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Thermal decomposition of tetraalkyl ammonium tetrafluoroborates

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Abstract

The thermal decomposition of tetraalkyl ammonium tetrafluoroborates (R_4NBF_4), where R=methyl, ethyl, *n*-propyl and *n*-butyl, were studied using thermogravimetric (TG) technique in an inert atmosphere of N_2 at a heating rate of 20 K min^{-1}. The decreasing order of thermal stability and activation energy (E) with increase in size of the substituted alkyl group are consistent with each other. The probable causes for higher activation energy observed in the case of *n*-butyl substituted compound are discussed. © 1997 Elsevier Science B.V.

Keywords: Quaternary ammonium compounds; Tetrafluoroborates; Thermalstability; Thermogravimetric; DTA

1. Introduction

Ammonium perchlorate (AP), as an oxidant, has found widespread application in solid propellant technology. Differential thermal-analysis (DTA) studies on AP revealed that it undergoes an endothermic crystallographic phase transition from orthorhombic to cubic structure at 513 K. The first exotherm appears at 553–573 K, immediately after the phase change and the second exotherm appears at about 713 K [1].

It is a characteristic feature of AP that its stability is very sensitive to the presence of various additives. This property provides a possibility for the elucidation of the regularities of solid-phase catalytic processes, an area of catalytic reactions which is of continuing interest to all researchers in this field[1]. The effect of various additives on the thermal decomposition of AP has been studied widely [2–7]. This is mainly because of the belief that the key reaction in the ignition process of AP-based composite solid propellants is the low-temperature decomposition (LTD) of AP [8].

It is well accepted that quaternary ammonium compounds of the type R_4N+X^- decompose thermally to yield an amine (R_3N) and the corresponding alkyl compound [9–12]. The amine (R_3N) thus formed can interact with the $HClO_4$ produced during the thermal decomposition of AP, thus forming an amine perchlorate which causes inhibition of the first exotherm of AP [13].

Sheikh [11] studied the thermal decomposition of R_4NBX_4s, where R=ethyl and X=Cl, Br, and phenyl dichloride. Zabinska et al. [14] have studied the thermal stability, phase-transition and fusion properties of $R_4N^+BF_4^-$, where R=methyl, ethyl, *n*-propyl and *n*-butyl. However, kinetics of thermal decomposition of these compounds were not discussed by these authors [14].

Therefore, in a prelude to the study of the effect of $R_4N^+BF_4^-$ on AP decomposition, this paper deals with

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the thermal decomposition kinetics of these compounds, where R=methyl, ethyl, *n*-propyl and *n*-butyl.

2. Experimental

Thermogravimetric (TG) studies were carried out using the DuPont-990 Thermal Analyser System, with pure N_2 as purge gas and a flow rate of 30 ml min^{-1}. The heating rate employed was 20 K min^{-1} and a sample mass of 3.5–4.0 mg was used in all TG experiments.

The tetraalkyl ammonium tetrafluoroborates (Fluka, Switzerland) were used as received. The kinetic parameters were evaluated using a FORTRAN IV computer program for the Coats–Redfern [15] and MacCallum–Tanner [16] equations.

3. Results and discussion

Fig. 1 shows the TG-curves of tetramethyl ammonium tetrafluoroborate (TMATFB), tetraethyl ammonium tetrafluoroborate (TEATFB), tetrapropyl ammonium tetrafluoroborate (TPATFB), and tetrabutyl ammonium tetrafluoroborate (TBATFB).

The onset temperatures of thermal decomposition, 50% decomposition and the end of decomposition are shown in Table 1. It is evident that, as the size of the substituted alkyl group increases, the thermal stability of these compounds decreases. The order of their thermal stability is: TMATFB>TEATFB>TPATFB>TBATFB.

The kinetic parameters of thermal decomposition were evaluated using Coats–Redfern [15] and MacCallum–Tanner [16] equations and are presented in Table 2. For the purpose of discussion, activation-energy (*E*) values obtained through the use of Coats–Redfern equation were used. However, similar observations can be made even from the data obtained through the use of MacCallum–Tanner equation.

As the alkyl substitution proceeds from methyl to *n*-propyl, the thermal stability is reduced. This is in agreement with the gradual lowering of activation-energy values from 232 kJ mol^{-1} for TMATFB to 218 kJ mol^{-1} for TPATFB (Table 2). However, in the case of TBATFB, even though the thermal stability of this compound is more or less the same as that of TPATFB, an activation-energy value closer to TMATFB (232 kJ mol^{-1}) was observed.

These observations can be explained on the following lines: In the thermal decomposition of quaternary ammonium compounds of the type $R_4N^+BF_4^-$, where R=ethyl and X=Cl, Br or phenyl dichloride, the first stage decomposition according to Sheikh [11] involves loss of one mole of ethyl halide with the formation of triethylamine trihaloborate:

$$(C_2H_5)_4N^+BF_4^- \rightarrow (C_2H_5)_3NBX_3 + C_2H_5X.$$

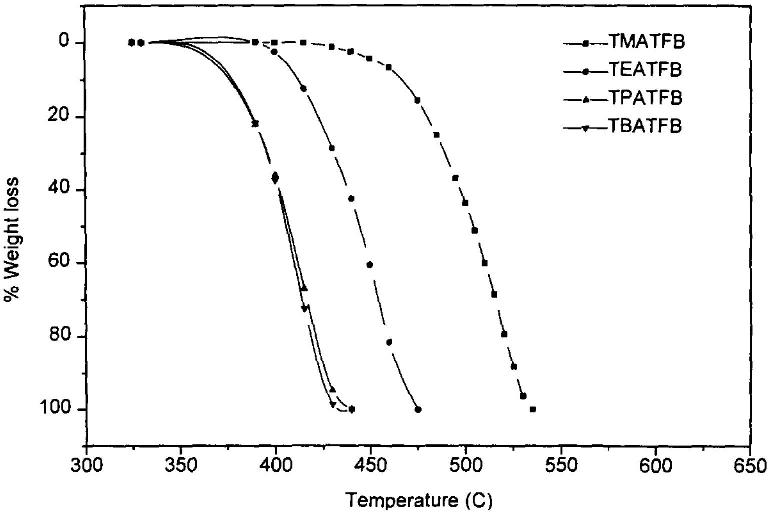


Fig. 1. TG-curves of tetraalkyl substituted ammonium tetrafluroborates.

Table 1
Temperatures at various stages of thermal decomposition of $R_4N^+BF_4^-$

Compound	T_i (K)	T_{50} (K)	T_f (K)
TMATFB	688	778	808
TEATFB	663	718	745
TPATFB	605	680	710
TBATFB	598	679	705

T_i – Temperature at onset of decomposition.
T_{50} – Temperature at 50% decomposition.
T_f – Temperature at completion of decomposition.

Table 2
Kinetic data on thermal decomposition of tetraalkyl substituted ammonium tetrafluoroborates

Compound	Kinetic equation	Activation energy (E) (kJ mol^{-1})	Frequency factor (A)
TMATFB	1[a]	232	4.54×10^{13}
	2[b]	238	1.50×10^{14}
TEATFB	1[a]	223	2.29×10^{14}
	2[b]	228	6.27×10^{14}
TPATFB	1[a]	218	7.40×10^{14}
	2[b]	222	1.78×10^{15}
TBATFB	1[a]	233	1.32×10^{16}
	2[b]	237	3.31×10^{16}

[a] Eq. (1): Coats–Redfern [15].
[b] Eq. (2): MacCallum–Tanner [16].

The formation of boron trihalide (BX_3) was explained by Sheikh [11] by the following reaction scheme:

$$R_4N^+BX_4^- \rightarrow R_3NBX_3 + RX$$

$$R_3NBX_3 \rightarrow R_2NBX_2 + RX$$

$$2R_2NBX_2 \rightarrow R(NRBX)_2X + RX$$

$$R(NRBX)_2X + R_2NBX_2 \rightarrow R(NRBX)_3X + RX$$

$$R(NRBX)_nX + R_2NBX_2 \rightarrow R(NRBX)_nNR_2 + BX_3$$

where R=ethyl and n-butyl and, n=1–5.

However, in the case of the n-butyl substituted compound, instead of formation of 1 : 1 complex, two molecules of C_4H_9X are ejected out in one single step [11]:

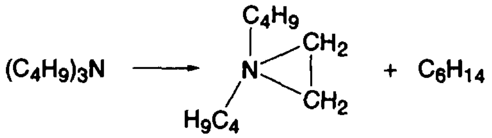
$$(C_4H_9)_4NBX_4 \rightarrow (C_4H_9)_2NBX_2 + 2C_4H_9X.$$

This indicates that when the size of the substituted alkyl group increases, steric factors come into play and stripping off of two molecules of C_4H_9X in one single step occurs, leading to relief in the molecular strain and consequent attainment of molecular stability.

Also, the fact that the thermal decomposition of similar compounds yields a trialkylamine was confirmed by various studies [9,12,13,17]. Kassen et al. [18] reported that in the case of tetrapropyl ammonium bromide (TPAB), while carrying out thermal studies on the state of tripropylamine (TPA) phase in ZSM-5, the TPA decomposes first at a temperature of 550 K with an activation energy (E) of 113 kJ mol^{-1}. In a similar study on the thermal decomposition of $(C_3H_7)_3N$-AlPO$_4$-5, Choudhary et al. [19] have reported that the cracking of TPA is expected to proceed in the following manner:

$$(C_3H_7)_3N \rightarrow 3C_3H_6 + NH_3.$$

However, in the case of the n-butyl substituted compound, there is a possibility of cyclization of the triamine formed [12], leading to the formation of an aziridine ring in addition to the formation of n-hexane.



4. Conclusions

The thermal stability and activation energy for thermal decomposition of tetraalkyl substituted ammonium tetrafluoroborates are reduced in direct proportion to the increase in size of the alkyl group.

Even though the thermal stability of the n-butyl substituted compound is more or less the same as that of the n-propyl substituted compound, relatively higher activation-energy value (closer to that of the methyl substituted compound) in the case of the n-butyl substituted compound, is explained on the lines that there exists a possibility of the formation of a more stable cyclic product such as aziridine together with n-hexane. Further, the loss of two molecules of butyl halide in the case of the n-butyl substituted compound as suggested by Sheikh [11], resulting in the formation of a more stable intermediate, can also justify higher activation energy in this case. Also, the trends in kinetic parameters obtained for these compounds using both the Coats–Redfern and MacCallum–Tanner equations are comparable.

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