic stabilities. Neutz et al. described the synthesis and fundamental properties of GA in their work [7]. They also applied thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and evolved gas analysis (EGA) to investigate the thermal properties and the decomposition behavior of GA. They found that GA is thermally quite stable and insensitive to friction and impact. They also reported that it melts at  $\sim 397$  K, and its thermal decomposition has an onset temperature of 440 K. The decomposition is suggested to involve five steps, producing nitrogen ( $N_2$ ), ammonia ( $NH_3$ ), cyanamide ( $NH_2CN$ ) and hydrazoic acid ( $HN_3$ ), as well as other unidentified species as the final products. It is mentioned that HCN is also formed, but it could not be seen in the FTIR spectroscopy results due to a detector lower limit of  $750\text{ cm}^{-1}$ . The presence of HCN is thought to be indicated by the time-of-flight data due to the detected  $m/z=26$ . However, the time-of-flight data for  $m/z=16$  and  $m/z=26$  show the same temporal behavior for temperatures above 640 K, suggesting that  $m/z=26$  is likely caused by cyanamide. Furthermore, an examination of the results from FTIR spectroscopy reveals that the *P* and *R* branches from a band centered near  $3310\text{ cm}^{-1}$  should be visible if HCN is formed. No such band structure is evident. Thus it appears reasonable to

\* Corresponding author. Tel.: +1 814 863 0977.

E-mail address: [thynell@psu.edu](mailto:thynell@psu.edu) (S.T. Thynell).

### Nomenclature

$A$	pre-exponential constant for reaction rate
$c_p$	specific heat at constant pressure
$G$	Gibbs free energy
$h$	mass specific enthalpy
$h_p$	Planck constant
$H$	enthalpy
$k$	reaction rate constant
$k_B$	Boltzmann constant
$m$	mass
$N$	number of chemical species
$\dot{Q}$	rate of external heat supplied
$S$	entropy
$T$	temperature
$t$	time
$y$	mass fraction of species
$\kappa$	transmission coefficient
$\sigma$	species mass fraction sensitivity coefficient to chemical reaction
$\dot{\omega}$	species generation rate in terms of mass fraction (unit: 1/s)

### Subscripts

$b$	backward reaction
$evap$	evaporation
$f$	forward reaction
$g$	gas phase
$i, j$	subscripts denoting species $i$ and $j$ respectively
$l$	liquid phase

### Superscripts

$\ddagger$	transition state
------------	------------------

assume that HCN is not an important decomposition product of GA.

The  $ATz^-$  anion in GA consists of a tetrazole ring with an amino ( $-NH_2$ ) group attached to the carbon atom as shown in Fig. 1. Compounds having structure similar to this ion have received considerable attention in literature. For example, Kiselev and Gristan studied the thermal decomposition of 5-aminotetrazole (5-ATZ) using quantum mechanics, including the G3 multilevel procedure and density functional theory. It was demonstrated that bimolecular reactions are important, especially in the condensed phase [8]. Paul et al. employed quantum mechanics based calculations using various levels of theory to identify the principal unimolecular decomposition pathways of 5-ATz in the gas phase [9]. They also predicted activation barriers for these pathways. Zhang et al. used ab initio methods to investigate the kinetics of the decomposition of 5-ATZ to  $HN_3$  and cyanamide [10]. They evaluated rate constants using conventional and canonical variational transition-state theories covering temperatures ranging from 300 to 2500 K. Piekil

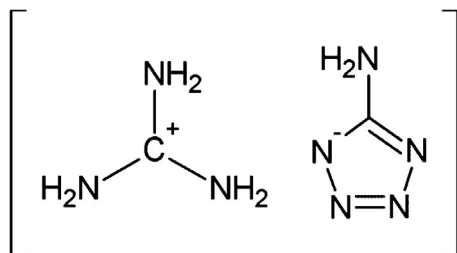


Fig. 1. Guanidinium 5-amino tetrazolate.

and Zachariah, using a T-Jump/time-of-flight mass spectrometry, studied the thermal decomposition of several tetrazole containing energetic salts under very high heating rate conditions [11]. They found two different reaction pathways involving ring opening; one involving the expulsion of  $N_2$  and the other producing  $HN_3$ . The pathway that was followed depended on the placement of functional groups on the ring.

Knowledge of the decomposition behavior of ingredients used in propellants is of significant interest for a wide variety of reasons. First, there is a long-term need to develop comprehensive ignition and combustion models of rocket motors and gas generators in order to facilitate the engineering systems design. Second, long-term storage of energetic materials requires a thorough understanding of the susceptibility to accidental ignition due to slow cook-off, impact and electrostatic discharge. Finally, knowledge of initiation of decomposition within a molecule can provide synthesis chemists a guide to the design of safer and more stable energetic materials. In most cases involving modeling of the ignition and combustion of energetic materials, comprehensive chemical reaction mechanisms are available only for the gas phase. In the solid or liquid phase, global reactions are most frequently used to simulate the ignition and combustion of energetic materials [30,31]. Current understanding of liquid-phase reactions is very limited regarding several aspects: (i) identities of the intermediate decomposition products, (ii) reaction pathways and (iii) rates of elementary reactions. Much additional work is needed regarding the development of liquid-phase decomposition and reaction models of energetic materials, which should improve the predictive capability of propellant ignition and combustion models. The present work on GA is an attempt in this direction. As a result, the motivation of this work is to formulate a chemical reaction mechanism for GA in the liquid phase by using molecular modeling ab initio methods and to compare the predicted results with the experimental results obtained by Neutz et al. [7].

## 2. Molecular modeling

Quantum mechanics calculations provide an avenue for corroborating existing experimentally measured data and providing information otherwise unavailable experimentally. The Gaussian 09 [12] suite of programs was utilized to this end. Molecular structures of species involved in the decomposition of GA were identified from transition-state calculations. The search for transition states was in most cases performed by using the B3LYP/6-31(d) level of theory. The obtained optimized structures served as an initial guess to higher-order methods, such as the MP2 perturbation theory. By using the MP2 method [13] and a triple split valence basis set with additional polarized functions, 6-311++G(d,p), the calculations account for the significant charge delocalization in the ions present. For cases in which convergence problems were encountered and the transition states could not be obtained using the MP2 method, the CBS-QB3 compound method developed by Montgomery et al. [14] was used. This method was chosen because it gives a good balance between accuracy and computational effort; however, calculations were also done by other methods including M062X. M062X is a high-nonlocality functional developed by Zhao and Truhlar for thermochemistry, thermochemical kinetics, noncovalent interactions, and excited states [15]. The computed structures were optimized and vibrational frequency calculations were performed to ensure that local energy minima (in case of reactants and products) and saddle points (in case of transition states) were achieved. Various thermodynamic properties of species including heat of formation, enthalpy, entropy, free energy and specific heat, which are required in the model describing the decomposition, were estimated in the gas and liquid phases from

Download English Version:

<https://daneshyari.com/en/article/673401>

Download Persian Version:

<https://daneshyari.com/article/673401>

[Daneshyari.com](https://daneshyari.com)