

A simultaneous TG-DTG-DSC-quadrupole mass spectrometric study

Thermal decomposition of benzyl-triethyl-ammonium tetrafluoroborate

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Abstract Mechanistic aspects of the thermal decomposition of benzyl-triethyl-ammonium tetrafluoroborate (BTEATFB) employing simultaneous TG-DSC coupled with a quadrupole mass spectrometer are considered in this work. The experiments were conducted in an inert atmosphere of helium. The decomposition of BTEATFB proceeds through several competing mechanisms. While nucleophilic substitution reaction occurs through the formation of a tertiary amine and plays an important role in the initial stages of the decomposition, and the probability of Hoffman elimination also exists.

Keywords Benzyl-triethyl · Ammonium · Tetrafluoroborate · Decomposition · Hoffman elimination · Nucleophilic substitution

Introduction

Among many other quaternary ammonium compounds: halides, hydroxides, and tetrafluoroborates of benzyl-triethyl-ammonium and benzyl-tri-*n*-butyl ammonium cations have been extensively used as phase-transfer catalysts [1–7]. Quaternary ammonium compounds such as choline are important in medical research [8]. Inclusion in the synthesis mixture of various quaternary salts, particularly bulky alkyl ammonium cations, has introduced a new structure-directing parameter into the synthesis mechanism [9], so that new type of zeolites have been patented [10–12] to widen up the scope of zeolite chemistry and applications. Toxicological evaluation was performed on human colon carcinoma cell line (CaCo-2) of ionic liquids based on imidazolium, guanidinium, ammonium, phosphonium, pyridinium, and pyrrolidinium cations [13].

The present work envisages studying the thermal decomposition of benzyl-tri-ethyl ammonium tetrafluoroborate (BTEATFB) in an inert atmosphere of Helium, and has not been considered hitherto. This is a prelude to using this compound as an additive for the modification of the thermal decomposition of ammonium perchlorate, a widely used oxidizer in composite solid rocket propellant technology even today.

Experimental

The pure compound BTEATFB was procured from M/s. Aldrich Chemicals. The thermal decomposition was studied using simultaneous TG-DSC coupled with Quadrupole Mass Spectrometer (QMS). Measurements were carried out at Netzsch's laboratory, Germany, employing STA/QMS 409-403 systems.

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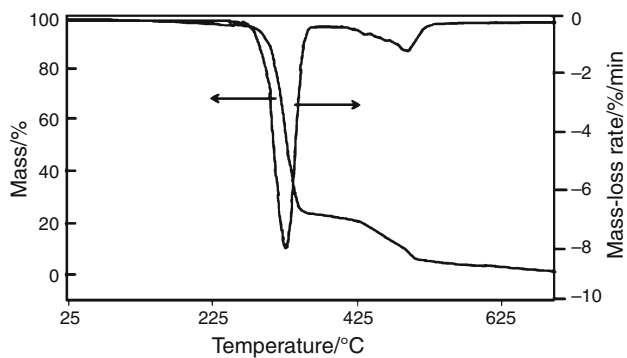


Fig. 1 TG curve of benzyl-triethyl-ammonium tetrafluoroborate. The derivative curve (mass-loss rate) is also plotted

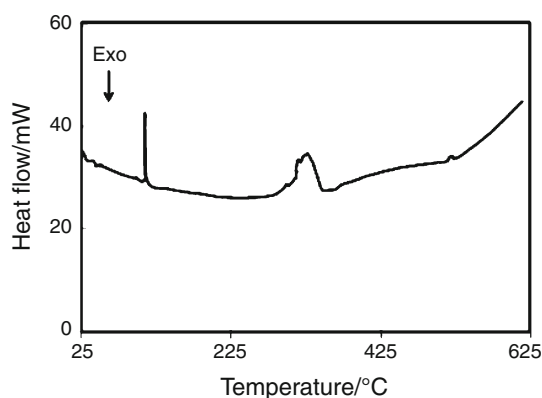


Fig. 2 DSC curve of benzyl-triethyl-ammonium tetrafluoroborate

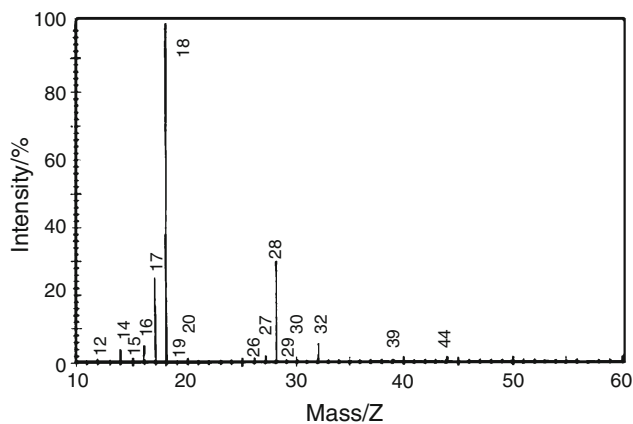


Fig. 3 Mass spectrum of evolved gases at a sample temperature of 324 °C

A sample heating rate of 5 °C min^{-1} , an inert atmosphere of Helium, and a gas flow rate of 75 mL min^{-1} were employed in this study. The QMS data acquisition was carried out in the scan mode, in the mass range of 10–200 amu.

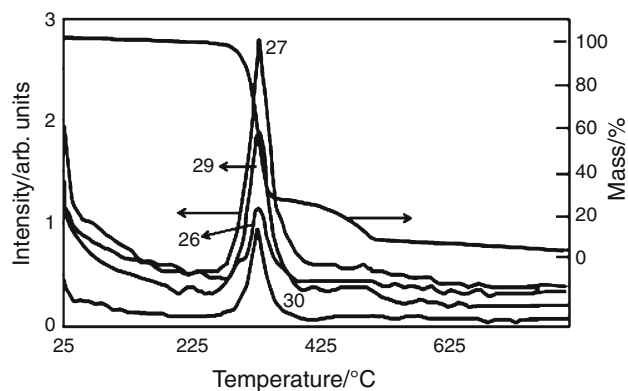


Fig. 4 Intensity of mass fragments with $m/z = 26, 27, 29,$ and 30 of evolved gases as a function of temperature

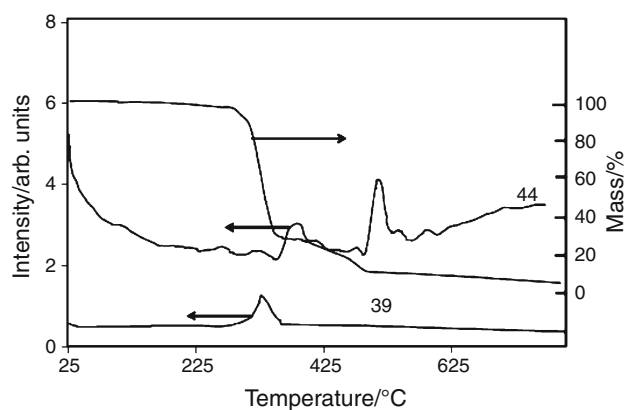


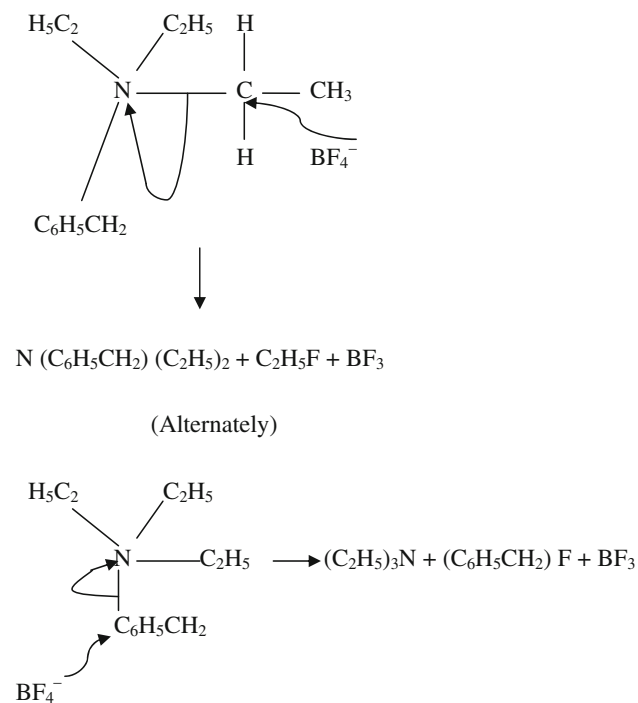
Fig. 5 Intensity of mass fragments with $m/z = 39$ and 44 of evolved gases as a function of temperature

Table 1 Assignment for the evolved mass fragments during thermal decomposition of benzyl-triethyl-ammonium tetrafluoroborate

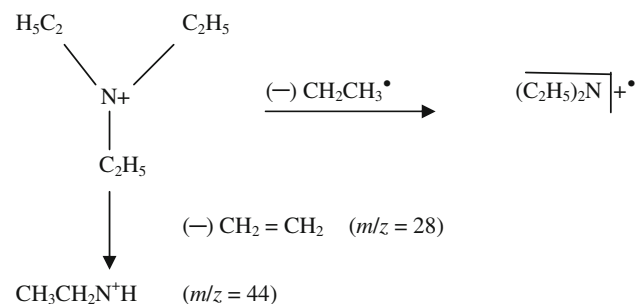
m/z value	Peak assignment
14	N^+
17	NH_3
18	H_2O
26	$\text{CH}\equiv\text{CH}$
28	$\text{CH}_2=\text{CH}_2$
30	$\text{CH}_2=\text{NH}_2$
39	C_2HN
44	$\text{CH}_3\text{CH}_2\text{N}^+\text{H}$
58	$\text{CH}_2=\text{NH}^+\text{C}_2\text{H}_5$
65	(C_7H_7) tropylium

Results and discussion

The TG-DTG curves of BTEATFB are shown in Fig. 1. This compound decomposes in two distinct steps with a mass loss of 78.5 and 20.3 % (as observed from TG).



Scheme 1 Decomposition pathways of benzyl-triethyl-ammonium tetrafluoroborate



Scheme 2 Degradation pathway of triethylamine

Maximum mass-loss rates were observed at 325 and 489 °C.

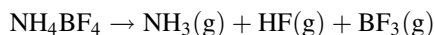
Figure 2 shows the DSC curve of BTEATFB. The enthalpy of fusion was found to be 172 J g^{-1} (DSC). A second endothermic (broad double peak) was observed between 280 and 350 °C (with peak temperature at 325 °C). This peak is caused by the decomposition of the compound BTEATFB. The endothermic decomposition enthalpy is $1,222 \text{ J g}^{-1}$. In the DSC curve, endothermic peaks occur at 109.4 and 325 °C, corresponding to fusion and decomposition processes of the compound BTEATFB.

Figure 3 shows the intensities of mass fragments formed in the quadrupole mass spectrometer as the sample undergoes thermal decomposition at 324 °C. Significant intensities were observed of mass fragments with $m/z = 14, 16, 17, 18, 28,$ and 32 . These peaks are due to the

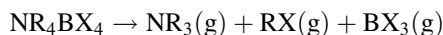
formation of $\text{H}_2\text{O}, \text{N}_2, \text{O}_2$ and C_2H_6 as decomposition products.

The intensities of mass fragments with $m/z = 26, 27, 29,$ and 30 as a function of sample temperature are shown in Fig. 4 along with TG-curve; those corresponding to $m/z = 39$ and 44 are shown in Fig. 5, and those corresponding to $m/z = 58, 63,$ and 65 are shown in Fig. 6. The significant intense peaks and their assignment are shown in Table 1.

The thermal decomposition of complex fluoro anions at temperatures of interest is characterized by the formation of gaseous components such as $\text{BF}_3, \text{NH}_3,$ and HF [14]. For example, the decomposition of NH_4BF_4 is represented by the reaction



It is well-accepted that the quaternary ammonium compounds of the type $\text{R}_4\text{N}^+\text{X}^-$ decompose thermally to yield an amine (R_3N) and the corresponding alkyl compound [15].



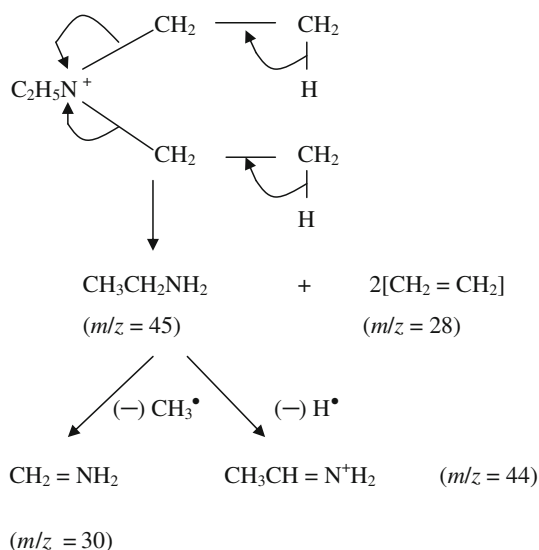
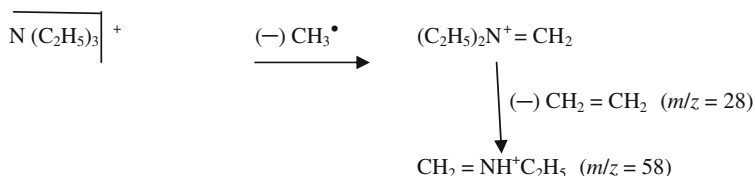
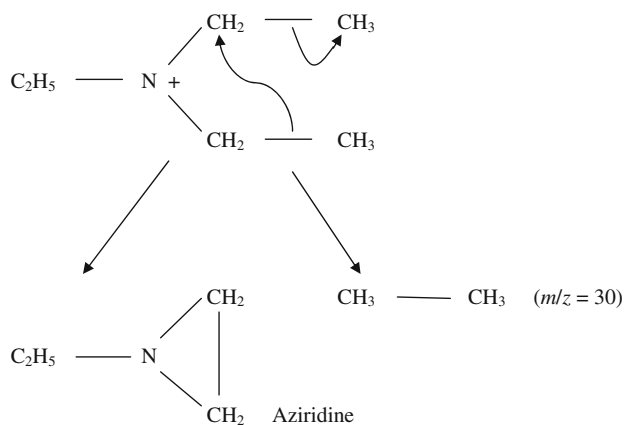
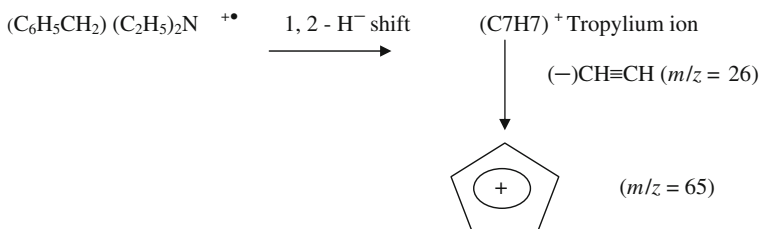
As BTEATFB is analogous to tetra alkyl ammonium compounds, its thermal decomposition can be predicted to follow similar pattern as for NH_4BF_4 or for NR_4BX_4 .

The thermal decomposition of benzyl quaternary-ammonium compounds proceeds through several competing reaction mechanisms. The products formed depend on the temperature of pyrolysis and the bulkiness of the alkyl substituent about the quaternary ammonium center. The major components are mainly those from a simple nucleophilic substitution reaction between the fluoroborate anion and the bulky quaternary ammonium cation. The reaction path and the possible products are shown in Scheme 1.

The formation of an intermediate amine in the thermal decomposition of quaternary ammonium compounds was reported by Haskins and Mitchell [8], Udupa [16], Nambiar et al. [17], and Prasad and Krishnamurthy [18]. Similar observations were made in the thermal decomposition of tetra alkyl ammonium thiomolybdates [19] and thiotungstates [20].

Due to the bulkiness of the benzyl group, the possibility of formation of its corresponding amine is doubtful. The triethyl amine formed according to Scheme 1 boils at 88.8 °C, and hence under experimental conditions (at higher temperatures), being unstable, undergoes further fragmentation according to Scheme 2.

Further, the C–C bond next to the heteroatom (nitrogen) is frequently cleaved, leaving the charge on the fragment containing the heteroatom (nitrogen) whose non-bonding electrons provide resonance stabilization. Accordingly, the triethyl amine formed as per Scheme 1 can yield

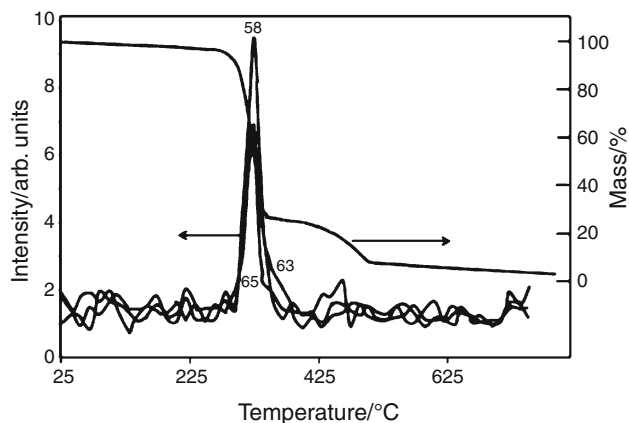
Scheme 3 Cleavage at C–C bond next to heteroatom**Scheme 4** Alternate path for triethylamine decomposition**Scheme 5** Stable cyclic aziridine formation**Scheme 6** Formation of Tropylium ion

Alternately, the ionized triethyl amine, with the elimination of two molecules of ethylene (Scheme 4) can yield ethylamine which boils at 16.6 °C can further yield fragments $\text{CH}_2=\text{NH}_2$ ($m/z = 30$) and $\text{CH}_3\text{CH}=\text{N}^+\text{H}_2$ ($m/z = 44$).

A peak corresponding to $m/z = 30$ is good though not conclusive evidence for a straight chain primary amine.

Yet another possibility for intermediary amine so formed according to Scheme 1 to undergo cyclization [18] as per Scheme 5 which explains for the appearance of molecular fragment corresponding to $m/z = 30$.

The most studied reaction of quaternary ammonium salts is the Hofmann degradation [21] which would give rise to benzyldimethylamine, hydrogen fluoride, and the corresponding alkene (Scheme 2). The evidence for the Hofmann elimination depends on the detection of the alkene. The appearance of the mass fragment corresponding to $m/z = 28$ is the evidence to conclude that the Hofmann elimination is taking place (Fig. 2). Further, in alkyl

**Fig. 6** Intensity of mass fragments with $m/z = 58$, 63, and 65 of evolved gases as a function of temperature

substituted aromatic compounds, cleavage is possible at the bond β to the ring, giving the resonance stabilized benzyl ion, or more likely, the tropylium ion [22]. These are again relatively high temperature processes taking place.

The appearance of a peak corresponding to $m/z = 26$ and 65 (Fig. 6) supports the above hypothesis.

Conclusions

In the thermal decomposition of BTEATFB, while at low temperatures simple displacement reactions appear to be predominant. At higher temperatures, more complex multi-center reactions are the probability. Observation of a strong peak corresponding to $m/z = 28$ is confirmative of the existence of Hofmann elimination process.

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