Direct Synthesis of Ammonium Monofluorophosphate Monohydrate, $[NH_4]_2[PO_3F]\cdot H_2O$, and Potassium Monofluorophosphate, $K_2[PO_3F]$

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A new direct general method for the synthesis of crystalline $[NH_4]_2[PO_3F]\cdot H_2O$ and $K_2[PO_3F]$, based on the reaction of H_3PO_4 and AHF_2 (A = NH_4 or K) followed by precipitation with ethanol, is described. The identity of the compounds has been established from the results of elemental analyses, molar conductance measurements, i.r. and laser Raman spectroscopic studies. Advantages of the new method are highlighted.

Monofluorophosphate, $[PO_3F]^{2-}$, is important particularly because of its use as an additive in dentifrice formulations for the inhibition of dental caries. Alkali monofluorophosphates have been known for quite some time,[1-5] however, there is no simple and easily accessible route to such compounds. The recommended methods[1-5] for their synthesis involve either a high-temperature fusion reaction, or fluorophosphoric acid as the starting material which requires extra preparation and purification, in addition to one or more steps to remove unwanted products, inevitably formed in either of the methods, to obtain the pure products. While studying the chemistry of fluoro compounds of some other elements,[6] it became necessary to synthesise alkali monofluorophosphates. The present work deals with the direct synthesis of ammonium monofluorophosphate monohydrate, $[NH_4]_2[PO_3F]\cdot H_2O$, and potassium monofluorophosphate, $K_2[PO_3F]$, and also highlights the advantages of the new method over those previously reported.

Experimental

Concentrated phosphoric acid (88%, 1.75 g cm^{-3}) used was of reagent-grade quality. The difluorides AHF_2 (A = NH_4 or K) were synthesised by the method developed in this laboratory.[7] Freshly distilled ethanol was used as a precipitant. Molar conductance was measured in conductivity-grade water using a Systronic type 304 digital direct reading conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. The laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrophotometer. The 5 154-Å laser line from a Spectra-Physics model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds.

Synthesis of $[NH_4]_2[PO_3F]\cdot H_2O$ *and* $K_2[PO_3F]$.—Since the method of synthesis is a general one only a representative procedure is described.

In a typical procedure 88% phosphoric acid (1.0 cm^3, 17.9 mmol; density 1.75 g cm^{-3}) was thoroughly mixed with AHF_2 (72 mmol; A = NH_4 or K), followed by the addition of water (*ca.* 10 cm^3). The solution thus obtained was stirred for 15 min. An amount of ~95% ethanol (*ca.* 20 cm^3) was added with stirring, whereupon white crystalline $[NH_4]_2[PO_3F]\cdot H_2O$ or $K_2[PO_3F]$ was precipitated. Stirring was continued for a further 15—20 min and the mixture was then allowed to stand for *ca.* 10 min. The compound was separated by centrifugation, washed 3—4 times with ethanol, and finally dried *in vacuo* over P_4O_{10}. The yields of $[NH_4]_2[PO_3F]\cdot H_2O$ and $K_2[PO_3F]$ were 1.8 g (66%) and 1.9 g (60%) respectively {Found: F, 12.7; N, 18.55; P, 20.6. Calc. for $[NH_4]_2[PO_3F]\cdot H_2O$: F, 12.5; N, 18.4; P, 20.35%. Molar conductance (Λ_M): 230 Ω^{-1} cm^2 mol^{-1}. Found: F, 11.1; K, 44.55; P, 17.8. Calc. for $K_2[PO_3F]$: F, 10.80; K, 44.40; P, 17.60%. Molar conductance (Λ_M): 225 Ω^{-1} cm^2 mol^{-1}}.

Elemental Analyses.—Phosphorus was estimated gravimetrically as $Mg_2[P_2O_7]$.[8] Fluoride was precipitated as PbClF and chloride was estimated by Volhard's method, from which the fluoride content was calculated.[9] Nitrogen and potassium were determined by the methods described earlier.[10]

Results and Discussion

Reaction of phosphoric acid, H_3PO_4, with hydrofluoric acid, under the appropriate conditions, gives rise to the formation of monofluorophosphoric acid, H_2PO_3F.[11] Substitution of ionisable protons by ammonium or alkali-metal ions (A) then provides the corresponding $A_2[PO_3F]$, if the wet methods are chosen. Alkali hydrogenfluorides, sources of HF, possess some special qualities as reagents, as they can not only act as fluorinating agents[6] but also maintain an acidic environment in a polar medium thus providing conditions conducive to some syntheses which are otherwise difficult.[6] Thus it was expected that interaction of an alkali hydrogenfluoride with phosphoric acid might lead directly to the title compounds. Accordingly, in line with the synthetic strategy, AHF_2 (A = NH_4 or K) were treated with H_3PO_4 which underwent a very facile fluorination and led to the direct synthesis of $A_2[PO_3F]$. The alkali hydrogenfluoride acted here not only as a fluorinating agent but also as the source of counter cation. The role of ethanol in the present synthesis was to bring about precipitation of the desired compounds. It may be mentioned that while the ammonium salt was obtained as a monohydrate the corresponding potassium salt was anhydrous. The new method, which can be scaled up if desired, is a straight one, and it neither involves any extra preparation step nor the use of hydrofluoric acid, rendering it easy to handle.

The results of elemental analyses are satisfactory (see Experimental section) and no recrystallisation is necessary. The compounds are stable for a prolonged period and are soluble in water. They permit molar conductance measurements, and the values were found to lie in the range 220—235 Ω^{-1} cm^2 mol^{-1}, in complete agreement with a 2:1 electrolye. Further, these results suggest that the compounds are also stable in solution and do not undergo decomposition, at least under the experimental conditions employed. I.r. spectra of the compounds synthesised by the new method are in order.[12] Laser Raman spectra, recorded on the solids between 1 200 and 600 cm^{-1}, show signals at *ca.* 922 and *ca.* 950 cm^{-1} which have been assigned [13] to ν(P–F) and ν(P=O) vibrations, respectively. Thus the results suggest that the compounds are the same as those described earlier.[2,3,5]

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