Reactions of Boron Compounds with Difluorophosphoric Acid; Characterisation of the Tetrakis(difluorophosphato)borate Anion by Multinuclear (^{11}B, ^{19}F, and ^{31}P) Nuclear Magnetic Resonance Spectroscopy

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The tetrakis(difluorophosphato)borate anion, $[B(PO_2F_2)_4]^-$ (1), has been identified and characterised in solution by means of ^{11}B, ^{19}F, and ^{31}P n.m.r. spectroscopy. (1) is formed from H_3BO_3 and $P_2O_3F_4$ in HPO_2F_2. It is also the initial product of the reaction of BBr_3 or BCl_3 with excess HPO_2F_2; however, it is gradually converted to (2), which is believed to be $[BF(PO_2F_2)_3]^-$. (2) is also generated directly from either BF_3 or BF_4^- in $P_2O_3F_4$–HPO_2F_2 mixtures, in which it is gradually converted to (1).

Difluorophosphoric acid has been the subject of a number of reviews.[1-4] The study of solutes in this medium is made more difficult owing to the tendency of this compound to decompose,[5] equation (i), even at room temperature. No simple anionic difluorophosphato-species, $[M(PO_2F_2)_n]^{m-}$, have been characterised. However, Russian workers [6] have recently identified the mixed complexes $[MF_5(PO_2F_2)]^-$ (M = P, As, or Sb) in HPO_2F_2–MeCN mixtures.

$$2HPO_2F_2 \longrightarrow H_2PO_3F + POF_3 \qquad \text{(i)}$$

This paper describes the reactions of some simple boron compounds with HPO_2F_2, with or without the anhydride $P_2O_3F_4$, and presents evidence from multinuclear n.m.r. spectroscopic studies for the formation of $[B(PO_2F_2)_4]^-$ and $[BF(PO_2F_2)_3]^-$.

Experimental

Reagents.—Commercial grade difluorophosphoric acid (Ozark-Mahoning) was purified by the method of Desmarteau and co-workers.[5] The anhydride $P_2O_3F_4$ was produced from the acid according to Robinson;[7] fractional distillation of the $P_2O_3F_4$–HPO_2F_2 mixture was not carried out since this mixture was suitable for our purposes. Commercial grade (BDH) BBr_3 and BCl_3 were distilled *in vacuo* before use. Commercial grade H_3BO_3 (BDH) and BF_3 (Cumbria Gases) were used without further purification. NMe_4BF_4 was prepared from H_3BO_3, NMe_4OH, and AR grade hydrofluoric acid.

Sample Preparation.—All reactions were carried out on millimolar quantities of the boron compounds in valved 5-mm glass n.m.r. tubes. The moisture-sensitive reagents were transferred *in vacuo*. The reactions of BBr_3 and BCl_3 with HPO_2F_2 were vigorous and each resulted in the formation of a two-phase system, which became homogeneous only when shaken at room temperature.

N.M.R. Measurements.—All spectra were obtained using a Bruker WM250 pulsed Fourier-transform spectrometer with the samples at 22 °C. ^{11}B, ^{31}P, and ^{19}F spectra were obtained at 80.2, 101.2, and 235.36 MHz respectively. High-frequency chemical shifts were taken to be positive relative to the external standards $BF_3\cdot OEt_2$, 85% phosphoric acid, and $CFCl_3$, respectively. The sealed 5-mm sample tubes were mounted coaxially in a 10-mm tube containing $CDCl_3$, to provide the deuterium lock for the spectrometer. Spectra of the samples were obtained at monthly intervals for up to 12 months.

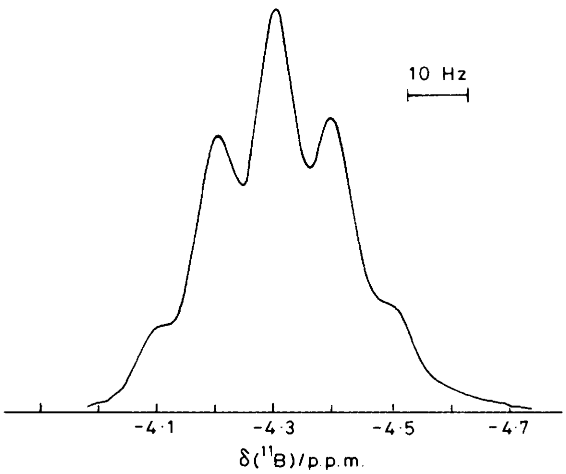


Figure 1. Boron-11 n.m.r. spectrum of species (1)

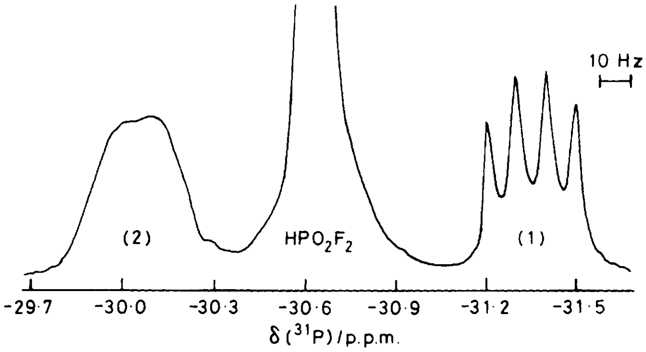


Figure 2. Phosphorus-31 n.m.r. spectrum (central resonances only) of the BCl_3–HPO_2F_2 (mole ratio 1 : 24) system

Results

(*a*) BBr_3– *and* BCl_3–HPO_2F_2 *Systems.*—At mole reactant ratios HPO_2F_2 : BX_3 (X = Br or Cl) above 9 : 1 the n.m.r. spectra demonstrated that these two systems are similar; only one boron-containing product, (1), was detected initially and this gave rise to multiplets in the ^{11}B, ^{31}P, and ^{19}F spectra: a 1 : 4 : 6 : 4 : 1 quintet in the ^{11}B spectrum (Figure 1), a 1 : 2 : 1 triplet of 1 : 1 : 1 : 1 quartets in the ^{31}P spectrum (one quartet appears in Figure 2), and a doublet in the ^{19}F spectrum. With

Table 1. N.m.r. data * for the principal boron-containing products in BX_3–HPO_2F_2 (X = Br or Cl) systems

	^{11}B		^{31}P			^{19}F		
X	δ	^2J(B–P)	δ	^1J(P–F)	^2J(P–B)	δ	^1J(F–P)	Species
Br	−4.4 (quin)	8	−31.5 (t of q)	986	8	−85.1 (d)	984	(1)
	−3.1 (s)	—	−30.3 (t)	980	—	−86.2 (d)	980	(2)
						−140.2 (s)		
Cl	−4.3 (quin)	9	−31.4 (t of q)	985	9	−85.2 (d)	986	(1)
	−2.9 (s)	—	−30.2 (t)	986	—	− 86.2 (d)	982	(2)
						−140.6 (s)	—	

* δ Values in p.p.m. (variations ±0.4 p.p.m. for ^{31}P and ^{19}F, ±0.2 p.p.m. for ^{11}B); *J* values in Hz [variations ±6 Hz for ^1J(P–F) and ±2 Hz for ^2J(B–P)]; quin = quintet, t of q = triplet of 1 : 1 : 1 : 1 quartets, d = doublet, s = singlet, and t = triplet.

Table 2. ^{31}P N.m.r. data [a] for by-products in BX_3–HPO_2F_2 (X = Br or Cl) systems

		δ/p.p.m.		^1J(P–F)/Hz	
X	Product	Observed	Literature	Observed	Literature
Br	$POBr_2F$	−45.4 (d)	−48.3 [b]	1 250	1 263 [b]
	$POBrF_2$	−26.6 (t)	−28.0 [b]	1 195	1 203 [b]
Cl	$POCl_2F$	4.8 (d)	0.0 [b]	1 192	1 180 [b]
	$POClF_2$	−10.9 (t)	−15.0 [b]	1 141	1 138 [b]
	HPO_2ClF	3.1 (d)	−2.0 [c]	1 068	1 050 [c]
Br,Cl	POF_3	−34.2 (q)	−35.5 [d]	1 053	1 058 [d]
	H_2PO_3F	−5.8 (d)	−8.3 [e]	960	955 [e]

[a] q = Quartet (1 : 3 : 3 : 1); for other symbols see Table 1. [b] G. Mavel, *Ann. Rep. NMR Spectrosc., Sect. B*, 1973, **5**, 1. [c] Ref. 4. [d] Ref. 1. [e] G. A. Olah and C. W. McFarland, *Inorg. Chem.*, 1972, **2**, 845.

time a second boron-containing species, (2), was detected which eventually (after *ca.* 3 months) became the major product. The ^{11}B, ^{31}P, and ^{19}F spectra of (2) comprised a broadened singlet, a triplet, and a doublet, respectively (Table 1); in addition there was a broadened singlet F resonance in the B–F region.

A number of other reaction products was detected by ^{31}P and ^{19}F n.m.r. spectroscopy in the two series of reactions after *ca.* 3 months. The ^{31}P n.m.r. parameters, as well as the assignments to known phosphorus(V) species are shown in Table 2. Additional resonances grew in the ^{31}P and ^{19}F spectra: the phosphorus resonances are probably doublets, but tend to be overlapped by adjacent resonances, whereas the fluorine resonances are well defined doublets, in the P–F region, with coupling constants between 940 and 960 Hz, and singlets in the B–F region.

(*b*) H_3BO_3–$P_2O_3F_4$–HPO_2F_2 *System*.—The only boron-containing product formed in this system was species (1) on the basis of the ^{11}B, ^{31}P, and ^{19}F n.m.r. spectra. It was evident that this species is stable for at least nine months at room temperature in a solution containing 1 mmol H_3BO_3 dissolved in $P_2O_3F_4$ (5 mmol) and HPO_2F_2 (3 mmol). No other products were detected in this reaction system.

(*c*) BF_3–$P_2O_3F_4$–HPO_2F_2 *and* NMe_4BF_4–$P_2O_3F_4$–HPO_2F_2 *Systems*.—The reaction of BF_3 with HPO_2F_2, in the absence of $P_2O_3F_4$, does not generate either (1) or (2) and will not be discussed further here. NH_4BF_4 and NMe_4BF_4 were found to be insoluble in pure HPO_2F_2; however, the reaction of either BF_3 or NMe_4BF_4 with $P_2O_3F_4$–HPO_2F_2 mixtures gives rise to solutions showing resonances attributable to (2) as well as POF_3. It was noticed that in the presence of excess $P_2O_3F_4$ ($P_2O_3F_4$: B > 7 : 1) (2) was gradually converted to (1). The n.m.r. parameters for these reaction products are essentially identical with those listed in Table 1; however, the ^{11}B couplings in the ^{31}P spectra were less well resolved.

Discussion

The only boron-containing product common to all of the five sets of reactions described above is species (1). From the ^{11}B, ^{31}P, and ^{19}F n.m.r. spectra it can be unambiguously identified as $[B(PO_2F_2)_4]^-$: the ^{11}B–^{31}P coupling constant, 8.5 ± 0.5 Hz, is evident in both the ^{11}B (a binomial quintet) and ^{31}P (a 1 : 1 : 1 : 1 quartet) n.m.r. spectra and the ^{31}P–^{19}F coupling constant, 986 Hz, in both the ^{31}P (a 1 : 2 : 1 triplet) and the ^{19}F (a doublet) spectra (Figures 1 and 2, Table 1). Its formation from BX_3 (X = Cl or Br) and HPO_2F_2 can be described by equation (ii); the fate of HX is discussed below. The production of the same species from H_3BO_3, BF_3, and BF_4^- by reaction with HPO_2F_2 in the presence of the anhydride, $P_2O_3F_4$, is shown in equations (iii), (iv), and (v), respectively. It is assumed that the protonic acid $HB(PO_2F_2)_4$ will function as a strong acid in HPO_2F_2 and will protonate not only $[PO_2F_2]^-$, equation (v), but even HPO_2F_2 to form the conjugate acid, $[PF_2(OH)_2]^+$. This behaviour is analogous to that of $HB(HSO_4)_4$ in H_2SO_4.[8] The tetrakis(difluorophosphato)-borate anion identified in these systems takes its place alongside other BZ_4^- species, Z = NO_3,[9] SO_3Cl,[10] ClO_4,[11] and $OTeF_5$.[12] Both the new anion as well as the $OTeF_5$ derivative are of interest in that the two-bond spin–spin coupling of ^{11}B is apparent in both the ^{11}B and ^{31}P or ^{125}Te n.m.r. spectra.

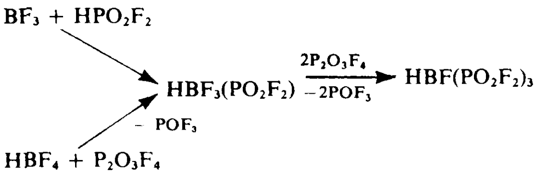
$$BX_3 + 4HPO_2F_2 \longrightarrow 3HX + HB(PO_2F_2)_4 \tag{ii}$$

$$H_3BO_3 + 3P_2O_3F_4 \xrightarrow{HPO_2F_2} 2HPO_2F_2 + HB(PO_2F_2)_4 \tag{iii}$$

$$BF_3 + HPO_2F_2 + 3P_2O_3F_4 \xrightarrow{P_2O_3F_4(\text{excess})} 3POF_3 + HB(PO_2F_2)_4 \tag{iv}$$

$$BF_4^- + HPO_2F_2 + 4P_2O_3F_4 \xrightarrow{P_2O_3F_4(\text{excess})} 4POF_3 + PO_2F_2^- + HB(PO_2F_2)_4 \tag{v}$$

The identity of species (2), which is formed initially from BF_3 or BF_4^- with $P_2O_3F_4$–HPO_2F_2 mixtures and eventually from BX_3 (X = Cl or Br) and HPO_2F_2, is not immediately obvious. The ^{31}P n.m.r. spectrum shows a broadened triplet, *J* = 980 ± 5 Hz, confirming the presence of one or more difluorophosphato-groups, although there is no resolved ^{11}B–^{31}P coupling in either the ^{11}B or the ^{31}P spectra. The ^{19}F spectrum shows the doublet, *J* = 980 Hz, expected for a PO_2F_2 group but also a resonance in the B–F region, the width of which is consistent with ^1J(B–F) < 15 Hz. It must therefore be inferred that (2) is a species of the type $[BF_{4-x}(PO_2F_2)_x]^-$



Scheme.

or a related neutral species: the lack of resolvable ^{11}B–^{31}P coupling in the spectra would reflect the quadrupolar broadening expected for these lower symmetry species.

Estimates of the ratios of $PO_2F_2 : F : B$ in species (2) were obtained from the ^{11}B,^{31}P, and ^{19}F n.m.r. spectra of samples in which the only boron-containing species detectable were (1) and (2). The relative concentrations of (1) and (2) in each sample were derived from the areas in the ^{11}B spectra; the ratio $PO_2F_2 : B = 2.9 \pm 0.4$ was then obtained from the ^{31}P spectra assuming that species (1) is indeed $[B(PO_2F_2)_4]^-$; similarly the ratio $PO_2F_2 : F = 2.9 \pm 0.4$ was calculated from the areas under the P–F and B–F resonances for species (2). The ratios derived in this way are based upon measurements from three different solutions and three sets of spectra. We must conclude that the available evidence is consistent with the formulation $[BF(PO_2F_2)_3]^-$ for species (2).

Our observation that $[BF(PO_2F_2)_3]^-$ is the initial product in the reactions of either BF_3 or BF_4^- with $P_2O_3F_4$–HPO_2F_2 mixtures is readily understood if the replacement of the first three fluorines of BF_4^- takes place in the time required to prepare the samples for study (Scheme). The substitution of the remaining fluorine by PO_2F_2 is a relatively slow reaction; it can be hastened by adding excess $P_2O_3F_4$ whose reactivity towards non-metal fluorides, *e.g.* XeF_2,[13] helps to compensate for the great affinity boron shows for fluoride.

The course of the reaction of BX_3 (X = Br or Cl) is clearly different; the initial product, $[B(PO_2F_2)_4]^-$, is formed because the B–X bonds are readily cleaved by HPO_2F_2. However, our results show that species (1) is gradually converted to (2) and this must be associated with the presence of HX, equation (ii), as well as the absence of $P_2O_3F_4$. Reactions (vi)—(x) are consistent with these observations and also with the formation of $POXF_2$, POX_2F, and HPO_2ClF (HPO_2BrF is said to be unstable [14]) which are phosphorus-containing by-products of these reactions. Hydrogen fluoride was not detected by ^{19}F n.m.r. spectroscopy nor were the reaction tubes etched so we infer that reaction (x) is rapid. It must be recognised that processes other than (x) may lead to transfer of fluoride to boron. There is evidence that the replacement of PO_2F_2 by F does not stop at the monofluoro-compound, species (2); our results do not allow us to characterise the subsequent products satisfactorily.

$$HX + HPO_2F_2 \xrightarrow{\text{slow}} POXF_2 + H_2O \qquad \text{(vi)}$$

$$HX + HPO_2F_2 \xrightarrow{\text{slow}} HPO_2XF + HF \qquad \text{(vii)}$$

$$HX + HPO_2XF \xrightarrow{\text{slow}} POX_2F + H_2O \qquad \text{(viii)}$$

$$H_2O + HPO_2F_2 \longrightarrow H_2PO_3F + HF \qquad \text{(ix)}$$

$$HF + [B(PO_2F_2)_4]^- \xrightarrow{\text{fast}} [BF(PO_2F_2)_3] + HPO_2F_2 \qquad \text{(x)}$$

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