Novel synthesis, characterization and thermal degradation of hydrazinium hexafluorophosphate*

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Abstract

Hydrazinium hexafluorophosphate has been synthesised for the first time in quantitative yields in a direct reaction between ammonium hexafluorophosphate and hydrazine hydrate. Chemical analysis and infrared spectroscopy characterizes the white crystalline solid as $\text{N}_2\text{H}_5\text{PF}_6$.

Thermal decomposition in air has been studied by TG and DTA techniques. A stepwise decomposition is observed with an intermediate formation of $\text{NH}_4\text{PF}_6$. The final products are, however, all gases, ammonia, hydrogen fluoride and phosphorus pentafluoride which makes it an interesting species for thermal reaction studies.

Key words: Hydrazinium hexafluorophosphate, thermal degradation.

1. Introduction

Salts of hydrazine with a number of anions, such as $\text{BF}_4^-$, $\text{SiF}_5^-$ and $\text{TiF}_6^-$, have been reported. Though 1,1,1-tri-substituted (alkyl and aryl) hydrazinium hexafluorophosphate has been reported, no report on the simple hydrazinium hexafluorophosphate is available. In the present investigation, a simple and efficient method has been developed for the preparation of hydrazinium hexafluorophosphate. The other products, being gases, can be pumped out leaving a pure sample of solid $\text{N}_2\text{H}_5\text{PF}_6$.

2. Materials and methods

Ammonium hexafluorophosphate ($\text{NH}_4\text{PF}_6$) was prepared by reacting pyridinium hexafluorophosphate with ammonium hydroxide. AR grade hydrazine hydrate and chloroform were used.

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2.1. Method

Ammonium hexafluorophosphate, 5 g (0.0306 M) was taken in a beaker (50 ml) and treated with 1.9 ml (0.0304 M) of hydrazine hydrate (80%). An instantaneous reaction occurred with the evolution of ammonia gas and formation of a semi-solid. The reaction could be represented by the equation

\[ \text{NH}_4\text{PF}_6 + \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_5\text{PF}_6 + \text{NH}_3 + \text{H}_2\text{O}. \]

Water and ammonia formed during this reaction were removed under vacuum and the resulting hydrazinium hexafluorophosphate was stored over phosphorus pentoxide. The weight of the white crystalline solid was 5.05 g corresponding to an yield of 93% based on the ammonium hexafluorophosphate used.

The melting point of the sample was found to be 110°C. Analysis indicated a content of more than 99% of hydrazinium hexafluorophosphate. Hydrazine and PF$_6^-$ contents of the sample were estimated volumetrically$^{10}$ and gravimetrically$^{11}$, respectively; hydrazine (\%) calcd 17.97, found: 18.00; PF$_6^-$(\%) calcd 80.46, found: 79.60. The infrared spectrum of hydrazinium hexafluorophosphate recorded on a Perkin Elmer Model 599 spectrophotometer, in Nujol, is given in fig. 1. Thermal decomposition in air has been studied with ULVAC Sinku-Rikota 1500 thermal analyser which records DTA, TGA (fig. 2) and DTGA simultaneously. A platinum cup was used as sample holder and the heating rate was 10°/min in the temperature range 25–500°C.

![Infrared spectrum of hydrazinium hexafluorophosphate (Nujol).](image)
3. Results and discussion

3.1. Infrared spectral data

Various infrared absorptions noted on the IR spectrum have been assigned. The two prominent strong peaks at 830 and 560 cm\(^{-1}\) of the octahedrally symmetric PF\(_6^-\) anion\(^{12}\) have been assigned \(v_3\) (\(F_{1u}\)), P–F stretching and \(v_4\) (\(F_{1u}\)), P–F bending vibrations, respectively.

The peaks at 3390, 3345 and 3300 cm\(^{-1}\) have been assigned to the N–H stretching vibrations, and those at 1610 and 1540 cm\(^{-1}\) to NH\(_2\)- and NH\(_3\)-bending vibrations, respectively. The NH\(_2\)-rocking vibration of the N\(_2\)H\(_5^+\) ion has appeared at 1115 cm\(^{-1}\). The peak at 965 cm\(^{-1}\) has been assigned to the N–N stretching vibration of the N\(_2\)H\(_5^+\) ion based on an earlier observation\(^{13,14}\).

3.2. Thermal degradation behaviour of hydrazinium hexafluorophosphate

The DTA shows an endotherm at 111°C which corresponds to the melting of the compound and an exotherm at 248°C followed by a large endotherm with the peak temperature at 342°C attributable to decompositions.

\[
3N_2H_5PF_6 \xrightarrow{348^\circ C} 3NH_4PF_6 + NH_3 + N_2;
\]

\[
NH_4PF_6 \xrightarrow{342^\circ C} NH_4F + PF_5.
\]

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![Fig. 2. DTA and TG curves of hydrazinium hexafluorophosphate.](image1)

![Fig. 3. DTA and TG curves of ammonium hexafluorophosphate.](image2)
To substantiate the above mechanism, thermal decomposition of \( \text{NH}_4\text{PF}_6 \) was also carried out under similar conditions (fig. 3). The DTA shows a large endotherm with the peak temperature at 352°C and the TG curve a 100% weight loss. This endotherm could be due either to sublimation of \( \text{NH}_4\text{PF}_6 \) or to decomposition giving rise to gaseous products such as \( \text{NH}_3 \), HF and PF₅.

In a separate experiment, the decomposition of ammonium hexafluorophosphate was carried out at 360°C. A white sublimate was deposited on the cooler parts of the reaction vessel. The infrared spectrum of the gas phase showed the presence of phosphoryl fluoride with traces of ammonia. The sublimate, when analysed quantitatively, tested positively for the presence of ammonium and fluoride radicals. Non-formation of any violet precipitate with methylene blue¹¹ indicated that the sublimate did not contain the PF₆⁻ radical ion. The sublimate, therefore, is considered to be ammonium fluoride and the gaseous component PF₅ which in the presence of moisture forms POF₃ which is shown on the IR spectrum.

The TG curve of hydrazinium hexafluorophosphate shows a continuous weight loss (up to 100%) in the temperature range 180–408°C, and leaves no residue after decomposition. This is in conformity with the expectation from the above proposed scheme wherein the products are all gases.

The decomposition endotherms of \( \text{N}_2\text{H}_5\text{PF}_6 \) appear at 342°C and that of \( \text{NH}_4\text{PF}_6 \) at 353°C and the shapes of the endotherms also being similar, clearly indicate that \( \text{N}_2\text{H}_5\text{PF}_6 \) thermally decomposes to \( \text{NH}_4\text{PF}_6 \), which further decomposes to ammonium fluoride and phosphorus pentafluoride. Such behaviour is noted in a few other hydrazinium salts¹⁵⁻¹⁸ and it is of interest to note that \( \text{NH}_4\text{PF}_6 \) decomposes with dissociation, as other alkali metal hexafluorophosphates¹⁹.

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