



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



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ABSTRACT

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

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Nomenclature

Symbols

γ out-of-plane bending vibration

δ in-plane bending vibration

ν stretching vibration

Subscripts

a asymmetric

s symmetric

1. Introduction

Recently, research on nitrogen-rich energetic materials has received significant attention because of their high positive heats of formation which provide the potential for releasing a large

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

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

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

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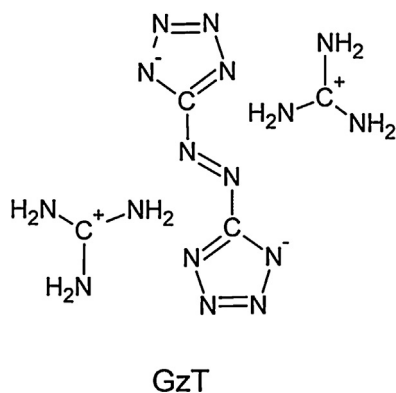


Fig. 1. Molecular structure of GzT.

decomposition of GzT [4]. According to these investigators, the first stage of GzT decomposition corresponds to an exothermic reaction involving abstraction of protons available at the guanidinium cation (Gu^+) by the azotetrazolate ring. They further state that proton transfer leads to the formation of a highly unstable product which then decomposes to release molecular nitrogen and cyanamide via ring-opening reactions. Hammerl et al. studied the structure of several GzT based salts [10]. Based on vibrational spectroscopy, they identified several important absorption bands. They also investigated the thermal behavior of GzT using DSC. The products were analyzed using infrared (IR) spectroscopy and mass spectrometry. The major decomposition products were found to be molecular nitrogen (N_2), ammonia (NH_3), and hydrogen cyanide (HCN); carbodiimide (HNCNH) was also detected as a gaseous product. It was suggested that decomposition of azotetrazolate dianion (AzT^{2-}) was initiated via the protonated species. The same products were observed by Sivabalan et al. in their work on GzT [11]. Decomposition pathways for GzT were investigated using computational methods by Liu et al. [12]. Quantum chemical ab initio methods were used to suggest a decomposition mechanism. The computational analysis was based on the assumption that decomposition occurred in the gas phase. The first decomposition step was identified as a “cracking” process to form two guanidinium cations and the azotetrazolate dianion. Very recently, Ting et al. proposed a reaction scheme for the decomposition of GzT based on their TG, differential scanning calorimetry (DSC), condensed-phase thermolysis using Fourier-transform infrared spectrometry (FTIR) and mass spectrometry experiments [13]. Their reaction scheme is very similar the ones discussed previously [4,10].

The literature survey on GzT decomposition presented here indicates that most of these studies are experimental and involve some degree of speculation concerning the chemical reactions that take place during the decomposition based on the observed products. It is essential, however, to explore other approaches to interpret the experimental information. Here we adopt recently developed methods based on the use of quantum mechanics. As described in several works, quantum mechanics techniques have been used to analyze the decomposition of guanidinium 5-aminotetrazolate as well as hypergolic reactions between monomethyl hydrazine and nitrogen dioxide [14,15]. These results can subsequently be used to formulate comprehensive chemical reaction mechanisms that are needed to simulate ignition and combustion of energetic materials. However, comprehensive chemical reaction mechanisms are available only for the gas phase. In the solid or liquid phase, global reactions are most frequently used to simulate the ignition and combustion of energetic materials [16,17]. Current understanding of liquid-phase

reactions is very limited regarding several aspects: (i) identities of the intermediate decomposition products, (ii) reaction pathways, and (iii) rates of elementary reactions. Much additional work is needed regarding the development of liquid-phase decomposition and reaction models of energetic materials, which should improve the predictive capability of propellant ignition and combustion models. The present work on GzT is an attempt in this direction. FTIR spectroscopy and time-of-flight mass spectrometry (ToFMS) experiments have been performed on GzT to analyze its decomposition in the liquid phase, and formation of the observed products has been explained by formulating elementary chemical reactions based on quantum mechanics based calculations.

2. Experimental

2.1. Materials

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

2.2. Fourier transform infrared (FTIR) spectroscopy

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

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

- i) About 0.5–1 mg of GzT sample was subjected to preset temperatures (563–593 K) in the CRT chamber and the corresponding FTIR spectra were obtained by passing the infrared beam through the FTIR probe volume. The goal is to subject the sample to decomposition under isothermal conditions. The total measurement time is about 10 s, and the time required for achieving isothermal conditions is about 0.2–0.3 s.
- ii) About 0.5 mg of GzT sample was subjected to preset temperatures (563–593 K) in the CRT chamber and the evolved gases were allowed to condense on a glass slide. The condensate on the slide was then mixed with 150 mg of potassium bromide (KBr) and pressed into a pellet. The CRT chamber in the path of infrared beam from the spectrometer was replaced by a specially designed fixture. The pressed pellet was then placed

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