J. Indian Inst. Sci., Mar.–Apr. 1989, 69, 125–129

Novel synthesis, characterization and thermal degradation of hydrazinium hexafluorophosphate*

K. SYED MOHAMED AND D. K. PADMA
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

Received on April 13, 1988; Revised on August 8, 1988.

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 $N_2H_5^+PF_6^-$. Thermal decomposition in air has been studied by TG and DTA techniques. A stepwise decomposition is observed with an intermediate formation of NH_4PF_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[1,2], such as BF_4[3,4], SiF_6[5] and TiF_6[6], have been reported. Though 1, 1, 1-tri-substituted (alkyl and aryl) hydrazinium hexafluorophosphate has been reported[7,8], 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 $N_2H_5^+PF_6^-$.

2. Materials and methods

Ammonium hexafluorophosphate (NH_4PF_6) was prepared by reacting pyridinium hexafluorophosphate with ammonium hydroxide[9]. AR grade hydrazine hydrate and chloroform were used.

---

*Accepted for presentation at the 11th International Conference on Phosphorus Chemistry at Tallinn, USSR, July 1989.

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

$$NH_4PF_6 + N_2H_4 \cdot H_2O \rightarrow N_2H_5PF_6 + NH_3 + H_2O.$$

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.

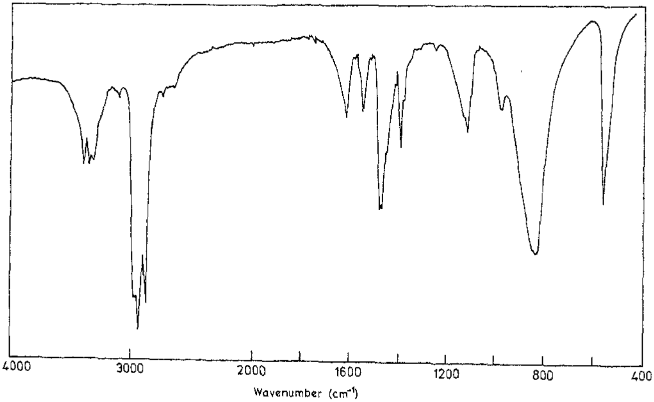

FIG. 1. Infrared spectrum of hydrazinium hexafluorophosphate (Nujol).

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 ν_3 (F_{1u}), P–F stretching and $\nu_4(F_{1u})$, 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 $N_2H_5^+$ ion has appeared at 1115 cm^{-1}. The peak at 965 cm^{-1} has been assigned to the N–N stretching vibration of the $N_2H_5^+$ 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.

$$3N_2H_5PF_6 \xrightarrow{248^\circ C} 3NH_4PF_6 + NH_3 + N_2;$$

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

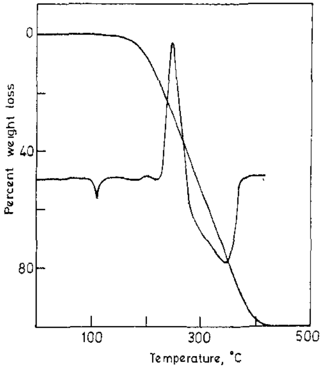

FIG. 2. DTA and TG curves of hydrazinium hexafluorophosphate.

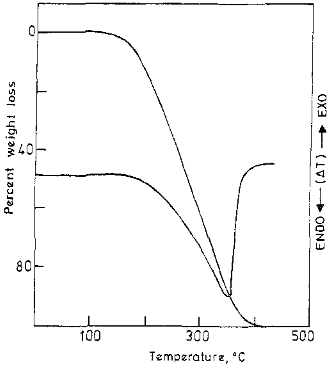

FIG. 3. DTA and TG curves of ammonium hexafluorophosphate.

To substantiate the above mechanism, thermal decomposition of NH_4PF_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 NH_4PF_6 or to decomposition giving rise to gaseous products such as NH_3, HF and PF_5.

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 blue[11] indicated that the sublimate did not contain the PF_6^- radical ion. The sublimate, therefore, is considered to be ammonium fluoride and the gaseous component PF_5 which in the presence of moisture forms POF_3 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 $N_2H_5PF_6$ appear at 342°C and that of NH_4PF_6 at 353°C and the shapes of the endotherms also being similar, clearly indicate that $N_2H_5PF_6$ thermally decomposes to NH_4PF_6, which further decomposes to ammonium fluoride and phosphorus pentafluoride. Such behaviour is noted in a few other hydrazinium salts[15–18] and it is of interest to note that NH_4PF_6 decomposes with dissociation, as other alkali metal hexafluorophosphates[19].

Acknowledgements

KSM thanks the UGC for teacher fellowship.

References

1. AUDRIETH, L. F. AND OGG, B. A. *The chemistry of hydrazine*, John Wiley, 1951
2. SCHIMDT, E. W *Hydrazine and its derivatives: Preparation, properties and applications*, Wiley, 1984.
3. FUNK, H. AND BINDER, F Preparation of salts of fluoroboric acid(II), *Z. Anorg. Allgem. Chem.*, 1926, **159**, 121–124.
4. FRLEC, B., GANTAR, D., GOLIC, L. AND LEBAN, I. Synthesis and characterization of hydrazinium (2+)tetrafluoroborate(III), *J. Fluor. Chem.*, 1984, **24**, 271–279.
5. FRLEC, B., GANTAR, D., GOLIC, L. AND LEBAN, I. Hydrazinium (2+)hexafluorosilicate(IV), *Acta Cryst.*, 1980, **36B**, 1917–1918.
6. SLIVNIK, J., MACEK, J., OREL, B AND SEDEJ, B. Synthesen und einige thermische und strukturelle eigenschaften von hydrazinium fluorotitanate (IV), *Monatsh Chem.*, 1973, **104**, 624–632.

7. OMIETANSKI, G. M. AND SISLER, H H. The reaction of chloramine with tertiary amines, 1, 1, 1, trisubstituted hydrazinium salts, *J. Am. Chem. Soc*, 1956, **78**, 1211–1213.

8. OMIETANSKI, G. M. *US Patent* 2885399 (March 5, 1959).

9 SYED MOHAMED, K., PADMA, D. K, KALBANDKERI, R. G. AND VASUDEVAMURTHY, A. R. Pyridinium poly(hydrogen fluoride)—A reagent for the preparation of hexafluorophosphates, *J. Fluor. Chem*, 1983, **23**, 509–514.

10. VOGEL, A I. *A textbook of quantitative inorganic analysis* Third edition, ELBS and Longman, 1975, p. 380.

11. LANGE, W. AND MÜLLER, E. Über die salze der phosphor-hexafluorwasserstoffsäure, HPF_6, *Ber Chem*, 1930, **63**, 1058–1070.

12. SHURVELL, H. F. Infrared spectra of some hexafluorophosphates and hexafluorosilicates, *Can J. Spectrosc.*, 1967, **12**, 156–162.

13. DECIUS, J C. Relation between force constant and bound length for the nitrogen-nitrogen bond, *J. Chem Phys.*, 1966, **45**, 1069

14. THOMAS, T. H, LADD, J. A, JONES, V. I P. AND ORVILLE THOMAS, W. J. Molecular parameters and bond structure VII Force constant-bond lengths relation for nitrogen-nitrogen bonds and the polar nature of nitrous oxide, *J. Mol. Str.*, 1969, 3, 47–56.

15 MILOJEVIC, M. AND SLIVNIK, J. Preparation and thermal properties of hydrazine mono and dihalides, Thermal Anal. Proc. Int. Conf. 3rd eds H G. Wiedemann and B S. Birkhauser, 1971 (Publ 1972) p 19

16. HOFMANN, K. A. AND FRIEDRICH, K. Über den thermischen zerfall von hydroxylamin-und hydrazinsalzen, *Ber. Chem.*, 1924, **57B**, 937–944.

17. PATIL, K. C, SOUNDARARAJAN, R. AND PAI VERNEKER, V. R. Differential thermal analysis of hydrazinium derivatives, *Thermochim. Acta*, 1979, **31**, 259–261.

18 RUBSTSOV, YU I, AND MANELIS, G. B. (a) Kinetics of the thermal decomposition of hydrazinium chloride, *Russ. J. Phys. Chem*, 1972, **46**, 359–361.
(b) Kinetics of the thermal decomposition of hydrazinium iodide, *Russ. J. Phys. Chem.*, 1971, **45**, 1724–1725.
(c) Effect of hydrazine, water and other additives on the thermal decomposition of hydrazinium iodide, *Russ. J. Phys. Chem.*, 1971, **45**, 1453–1455.

19. THOMAS, E. C. AND MING-MING HISA. Thermal decomposition of alkali metal hexafluorophosphates, *J. Chem. Engng Data*, 1972, **17**, 18–21