Investigation of Thermal Decomposition of Solid Propellant Components by Online Atmospheric Pressure Photoionization Mass Spectrometry

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1 Introduction

Solid propellants are the primary power source for propulsion systems, generally comprising fuel, oxidisers, binders and other additives.[1] As technology advances, there is an increasing demand for higher energy outputs, which creates significant safety challenges. Energetic materials are often incorporated into the inert matrix to enhance the energetic properties and minimize mechanical sensitivity, such as glycidyl azide polymer (GAP) and 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane (HMX). [2, 3] In order to explore the effectiveness of alternative components in solid propellants, the thermal decomposition process of energetic materials requires more in-depth investigation.

Understanding the pyrolysis mechanisms of GAP and HMX is crucial, as they will help determine the operational temperature, characterize major products, and construct combustion and aging models. The detection of key intermediates produced during pyrolysis is a vital process for the analysis of pyrolysis reaction network. Intermediates play a crucial role in the chemical reaction network, but their rapid reaction rates make it challenging to obtain valid results using conventional measurement techniques. Nonetheless, prior research has successfully measured several pyrolysis products of HMX through various methods, significantly contributing to the understanding of HMX pyrolysis mechanism. Tang [4] obtained a series of characteristic parameters related to the thermal decomposition of HMX using thermogravimetry (TG) and differential scanning calorimetry (DSC). Similarly, Liu [5] measured several gaseous pyrolysis products of HMX, including NO, NO_2, CO, HONO, and N_2O, using in-situ infrared spectroscopy. The experimental results revealed that the breaking rate of C-N bonds is considerably higher than that of N-N bonds as the temperature increases, and an intramolecular recombination phenomenon of the broken HMX molecules was observed. Some researchers have suggested that the breaking of the C-N bonds is the primary mechanism, specifically ring cleavage into two equal m/z 148 species, based on experimental results obtained through Langmuir evaporation and mass spectrometry (MS). [6, 7] However, the existing experimental evidence is insufficient to clearly delineate the thermal decomposition pathways of HMX.

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Two pyrolysis decomposition stages of GAP have been identified using Fourier Transform Infrared Spectrometer (FTIR) and thermogravimetric analysis[2, 8]. The first stage is an exothermic reaction primarily driven by the decomposition of side-chain azide groups, while the second comprises the main-chain degradation [9]. However, Liu et al. [10] conducted ReaxFF MD simulations, revealing that the initial reactions of GAP involve the bond decomposition at both side- and main chains. Nonetheless, this theoretical evidence lacks experimental support. Molecular beam mass spectrometry (MBMS) has been used to identify decomposition products, including gaseous species such as N_2, HCN, CH_2O, CO_2, H_2O, NH_3, CO, and small molecules (such as acetonitrile and acrylonitrile). Polyatomic molecules containing N atoms, like pyrroles and furans, have also been detected [11, 12]. However, identifying the products with larger molecular weights remains challenging.

The pyrolysis process of energetic materials occurs extremely rapidly, generating products with complex structures, thereby necessitating higher resolution in measurement equipment. However, the FTIR method can only provide the composition of small gaseous products, and chromatographic methods are time-consuming. Thus, directly connecting reactors to mass spectrometry for online measurement of pyrolysis products presents a more efficient approach. Conventional ionization methods for mass spectrometry typically employ electron impact ionization (EI) at an energy of 70 eV. However, this ionization process often generates numerous fragments, complicating product analysis. In contrast, the photoionization (PI) method usually uses vacuum ultraviolet (VUV) light with lower energy (7-18 eV) as the ionization source, effectively covering the ionization energy of most organic compounds and producing minimal fragments during ionization. [13] Currently, photoionization mass spectrometry (PIMS) is widely used in various fields, including combustion and catalysis. [14, 15]

In this paper, atmospheric photoionization ultra-high resolution mass spectrometer (APPI-HRMS) was applied to measure the pyrolysis products of GAP and HMX. Based on the experimental findings, the primary pyrolysis pathways were analyzed, providing a foundation for constructing the reaction networks of GAP and HMX.

2 Method

Heavier pyrolysis products were in situ and online identified by a combination of atmospheric pressure photoionization and high-resolution mass spectrometry (APPI-HRMS) [16, 17], as shown in Figure 1. The HRMS (Orbitrap Fusion, ThermoFisher Scientific) operated with a resolution of 500,000 @ 200 Da. The reactor featured a quartz tube with a 0.5 mm hole insulated by a boron nitride layer, creating a thermostatic zone (~5 cm). A VUV lamp (10.6 eV) was aligned with the hole to ensure immediate ionization of products exiting the reactor. The MS sampling interface, positioned 10 mm from the hole, enabled efficient online sampling. In the APPI-HRMS experiments, the ionization mode of the detected compounds was $[M\text{-}H]^+$, so the product peaks should be treated with +H for subsequent analysis.

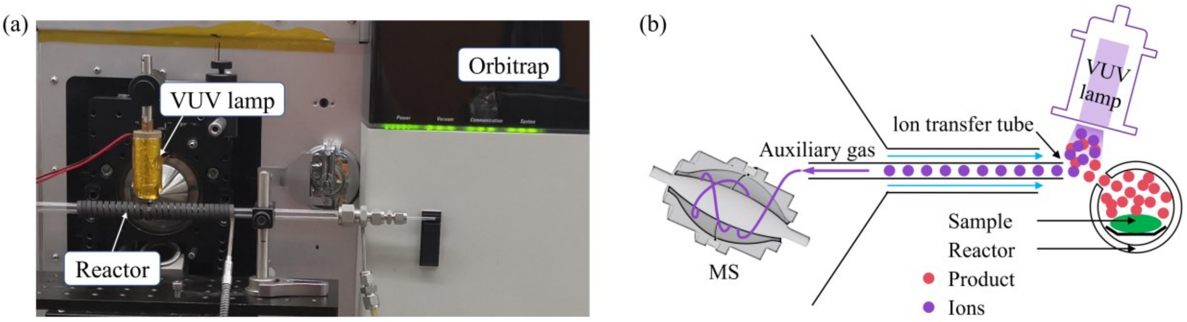

Figure 1: Photograph (a) and schematic diagram (b) of the APPI-HRMS setup.

3 Results and discussions

3.1 Primary pathways of GAP thermal decomposition

The results of the primary stage of GAP pyrolysis, detected using APPI-HRMS, are presented in Fig. 2. Signals with compositions of $C_aH_bO_cN_d$ were identified. It is observed that there are some high abundance peaks, present i.e., $[C_6H_{11}O_2N_2]^+$, $[C_9H_{16}O_3N_5]^+$, $[C_{12}H_{21}O_4N_8]^+$ and $[C_{15}H_{26}O_5N_{11}]^+$, which differ by a -$C_3H_5ON_3$ unit. Additionally, a similar peak pattern with the compositions of $[C_7H_{13}O_2N_2]^+$, $[C_{10}H_{18}O_3N_5]^+$, and $[C_{13}H_{23}O_4N_7]^+$ are also observed. Notably, the $C_3H_5ON_3$ unit matches the composition of one repeating unit of GAP, suggesting that these products are produced from the primary depolymerization reaction of GAP.

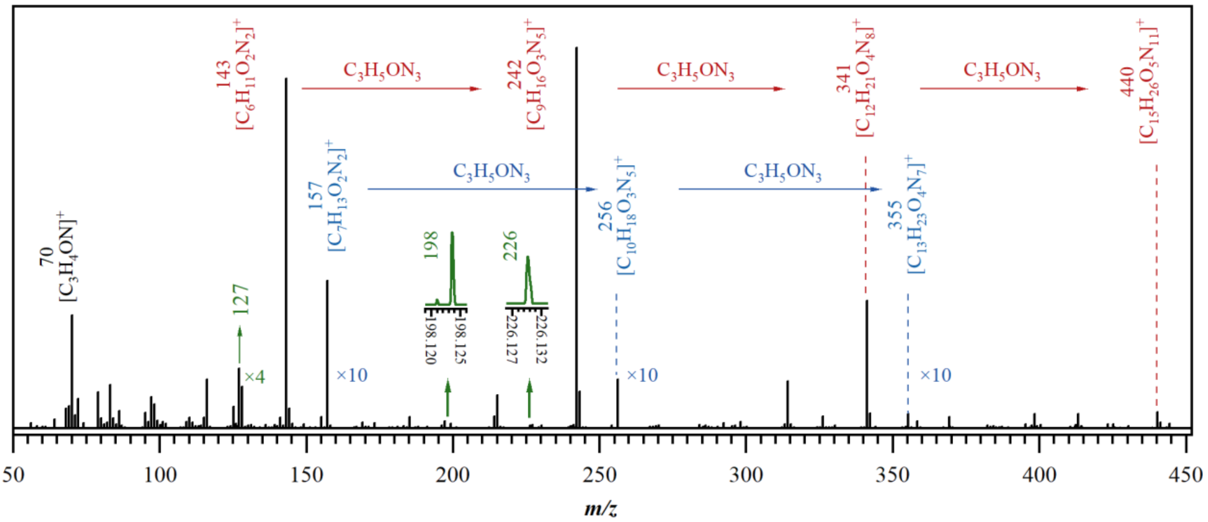

Figure 2: Initial pyrolysis stage of GAP detected using APPI-HRMS at 300 °C.

Using DFT, Fu et al. [17] calculated the bond dissociation energies (BDEs) of the C-O-C bonds in the GAP. Moreover, the BDEs of the main chain C-C bond(s) are significantly higher than those of C-O-C bonds [12], indicating that the decomposition of C-O-C bonds predominantly drives the main chain depolymerization. In Fig. 2, the red peaks, resulting from the homolytic dissociation of C-O-C bonds, are more abundant. The blue peaks represent products formed by the breakage of C-C bonds intra-units. Other products exhibiting regular patterns are labeled in green in Fig. 2. Notably, the peaks of $[C_9H_{16}O_2N_5]^+$ (m/z 127.09) and $[C_9H_{16}O_2N_3]^+$ (m/z 226.13) differ with a N_2 unit (m/z 28.00), indicating that the depolymerization and the decomposition of the -N3 group occur in the same reaction stage. This contrasts the previous mechanism [6, 9, 11] that proposed the decomposition of the -N_3 group as the sole primary pathway. In other words, the detection of featured $C_aH_bO_cN_d$ intermediates can serve as crucial indicators for the existence of depolymerization reactions by breaking C-O-C and C-C bond(s) as primary initiation steps of GAP.

The depolymerization pathways are illustrated in Scheme 3. Since GAP is a hydrogen-rich system, biradicals formed by the main chain bonds dissociation recombine with H atoms to form stable products [11, 18]. The products are formed via different bond-breaking at different sites. First, the bond dissociation reactions at the inter-unit C-O sites (denoted as D1, D1') generate products. Second, the dissociation reactions at C-C sites (denoted as D2, D2') and inter-unit C-O sites generate products in blue. Last, these inter-unit C-O bonds (denoted as D3, D3') and intra-unit C-O bonds contribute to the formation of $[C_6H_{12}ON_2]^+$.

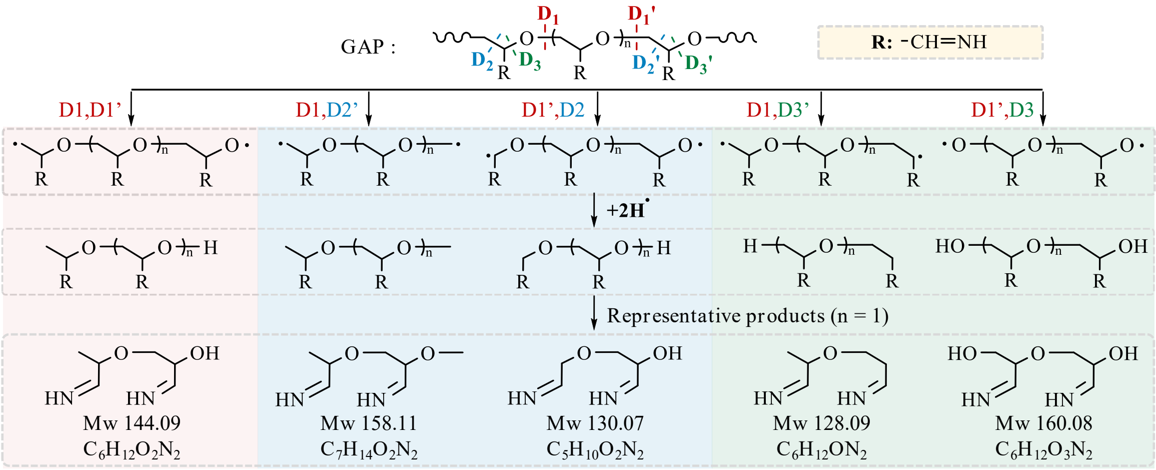

Figure 3: Primary reaction pathways of initial depolymerization products of GAP.

3.2 Primary pathways of HMX thermal decomposition

Since the high resolution of APPI-HRMS, the molecular weights and molecular formulas of pyrolysis products have been essentially determined. Figure 4 shows the mass spectrum of HMX pyrolysis products under atmospheric pressure obtained by APPI-HRMS. The specific molecular structure of each product is derived by combining the molecular formula with the tandem mass spectrum results.

The species at m/z 98 is a seven-membered C-N heterocyclic ring. The m/z 141 and 186 features a bicyclic ring structure, with an NO_2 group still retained on m/z 186. It can be observed that both the contraction and growth of the rings in the HMX molecules occur during the early stage of thermal decomposition, while the nitro groups have not yet been completely detached from the parent compound. In the middle stages of thermal decomposition, reactions primarily involve the formation of six-membered rings, such as m/z 83 and m/z 85, alongside the breakage of existing rings. As the reactions progress to the late stage, characteristic products m/z 135 and m/z 182 emerge. The m/z 135 product features a bicyclic ring structure containing three double bonds, while m/z 182 consists of a tricyclic ring. The increase in the number of double bonds and rings indicates a significant growth of nitrogen heterocycles during the late pyrolysis of HMX.

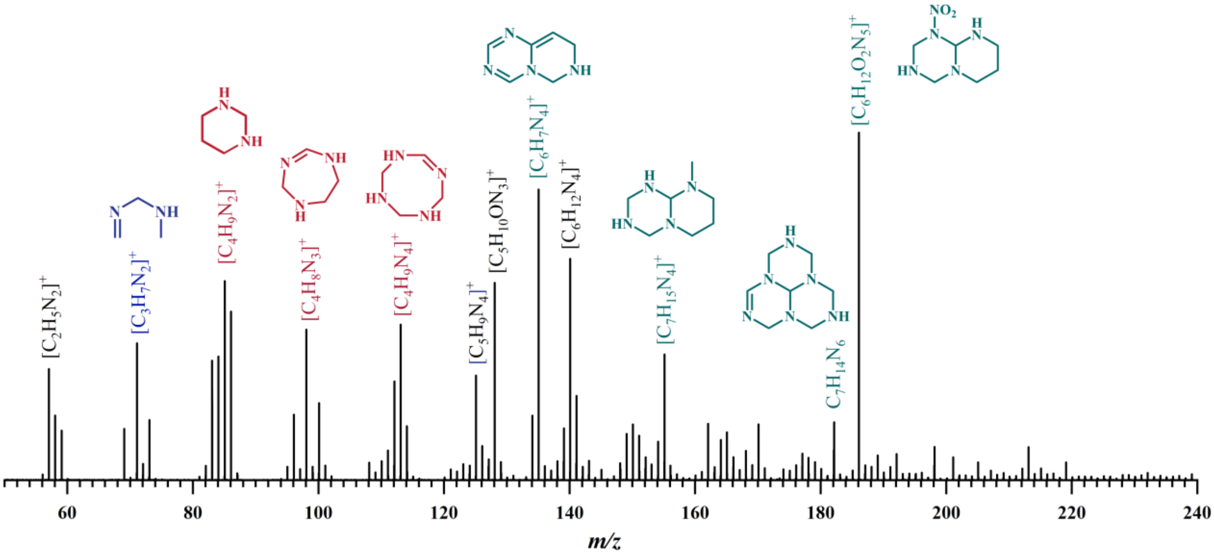

Figure 4: Primary thermal decomposition products of HMX detected by APPI-HRMS at 300 °C.

Combined with the previous research[6, 19], the initial decomposition process of HMX involves three possible pathways: (i) HONO-elimination; (ii) N-NO_2 bond breaking; and (iii) cleavage of HMX along the symmetry axis into two INT148 fragments. Furthermore, using APPI-HRMS, the presence of polycyclic structures was detected, such as m/z 85, m/z 135, and m/z 182, suggesting that the formation of nitrogen heterocycles occurred during the pyrolysis process of HMX and the contraction of the eight-membered ring in the HMX molecule into a six-membered ring. Finally, the thermal decomposition pathways mentioned above are summarized and illustrated in Figure 5.

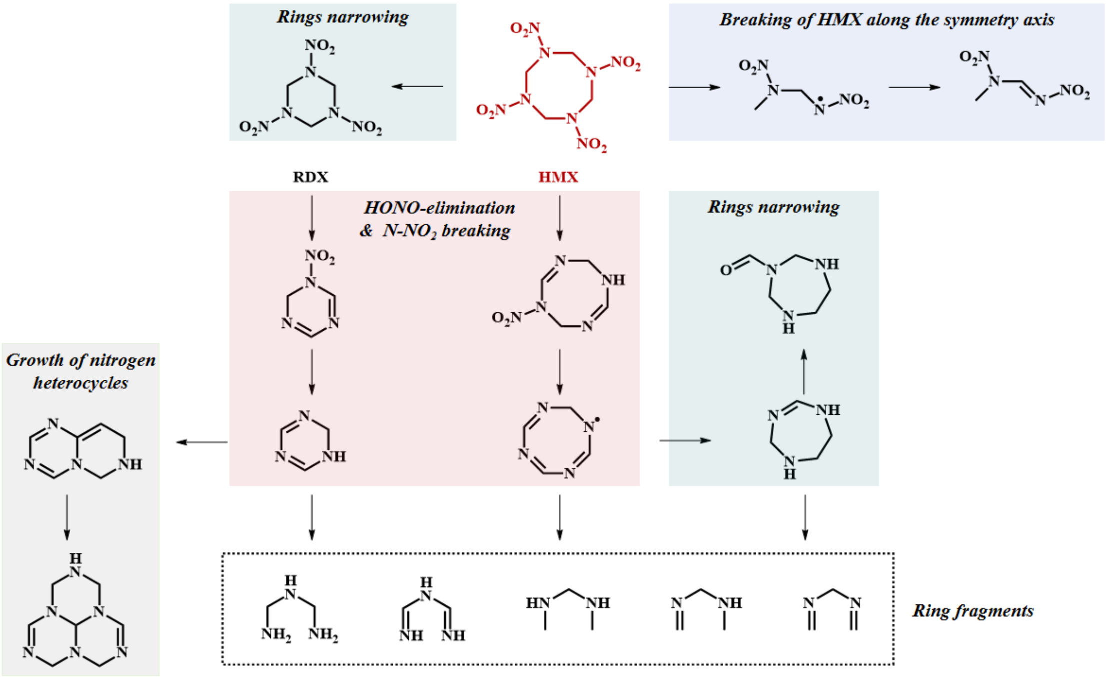

Figure 5: Primary thermal decomposition pathways of HMX.

4 Conclusions

This work investigated the pyrolysis products of a model energetic binder GAP and an energetical additive HMX using APPI-HRMS. The experiment evidence confirms that the bond dissociation at both side-chain -N_3 groups and main-chain C-O-C and C-C sites are primary decomposition pathways of GAP. Additionally, the presence of polycyclic structures suggests the growth of nitrogen heterocycles occurred during the pyrolysis process of HMX and the contraction of the eight-membered ring in the HMX molecule into a six-membered ring. These findings lay the theoretical groundwork for developing a kinetic model and offer a solid foundation for further exploration of multi-component interaction mechanisms in propellants.

Acknowledgements

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