

Received: January 19, 1983; accepted: March 16, 1983

PYRIDINIUM POLY(HYDROGEN FLUORIDE) - A REAGENT FOR THE PREPARATION OF HEXAFLUOROPHOSPHATES

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SUMMARY

Pyridinium poly(hydrogen fluoride) has been found to be an efficient and versatile reagent for the preparation of hexafluorophosphates. Pyridinium hexafluorophosphate has been prepared by the reaction between phosphorus (V) halides (POCl_3 , POBr_3 , PSCl_3 , PCl_5 , PBr_5) and pyridinium poly(hydrogen fluoride). This in turn is used to prepare the hexafluorophosphates of ammonium, sodium, potassium, rubidium and cesium in good yield and high purity.

INTRODUCTION

Hexafluorophosphates are well known to be an interesting class of compounds and find extensive applications in catalysis [1] and biological systems [2]. Conventional methods for the preparation of hexafluorophosphates require either the handling of hazardous liquid hydrogen fluoride and/or anhydrous hydrogen fluoride gas under pressure with phosphorus pentachloride and metal chloride [3]. Ammonium and alkali metal hexafluorophosphates have also been prepared in low yields by the reaction of ammonium or alkali metal fluorides with phosphorus pentachloride and isolated by tedious and time consuming processes [4].

Recently Olah et al. [5] have shown that pyridinium poly(hydrogen fluoride) can be conveniently and safely used at atmospheric pressure for the preparation of a variety of organic fluorine compounds. During the course of our investigations on the preparation and characterisation of fluorine compounds, it has been observed that this versatile reagent could be used for the preparation of pyridinium hexafluorophosphate from several phosphorus(V) halides in good yield and high purity.

The reaction of pyridinium hexafluorophosphate with ammonium hydroxide and alkali metal hydroxides/chlorides has been extended to prepare the corresponding ammonium and alkali metal hexafluorophosphates in almost quantitative yields. The details of the preparative methods and characterisation of these compounds are presented in this paper.

EXPERIMENTAL

(a) General

All the experiments were carried out in polythene ware in an efficient hood with proper precautions against spillage and fumes of hydrogen fluoride. Polythene separatory funnels were used for extraction.

Infra-red spectra were recorded on Perkin Elmer 599 spectrophotometer. ^1H NMR spectrum of pyridinium hexafluorophosphate was obtained on a Varian T60 NMR spectrometer using DMSO-d_6 as solvent. X-ray powder pattern diffractograms for all the samples were recorded on Phillips 1050/70 X-ray diffractometer. All the compounds were analysed for the PF_6^- content gravimetrically using nitron as precipitant.

(b) Preparation of pyridinium poly(hydrogen fluoride) reagent [5]

100g (5 mole) of liquid hydrogen fluoride drawn from a cylinder was added in portions to 148g (1.87 mole) of dry pyridine cooled to -80°C with magnetic stirring. This reagent solution A (mole ratio of pyridine to HF is 3:8) was employed for the preparation of pyridinium hexafluorophosphate.

(c) Preparation of pyridinium hexafluorophosphate using phosphoryl chloride (POCl_3)

40 ml of chilled reagent solution A was reacted with 16g of phosphoryl chloride added dropwise. The separated white pyridinium hexafluorophosphate was washed with chloroform and recrystallised from water. This sample was compared with that prepared by the method reported by Lange et al [6] by mixing pyridine in acetic acid with a concentrated solution of ammonium hexafluorophosphate. The melting point, infra-red and ^1H NMR spectra of both samples were in good agreement.

A new analytical procedure was evolved for the analysis of pyridinium hexafluorophosphate by titrating a known amount of the sample in water (pH of 0.1 N solution was 3.6) with a standard solution (0.1N) of sodium hydroxide using phenolphthalein as indicator. In a separate experiment the PF_6^- content was estimated. The analytical results indicated that the sample was 99.89% pure.

Pyridinium hexafluorophosphate was also prepared under similar experimental conditions by substituting POCl_3 with the corresponding amounts of (i) POBr_3 , (ii) PSCl_3 , (iii) PCl_5 and (iv) PBr_5 . The experimental results are given in Table I. In the case of PSCl_3 , a quantitative amount of hydrogen sulphide was liberated which was swept off by a current of nitrogen and estimated iodometrically.

Table I

Preparation of pyridinium hexafluorophosphate from the reaction between pyridinium poly(hydrogen fluoride) and phosphorus (V) halides

S. No.	Phosphorus (V) halide	Amount of phosphorus (V) halides taken g (mole)	Volume of pyridinium poly(hydrogen fluoride) solution ml	Amount of pyridinium hexafluorophosphate (g)		Yield %*
				Expected	Obtained	
1	POCl ₃	16 (0.1)	40	23.47	19.95	85
2	POBr ₃	5 (0.0174)	20	3.92	3.33	85
3	PSCl ₃	8 (0.0472)	20	10.62	9.55	90
4	PCl ₅	10 (0.0480)	20	10.80	9.72	90
5	PBr ₅	20 (0.0464)	30	10.44	8.35	80

* The purified product appears as bright colourless needles, starts melting in the range 170-175°C and decomposes around 208°C.

(d) Preparation of ammonium and alkali metal hexafluorophosphates

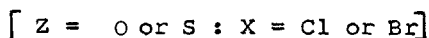
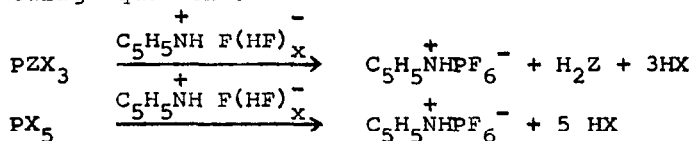
Recrystallised pyridinium hexafluorophosphate (0.05 mole) was suspended in water and treated with the calculated quantity of alkali metal hydroxides and a slight excess in the case of ammonium hydroxide. The pyridine liberated was extracted with chloroform and the aqueous solution was evaporated to dryness in vacuo. The salts (NaPF₆, KPF₆ and NH₄PF₆) were preserved over conc. H₂SO₄. In a similar manner rubidium and cesium hexafluorophosphates were prepared by using the corresponding chlorides and pyridinium hexafluorophosphate in

the presence of ammonium hydroxide. The salts were characterised by comparison of their infra-red spectra and X-ray powder patterns with those reported [7-10]. All the salts were analysed for their PF_6^- content. It was found to be rather difficult to isolate solid LiPF_6 by this cation exchange method.

RESULTS AND DISCUSSION

The results in Table I indicate that pyridinium hexafluorophosphate (10-20g) can be conveniently prepared in about 90% yields from all the phosphorus (V) halides taken for the reaction with the reagent pyridinium poly(hydrogen fluoride). The ammonium and alkali metal hexafluorophosphates have been prepared in more than 90% yield and of purity more than 99%. This preparative route is much simpler and the yields are much higher.

The formation of pyridinium hexafluorophosphate from phosphorus (V) halides could be explained in terms of the following equations.



The infra-red spectrum of pyridinium hexafluorophosphate recorded for the first time in the range 400-4000 cm^{-1} shows the following major absorption frequencies (cm^{-1}); 3330s, 3210s, 3150s, 3120s, 1638s, 1610s, 1540s, 1490s, 1400m, 830 vs, 740s, 670s, 558s. The band at 3330 cm^{-1} may be assigned to $\nu(\text{N-H})$ and the bands at 830 and 558 cm^{-1} have been assigned to $\nu(\text{P-F})$ and $\delta(\text{P-F})$ respectively [11]. The other bands are due to the pyridine moiety with the expected shifts due to salt formation.

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