Thermal decomposition and pyrolysis-GC studies on tetraalkyl-substituted ammonium hexafluorophosphates

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Abstract

Thermal decomposition (TD) and pyrolysis-GC studies on $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$ were carried out using a Du Pont-990 thermal analyser system and a Shimadzu PYR-2A coupled with a Shimadzu GC-5A gas chromatograph, respectively. Based on these studies, the thermal decomposition mechanism of compounds of type R_4NPF_6, where R = alkyl, aryl, alkaryl groups, or H, was predicted to be $R_4NPF_6 \rightarrow R_3N + RF + PF_5$.

The kinetic parameters of TD of ethyl- and butyl-substituted tetraalkyl ammonium compounds were evaluated using the Coats–Redfern and MacCallum–Tanner equations and the data were found to be comparable with each other. The higher activation energy value for the second-stage decomposition of $(C_4H_9)_4NPF_6$ was attributed to thermal cyclisation of the tetrabutyl amine that is formed during the first-stage decomposition of this compound, yielding an aziridine ring compound and hexane.

INTRODUCTION

Tetraalkyl-substituted quaternary ammonium as well as phosphonium salts find wide application as phase-transfer catalysts. These compounds catalyse two-phase reactions such as the dichlorocyclo-propanation of al-kenes with chloroform and aqueous NaOH, the deuterium exchange of the active hydrogens of ketenes with D_2O; the hydrolysis of esters and alkene-sulphonyl chlorides with aqueous NaOH and the borohydride reduction of ketones [1].

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Alkyl ammonium salts, especially tetraalkyl ammonium tetrafluoroborates, have been successfully and widely used in electrochemistry over the last thirty years as supporting electrolytes in non-aqueous solvent systems of both analytical and industrial interest [2].

Hexafluorophosphate ions, PF_6^- (octahedral anions), are extremely stable and inert to chemical attack. In the case of substituted ammonium hexafluorophosphates having compositions represented by the formula R_4NPF_6 (where R = alkyl, aryl, alkaryl groups or H), unusual thermal stability is found when the R groups are the lower alkyl radicals. For example, $(CH_3)_4NPF_6$ is stable up to around 400°C [3]. In this presentation an attempt is made to study the thermal stability of tetraethyl- and tetrabutyl-substituted ammonium hexafluorophosphates and to establish the mechanism of their decomposition stages from pyrolysis-GC studies.

EXPERIMENTAL

Materials

The pure compounds, $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$, used in this study were from M/s Fluka, Switzerland.

Instrumentation

Thermal decomposition studies were carried out using a Du Pont-990 thermal analyser system, in an inert atmosphere of nitrogen, at a heating rate of 20°C min^{-1}, and a constant sample mass of ≈ 5 mg. The pyrolysis-GC studies on these pure compounds were carried out using a low-resolution pyrolysis-GC (a furnace pyrolyser), Shimadzu PYR-2A, coupled with a Shimadzu GC-5A gas chromatograph, using a flame ionisation detector.

A stainless steel column (3 mm $\phi \times$ 2 m) packed with PORA PAK-Q on 80–100 mesh support was used. The experimental conditions used were: column temperature, 50–180°C at 15°C min^{-1}; injection-port temperature, 200°C; and helium flow rate, 40 ml min^{-1}.

RESULTS

The thermogravimetric (TG) curves (Fig. 1) of $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$ indicate that their thermal stabilities are in the order $(C_2H_5)_4NPF_6 > (C_4H_9)_4NPF_6$.

Differential thermal analysis (DTA) patterns of these compounds (Fig. 2) indicate the shift of phase-transition temperatures (T_p) and fusion temperatures (T_f) to lower temperature regions as the alkyl substitution changes from tetraethyl to tetrabutyl groups. Fusion occurs at ≈ 320°C in the case
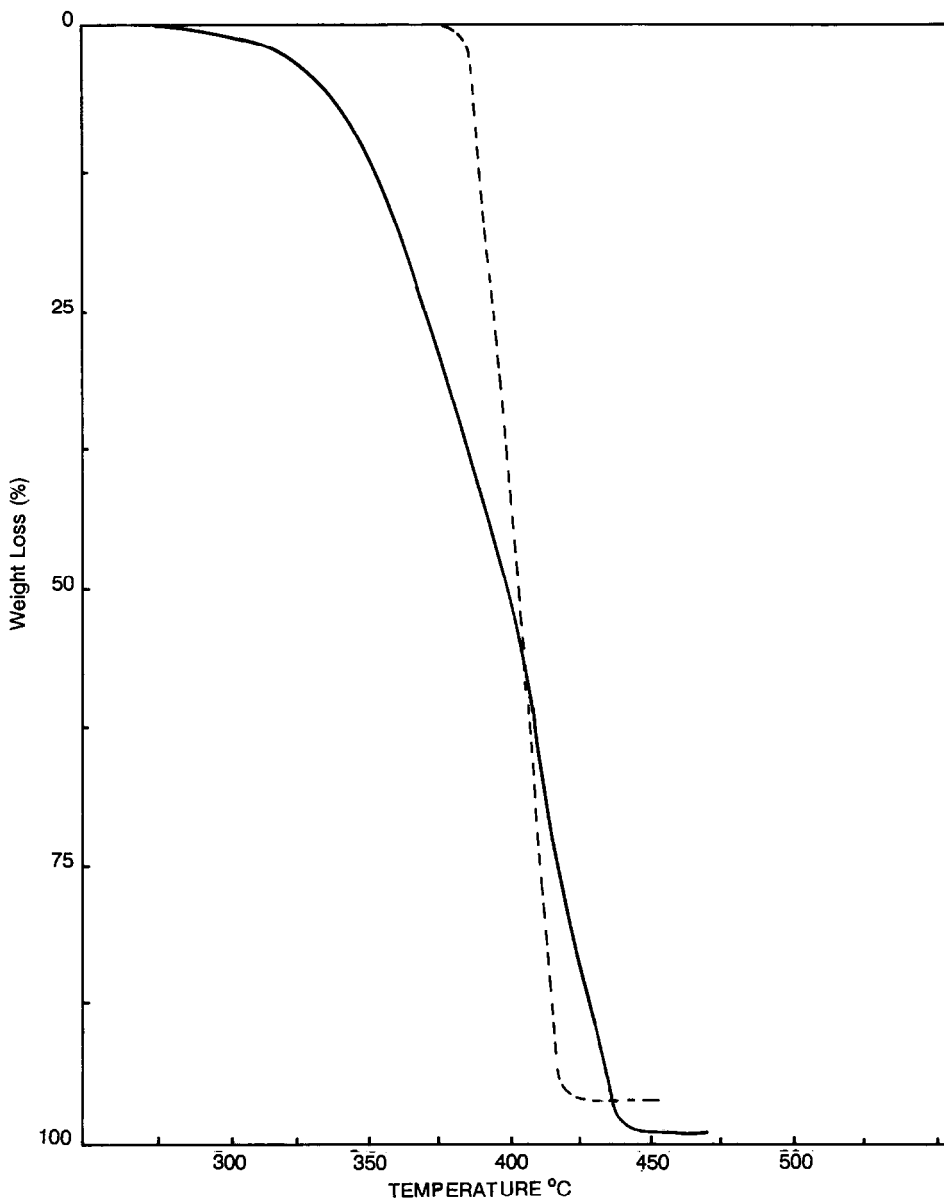
Fig. 1. TG curves of $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$.

of $(C_2H_5)_4NPF_6$, compared with $\approx 250\,^\circ C$ for the tetrabutyl compound. Similarly, the endothermic crystallographic phase transition that occurs at $\approx 80\,^\circ C$ in the case of $(C_2H_5)_4NPF_6$ shifts to $95\,^\circ C$ in the case of the tetrabutyl-substituted compound, in agreement with the value reported in the literature [4].

Also, the DTA thermograms (Fig. 2) indicate that both $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$ decompose endothermically. The endothermic decomposition
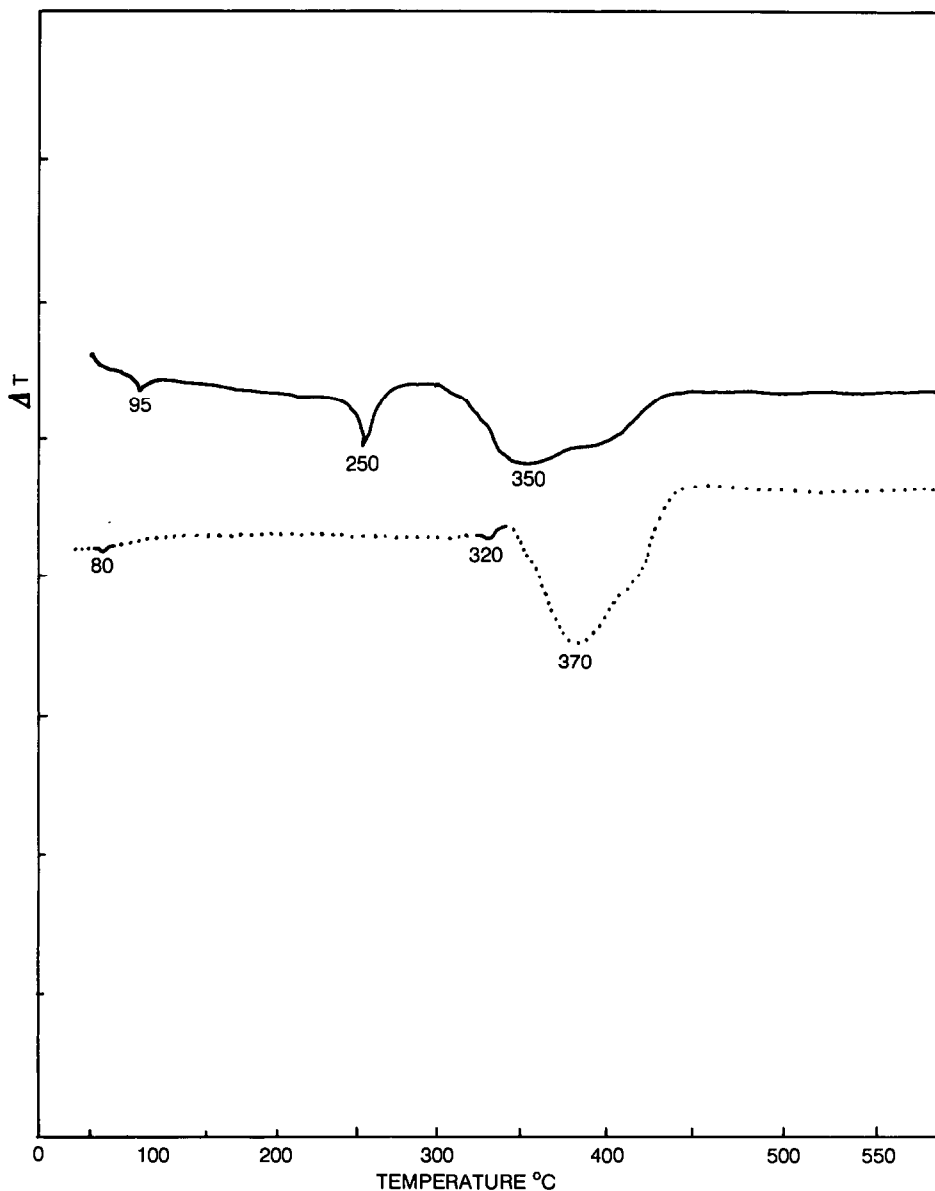
Fig. 2. DTA curves of $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$.

peaks of the tetraethyl- and tetrabutyl-substituted compounds indicate that the decomposition may occur in two stages, as seen from the humps at about 410 and 380°C, respectively.

In the case of the tetraethyl-substituted compound, the temperature interval for the apparent second-stage decomposition from the point of occurrence of the hump is not great and, hence, the kinetic parameters were evaluated from TGA data corresponding to the temperature range consider-

TABLE 1

Kinetic parameters for thermal decomposition of tetraethyl and tetrabutyl ammonium hexafluorophosphates

Compound	Decomposition stage	Order of reaction	Coats–Redfern equation			MacCallum–Tanner equation		
			E^a	A^b	r^c	E^a	A^b	r^c
Tetraethyl ammonium hexafluorophosphate	Single stage (683–723 K)	1.5	63.6	9.97×10^{17}	0.9996	64.9	3.17×10^{18}	0.9996
Tetrabutyl ammonium hexafluorophosphate	First-stage (598–643 K)	1.7	52.4	2.66×10^{16}	0.9997	53.2	5.49×10^{16}	0.9997
Tetrabutyl ammonium hexafluorophosphate	Second stage (665–698 K)	1.85	83.0	6.78×10^{24}	0.9990	84.2	2.76×10^{25}	0.9990

[a] Activation energy (kcal mol^{-1}).
[b] Frequency factor.
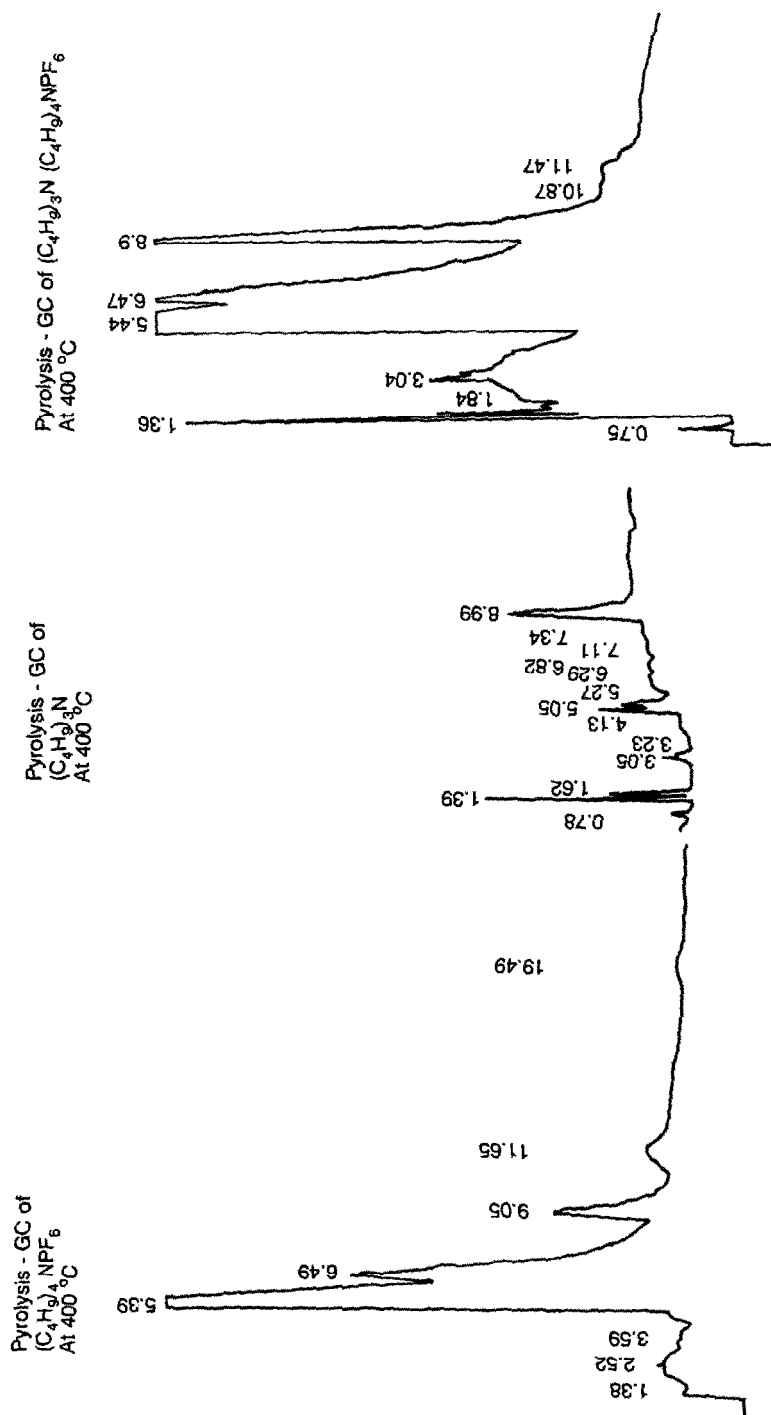[c] Correlation coefficient.

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Pyrolysis-GC at 400°C of $(C_4H_9)_4NPF_6$, $(C_4H_9)_3N$ and a mixture of $(C_4H_9)_4 NPF_6$ and $(C_4H_9)_3N$.
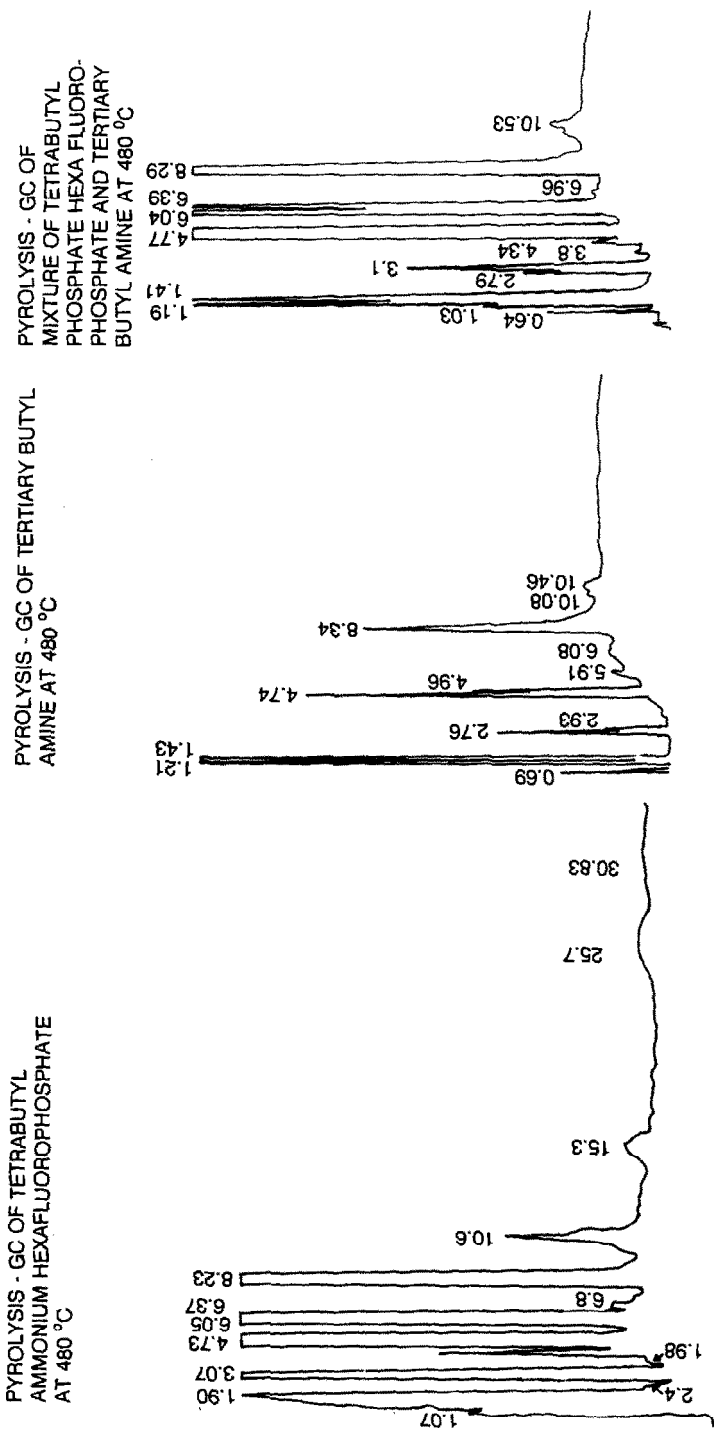
Fig. 3.

Fig. 4. Pyrolysis-GC at 480°C of $(C_4H_9)_4NPF_6$, $(C_4H_9)_3N$ and a mixture of $(C_4H_9)_4NPF_6$ and $(C_4H_9)_3N$.

ing this to be a single decomposition peak. However, in the case of the tetrabutyl-substituted compound, because the temperature interval corresponding to the apparent second-stage decomposition is relatively large, the kinetic parameters were evaluated for both stages separately from the TGA data corresponding to these temperature intervals.

The kinetic parameters evaluated using the MacCallum–Tanner [5] and Coats–Redfern [6] equations are listed in Table 1. The results obtained were found to be in close agreement with each other.

The pyrolysis-GC data on $(C_4H_9)_4NPF_6$, $(C_4H_9)_3N$ and a mixture of $(C_4H_9)_4NPF_6$ and $(C_4H_9)_3N$ at 400 and 480°C are shown in Figs. 3 and 4. At both temperatures, it can be seen that, in the mixture, the peak heights corresponding to pure tertiary amine, at about 1.39, (5.05, 5.27) and 8.99 retention times, were found to be enhanced. This suggests that tertiary amine is one of the decomposition products in the thermal decomposition of $(C_4H_9)_4NPF_6$.

DISCUSSION

Thermal decomposition of ammonium tetrafluoroborate (NH_4BF_4) and ammonium hexafluorophosphate (NH_4PF_6) produces gaseous products in accordance with the following equations [7]

$$NH_4BF_4(S) \rightarrow NH_3(g) + HF(g) + BF_3(g) \tag{1}$$

$$NH_4PF_6(S) \rightarrow NH_3(g) + HF(g) + PF_5(g) \tag{2}$$
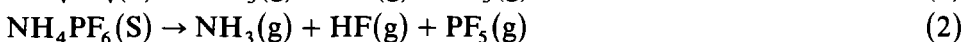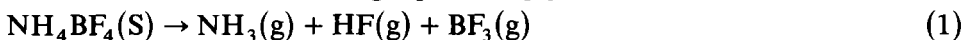
Considering that the tetraalkyl substituted ammonium hexafluorophosphates (R_4NPF_6) are analogous to NH_4PF_6, their thermal decomposition can be expected to proceed on similar lines. Accordingly, thermal decomposition reaction of these compounds can be written as

$$R_4NPF_6 \rightarrow R_3N + RF + PF_5 \tag{3}$$

This assumption is supported by the decomposition studies on tetramethyl phosphonium perchlorate, nitrate and picrate which proceed as shown in eqn. (4) [8]


$$\tag{4}$$
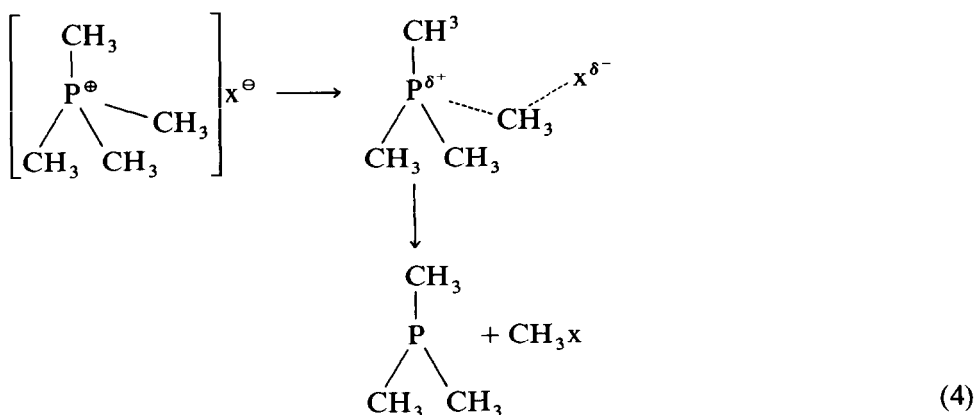
Also, in the case of $(CH_3)_4NClO_4$, Jain and Nambiar [9] postulated that a methyl group transfer as the rate-determining step and showed evidence for the formation of $(CH_3)_3N$ as one of the decomposition products.
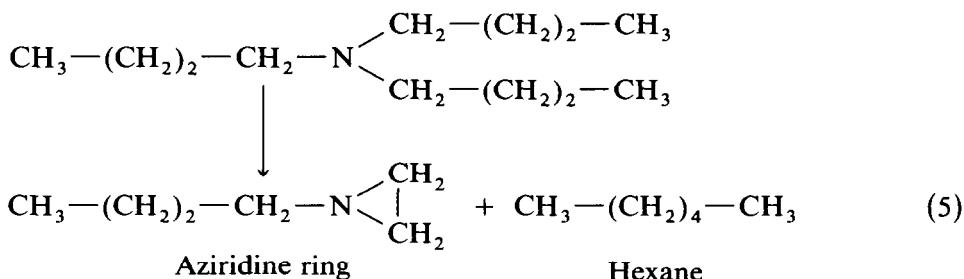
The assumption that tertiary amine is one of the decomposition products in the thermal decomposition of R_4NPF_6 is further confirmed from the pyrolysis-GC data obtained at 400 and 480 °C for pure $(C_4H_9)_4NPF_6$, $(C_4H_9)_3N$ and the mixture of $(C_4H_9)_4NPF_6$ with $(C_4H_9)_3N$. From Fig. 3, it can be seen that the peaks characteristic of $(C_4H_9)_3N$ at 1.39, (5.05, 5.27) and 8.99 elution times, are enhanced for both $(C_4H_9)_4NPF_6$ and its mixture with $(C_4H_9)_3N$, indicating that the enhanced peak heights are due to the formation of additional $(C_4H_9)_3N$ from the $(C_4H_9)_4NPF_6$ decomposition. Similar observations were made in the case of $(C_4H_9)_4NPF_6$ decomposing at 480 °C (Fig. 4).

In eqn. (3), it is proposed that alkyl fluoride is also one of the products of decomposition of R_4NPF_6-type compounds.

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 trihalide [10]. As $R_4N^+PF_6^-$-type compounds are analogous to $R_4N^+BX_4^-$, the proposed thermal decomposition reaction in eqn. (3) is justified. Furthermore, in the case of $R_4N^+BX_4^-$, the final products were polymeric materials of the type

$$
\begin{array}{ccc}
R & X & R \\
| & | & | \\
R-(N-B &)_n & N-R.
\end{array}
$$
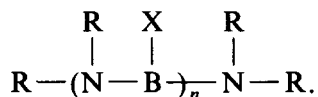
Polymers with these end groups were not isolated in the case of R = ethyl, but were obtained in the n-butyl system [10]. The higher activation energy value for the second-stage decomposition of $(C_4H_9)_4NPF_6$ (Table 1) could be explained by the cyclisation of the $(C_4H_9)_3N$ formed during the first-stage decomposition followed by its decomposition at elevated temperatures

$$
CH_3-(CH_2)_2-CH_2-N \Big\langle \begin{array}{l} CH_2-(CH_2)_2-CH_3 \\ CH_2-(CH_2)_2-CH_3 \end{array}
$$

$$
\downarrow
$$

$$
CH_3-(CH_2)_2-CH_2-N \Big\langle \begin{array}{l} CH_2 \\ CH_2 \end{array} \quad + \quad CH_3-(CH_2)_4-CH_3 \tag{5}
$$

Aziridine ring   Hexane

CONCLUSIONS

Thermal decomposition and pyrolysis-GC studies on $(C_2H_5)_4NPF_6$ and $(C_4H_9)_4NPF_6$ proceed via the reaction proposed in eqn. (3). The proposed decomposition mechanism is in agreement with the observations of Nambiar and Jain [8], Jain and Nambiar [9] and Sheikh [10].

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