Ammonium Fluoroperoxomonophosphate Dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$. First Chemical Synthesis of a Fluorinated Peroxophosphate

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The salt $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$ has been synthesised from the reaction of $[NH_4][H_2PO_4]$ with 48% HF and 30% H_2O_2 at pH 10—11, maintained by the addition of aqueous ammonia, at an ice-bath temperature. The compound has been characterised by chemical analysis, i.r., and laser-Raman spectroscopic studies. Some properties of the compound are also reported.

In contrast to a host of reports concerning the synthesis, characterisation, and reactivity of peroxometal compounds, information on the corresponding aspects of non-metals is scanty, probably because of a limited access to such compounds. Some peroxo compounds of carbon, sulphur, and phosphorus, for example, are known[1,2] in addition to a few fluorinated peroxides of carbon and sulphur[3] which were generally synthesised by fluorination of oxo-compounds of the corresponding elements, a method which requires a very careful manipulation. It was reported over half a century ago[4] that anodic oxidations of fluorophosphoric acids produced fluoroperoxophosphoric acids $H_2PO_2(O_2)F$ and $H_2P_2O_4(O_2)F_2$, only in *ca.* 2% yields. The compounds are poorly characterised and to our knowledge neither salts of the acids nor chemical syntheses of fluorinated peroxophosphates, have been reported. We report herein a simple and efficient synthesis for the heretofore unknown ammonium fluoroperoxomonophosphate dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$, the first chemically synthesised fluoroperoxophosphate, along with its structural assessment and some results of our studies of its chemistry.

Experimental

Reagent-grade chemicals were used throughout. I.r. and laser-Raman spectra were recorded on instruments and under conditions already described.[5,6] The pH measurements were accomplished with a Systronics type 335 digital pH meter as well as with pH indicator (BDH) paper.

Synthesis of Ammonium Fluoroperoxomonophosphate Dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$.—A mixture of ammonium dihydrogenphosphate, $[NH_4][H_2PO_4]$ (1 g, 8.69 mmol), and 48% HF (1 cm^3, 24 mmol) was allowed to react with 30% hydrogen peroxide (15 cm^3 132.3 mmol) in an ice-bath, at pH 10—11 maintained by careful addition of aqueous ammonia (sp. gr. 0.9) with stirring. Stirring was continued for *ca.* 7 min followed by the addition of ice-cold ethanol (*ca.* 25 cm^3), whereupon white crystals were precipitated. These were filtered off, washed five to six times with ethanol, and dried *in vacuo* over concentrated H_2SO_4. Yield 1.3 g (81%) {Found: H, 6.6; F, 9.9; N, 14.7; O_2^{2-} (active oxygen), 16.9; P, 16.8. Calc. for $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$: H, 6.5; F, 10.2; N, 15.05; O_2^{2-} (active oxygen), 17.2; P, 16.65%}.

Elemental Analyses.—The fluoride and phosphorus[6] and peroxide, nitrogen, and hydrogen[7] contents were determined by methods described earlier.

Results and Discussion

It was shown recently[6] that a direct interaction of phosphoric acid with alkali hydrogenfluoride, AHF_2, afforded monofluorophosphate, PO_3F^{2-}. A similar reaction conducted in the presence of hydrogen peroxide, however, did not give access to a fluoroperoxophosphate. Subsequently it was noticed that a rise in pH of the reaction medium and thence isolation of a solid indicated the formation of the kind of product looked for. Accordingly, the first chemical synthesis of a fluoroperoxophosphate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$, was achieved by the reaction of ammonium dihydrogenphosphate with 48% HF and hydrogen peroxide at pH 10—11 maintained by the addition of aqueous ammonia [equation (1)]. The role of ammonia was not only to raise the pH to facilitate formation of fluoroperoxophosphate but also to act as the source of counter cations, while ethanol helped in precipitating the product. The compound can be stored for a prolonged period in a sealed polyethylene envelope in a freezer, and is insoluble in common organic solvents. It decomposes in water, and quantitatively liberates H_2O_2 in the presence of sulphuric acid, rendering it easy to determine the active oxygen content. The results of peroxide estimation and elemental analyses are in complete agreement with the formula given.

$$[NH_4][H_2PO_4] + HF + H_2O_2 + NH_4OH \longrightarrow [NH_4]_2[PO_2(O_2)F] + 3H_2O \quad (1)$$

The i.r. spectrum of the compound indicates the presence of peroxide, P–F, and P=O vibrations. Features at 960—1 060s and 900s cm^{-1} are similar in shape and position to those expected for the stretching modes of P=O and P–F, respectively.[8] Quite significant is the medium-intensity absorption at 853 cm^{-1} which has been assigned to ν(O—O) originating from a peroxide group bonded to the phosphorus centre. The doublet at 550s and 530s cm^{-1} is believed to arise from δ(OPO) modes. The i.r. spectrum also provides evidence for NH_4^+ and lattice water.

The laser-Raman spectrum of the solid is in close agreement with its i.r. spectrum and shows signals at 950 and 900 cm^{-1} due[9] to ν(P=O) and ν(P–F), respectively, at 858 cm^{-1} assigned to ν(O–O), and 556 and 528 cm^{-1} attributed to δ(OPO) modes. These results confirm the formulation of the compound, with the peroxide (O_2^{2-}) group being presumably bonded in an end-on manner as encountered in simple monoperoxo derivatives of sulphur and phosphorus.

It was of interest that this compound, in the presence of an acid, was capable of oxidising an hydrocarbon, alcohols, and olefins. Thus in stoicheiometric reactions it oxidised anthracene to anthraquinone, 2-propanol to acetone, n-butanol to butanal, cyclohexene to 1,2-cyclohexanediol, and styrene to 1-phenylethylene glycol, generally in *ca.* 40% yield. Equally interesting is the phosphorus product isolated after working up of the oxidation product in each of the above reactions. This has been identified as the monofluorophosphate, PO_3F^{2-}, a species important because of its use as an additive in dentifrice formulations. In the absence of air, the peroxo compound in water reacts with SO_2 to produce sulphate.

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