



Thermal Decomposition of Ammonium Perchlorate – Benzyl Triethyl Ammoniumtetrafluoroborate Mixture: A Simultaneous TG-MS Approach

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ABSTRACT

Focus is on the search for materials that can suppress the first exotherm of ammonium perchlorate, a factor contributing to the premature re-ignition of extinguishable solid propellant rocket motors. In this context, the role of benzyl-triethyl-ammonium tetrafluoroborate in modifying thermal decomposition of ammonium perchlorate is considered. The mechanistic aspect of thermal decomposition of mixture of AP and Benzyl-triethyl-ammoniumtetrafluoroborate are discussed based on simultaneous TG – MS studies. The formations of trialkyl amine, corresponding alkyl halide, together with boron trifluoride are the suggested intermediate products.

Keywords: Ammonium perchlorate, Benzyl triethyl ammoniumtetrafluoroborate, decomposition.

INTRODUCTION

Quaternary ammonium compounds such as Choline are important in medical research [1]. Quaternary ammonium compounds are extensively used in domestic, agricultural, healthcare, and industrial applications as surfactants, emulsifiers, fabric softeners, disinfectants, pesticides, corrosion inhibitors, and personal care products [2, 3]. Benzyltrimethyl ammonium hydroxide, a known organic base, is used in aldol condensation reactions and base-catalyzed dehydration reactions. It is also used as a base in Ando's Z-selective variant of Horner-Wadsworth-Emmons Olefination reactions [4]. Thermal decomposition of benzyl-triethyl-ammonium tetrafluoroborate was reported by Prasad et al [5]. Present work focuses on the effect of benzyl-triethyl-ammonium tetrafluoroborate on thermal decomposition of ammonium perchlorate, an inorganic oxidizer, extensively used in composite solid rocket propellant technology.

MATERIALS AND METHODS

Ammonium perchlorate used in this study is from Ammonium perchlorate Experimental Plant (APEP), Always, Indian Space Research Organization (ISRO), Department of Space (DOS), Government of India. Benzyl - triethyl ammonium tetrafluoroborate (BTEATFB) is from M/s. Aldrich Chemicals.

The TG – SDTA - QMS experiments were conducted in a Mettler - 851e system coupled to Balzers Mass spectrometer, and DSC in Mettler 821e system; in an inert atmosphere of pure nitrogen, at a sample

heating rate of $10^{\circ}\text{C min}^{-1}$, and a gas flow rate of 30 mL min^{-1} . The sample holder is made up of alumina and the thermocouples employed are of Pt-Rh.

RESULTS AND DISCUSSION

The thermo gravimetric (TG) and differential thermo gravimetric curves of Benzyl-triethyl-ammonium tetrafluoroborate (BTEATFB) are shown in fig. 1(a) and fig.1 (b). The temperatures of onset and completion of thermal decomposition of BTEATFB are at 317°C and 370°C . The peak decomposition rate occurs at about 361°C . The TG-DTG curves of pure ammonium per chlorate (AP) are shown in fig.2.

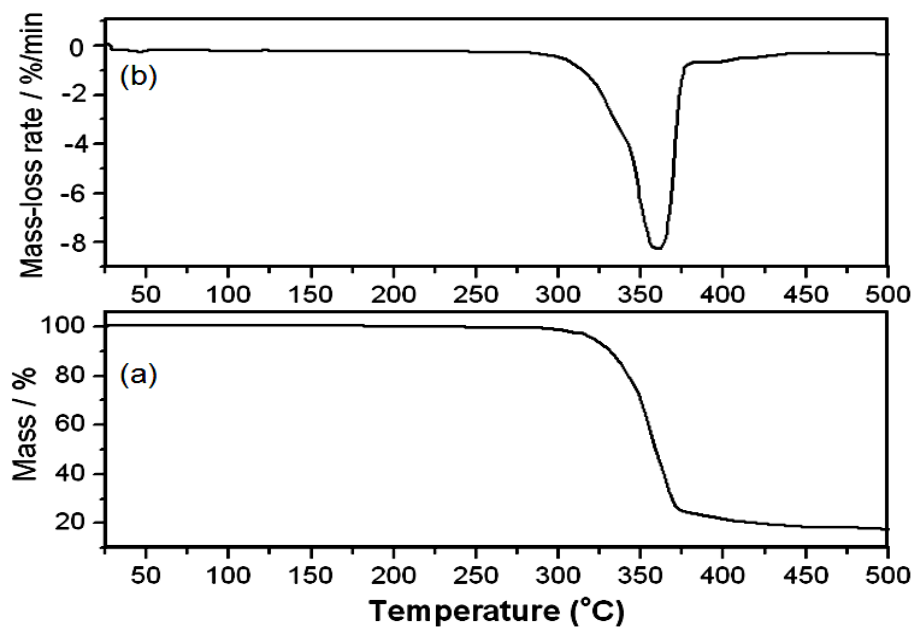


Fig.1 (a) , 1 (b) TG and DTG Curves of BTEATFB

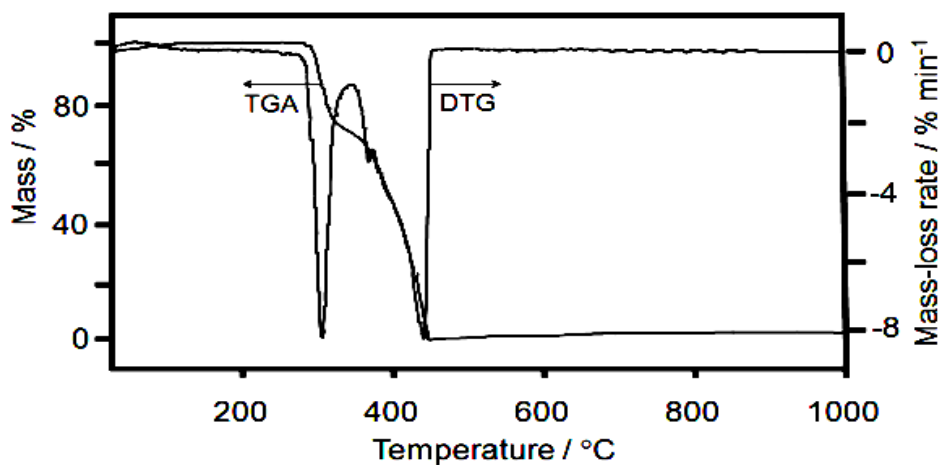


Fig.2. TG – DTG Curves of Ammonium Per chlorate

The onset and end set temperatures of decomposition of AP are 277.1°C and 442.6°C, respectively. Ammonium per chlorate decomposes in two distinct stages. The DSC curves of pure AP and AP-BTEATFB mixture (BTEATFB is 0.5 per cent by weight of AP) are shown in fig.3 and fig.4.

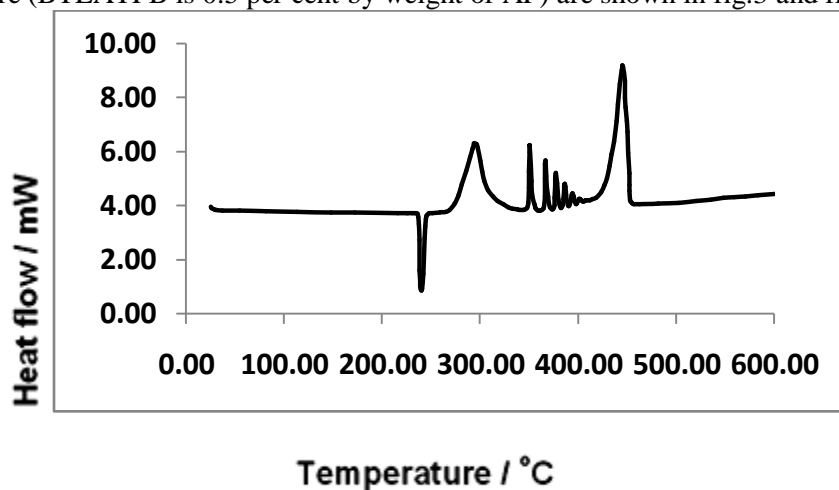


Fig.3. DSC Curve of Ammonium Per chlorate

From Fig.3, the crystallographic phase-transition from ortho-rhombic to cubic phase occurs at 240°C with an enthalpy of (−) 203.6 J g^{−1}. The low temperature decomposition (LTD) peak occurs at 295.3°C with an enthalpy of 864.4 J g^{−1}. The high temperature decomposition (HTD) peak occurs at 447.7°C with an enthalpy of 1418.4 J g^{−1}. The total enthalpy of AP decomposition is 2282.8 J g^{−1}.

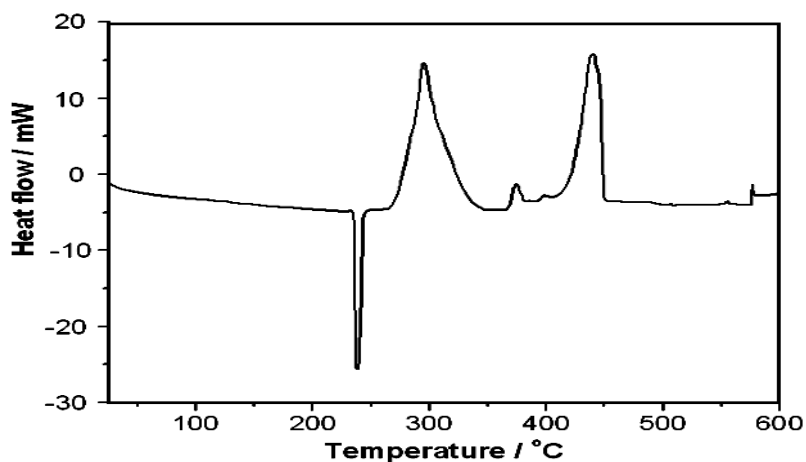


Fig.4. DSC Curve of AP – BTEATFB Mixture

In the case of AP – BTEATFB mixture (Fig.4), the small endothermic peak corresponds to the melting of BTEATFB (106.2°C) with an enthalpy of (−) 0.73 J g^{−1}. The sharp endothermic peak at 239°C corresponds to the crystallographic phase-transition from ortho-rhombic to cubic phase of AP, with an enthalpy of (−) 100.14 J g^{−1}.

The enthalpies of decomposition of LTD and HTD of AP- BTEATFB mixture are 567.4 J g^{−1} and 429.2 J g^{−1}, respectively (Fig.4). The total enthalpy of decomposition of AP-BTEATFB mixture is 996.6 J g^{−1}. There is a considerable amount of reduction in energy content due to the presence of BTEATFB. There is no effect of BTEATFB on the first exothermic peak of AP (which occurs at 295.3°C). However, it has a

marginal effect on the HTD of AP (from 447.7°C in the case of pure AP to 440.4°C in the case of AP – BTEATFB mixture).

The simultaneous TG-DTG-DTA curves of AP – BTEATFB mixture are shown in fig.5. The mixture decomposes in two steps; the temperatures corresponding to these two stages of decomposition being 307.4°C, and 464°C, respectively (from DTA curve).

The corresponding DTG peak temperatures are 301.1°C and 467.6°C (from DTG curve). The mass fragments evolved during thermal decomposition of AP – BTEATFB mixture are shown in fig.6. The important fragments assignment is given in table -1.

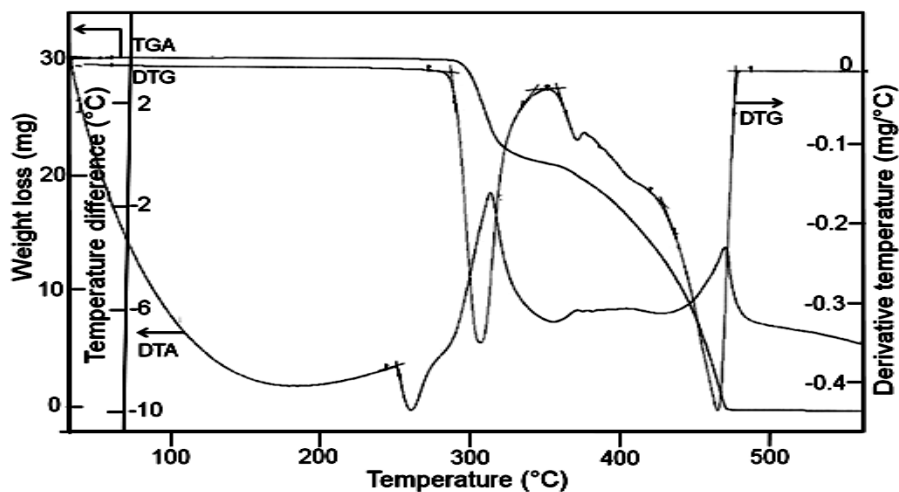


Fig.5. Simultaneous TG – DTG – DTA Curves of AP – BTEATFB Mixture

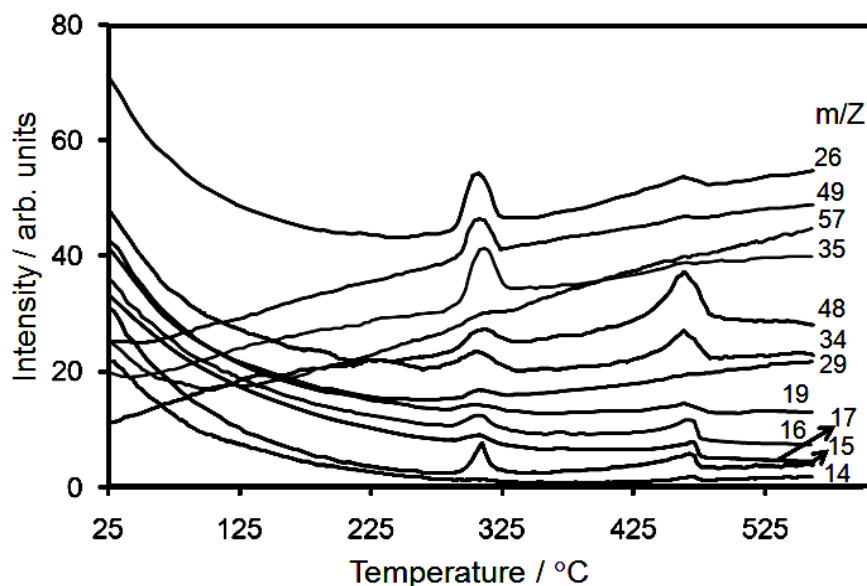


Fig.6. Mass Fragments Evolved during thermal decomposition of AP - BTEAATFB Mixture

Table 1: Probable Mass Assignments for the Evolved Species during thermal decomposition of AP – BTEATFB mixture

Mass Fragment (m/Z)	Fragment Assignment
14	N ⁺
15	CH ₃
16	NH ₂
17	NH ₃
19	H ₃ O ⁺
26	CH≡CH
29	CH ₃ CH ₂ ⁺
35	Cl ⁺
48	H ₂ NO ₂ / H ₄ N ₂ O
49	BF ₂
57	C ₄ H ₉

The probable pathways of thermal decomposition of BTEATFB have been discussed by Prasad et al [5]. It is a well accepted fact that the quaternary ammonium compounds of the type R₄N⁺BF₄⁻ decompose thermally to yield an amine and the corresponding alkyl halide [1, 6 -14]. The proof for the occurrence of Hofmann elimination in the thermal decomposition of AP – BTEATFB mixture is provided by the observation of mass fragment corresponding to m/Z=26 (acetylene), an alkene. The liberation of acetylene (m/Z=26) was observed in the thermal decomposition of BTEATFB as well as Tetraethyl ammonium tetrafluoroborate (TEATFB) [13, 15]. The triethylamine, which is most likely formed as an intermediate, being basic in nature and boils at 88.8°C, can interact with the HClO₄ formed during thermal decomposition of NH₄ClO₄ present in the mixture and lead to the formation of triethylamine per chlorate that undergoes subsequent decomposition. Also, there is a probability of forming an intermediate triethylamine tetrafluoroborate, when the triethylamine interacts with the tetrafluoroborate anion, which has a melting point of 104.3°C and decomposes at about 286.7°C [16].

The appearance of a molecular fragment corresponding to m/Z=49 is indicative of the formation of BF₂. A similar observation was made in the study of thermal decomposition of NH₄ClO₄ – (CH₃)₄NBF₄ mixture [17] and thermal decomposition of (C₄H₉)₄NBF₄ [18]. Interaction between the products of decomposition of BTEATFB, namely, NH₃, H₂O, C₂H₂, C₂H₄, CH₂NH₂, C₂HN, CH₃CH₂N⁺H, CH₂N⁺HC₂H₅, and C₇H₇ [15]; and that of NH₄ClO₄ (NH₃ and HClO₄ – rate controlling step) [19] can lead to multi-step intermediate processes. Thus, we notice multiple parallel processes taking place that contribute to the overall reduction in the energy level of the mixed system under present study.

CONCLUSIONS

The DTA curve of AP – BTEATFB mixture is indicative of having no influence on the first-stage decomposition of AP, while the second-stage decomposition is slightly inhibited as evident from the peak heights and areas under the peaks. The triethyl- amine formed as an intermediate during the decomposition

of BTEATFB, interacts with the perchloric acid formed during the decomposition of NH_4ClO_4 , forming an intermediate trialkyl amine per chlorate which undergoes further decomposition leading to the final decomposition products. Multiple parallel reactions do occur between the products of decomposition of BTEATFB and AP.

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