

## Multinuclear Nuclear Magnetic Resonance Study of the Interaction of Some Phosphorus(v) Compounds with Inorganic Acids. The Protonating Abilities of $\text{HNO}_3$ , $\text{MeSO}_3\text{H}$ , and $\text{HPO}_2\text{F}_2$ towards the Phosphoryl Group

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The influence of protonation upon  $^{31}\text{P}$  and  $^{17}\text{O}$  n.m.r. parameters of the phosphoryl compounds  $\text{POCl}_3$  and  $\text{HPO}_2\text{F}_2$  has been investigated. For  $\text{POCl}_3$ ,  $\delta(^{17}\text{O})$  and  $^1J(\text{P}-\text{O})$  decrease whereas  $\delta(^{31}\text{P})$  increases with increasing protonation of the phosphoryl group. For  $\text{HPO}_2\text{F}_2$  the changes in  $\delta(^{17}\text{O})$  and  $\delta(^{31}\text{P})$  were less informative although  $^1J(\text{P}-\text{F})$  appears to increase smoothly with increasing protonation. The same trend in  $^1J(\text{P}-\text{F})$  is observed for solutions of  $\text{Na}_2\text{PO}_3\text{F}$  in some inorganic acids ( $\text{MeSO}_3\text{H}$ ,  $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{HNO}_3$ ,  $\text{HSO}_3\text{Cl}$ , and 25 oleum). The  $\text{POCl}_3$  results indicate that the ability of  $\text{HNO}_3$  to protonate the phosphoryl group is significantly greater than would be anticipated on the basis of Hammett acidity-function measurements, whereas the protonating ability of  $\text{MeSO}_3\text{H}$  is as anticipated on the basis of its Hammett function and that of  $\text{HPO}_2\text{F}_2$  is lower than those of  $\text{HNO}_3$  and  $\text{MeSO}_3\text{H}$ , comparable with that of liquid  $\text{HCl}$ . The values of  $\delta(^{31}\text{P})$  of  $\text{POBr}_3$  in  $\text{HNO}_3$ ,  $\text{MeSO}_3\text{H}$ , and  $\text{HPO}_2\text{F}_2$  are in agreement with the above conclusions.

The use of  $^{31}\text{P}$  n.m.r. spectroscopy as a means of investigating the reactions of phosphorus compounds with inorganic acids is well established.<sup>1</sup> The  $\delta(^{31}\text{P})$  value of  $\text{POCl}_3$  and  $\text{POBr}_3$  in strong acids has been shown to be markedly sensitive to acid strength.<sup>1</sup> Olah and McFarland<sup>2</sup> noted appreciable changes in  $^1J(\text{P}-\text{F})$  for  $\text{HPO}_2\text{F}_2$  and  $\text{H}_2\text{PO}_3\text{F}$  in fluorosulphuric and fluorosulphuric acid-antimony pentafluoride ('magic' acid)<sup>2</sup> relative to the pure acids. However, until the work reported here the use of  $^{17}\text{O}$  n.m.r. spectroscopy as a means of probing the effect of protonation upon the phosphoryl group had not been exploited.

### Experimental

All manipulations were carried out in an atmosphere of dry nitrogen. The preparations of  $\text{HNO}_3$  and  $\text{HPO}_2\text{F}_2$ <sup>3</sup> have been described previously. Commercial  $\text{PCl}_5$  was purified by sublimation prior to use. All other chemicals were of the best commercial grade available and were used without further purification. Oxygen-17 n.m.r. spectra were recorded on a Bruker WH 400 FT spectrometer at 54.24 MHz, phosphorus-31 and fluorine-19 spectra using a Bruker WM 250 FT spectrometer at 101.27 and 235.39 MHz respectively, and  $^{13}\text{C}$  spectra using the WM 250 at 62.87 MHz. The  $^{17}\text{O}$  spectra were recorded without field-frequency lock. Enough free induction decays were accumulated for each nucleus for the production of a high quality spectrum.

Shifts were measured with the high-frequency direction taken as positive relative to the external standards tetramethylsilane ( $^{13}\text{C}$ ),  $\text{CFCl}_3$  ( $^{19}\text{F}$ ), 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), and water ( $^{17}\text{O}$ ). Carbon-13 n.m.r. spectra were recorded with broad-band proton decoupling. Raman spectra were recorded using a Spex Ramalog spectrometer using a Spectra Physics model 164 (blue-green) argon-ion laser (514.5 nm).

### Results and Discussion

*Trichlorophosphine Oxide and Tribromophosphine Oxide.*—The compounds  $\text{POCl}_3$  and  $\text{POBr}_3$  dissolve in  $\text{HNO}_3$ ,  $\text{MeSO}_3\text{H}$ , and  $\text{HPO}_2\text{F}_2$  to give initially colourless solutions. The  $^{13}\text{C}$  n.m.r. spectra of freshly prepared solutions of  $\text{POCl}_3$  in  $\text{MeSO}_3\text{H}$  contained a single peak attributable to  $\text{MeSO}_3\text{H}$  but additional peaks appeared with time. The  $^{31}\text{P}$  and  $^{17}\text{O}$

**Table 1.** Phosphorus-31 and oxygen-17 n.m.r. parameters for  $\text{POCl}_3$  and  $\text{POBr}_3$  in acid solvents

Acid	$\text{POCl}_3$			$\text{POBr}_3$ $\delta(^{31}\text{P})$ /p.p.m.
	$\delta(^{31}\text{P})$ /p.p.m.	$\delta(^{17}\text{O})$ /p.p.m.	$^1J(\text{P}-\text{O})$ /Hz	
Pure $\text{POX}_3$	3.6 <sup>a</sup>	215 <sup>b</sup>	205 <sup>c</sup>	-103.4 <sup>d</sup>
$\text{HCl}$	6.9 <sup>d</sup>	—	—	—
$\text{HPO}_2\text{F}_2$	5.3 <sup>a</sup>	208 <sup>a</sup>	199 <sup>a</sup>	-95.3 <sup>a</sup>
$\text{MeSO}_3\text{H}$	12.8 <sup>a</sup>	202 <sup>a</sup>	188 <sup>a</sup>	-88.4 <sup>a</sup>
100% $\text{H}_2\text{SO}_4$	20.0 <sup>d</sup>	—	—	-80 <sup>d</sup>
$\text{HNO}_3$	21.6 <sup>a</sup>	187 <sup>a</sup>	177 <sup>a</sup>	-78.6 <sup>a</sup>
$\text{HSO}_3\text{Cl}$	24.1 <sup>a</sup>	177 <sup>a</sup>	173 <sup>a,e</sup>	-76 <sup>d</sup>
65 Oleum	55.9 <sup>d</sup>	—	—	-57 <sup>d</sup>

<sup>a</sup> This work,  $\text{POCl}_3$  solutions ca. 1 mol  $\text{kg}^{-1}$ ;  $\delta(^{31}\text{P})$  for  $\text{POCl}_3$  increases by ca. 2 p.p.m. for 0.25 mol  $\text{kg}^{-1}$  solutions. <sup>b</sup> G. Grossman, M. Gruner, and G. Seifert, *Z. Chem.*, 1976, **16**, 362. <sup>c</sup> Ref. 13. <sup>d</sup> Ref. 1. <sup>e</sup>  $^1J(\text{P}-\text{O})$  only resolved using resolution-enhancement techniques.

n.m.r. parameters for freshly prepared solutions of  $\text{POCl}_3$  and  $\text{POBr}_3$  in  $\text{HPO}_2\text{F}_2$ ,  $\text{MeSO}_3\text{H}$ ,  $\text{HNO}_3$ , and  $\text{HSO}_3\text{Cl}$  are collected in Table 1. Data of Waddington and co-workers<sup>1</sup> are included for comparison.

Freshly prepared solutions of  $\text{PCl}_5$  in  $\text{HPO}_2\text{F}_2$ ,  $\text{MeSO}_3\text{H}$ , and  $\text{HNO}_3$  gave singlet  $^{31}\text{P}$  resonances in similar positions to those of the  $\text{POCl}_3$  solutions. The  $^{31}\text{P}$  spectra of  $\text{PCl}_5$  in  $\text{HPO}_2\text{F}_2$  also contained a triplet assignable to  $\text{POF}_2\text{Cl}$  [ $\delta(^{31}\text{P}) = -12.3$  p.p.m.,  $^1J(\text{P}-\text{F}) = 1139$  Hz; lit.,<sup>4</sup>  $\delta(^{31}\text{P}) = -14.8$  p.p.m.,  $^1J(\text{P}-\text{F}) = 1138$  Hz]. The assignment of the singlet  $^{31}\text{P}$  resonances observed in  $\text{POCl}_3$ - and  $\text{PCl}_5$ -containing solutions to partially protonated  $\text{POCl}_3$  was confirmed by Raman spectroscopy. The spectra of freshly prepared  $\text{POCl}_3$  solutions in 25 oleum (25%  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ ),  $\text{HNO}_3$ ,  $\text{MeSO}_3\text{H}$ , and  $\text{HPO}_2\text{F}_2$  below 500  $\text{cm}^{-1}$  contained only the four bands expected for  $\text{POCl}_3$ <sup>5</sup> (observation of the phosphoryl stretching mode by vibrational spectroscopy was complicated by overlap of strong solvent bands).

As can be seen from Table 1, if we take an increase in  $\delta(^{31}\text{P})$  to be indicative of an increase in the degree of protonation of  $\text{POX}_3$ , the protonating abilities of  $\text{HPO}_2\text{F}_2$ ,  $\text{MeSO}_3\text{H}$ , and  $\text{HNO}_3$  are in the order  $\text{HPO}_2\text{F}_2 < \text{MeSO}_3\text{H} < \text{HNO}_3$ . The protonating ability of  $\text{HPO}_2\text{F}_2$  towards  $\text{POCl}_3$  and  $\text{POBr}_3$  is

comparable with that of liquid HCl, whereas HNO<sub>3</sub> appears to be able to protonate POCl<sub>3</sub> and POBr<sub>3</sub> to a similar extent as the highly acidic 100% H<sub>2</sub>SO<sub>4</sub> and even HSO<sub>3</sub>Cl. The protonating ability of MeSO<sub>3</sub>H towards POCl<sub>3</sub> and POBr<sub>3</sub> is intermediate between HPO<sub>2</sub>F<sub>2</sub> and HNO<sub>3</sub> and is in accordance with Hammett acidity-function measurements which indicate that MeSO<sub>3</sub>H ( $H_0 = -7.86$ )<sup>6</sup> is considerably less acidic than 100% H<sub>2</sub>SO<sub>4</sub> ( $H_0 = -11.12$ )<sup>7</sup> and HSO<sub>3</sub>Cl ( $H_0 = -12.78$ ).<sup>8</sup> The protonating ability of HNO<sub>3</sub> ( $H_0 = -6.3$ )<sup>9</sup> towards the phosphoryl group in the trihalogenophosphine oxides is unexpectedly high. This may be at least partly explained by the following factors. (a) The difficulties in finding suitable indicators for nitric acid concentrations greater than 65%,<sup>9</sup> leading to inaccurate Hammett function measurements. (b) The high degree of self-ionisation of HNO<sub>3</sub> which is greater than for any of the other acids examined.<sup>10</sup> As has been discussed by Gillespie and Peel<sup>11</sup> for H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, extensively self-dissociated acids may be said to be highly buffered whereas for less self-dissociated acids even a very small amount of added base causes a considerable reduction in the acidity of the medium.

Oxygen-17 n.m.r. spectroscopy is obviously valuable in studying the protonation of POCl<sub>3</sub> in acidic solvents. As can be seen from Table 1,  $\delta(^{17}\text{O})$  and  $^1J(\text{P}-\text{O})$  smoothly decrease with increasing acidity of the solvent. A plot of  $\delta(^{31}\text{P})$  against  $\delta(^{17}\text{O})$  has a negative slope. This indicates a phosphoryl  $\pi$ -bond polarity effect in the POCl<sub>3</sub> systems analogous to that observed for the carbonyl group in the acetone-water system.<sup>12</sup> Also in the POCl<sub>3</sub> acidic solvent systems the energy of the P=O  $n \rightarrow \pi^*$  transition (a dominant contributor to the paramagnetic part of  $\delta$ ) would be expected to increase with increasing protonation. A similar increase in the C=O  $n \rightarrow \pi^*$  transition energy has been observed upon hydrogen-bond formation in the acetone-water system. Thus changes in  $\delta(^{17}\text{O})$  and  $\delta(^{31}\text{P})$  upon protonation of POCl<sub>3</sub> should be in the same direction as  $\delta(^{17}\text{O})$  and  $\delta(^{13}\text{C})$  for acetone upon hydrogen-bond formation. This is indeed found to be the case experimentally. The decrease in  $^1J(\text{P}-\text{O})$  with increasing protonation may be due to a progressive decrease in the P-O bond order.

**Difluorophosphoric Acid.**—N.m.r. parameters for HPO<sub>2</sub>F<sub>2</sub> in various solvents are collected in Table 2(a). The trends in  $\delta(^{31}\text{P})$  and  $\delta(^{17}\text{O})$  are not well defined as in the POCl<sub>3</sub> systems. This acid is a weaker base than POCl<sub>3</sub> and consequently contributions to  $\delta(^{31}\text{P})$  and  $\delta(^{17}\text{O})$  other than differential protonation are presumably more important. These other contributions may include the different degrees of polymerisation of HPO<sub>2</sub>F<sub>2</sub> and differences in hydrogen bonding. However,  $^1J(\text{P}-\text{F})$  does appear to be sensitive to the acid strength of the solvent, increasing with increasing acidity. In the basic solvent diethyl ether it was possible to measure  $^1J(\text{P}-\text{O})$  for HPO<sub>2</sub>F<sub>2</sub> [see Table 2(a)] but in the acidic solvents and in pure HPO<sub>2</sub>F<sub>2</sub> coupling was not resolved.

**Sodium Monofluorophosphate.**—N.m.r. parameters for Na<sub>2</sub>PO<sub>3</sub>F in various acid solvents are presented in Table 2(b). The trend in  $^1J(\text{P}-\text{F})$  noted for the HPO<sub>2</sub>F<sub>2</sub> solutions is observed for the sodium monofluorophosphate solutions also. It is significant to note that  $^1J(\text{P}-\text{F})$  is lower in CF<sub>3</sub>CO<sub>2</sub>H and MeSO<sub>3</sub>H than for pure H<sub>2</sub>PO<sub>3</sub>F.<sup>4</sup> In HNO<sub>3</sub>, 25 oleum, and HSO<sub>3</sub>Cl the values of  $^1J(\text{P}-\text{F})$  indicate that the monofluorophosphate species present is probably partially protonated H<sub>2</sub>PO<sub>3</sub>F. In HNO<sub>3</sub>, monofluorophosphate was increasingly hydrolysed to P(OH)<sub>4</sub><sup>+</sup>, identified by its characteristic <sup>31</sup>P resonance position [ $\delta(^{31}\text{P}) = +2.3$  p.p.m.]<sup>3,13</sup> although freshly prepared solutions contained only low concentrations of

**Table 2.** N.m.r. parameters in various solvents

(a) Difluorophosphoric acid (ca. 2 mol kg<sup>-1</sup>)

Solvent	$\delta(^{31}\text{P})$ /p.p.m.	$^1J(\text{P}-\text{F})$ /Hz	$\delta(^{17}\text{O})$ /p.p.m.	$^1J(\text{P}-\text{O})$ /Hz	$\delta(^{19}\text{F})$ /p.p.m.
Pure HPO <sub>2</sub> F <sub>2</sub>	-21.7	984	62.1	—	-87.2
Et <sub>2</sub> O	-19.0	980	75.3	117	-85.0
CF <sub>3</sub> CO <sub>2</sub> H	-20.1	986	68.2	—	-87.2
HNO <sub>3</sub>	-18.6	993	66.6	—	-82.9
HSO <sub>3</sub> Cl	-21.7	1 001	66.9	—	-84.8
25 Oleum	-21.9	1 008	68 ± 2 <sup>a</sup>	—	-84.8
HSO <sub>3</sub> F	-22.6 <sup>b</sup>	1 002 <sup>b</sup>	—	—	—
HSO <sub>3</sub> F-SbF <sub>5</sub>	—	1 048 <sup>b</sup>	—	—	-83.6 <sup>b</sup>

(b) Sodium monofluorophosphate (ca. 0.3 mol kg<sup>-1</sup>)

Solvent	$\delta(^{31}\text{P})$ /p.p.m.	$^1J(\text{P}-\text{F})$ /Hz
CF <sub>3</sub> CO <sub>2</sub> H	-5.3	945
MeSO <sub>3</sub> H	-7.5	951
HNO <sub>3</sub>	-5.4	966
25 Oleum	-6.6	988
HSO <sub>3</sub> Cl	-6.1	992
Pure H <sub>2</sub> PO <sub>3</sub> F	-8.3 <sup>b</sup>	955 <sup>b</sup>

<sup>a</sup> Broad resonance  $\delta(^{17}\text{O})$  difficult to measure. <sup>b</sup> Ref. 2.

P(OH)<sub>4</sub><sup>+</sup>. Time-dependent hydrolysis of HPO<sub>2</sub>F<sub>2</sub> in HNO<sub>3</sub> also occurs as reported previously.<sup>3</sup> In addition to monofluorophosphate a phosphate species [ $\delta(^{31}\text{P}) = +3.7$  p.p.m.] was also produced along with some HPO<sub>2</sub>F<sub>2</sub> in Na<sub>2</sub>PO<sub>3</sub>F-MeSO<sub>3</sub>H solutions (<sup>19</sup>F n.m.r. spectroscopy gave no evidence for F<sup>-</sup> or HF). A more detailed investigation into the nature of the phosphate species is merited. Its <sup>31</sup>P shift precludes it from being either H<sub>3</sub>PO<sub>4</sub> or P(OH)<sub>4</sub><sup>+</sup>.<sup>13</sup>

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