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Effect of Tetra-n-butyl Ammonium Tetrafluoroborate on Thermal Decomposition of Ammonium Perchlorate

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ABSTRACT

Effect of tetra – n- butyl ammonium tetrafluoroborate on thermal decomposition of ammonium perchlorate is studied. Simultaneous thermo-analytical techniques of TG-DTG-DTA system coupled to Blazers Mass Spectrometer are employed in this study. Evidence for the liberation of tri-butyl amine, butyl fluoride, and boron trifluoride as major decomposition products is provided through Mass Spectral data. The presence of TBATFB brings down the overall enthalpy of AP decomposition, indicating its suppressive role.

Keywords: Ammonium, perchlorate, tetra butyl, tetrafluoroborate, thermo-analytical, Decomposition.

INTRODUCTION

Direct pyrolysis mass spectrometric investigation of polypyrole films doped with tetrabytylammonium tetrafluoroborate (TBATFB) was carried out by Evren Aslan Gürel et al [1]. NMR studies on TBATFB by Szafranska et al [2] suggest that the large cation is rotationally disordered in the high temperature phase. In the case of tetra butyl cation, at (—) 3°C, branch disorder and methyl disorder were observed; while for the anion, rotational disorder was noticed in the temperature range of (—) 3°C to 60°C. For the tetra butyl cation, rotational, branched and methyl disorders were noticed; and for the anion (BF_4) only rotational disorder was observed. Same trend was observed in the temperature regime of 60°C to 164°C as well [3].
The overall rotational correlation times of symmetric tetraalkylammonium ions, R_4N^+ (R= ethyl, n-propyl, n-butyl, and n-pentyl), in various solvents were determined by the measurements of the ^{13}C NMR spin-lattice relaxation times and the nuclear Overhauser enhancement factors of each α – carbon, considering the contribution of the internal rotation around the N—C bond [4]. Tetraalkylammonium tetrafluoroborates are the commonly employed supporting electrolytes in the electrosynthesis of Polysilane [5]. The focus in the present study is on studying the effect of tetra-n-butyl ammonium tetrafluoroborate (TBATFB) on thermal decomposition of ammonium per chlorate (AP), an extensively used oxidizer in composite solid rocket propellants.

MATERIALS AND METHODS

Ammonium per chlorate used in this study is from the Ammonium Per chlorate Experimental Plant (APEP), Alwaye, Indian Space Research Organization (ISRO), Department of Space (DOS), Government of India. Tetra-n-butyl ammonium tetrafluoroborate (TBATFB) 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 $10^{\circ}C.min^{-1}$, 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 TG-DTG curves of pure tetra-n-butyl ammonium tetrafluoroborate (TBATFB) are shown in fig.1. The temperatures of onset of decomposition, peak rate of decomposition, and end set of decomposition are 348.4°C, 392.9°C, and 417.3°C respectively.

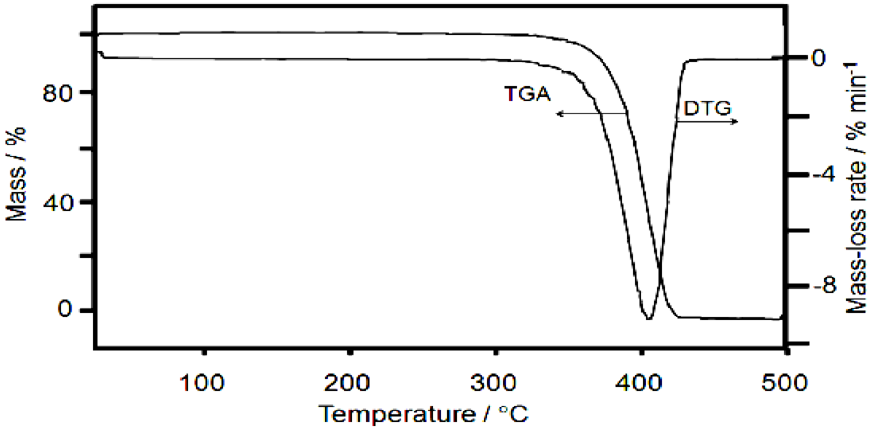

Fig.1. TG – DTG Curves of Thermal Decomposition of $(C_4H_9)_4NBF_4$

The TG-DTG curves of pure ammonium per chlorate are shown in fig.2. The decomposition occurs in two distinct stages. The low-temperature decomposition (LTD) peak is at about 310°C, and the subsequent high-temperature decomposition (HTD) occurs at about 440°C.

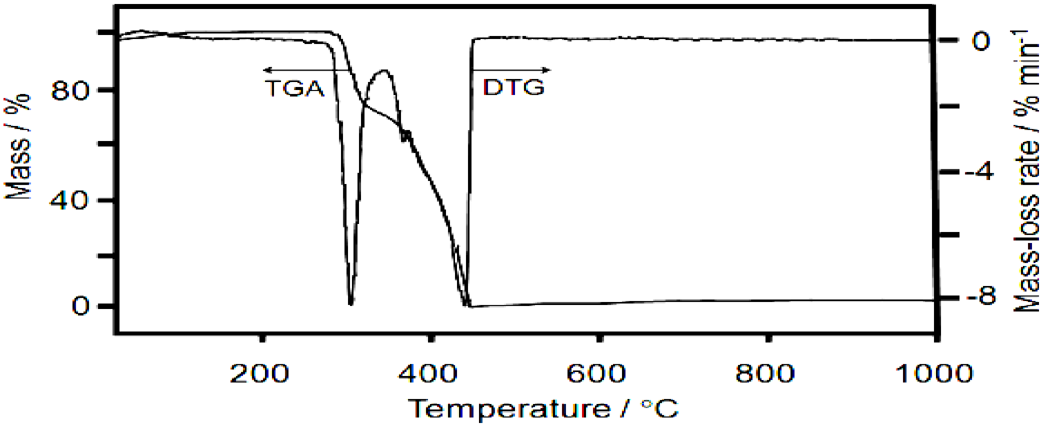

Fig.2. TG – DTG Curves of Thermal Decomposition of NH_4ClO_4

From fig.1 and fig.2, it can be seen that, the thermal decomposition of TBATFB falls in the temperature interval corresponding to the second-stage decomposition of AP. This suggests that there is a possibility for TBATFB to influence the second-stage decomposition of AP when their mixtures are considered.

Fig.3 shows the DSC curve of pure ammonium per chlorate (AP). The crystallographic phase-transition from ortho-rhombic to cubic phase occurs at 250°C with an enthalpy of (—) 203.59 J.g^{-1}. The low temperature decomposition (LTD) peak occurs at 295.32°C with an enthalpy of 864.41 J.g^{-1}. The high temperature decomposition (HTD) peak occurs at 447.66°C with an enthalpy of 1418.39 J.g^{-1}. The net enthalpy of AP is 2079.21 J.g^{-1}.

Fig.4 shows the DSC curve of AP in presence of 0.5 percent of tetra-n-butyl ammonium tetrafluoroborate (TBATFB) by weight of AP. In the case of the mixture, the phase transition occurs at 237.44°C with an enthalpy of —103.31J.g^{-1}; the first-exothermic peak at 294.89°C with an enthalpy of 413.94 J.g^{-1}; and the second major exothermic peak at 435.01°C with an enthalpy of 365.54J.g^{-1}. In the intermediary temperature regime, there is an oscillatory decomposition with peaks at 360.84°C and 417.63°C, and the corresponding enthalpy values are 116.03J.g $^{-1}$ and 644.60J.g^{-1}respectively. The net enthalpy of AP – TBATFB mixture is 1436.80 J.g^{-1}. Comparing enthalpies of pure AP decomposition (2079.2 J.g^{-1}) and that of TBATFB- AP mixture (1436.80 J.g $^{-1}$), there is a substantial drop of about 642.4 J.g^{-1}. In other words TBATFB acts as a suppressant.

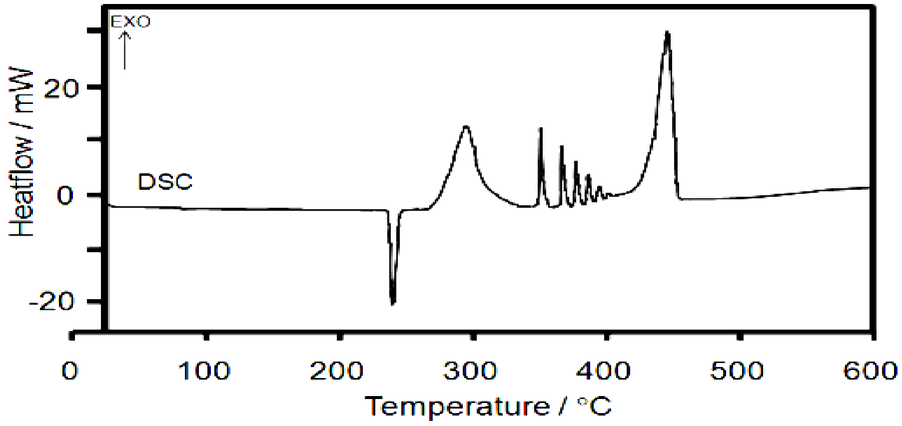

Fig.3. DSC Curve of pure NH_4ClO_4

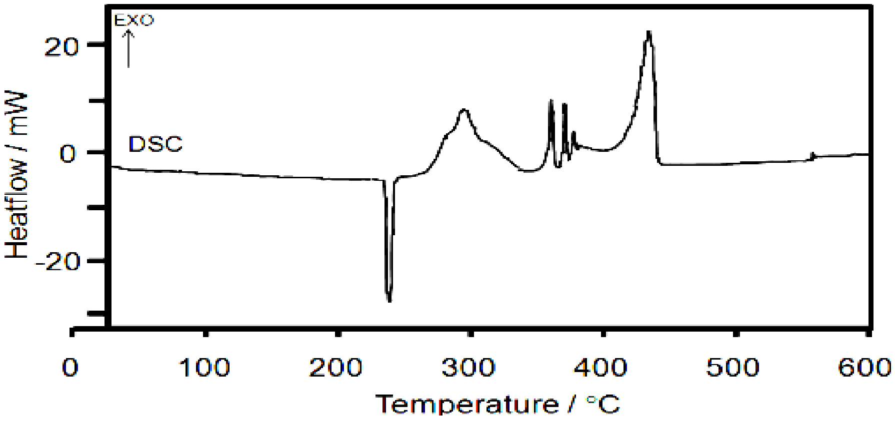

Fig.4. DSC Curve of NH_4ClO_4 -$(C_4H_9)_4NBF_4$ Mixture

The simultaneous TG-DTG-DTA of AP-TBATFB mixture containing 0.50 percent of TBATFB by weight of AP is presented in Fig.5. The endothermic peak at 248.59°C is due to the crystallographic phase-transition of AP from orthorhombic to cubic phase followed by exothermic peaks at 300.17°C, 366.10°C, 375.93°C, and 393.69°C.

TBATFB melts in the temperature range of 159 – 161°C which means it is in the molten phase before the crystallographic phase-transition of AP occurs. Since, in the case of trabutyl cation rotational, branch and methyl disorders were noticed in the temperature range (—3°C) to 60°C; and tetrafluoroborate anion undergo only rotation disorder was observed in the temperature range of 60°C – 164°C [3]. Since, the intermediate amine (tri-butyl amine) formed boils at 216°C, and can interact with the perchloric acid formed during the decomposition of AP, thereby forming an amine per chlorate that subsequently undergoes decomposition. Thus, it is seen that, the reaction system is in a dynamic situation just before the phase-transition of AP. The shift in the phase-transition temperature of AP is attributed to the synergistic effect, and there is a possibility of diffusion of molten TBATFB at the phase-transition temperature of AP. The exothermic peak at 300.17°C is a major one while the second major decomposition peak is lowered, an indication of the significant role played by TBATFB in controlling the overall decomposition of AP.

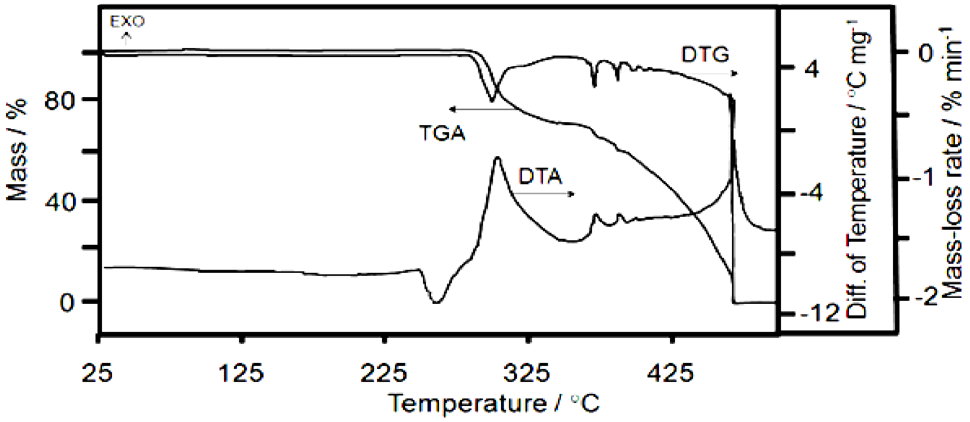

Fig.5. Simultaneous TG – DTG – DTA of NH_4ClO_4 - $(C_4H_9)_4NBF_4$ Mixture

The mass fragments evolution curves as a function of time were recorded and are shown in figs. 6 to 14 in the order of m/Z ratio.

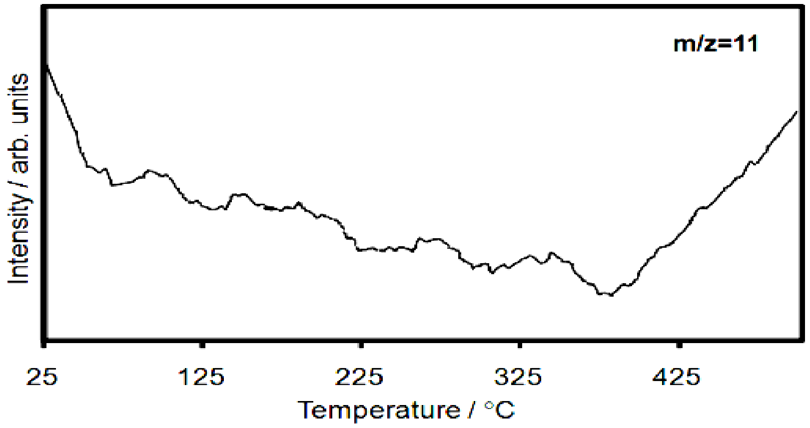

Fig.6. Evolution of Mass Fragment (m/z) =11 during thermal decomposition of AP – TBATFB Mixture

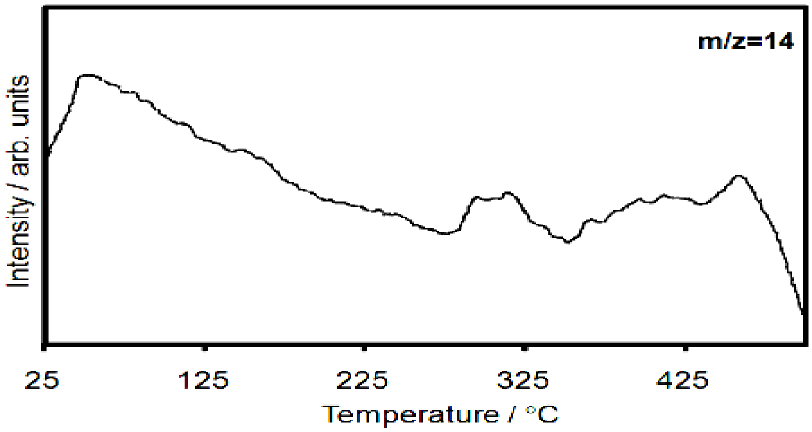

Fig.7. Evolution of Mass Fragment (m/z) =14 during thermal decomposition of AP – TBATFB Mixture

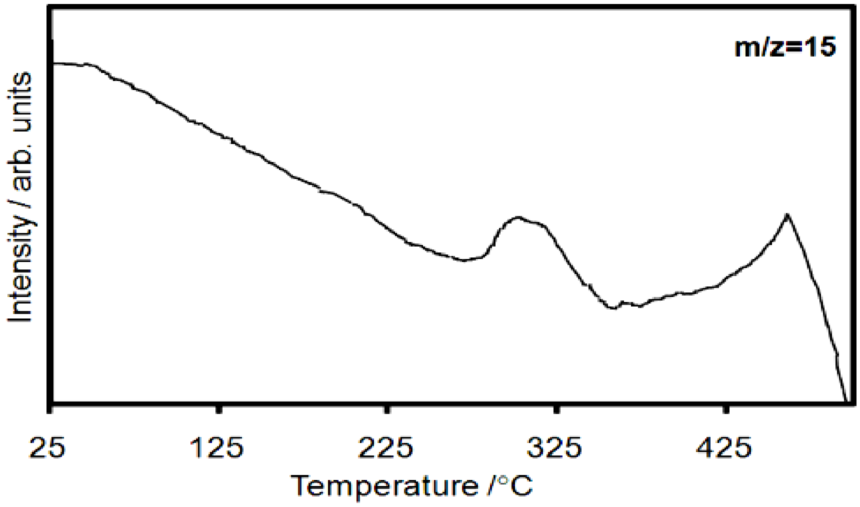

Fig.8. Evolution of Mass Fragment (m/z) =15 during thermal decomposition of AP – TBATFB Mixture

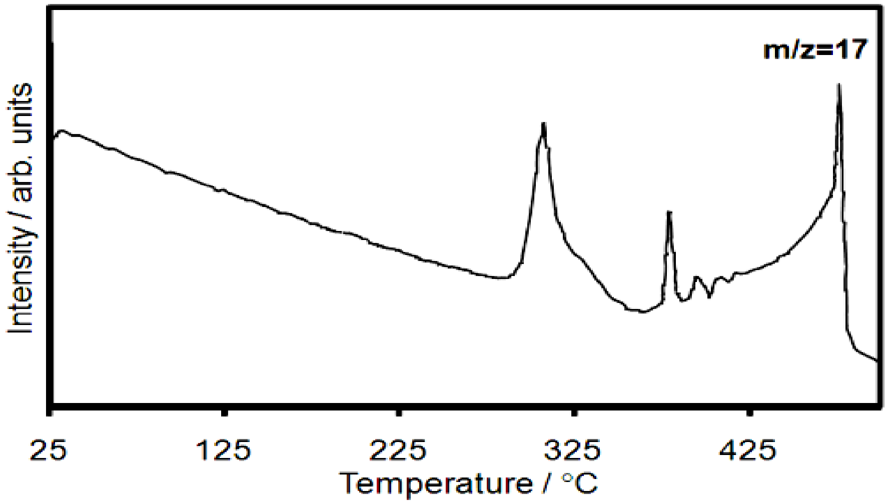

Fig.9. Evolution of Mass Fragment (m/z) =17 during thermal decomposition of AP – TBATFB Mixture

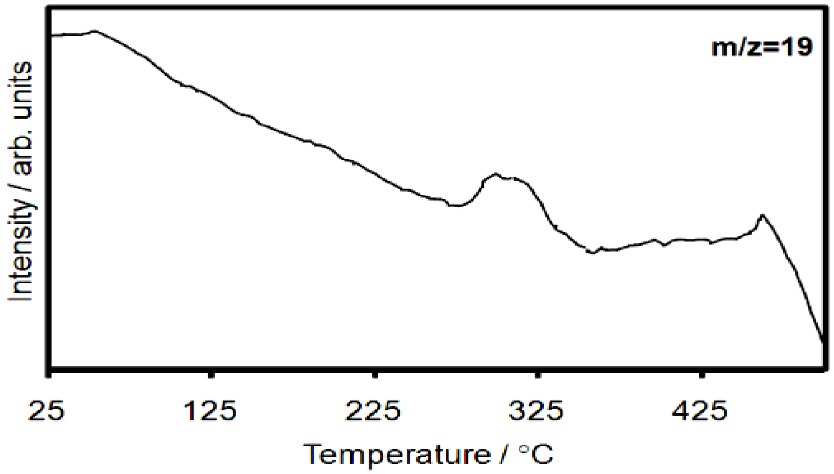

Fig.10. Evolution of Mass Fragment (m/z) =19 during thermal decomposition of AP – TBATFB Mixture

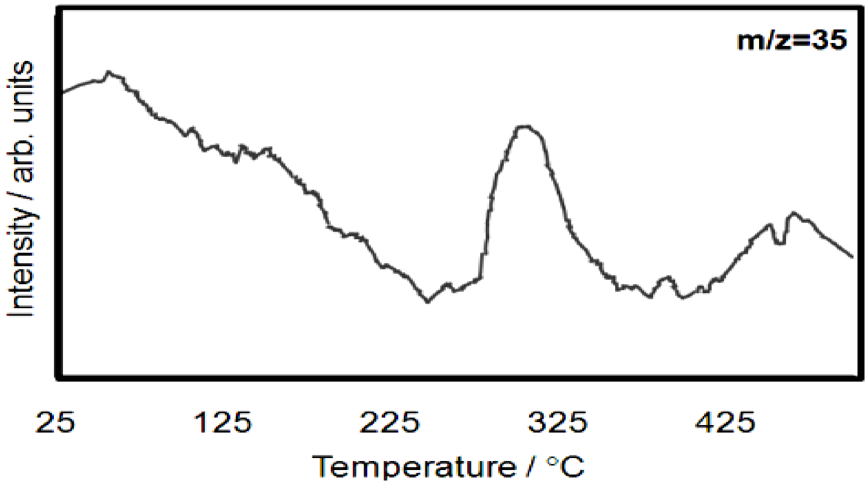

Fig.11. Evolution of Mass Fragment (m/z) =35 during thermal decomposition of AP – TBATFB Mixture

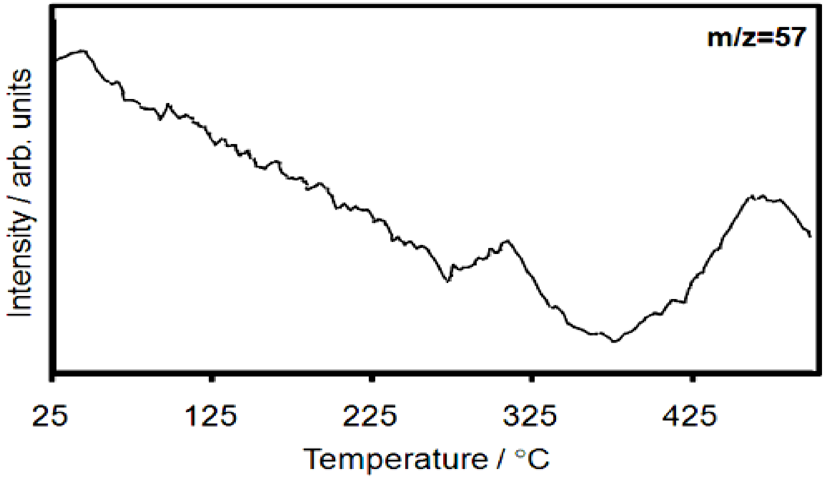

Fig.12. Evolution of Mass Fragment (m/z) =57 during thermal decomposition of AP – TBATFB Mixture

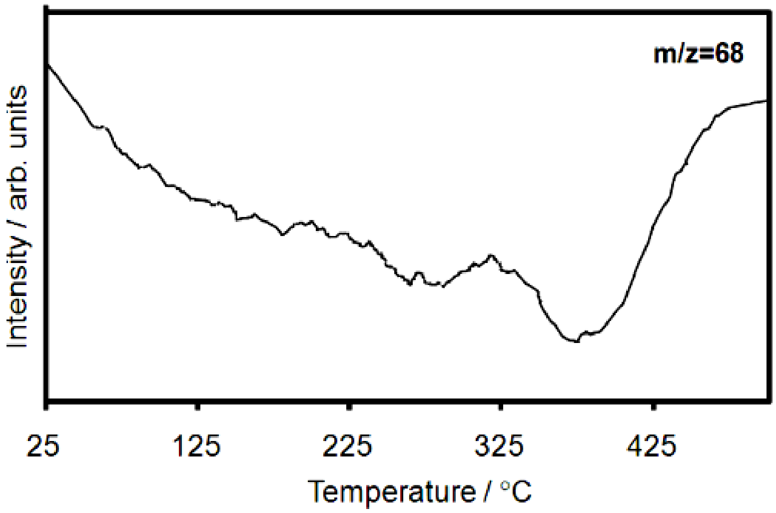

Fig.13. Evolution of Mass Fragment (m/z) =68 during thermal decomposition of AP – TBATFB Mixture

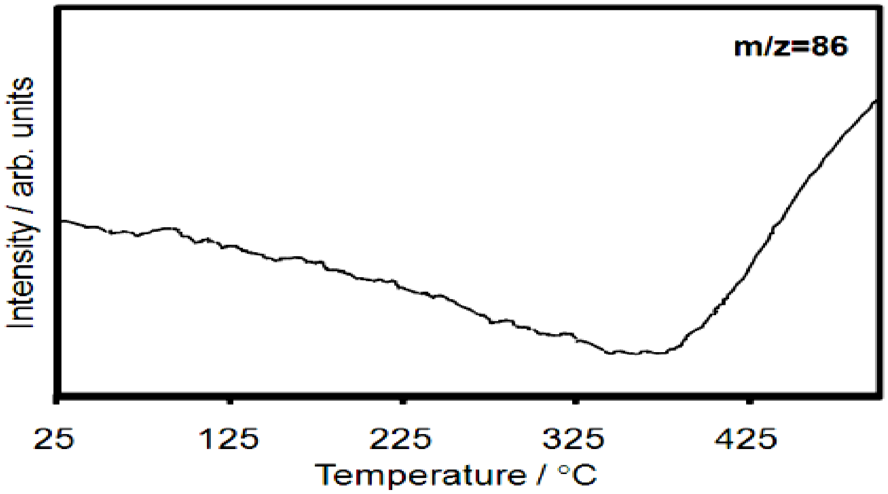

Fig.14. Evolution of Mass Fragment (m/z) =86 during thermal decomposition of AP – TBATFB Mixture

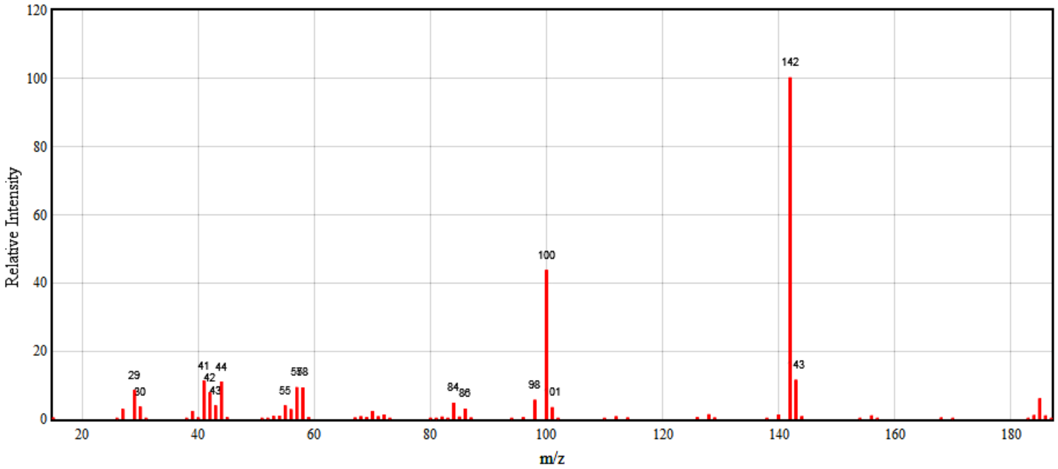

Fig.15. Mass Spectrum of Tri-butyl Amine [6]

The mass spectrum of Tetra-n-butyl ammonium Iodide is shown in Fig. 16.

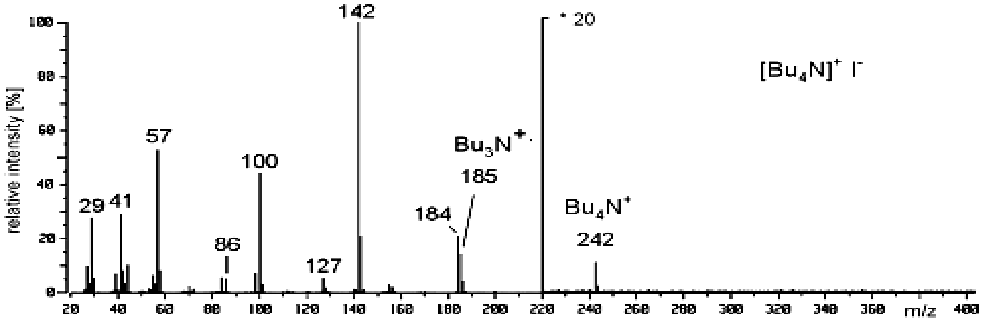

Fig.16. Mass Spectrum of Decomposition of Tetra-butyl ammonium Iodide

Here, in this case as well, we can see the peaks corresponding to m/z=57 and 86 [9]. In the understanding of the role of tributylamine bromide in the formation of structure of high –silica Zeolite TsVK-1, formation of molecular fragments of (C**4**H9)$_3$N and $C_4H_9^+$ were observed [10].

The decomposition path of NH_4BF_4 is well represented in terms of the equation

$$NH_4BF_4 = NH_3 + HF + BF_3$$

Tetra-n-butyl ammonium tetrafluoroborate being analogous to NH_4BF_4 can be expected to decompose in a similar fashion. Accordingly, the corresponding decomposition path can be represented as

$$N\,(C_4H_9)_4BF_4 = N\,(C_4H_9)_3 + (C_4H_9)\,F + BF_3$$

This indicates that tri-butyl amine is formed as one of the decomposition products. The mass spectrum of TBATFB is shown in Fig.15. [6], and the peak at m/Z=185 confirms the formation of tri-butyl amine. Similar observations are made in the pyrolysis – GC experiments on tetra-n-butyl ammonium hexafluorophosphate [7].

The evolution of alkyl halide together with boron tri-fluoride has been reported in the case of $R_4N^+BX_4^-$, where n=C_4H_9 and X= Cl, Br, $PhBCl_2$ [8].The mass fragment corresponding to m/Z=68 (Fig.16) confirms the formation of BF_3. The assignment of all evolved mass fragments is summarized in table-1.

Table 1: Evolved Mass Fragments and their Assignment

m / z Ratio	**Probable Fragment Assignment**
11	B^+
14	N^+
15	CH_3
17	NH_3
19	H_3O^+
35	Cl^+
49	BF_2
57	$C_4H_9^+$
68	BF_3
86	$CH_3(CH_2)_4CH_3$

CONCLUSIONS

The addition of 0.50 weight percent of TBATFB to AP reduces the enthalpy of the AP – TBATFB system, indicating its suppressive role in the thermal decomposition of such a mixture. Formation of tri-butyl amine, alkyl fluoride, and boron tri-fluoride as products of thermal decomposition of AP – TBATFB system is established.

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