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Thermal Decomposition of Tetrabutylammonium – tetrafluoroborate, hexafluorophosphate and perchlorate

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ABSTRACT

As a prelude to their use as additives for the modification of thermal decomposition of ammonium per chlorate (AP), a solid rocket propellant oxidizer; thermal decomposition of tetra-n-butyl ammonium hexafluorophosphate (TBAHFP), tetra-n-butyl ammonium tetrafluoroborate (TBATFB), and tetra-n-butyl ammonium per chlorate (TBAP) was studied at a sample heating of 10^{o}*c.min─1, in an inert gaseous atmosphere of pure nitrogen, in a DuPont – 990 and DuPont-2000 thermal analysis systems. Thermal stabilities of these compounds were found to be in the order of TBAP < TBAHFP <TBATFB. Formation of tributylamine is the primary decomposition product together with HF, other Lewis acid formed include -* BF_3 *or* PF_5 *depending upon the compound under consideration.*

Keywords: Tetra-n-butyl, ammonium, hexafluorophosphate, tetrafluoroborate, per chlorate, Lewis acid, thermal decomposition.

INTRODUCTION

In the controllable solid rocket motor combustion, premature reignition of the propellant has been attributed to the first-exotherm of ammonium per chlorate (AP), and this has been avoided by the addition of 1.5 percent by weight of ammonium hexafluorophosphate [1]. Tetraalkyl substituted ammonium compounds have not been exploited so far for this purpose and hence this study. Tetraalkylammonium per chlorates (R_4NClO_4), tetraalkylammonium tetrafluoroborates (R_4NBF_4), tetraalkylammonium hexafluorophosphates (R_4NPF_6) and the like are commonly employed as supporting electrolytes. Coker et al [2] reported the fusion properties of some ionic quaternary ammonium compounds that include: tetrabutylammonium – chloride, bromide, iodide, nitrate, tetrafluoroborate, hexafluorophosphate and tetraphenylborate. In a study of the factors affecting the ionization efficiency of quaternary ammonium compounds in electrospray/ion spray mass spectrometry[3], tetraalkylammonium salts gave the best sensitivity with no influence of sample-ion shape or counter ion. It appears that the large sizes of R_4N^+ ions, their low charge densities and the high relative permittivity of poly carbonate render these ions to be free, unassociated and almost unsolvated in this medium [4].

Formation of oxygen-free polysilanes is facilitated by the electro-reduction of dichloro-dimethyl-silane (DNDCS) under galvanostatic mode in the presence of triphenylchlorosilane (Ph_3SiCl) on a platinum cathode using tributylammonium tetrafluoroborate (TBATFB) as electrolyte [5, 6]. Thermal analysis and spectroscopic characteristics of tetrabutylammonium tetrachloroferrate (III) was studied by Wyrzykowski et al [7]. In the electrochemical reduction of 2-nitroimidazole in aqueous mixed medium tetrabutylammonium perchlorate has been employed [8]. The saturation of the electrode porosity limits the usable voltage of a super capacitor system and consequently the deliverable energy and power. A study on electric double-layer capacitors in organic electrolytes based on symmetrical bulky tetraalkylammonium cations, using activated carbons with adjusted pore size distribution was reported by Mysyk et al [9]. The catalytic decomposition of free chlorine was observed with the tertiary-ammonium-based anion-exchange resins [10]. In the present work, we report the thermal decomposition of tetrabutylammonium – tetrafluoroborate, hexafluorophosphate, and per chlorates as a prelude to using them as additives for the modification of thermal decomposition of ammonium per chlorate, an oxidizer, widely used in rocket propulsion.

MATERIALS AND METHODS

Pure compounds of tetra butyl substituted ammonium tetra – fluoroborate, hexafluorophosphate, and per chlorate were procured from M/s. Aldrich Chemicals. The, TG-DTG-DTA experiments on tetra-n-butyl ammonium hexafluorophosphate (TBAHFP) and tetra-n-butyl ammonium tetrafluoroborate (TBATFB) were carried out using DuPont-990 Thermal Analysis System, in an inert atmosphere of pure nitrogen gas at a flow rate of 100 ml. min^{-1}, and a sample heating rate of 20^{o}C.min^{-1}. In the case of TBAP, keeping in view of the sensitive nature of the compound, the TG-DTG experiments were conducted in a DuPont-2000 Thermal Analysis system at a sample heating rate of 10^{o}C.min^{-1}, in an inert atmosphere of pure nitrogen gas, at a gas flow rate of 50ml.min^{-1}, employing Pt/ Pt-13%Rh thermocouples. The melting and decomposition temperatures were followed for TBAP through a Mettler DSC system (821^{e}), at a heating rate of 10^{o}C.min^{-1}, in an inert atmosphere of pure nitrogen.

RESULTS AND DISCUSSION

The thermo gravimetric (TG) curves of tetrabutylammonium tetrfluoroborate (TBATFB), tetrabutylammonium hexafluorophosphate (TBAHFP), and tetrabutylammonium per chlorate (TBAP) are presented in figs. 1 to 3.

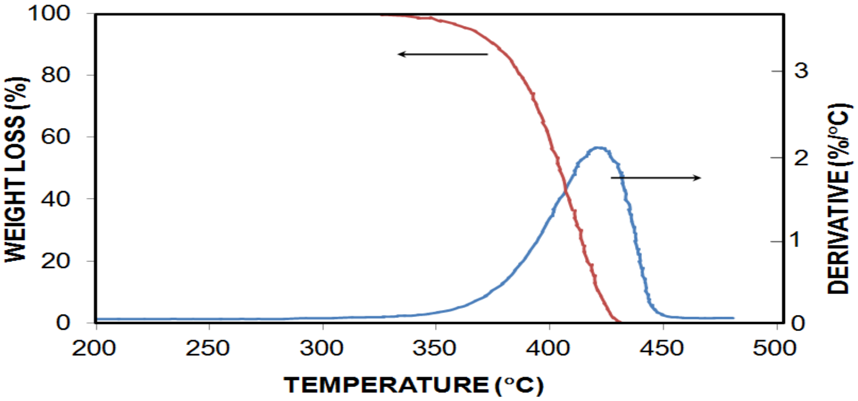

Fig.1: TG-DTG Curves of Tetra – n – butyl ammonium Tetrafluoroborate (TBATFB).

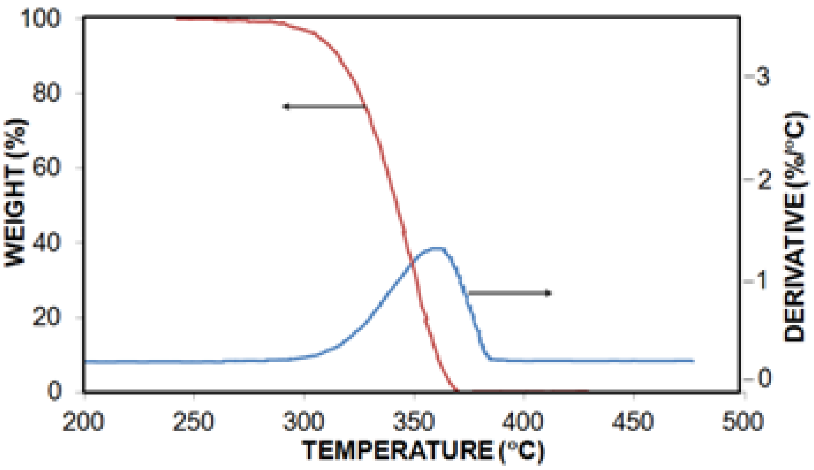

Fig.2: TG – DTG Curves of Tetra – n- butyl ammonium Hexafluorophosphate (TBAHFP).

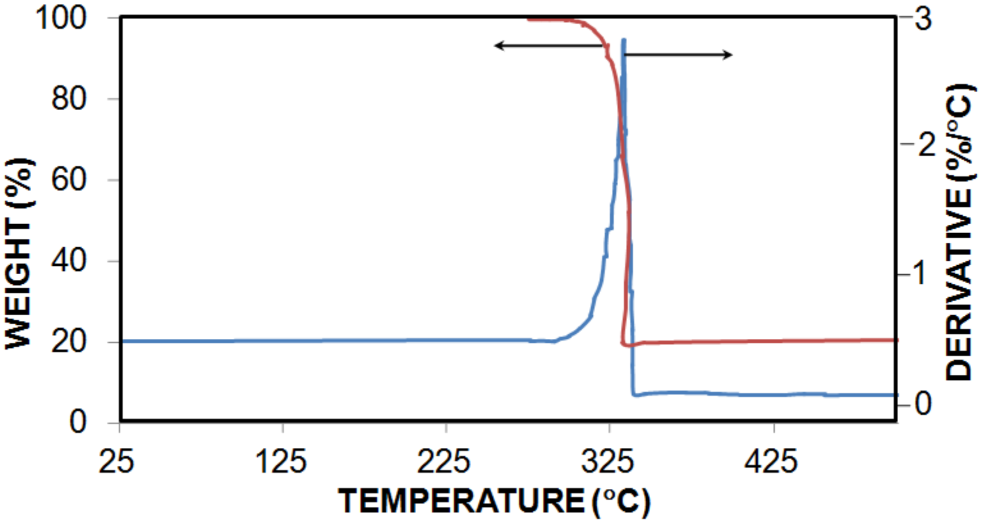

Fig.3: TG – DTG Curves of Tetra –n – butyl ammonium per chlorate (TBAP).

The onset temperatures of thermal decomposition of TBATFB, TBAHFP, and TBAP are: 320°C, 287.3°C, and 257.5°C, respectively. From this, the thermal stabilities can be said to be in the order of TBAP<TBAHFP<TBATFB. Of the three widely used non-coordinating anions (PF^{6-}, BF^{4-}, ClO^{4-}), the hexafluorophosphate ion has the least co-ordination activity. BF^{4-} owes its inertness to two factors: (i). it is symmetrical so that the negative charge is distributed equally over four fluorine atoms, (ii). It is composed of highly electronegative fluorine atoms that diminish basicity of the anion. Per chlorate ion is the least reactive oxidizer of the generalized chlorates.

The decomposition paths of ammonium compounds of NH_4PF_6, NH_4BF_4, and NH_4ClO_4 are reported to follow the paths described through equations here below [1].

$$NH_4PF_6 \longrightarrow NH_3 + HF + PF_5 \text{ (Lewis Acid)}$$

$$NH_4BF_4 \longrightarrow NH_3 + HF + BF_3 \text{ (Lewis Acid)}$$

$$NH_4ClO_4 \longrightarrow NH_3 + HClO_4$$

$$2HClO_4\text{ (s)} \rightleftarrows H_2O\text{ (s)} + ClO_3^+\text{ (s)} + ClO_4^-\text{ (s)}$$

and the ammonia is oxidized by the ClO_3^+ (s) [1]:

$$ClO_3^+ (s) + NH_3 \longrightarrow \text{Products.}$$

The tetrabutyl substituted compounds being analogous to ammonium compounds mentioned above, can be expected to follow similar decomposition paths. Accordingly, we can write the decomposition equations as follows:

$$(C_4H_9)_4NPF_6 \longrightarrow (C_4H_9)_3N + C_4H_9F + PF_5 (g)$$

$$(C_4H_9)_4NBF_4 \longrightarrow (C_4H_9)_3N + C_4H_9F + BF_3 (g)$$

$$(C_4H_9)_4NClO_4 \longrightarrow (C_4H_9)_3N + C_4H_9Cl + ClO_3$$

In all the above cases, the primary product is the tri-butyl amine. The evidence for the formation of such a triamine has been provided by the pyrolysis-GC studies on tetraalkyl-substituted ammonium hexafluorophosphates by Prasad et al [12], and supported by the decomposition studies on tetramethyl phosphonium - perchlorate, nitrate, and picrate which proceed in the similar path [13,14]; as well as NIST's Mass Spectral data on TBAHFP and TBATFB [15].

In the case of $R_4N^+BX_4^-$ (where R=Et or n-Bu, and X= Cl, Br or $PhBCl_2$), the first-stage thermal decomposition of the haloborates involves the loss of one mole of an alkyl halide with the formation of a 1:1 complex. Further stages of decomposition of haloborates lead to the evolution of further quantities of alkyl halides together with the corresponding boron trihalides [16]. Thus, the above proposed equations for the thermal decomposition of $(C_4H_9)_4NPF_6$, $(C_4H_9)_4NBF_4$, and $(C_4H_9)_4NClO_4$ are justified.The DTA curves for TBAHFP, TBAP and TBATFB are shown in figs. 4 to 6.

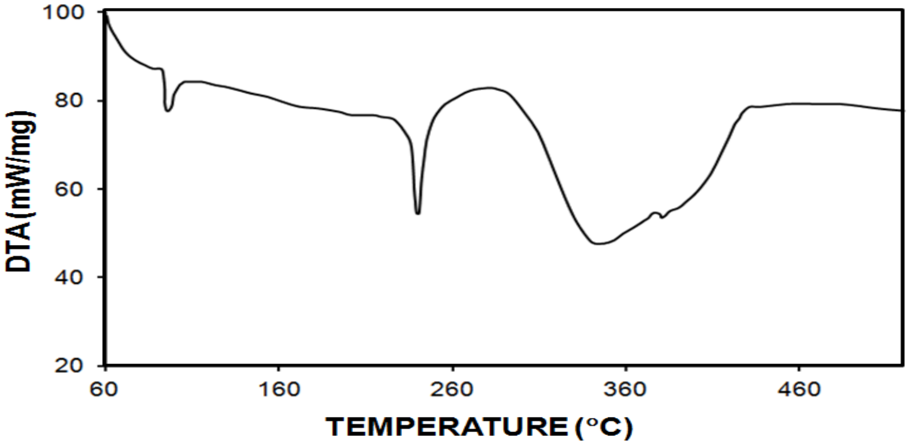

Fig.4: DTA Curve of tetra – n – butyl ammonium Hexafluorophosphate (TBAHFP).

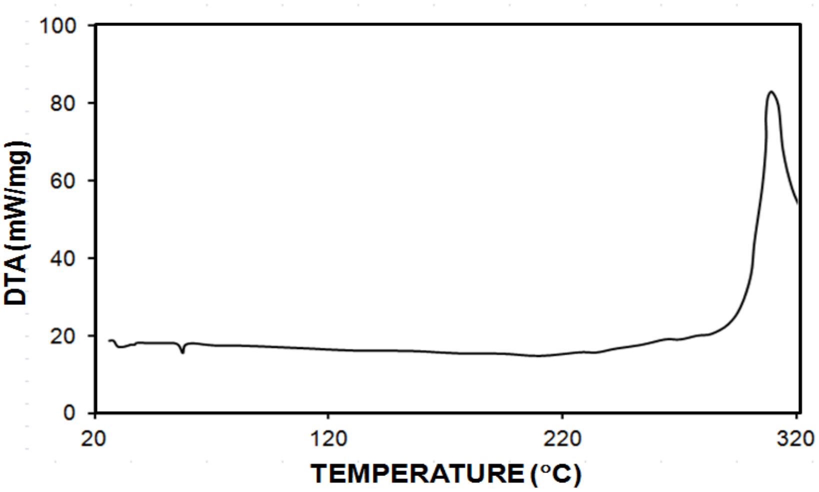

Fig.5: DTA Curve of Tetra – n – butyl ammonium per chlorate (TBAP).

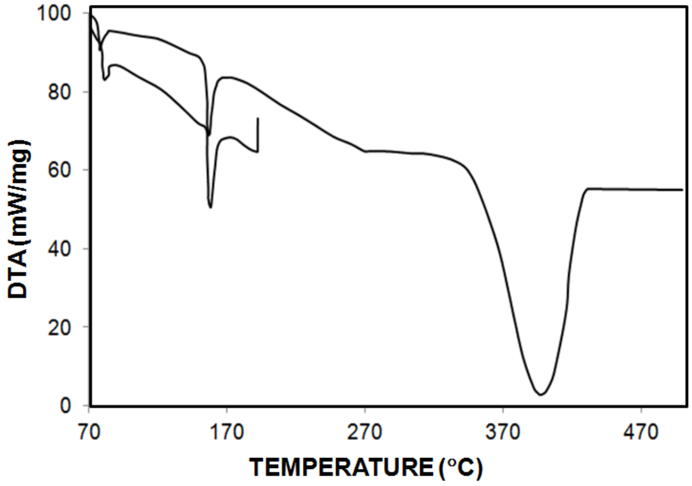

Fig.6: DTA Curve of Tetra – n- butyl ammonium Tetrafluoroborate (TBATFB).

The low – temperature peaks at 68°C for TBAHFP, 60°C for TBAP, and 95°C for TBATFB may be due to crystallographic phase-transitions; those at 162°C for TBAHFP, 211.9°C for TBAP, and 252°C for TBATFB are attributed to their melting. Both, TBAHFP and TBATFB undergo endothermic decomposition at 350°C and 400°C, respectively, while TBAP undergoes rapid exothermic decomposition at about 370°C.

The activation energy values were obtained from the above derivative curves employing Murray and White [17] equation (which is based on DTG maximum peak temperatures)

$$(d\alpha/dt)_{max} = [0.4 \times \beta \times E] / [R \times T^2_{max}] \quad \text{---------------} \; (1)$$

(or)

$$E = [2.5 \times (d\alpha/dt)_{max} \times R \times T^2_{max}] / \beta \quad \text{----------------} \; (2)$$

Since, (dα/dT) = (dα/dt) x (dT/dt) where (dT/dt) is nothing but heating rate 'β',
Equation (2) can be writtween as,

$$E = [2.5 \times (d\alpha/dT)_{max} \times R \times T^2_{max} \quad \text{-------------------} \; (3)$$

The kinetic parameters are tabulated in Table-1.

Table 1.

Compound	T_{Max} (T in 'K')	$(d\alpha/dT)_{Max}$	E_{Act} kJ.mol^{-1}.
TBAHFP	625.5	0.025	203.3
TBATFB	690.5	0.02375	235.4
TBAP	600.0	0.0389	291.2

The activatioin energy values obtained for TBAP, TBAHFP, and TBATFB are: 291.2, 203.3, and 235.4 kJ/mole, respectively.

APPLICATIONS

The thermal decomposition of tetrabutylammonium – tetrafluoroborate, hexafluorophosphate, and per chlorates as a prelude to using them as additives for the modification of thermal decomposition of ammonium per chlorate, an oxidizer, widely used in rocket propulsion.

CONCLUSIONS

- Tetra-n-butyl substituted ammonium compounds decompose giving out tri-n-butyl amine, HF and a corresponding Lewis acid as the products of decomposition.
- Thermal stabilities of compounds under study are in the order of TBAP< TBAHFP <TBATFB.

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