

INORGANIC SYNTHESIS
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Thermal Stability of Quaternary Ammonium
Hexafluorophosphates and Halides

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Abstract—Thermal decomposition of hexafluorophosphates of short-chain tetraalkylammonium salts of the general formula $R_3R'NPF_6$, where $R_3 = R' = CH_3, C_2H_5, C_4H_9$; $R_3 = C_2H_5, R' = CH_2C_6H_6$ or $CH_2CH=CH_2$, was studied by thermal gravimetric analysis. Measurements were performed in air in the temperature interval 20–500°C. The thermal stability of halides with the same cations in the same temperature interval was studied for comparison. The effect of cation on the thermal stability of the halides and hexafluorophosphates was examined. The mechanism of thermal decomposition of quaternary ammonium hexafluorophosphates was suggested.

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Quaternary ammonium, dialkylimidazolium, and alkyipyridinium hexafluorophosphates, which were prepared in the early 1990s, belong to the class of hydrophobic low-temperature ionic liquids (ILs) [1].

The stability and chemical inertness of these organic compounds, along with their commercial availability, largely favored the progress of studies concerning synthesis, catalysis, and other aspects of their chemistry [2, 3]. The hydrophobicity of hexafluorophosphates is their major advantage over tetrafluoroborates BF_4^- or aluminates $AlCl_4^-$ in application as ionic liquids. For example, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) in combination with organic reagents in aqueous solutions is used for extraction of alkali and alkaline-earth metals [4, 5]. The extraction of organic compounds of various classes into hexafluorophosphate ILs has been studied to a greater extent than their extraction into other ionic liquids [6]; as extractants of neutral organic compounds, hexafluorophosphate ILs behave similarly to esters and aromatic hydrocarbons.

Imidazolium and pyridinium hexafluorophosphates with long-chain radicals ($C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$), in contrast to other ionic liquids, are thermotropic liquids forming liquid crystal phases on melting [7]. Such salts are of particular interest as solvents for

phase-transfer catalysis, because they combine the properties of common ILs and liquid crystal solvents.

Quaternary ammonium hexafluorophosphates as ionic liquids are known and studied to a lesser extent; mainly these are salts of unsymmetrical cations with a long-chain radical or polyalkylammonium cation [8]. Hexafluorophosphates with short-chain tetraalkylammonium cation as ILs are unknown, because in going to highly symmetrical molecules the polarity increases considerably, and the crystallinity increases also; as a result, the melting point of such salts is beyond the temperature interval for ionic liquids, 0–100°C. However, if the salts contain as counterion acidic $AlCl_4^-$ anion instead of neutral PF_6^- anion, the salts acquire properties of typical ionic liquids and are used as catalysts. For example, trimethylammonium chloride is used in isomerization of n-alkanes [9]; tetrabutylammonium bromide, in phase-transfer catalysis in phosphorylation of alcohols [10]; tetrabutylammonium chloride, in hydrodechlorination of CCl_4 [11]. In some cases, ionic liquids based on ammonium salts, e.g., trioctylammonium chloride, are preferable as solvents even over BMIMPF₆ [12].

Because of the fact that in some organic processes it is necessary to use ionic liquids at elevated temperatures, their stability and decomposition temperature become im-

portant factors. Ionic liquids will exhibit different thermal stability depending on the kind of the cation and anion.

The decomposition of ionic liquids (like that of other quaternary salts) at high temperatures is determined by the structure of the organic amine (at the same anion). For example, alkylammonium salts are the least stable and can undergo alkyl interchange and dealkylation on heating to 150°C, whereas imidazolium and pyridinium salts are considerably more stable [13]. In the series of similar cations, the thermal stability of salts does not appreciably depend on the chemical structure of the cation but depends on the kind of the anion; bulky anions, as a rule, enhance the thermal stability of salts [14].

In this work we studied the thermal stability of quaternary ammonium hexafluorophosphates containing short-chain alkyl radicals in the cationic moiety in comparison with the related halides belonging to the class of ionic liquids. Also, we examined the relationship between the structure of the cation and the thermal stability of quaternary salts containing hexafluorophosphate PF_6^- and halide anions as counterions.

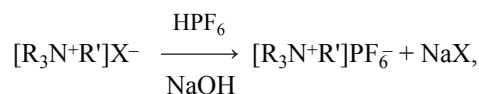
EXPERIMENTAL

The IR spectra were recorded with a Bruker Equinox 55 Fourier spectrometer; samples were prepared as KBr (ultrapure grade) pellets. Differential thermal gravimetric analysis was performed with a Netzsch STA 449 F3 device in the temperature interval 25–550°C at a heating rate of 5 deg min^{-1} in air. Elemental analysis was performed with a Hewlett–Packard 185 C,H,N-Analyser. Photomicrographs were taken with a JEOL JSM-6610LV scanning electron microscope.

Allyl- and benzyltriethylammonium chlorides. A solution of benzyl or allyl chloride (0.51 mol) in 20 mL of

acetone was added to a solution of triethylamine (0.5 mol) in 30 mL of dry acetone. The mixture was refluxed for 0.5–3 h. The precipitate of the quaternary salt was filtered off, washed with dry cold ether, recrystallized from a 1 : 2 ethanol–ethyl acetate mixture, and dried in a vacuum. Yield 72 and 94%, respectively. The products are white crystalline substances soluble in water and polar solvents and insoluble in nonpolar solvents (ether, hexane). The physicochemical properties are given in Table 1.

Quaternary ammonium hexafluorophosphates. A 0.05-mol portion of quaternary ammonium chloride was dissolved in 20 mL of water, 0.05 mol of 60% HPF_6 was added dropwise to the resulting solution with continuous stirring, and 0.05 mol of NaOH in the form of a 0.1 M solution was added to the mixture obtained. Quaternary ammonium hexafluorophosphate formed as a white amorphous mass was filtered off, washed with water, recrystallized from methanol, and vacuum-dried for 24 h. The yield varied from 70 to 95% depending on the structure of quaternary ammonium cation. The recrystallized reaction products are crystals of regular shape (Fig. 1). The synthesized quaternary ammonium hexafluorophosphates are hydrophobic substances immiscible with water and soluble in polar organic solvents. The composition and structure of the products were confirmed by elemental analysis and IR spectroscopy (Table 2). Quaternary ammonium hexafluorophosphates were prepared by the following scheme:



where $\text{R}_3 = \text{R}' = \text{C}_2\text{H}_5$, $\text{X} = \text{I}$ (**I**); $\text{R}_3 = \text{C}_2\text{H}_5$, $\text{R}' = \text{CH}_2\text{—CH=CH}_2$, $\text{X} = \text{Cl}$ (**II**); $\text{R}_3 = \text{C}_2\text{H}_5$, $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$, $\text{X} = \text{Cl}$ (**III**); $\text{R}_3 = \text{R}' = \text{C}_4\text{H}_9$, $\text{X} = \text{Cl}$ (**IV**); $\text{R}_3 = \text{R}' = \text{CH}_3$,

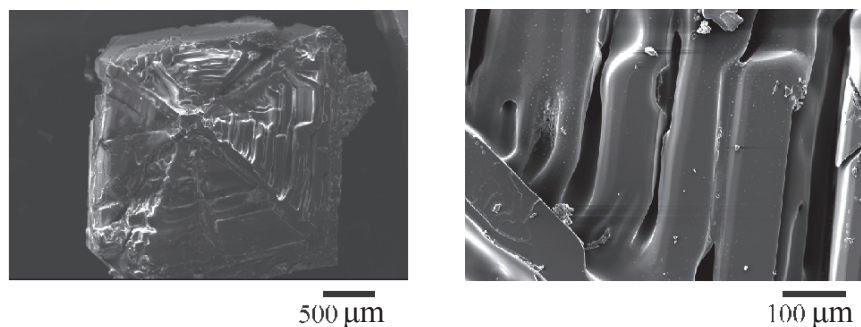


Fig. 1. Photomicrographs of a crystal of tetraethylammonium hexafluorophosphate (Table 2, compound no. 1).

Table 1. Physicochemical properties of quaternary ammonium hexafluorophosphates of the general formula $[R_3NR']^+PF_6^-$

Comdio no.	R	R'	M , g mol ⁻¹	T_m , °C	Found, %/Calculated, %		IR, ν , cm ⁻¹
					C	H	
1	C ₂ H ₅	C ₂ H ₅	336.7	334 (dec.)	<u>35.1</u> 34.9	<u>7.5</u> 7.3	ν_{C-Hal} 2960, 2940, 2905; $\nu_{PF_6^-}$ 844
2	C ₂ H ₅	CH ₂ -CH=CH ₂	370.8	142	<u>37.8</u> 37.7	<u>7.1</u> 6.9	ν_{C-Hal} 2990, 2973; ν_{C-H} 3010; $\nu_{C=C}$ 1647; $\nu_{PF_6^-}$ 846
3	C ₂ H ₅	C ₆ H ₅ CH ₂	337.0	185	<u>46.4</u> 46.3	<u>6.7</u> 6.5	ν_{C-Hal} 2988; ν_{C-Hap} 3027; ν_{C-Cap} 1589, 1479; $\nu_{PF_6^-}$ 845
4	C ₄ H ₉	C ₄ H ₉	387.1	251	<u>49.9</u> 49.7	<u>9.7</u> 9.3	ν_{C-Hal} 2968, 2949; $\nu_{PF_6^-}$ 841
5	CH ₃	CH ₃	219.0	377 (dec.)	<u>22.1</u> 21.9	<u>5.8</u> 5.5	ν_{C-Hal} 2930, 2905; $\nu_{PF_6^-}$ 847

X = I (V).

As seen from Table 1, the hexafluorophosphates obtained have relatively high melting points. This fact can be attributed to relatively high "ionicity" of the compounds, because the positive charge is virtually fully localized on the nitrogen atom, without delocalization to the periphery of the molecule. Furthermore, virtually all the organic cations in the compounds obtained have short-chain radicals and exhibit relatively high symmetry. These are, apparently, the major factors responsible for so high melting points.

The thermal stability of the starting quaternary ammonium halides and hexafluorophosphates was studied by thermal gravimetric analysis. The results obtained for tetraalkylammonium halides are shown in Fig. 2.

It follows from the TG and DTA curves of quaternary ammonium halides that the processes occurring on heating are similar in character. However, the compounds significantly differ in the thermal stability. For example, highly symmetrical salts (CH₃)₄NI and (C₂H₅)₄NI, containing iodide ion as counterion, are practically stable up to 360°C and decompose without melting at 440°C; the decomposition products burn out with an exothermic effect observed at 450°C. The chlorides are less stable, which is consistent with the general trend in the thermal stability of halides: $I^- > Br^- \gg Cl^- > F^-$ [14]. Despite the fact that the temperature of 150°C is considered as the maximal working temperature for the majority of quaternary ammonium chlorides [15], tetrabutylammonium

(Table 2, compound no. 4), triethylbenzylammonium (no. 3), and triethylallylammonium (no. 2) chlorides are stable up to 180°C and rapidly decompose at 240°C in one step. It should be noted that the thermal decomposition of salts with benzyl and allyl radicals occurs similarly, although they are significantly inferior in stability to the symmetrical salts (C₂H₅)₄NI and (C₄H₉)₄NCl, which may be due to weakening of Coulomb interactions of the cation and anion as a result of distortion of the cation symmetry upon introduction of benzyl or allyl group instead of ethyl group.

Data on the thermal stability of the synthesized quater-

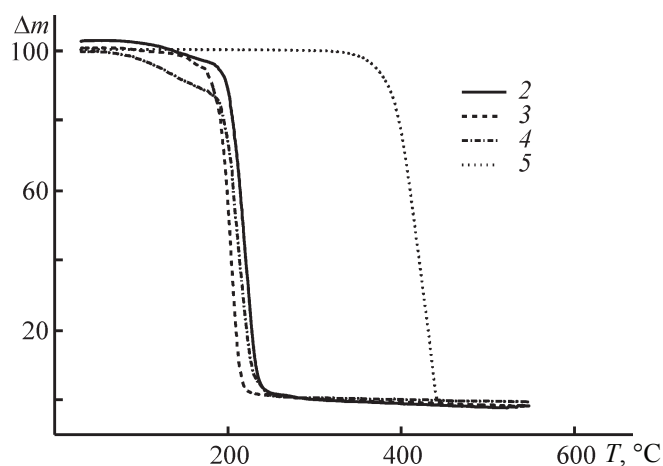


Fig. 2. TG curves of quaternary ammonium halides. (Δm) Weight loss and (T) temperature; the same for Fig. 3. Numerals at curves are compound nos. in Table 2.

Table 2. Thermal stability of quaternary ammonium halides of the general formula $[R_3NR']^+X^-$

Compd. no.	R	R'	X ⁻	T_m	T_{50}^*	Weight loss, %, at indicated T , °C		
				°C		100	200	300
1	C ₂ H ₅	C ₂ H ₅	I	>300	260	0	0	30
2	C ₂ H ₅	CH ₂ -CH=CH ₂	Cl	52	217	0	12	100
3	C ₂ H ₅	C ₆ H ₅ CH ₂	Cl	96	200	0	47	100
4	C ₄ H ₉	C ₄ H ₉	Cl	76	210	3	27	100
5	CH ₃	CH ₃	I	>300	415	0	0	0

^a (T_{50}) Temperature of 50% decomposition of the sample; the same for Table 3.

nary ammonium hexafluorophosphates are given in Fig. 3 and Table 3. As can be seen, all the salts surpass halides in the thermal stability. For example, tetramethylammonium hexafluorophosphate (CH₃)₄NPF₆ appeared to be the most stable. It is stable up to 380°C and rapidly decomposes without melting in one step with simultaneous combustion of decomposition products at 500°C (exothermic effect at 450°C).

The compounds (C₂H₅)₄NPF₆ and (C₄H₉)₄NPF₆ differ in the thermal behavior from all the other compounds studied. The DTA curves are shown in Fig. 4. These salts are stable up to 280–330°C and, in contrast to the other salts, decompose without melting in two steps. For (C₄H₉)₄NPF₆, the first step occurs at 280–370°C (endothermic effect at 340°C) and the second step, at 370–410°C. Tetraethylammonium hexafluorophosphate

(C₂H₅)₄NPF₆ is stable up to 330°C, and on further heating it decomposes in two steps. The first fast step is observed in the interval 330–385°C with an exothermic effect at 375°C (combustion of decomposition products), and the second, slower step, in the interval 385–430°C. The hexafluorophosphates with the benzyl and allyl substituents in the cation (Table 3, compound nos. 2, 3) decompose similarly: The salts are stable up to 280°C, after which they rapidly decompose in one step with an endothermic effect at 330°C, followed by combustion of the decomposition products at 370°C.

As follows from our results, replacement of the halide ion by bulky octahedral PF₆⁻ anion leads to a change in the physicochemical properties of tetraalkylammonium salts, namely, to an increase in their melting point (which does not allow them to be classed with low-temperature ionic liquids) and in the decomposition temperature.

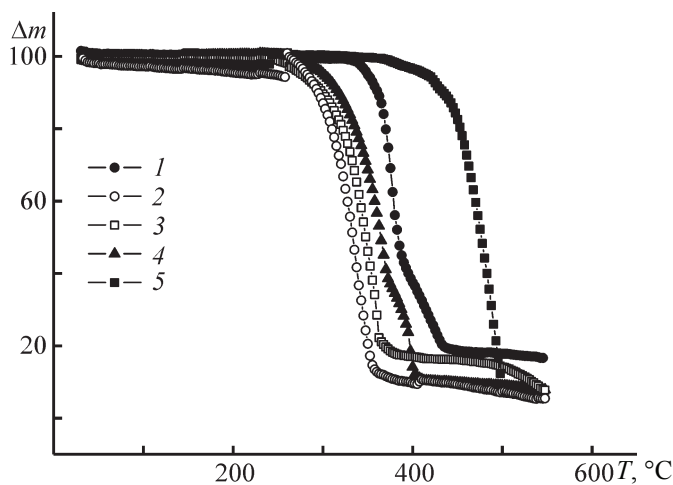


Fig. 3. TG curves of quaternary ammonium hexafluorophosphates. Numerals at curves are compound nos. in Table 3.

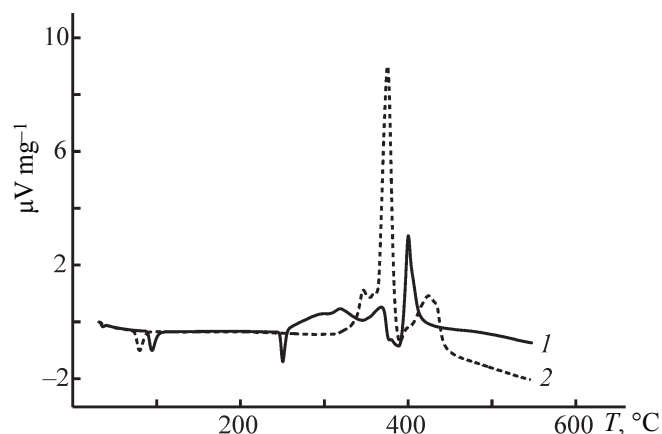


Fig. 4. DTA curves of (1) tetrabutylammonium and (2) tetraethylammonium hexafluorophosphates. (T) Temperature.

Table 3. Thermal stability of quaternary ammonium hexafluorophosphates of the general formula $[R_3NR']^+PF_6^-$

Compound no.	R	R'	T_{50} , °C	Weight loss, %, at indicated T , °C		
				200	300	400
1	C ₂ H ₅	C ₂ H ₅	384	0	0	63
2	C ₂ H ₅	CH ₂ -CH=CH ₂	334	4.5	13	90
3	C ₂ H ₅	C ₆ H ₅ CH ₂	348	1	10	83
4	C ₄ H ₉	C ₄ H ₉	365	0	4	85
5	CH ₃	CH ₃	476	0	0	4

According to published data [16], at equal charge of the anions, an increase in their size in most cases leads to a decrease in the melting point of the salts. For example, the melting points of EMIMBF₄, EMIMNO₃, and EMIMPF₆ are 87, 38, and 6°C, respectively. This trend is typical of salts with a planar cation (Im⁺, Py⁺) and is associated with the possibility of hydrogen bonding of the cation with the counterion. In the case of octahedral PF₆⁻ anion, all the equatorial fluorine atoms can participate in hydrogen bonding with 1-ethyl-3-methylimidazolium cation, whereas for the tetrahedral BF₄⁻ anion only three fluorine atoms are involved in hydrogen bonding. With respect to the H-bond strength, the anions can be ranked in the following order: CF₃COO⁻ > BF₄⁻ > PF₆⁻ > B(C₆H₅)₄⁻ [17].

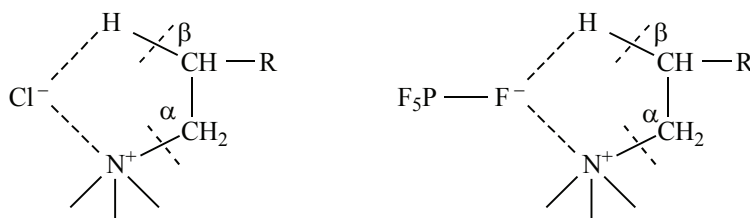
However, for quaternary ammonium hexafluorophosphates, we observed an opposite trend: increase in the melting and decomposition temperatures of the salts. This fact may be associated with the tetrahedral structure of ammonium cations and with the lack of any hydrogen bonds with the anion, which leads to enhancement of Coulomb interaction, formation of ordered structures by the ions, and increase in the melting and decomposition temperatures. In addition, high thermal stability of hexafluorophosphates can probably be attributed to the fact that decomposition of the salts is mainly determined by decomposition of the cation. According to published

data [14], the initial steps of the cation decomposition in quaternary ammonium salts start with cleavage of the alkyl-N⁺ bond and can occur along two pathways: β-elimination (E₂) and nucleophilic substitution at quaternary N atom (S_N) (Scheme 1)

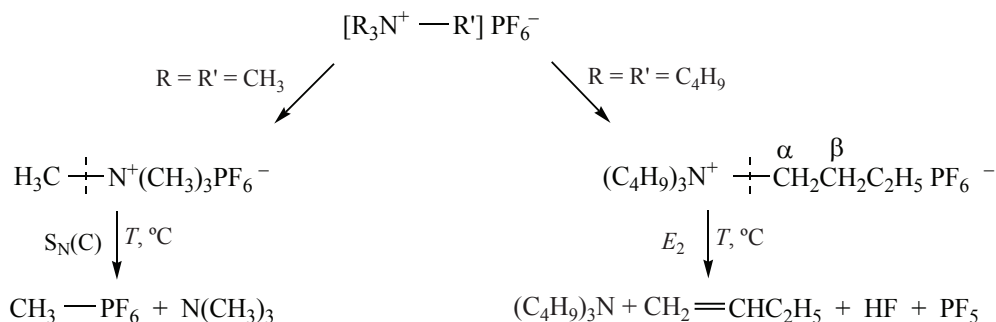
Presumably, thermal degradation of the quaternary salts studied occurs by the mechanism of intramolecular β-elimination via 5-centered transition state [18] (Scheme 2).

In this case, the PF₆⁻ anion acts as a nucleophile, with simultaneous heterolytic cleavage of the C_β-H and C_α-N⁺ bonds occurring in nucleophilic β-elimination reactions. In the case of hexafluorophosphate ions, the formation of the transition state is hindered, because the hexafluorophosphate ion is bulky (3.3 Å) and is difficultly incorporated in a three-dimensional structure [13]. On the contrary, the presence of Cl⁻ ion as counterion (radius 1.81 Å) leads to a considerable decrease in the thermal stability owing to easy formation of the transition state in the course of β-elimination. If there are no H atoms in the β-position and the elimination is impossible, the process preferentially occurs as nucleophilic substitution S_N(C).

Similar results were obtained in studying the thermal stability of quaternary ammonium tetrafluoroborates [19] and 1,3-disubstituted imidazolium tetrachlorofer-

Scheme 1.

Scheme 2.



rates [20]. Deceleration of the thermal decomposition of tetrafluoroborates and tetrachloroferrates is due to destabilization of the transition state, caused by steric repulsion of the bulkier anion.

Compound no. 2 containing the allyl substituent exhibits the lowest thermal stability among quaternary ammonium hexafluorophosphates. This may be due to the fact that one of the β -C atoms in this compound is in the state of sp^2 hybridization, which increases its C–H acidity. Therefore, in the transition state arising in the course of β -elimination the detachment of this proton requires smaller energy than the proton detachment from the sp^3 -hybridized C atom.

For all the compounds, decomposition of the cation leads to a decrease in the strength of electrostatic interaction with the anion. The PF_6^- anion cannot exist as separate species. This leads to elimination of F^- in the form of HF (with β -H atom of one of alkyl groups), which, in turn, favors formation of stable alkenes, tertiary amines, HF, and PF_5 . If there is no β -H atom (compound no. 5), the decomposition follows the $S_N(C)$ pathway. It is also known that thermal decomposition of quaternary salts at lower temperatures (200–300°C) preferentially occurs by the $S_N(C)$ mechanism, and at higher temperatures, by the E_2 mechanism [21]:

In tetramethylammonium hexafluorophosphate (Table 3, compound no. 5), there is no β -H atom, and the elimination is impossible. As a result, the thermal decomposition preferentially occurs as nucleophilic substitution.

It is not improbable that thermal decomposition of hexafluorophosphates occurs by both mechanisms, E_2 and $S_N(C)$, simultaneously, but at lower temperatures (200–300°C) the nucleophilic substitution mechanism is more probable, whereas at elevated temperatures the E_2 mechanism should be realized.

CONCLUSIONS

(1) All the quaternary ammonium hexafluorophosphates studied surpass in thermal stability quaternary ammonium halides and are stable up to 300°C.

(2) Tetrabutyl- and tetraethylammonium hexafluorophosphates, in contrast to the other salts studied, decompose without melting. The process occurs in two steps with complete decomposition above 400°C.

(3) The effect of cation on the thermal stability of quaternary ammonium hexafluorophosphates was determined. With symmetrical cations $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, and $(C_4H_9)_4N^+$, the Coulomb interactions with PF_6^- anions are enhanced, which leads to an increase in the crystallinity and in the decomposition temperature of the corresponding compounds.

(4) Quaternary ammonium hexafluorophosphates containing benzyl or allyl radical with C_{sp^2} atoms in the cationic moiety are less stable and decompose in the interval 280–360°C, with the decomposition pattern being similar.

(5) The mechanism of thermal decomposition of tetraalkylammonium hexafluorophosphates was suggested. The process presumably occurs as β -elimination (E_2) or as nucleophilic substitution (S_N) depending on the cation.

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