Hydrothiophosphoryl Difluoride, SPF_2H, a New, Stable Hydride of Quinquevalent Phosphorus

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THE reactions of dialkylamino-derivatives of phosphorus fluorides with hydrogen halides have been established as a convenient preparative route to the mixed fluorohalides of phosphorus.[1,2]

The reactions of the tervalent phosphorus fluorides[1] predictably follow the equation:

$$PF_2{\cdot}NR_2 + 2HX \rightarrow PF_2X + R_2NH_2X \qquad (1)$$

where X = Cl, Br, I, and it has recently been shown that the quinquevalent alkylaminophosphoryl and thiophosphoryl fluorides are converted into the mixed chloro- or bromo-fluorides:[2]

$$EPF_2{\cdot}NR_2 + 2HX \rightarrow EPF_2X + R_2NH_2X \qquad (2)$$

where in these cases E represents S or O, and X = Cl or Br.

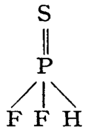
We have found that hydrogen iodide does not react with dimethylaminothiophosphoryl difluoride in the way indicated by reaction (2) but rather, molecular iodine is formed as one of the products. The phosphorus compound formed was identified as hydrothiophosphoryl difluoride, SPF_2H. Essentially complete conversion of the dimethylamino-compound into the hydride was obtained using the stoicheiometry expressed by the equation:

$$SPF_2{\cdot}N(Me)_2 + 3HI \rightarrow SPF_2H + Me_2NH_2I + I_2 \qquad (3)$$

Hydrothiophosphoryl difluoride was characterised by molecular weight (Found: *M*, 104; Calc. for HF_2SP: *M*, 102) and precise measurement of the parent ion in the mass spectrum, recorded on an AEI MS–9 mass spectrometer (Found: *m/e*, 101·9503; Calc. for $HF_2P^{32}S$: *m/e*, 101·9505).

The nuclear magnetic resonance spectra strongly support the formulation of the compound as a derivative of quinquevalent phosphorus. The ^{19}F spectrum is a doublet of doublets with coupling constants J (P–F) = 1153·3 c./sec. and J (F–H) = 99·0 c./sec. and a chemical shift of +46·1 p.p.m. relative to CCl_3C. The proton spectrum is a doublet of triplets with coupling constants J (P–H) = 725·4 c./sec. and J (F–H) = 98·9 c./sec. and a chemical shift of τ = 1·93 relative to tetramethylsilane (τ = 10·0). The low value of τ suggests P–H rather than P–S–H bonding since the latter are typically observed at $\tau \sim 7$. The large value of the P–H coupling constant is also consistent with hydrogen directly bonded to phosphorus and similarly the magnitude of F–H coupling indicates that the atoms are not separated by more than one atom, thus ruling out the phosphine structure, F_2P–S–H. The nuclear resonance parameters are similar to those recently reported[3] for PF_2H except that the P–H and F–H coupling constants are larger in SPF_2H. They are also quite similar to the values observed in the anion $CF_3PF_4H^-$ which is another example of a quinquevalent phosphorus hydride derivative.[4] The P–F coupling constant obtained for SPF_2H is somewhat high for quinquevalent phosphorus but is in keeping with the value of 1189 c./sec. observed for SPF_3.[2b]

The infrared spectrum of the vapour shows a medium-intensity band at 2458 cm.$^{-1}$ with typical PQR rotational structure. This band suggests a P–H rather than S–H stretching vibration since the former are usually found near 2400 cm.$^{-1}$ whereas the latter are usually found[5] near 2600 cm.$^{-1}$. A strong absorption band at 1016 cm.$^{-1}$ also with rotational structure is assigned to the P–H bending vibration. The observed value is more consistent with P–H bonding than with S–H bonding.[5] Other bands which support the thiophosphoryl structure are the strong band at 918 cm.$^{-1}$, assigned to P–F stretching, and the medium band at 705 cm.$^{-1}$ assigned to the P=S stretch.[5] In general all of the spectroscopic information supports the structure:



The compound is stable at room temperature for extended periods and thus is more stable than the recently reported tervalent analogue[3] PF_2H which is made by a reaction similar to reaction (3) but requiring mercury for removal of iodine. The increased stability of the sulphur derivatives may well be due to the electron delocalization in the phosphorus–sulphur bond.

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