

Multinuclear Nuclear Magnetic Resonance Study of the Interaction of Some Phosphorus(v) Compounds with Inorganic Acids. The Protonating Abilities of HNO₃, MeSO₃H, and HPO₂F₂ towards the Phosphoryl Group

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The influence of protonation upon ³¹P and ¹⁷O n.m.r. parameters of the phosphoryl compounds POCl₃ and HPO₂F₂ has been investigated. For POCl₃, δ(¹⁷O) and ¹J(P–O) decrease whereas δ(³¹P) increases with increasing protonation of the phosphoryl group. For HPO₂F₂ the changes in δ(¹⁷O) and δ(³¹P) were less informative although ¹J(P–F) appears to increase smoothly with increasing protonation. The same trend in ¹J(P–F) is observed for solutions of Na₂PO₃F in some inorganic acids (MeSO₃H, CF₃CO₂H, HNO₃, HSO₃Cl, and 25 oleum). The POCl₃ results indicate that the ability of HNO₃ 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 MeSO₃H is as anticipated on the basis of its Hammett function and that of HPO₂F₂ is lower than those of HNO₃ and MeSO₃H, comparable with that of liquid HCl. The values of δ(³¹P) of POBr₃ in HNO₃, MeSO₃H, and HPO₂F₂ are in agreement with the above conclusions.

The use of ³¹P n.m.r. spectroscopy as a means of investigating the reactions of phosphorus compounds with inorganic acids is well established.¹ The δ(³¹P) value of POCl₃ and POBr₃ in strong acids has been shown to be markedly sensitive to acid strength.¹ Olah and McFarland² noted appreciable changes in ¹J(P–F) for HPO₂F₂ and H₂PO₃F in fluorosulphuric and fluorosulphuric acid–antimony pentafluoride ('magic' acid)² relative to the pure acids. However, until the work reported here the use of ¹⁷O 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 HNO₃ and HPO₂F₂³ have been described previously. Commercial PCl₅ 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 ¹³C spectra using the WM 250 at 62.87 MHz. The ¹⁷O 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 (¹³C), CFCl₃ (¹⁹F), 85% H₃PO₄ (³¹P), and water (¹⁷O). 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 POCl₃ and POBr₃ dissolve in HNO₃, MeSO₃H, and HPO₂F₂ to give initially colourless solutions. The ¹³C n.m.r. spectra of freshly prepared solutions of POCl₃ in MeSO₃H contained a single peak attributable to MeSO₃H but additional peaks appeared with time. The ³¹P and ¹⁷O

Table 1. Phosphorus-31 and oxygen-17 n.m.r. parameters for POCl₃ and POBr₃ in acid solvents

Acid	POCl ₃			POBr ₃ δ(³¹ P) /p.p.m.
	δ(³¹ P) /p.p.m.	δ(¹⁷ O) /p.p.m.	¹ J(P–O) /Hz	
Pure POX ₃	3.6 ^a	215 ^b	205 ^c	–103.4 ^d
HCl	6.9 ^d	—	—	—
HPO ₂ F ₂	5.3 ^a	208 ^a	199 ^a	–95.3 ^a
MeSO ₃ H	12.8 ^a	202 ^a	188 ^a	–88.4 ^a
100% H ₂ SO ₄	20.0 ^d	—	—	–80 ^d
HNO ₃	21.6 ^a	187 ^a	177 ^a	–78.6 ^a
HSO ₃ Cl	24.1 ^a	177 ^a	173 ^{a,e}	–76 ^d
65 Oleum	55.9 ^d	—	—	–57 ^d

^a This work, POCl₃ solutions ca. 1 mol kg^{–1}; δ(³¹P) for POCl₃ increases by ca. 2 p.p.m. for 0.25 mol kg^{–1} solutions. ^b G. Grossman, M. Gruner, and G. Seifert, *Z. Chem.*, 1976, **16**, 362. ^c Ref. 13. ^d Ref. 1. ^e ¹J(P–O) only resolved using resolution-enhancement techniques.

n.m.r. parameters for freshly prepared solutions of POCl₃ and POBr₃ in HPO₂F₂, MeSO₃H, HNO₃, and HSO₃Cl are collected in Table 1. Data of Waddington and co-workers¹ are included for comparison.

Freshly prepared solutions of PCl₅ in HPO₂F₂, MeSO₃H, and HNO₃ gave singlet ³¹P resonances in similar positions to those of the POCl₃ solutions. The ³¹P spectra of PCl₅ in HPO₂F₂ also contained a triplet assignable to POF₂Cl [δ(³¹P) = –12.3 p.p.m., ¹J(P–F) = 1 139 Hz; lit.,⁴ δ(³¹P) = –14.8 p.p.m., ¹J(P–F) = 1 138 Hz]. The assignment of the singlet ³¹P resonances observed in POCl₃- and PCl₅-containing solutions to partially protonated POCl₃ was confirmed by Raman spectroscopy. The spectra of freshly prepared POCl₃ solutions in 25 oleum (25% SO₃ in H₂SO₄), HNO₃, MeSO₃H, and HPO₂F₂ below 500 cm^{–1} contained only the four bands expected for POCl₃⁵ (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 δ(³¹P) to be indicative of an increase in the degree of protonation of POX₃, the protonating abilities of HPO₂F₂, MeSO₃H, and HNO₃ are in the order HPO₂F₂ < MeSO₃H < HNO₃. The protonating ability of HPO₂F₂ towards POCl₃ and POBr₃ is

comparable with that of liquid HCl, whereas HNO₃ appears to be able to protonate POCl₃ and POBr₃ to a similar extent as the highly acidic 100% H₂SO₄ and even HSO₃Cl. The protonating ability of MeSO₃H towards POCl₃ and POBr₃ is intermediate between HPO₂F₂ and HNO₃ and is in accordance with Hammett acidity-function measurements which indicate that MeSO₃H ($H_0 = -7.86$)⁶ is considerably less acidic than 100% H₂SO₄ ($H_0 = -11.12$)⁷ and HSO₃Cl ($H_0 = -12.78$).⁸ The protonating ability of HNO₃ ($H_0 = -6.3$)⁹ 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%,⁹ leading to inaccurate Hammett function measurements. (b) The high degree of self-ionisation of HNO₃ which is greater than for any of the other acids examined.¹⁰ As has been discussed by Gillespie and Peel¹¹ for H₂S₂O₇, 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 POCl₃ 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 π -bond polarity effect in the POCl₃ systems analogous to that observed for the carbonyl group in the acetone-water system.¹² Also in the POCl₃ acidic solvent systems the energy of the P=O $n \rightarrow \pi^*$ transition (a dominant contributor to the paramagnetic part of δ) 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 POCl₃ 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 HPO₂F₂ 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 POCl₃ systems. This acid is a weaker base than POCl₃ 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 HPO₂F₂ 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 HPO₂F₂ [see Table 2(a)] but in the acidic solvents and in pure HPO₂F₂ coupling was not resolved.

Sodium Monofluorophosphate.—N.m.r. parameters for Na₂PO₃F in various acid solvents are presented in Table 2(b). The trend in $^1J(\text{P}-\text{F})$ noted for the HPO₂F₂ solutions is observed for the sodium monofluorophosphate solutions also. It is significant to note that $^1J(\text{P}-\text{F})$ is lower in CF₃CO₂H and MeSO₃H than for pure H₂PO₃F.⁴ In HNO₃, 25 oleum, and HSO₃Cl the values of $^1J(\text{P}-\text{F})$ indicate that the monofluorophosphate species present is probably partially protonated H₂PO₃F. In HNO₃, monofluorophosphate was increasingly hydrolysed to P(OH)₄⁺, identified by its characteristic ³¹P resonance position [$\delta(^{31}\text{P}) = +2.3$ p.p.m.]^{3,13} 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⁻¹)

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 ₂ F ₂	-21.7	984	62.1	—	-87.2
Et ₂ O	-19.0	980	75.3	117	-85.0
CF ₃ CO ₂ H	-20.1	986	68.2	—	-87.2
HNO ₃	-18.6	993	66.6	—	-82.9
HSO ₃ Cl	-21.7	1 001	66.9	—	-84.8
25 Oleum	-21.9	1 008	68 ± 2 ^a	—	-84.8
HSO ₃ F	-22.6 ^b	1 002 ^b	—	—	—
HSO ₃ F-SbF ₅	—	1 048 ^b	—	—	-83.6 ^b

(b) Sodium monofluorophosphate (ca. 0.3 mol kg⁻¹)

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

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

P(OH)₄⁺. Time-dependent hydrolysis of HPO₂F₂ in HNO₃ also occurs as reported previously.³ In addition to monofluorophosphate a phosphate species [$\delta(^{31}\text{P}) = +3.7$ p.p.m.] was also produced along with some HPO₂F₂ in Na₂PO₃F-MeSO₃H solutions (¹⁹F n.m.r. spectroscopy gave no evidence for F⁻ or HF). A more detailed investigation into the nature of the phosphate species is merited. Its ³¹P shift precludes it from being either H₃PO₄ or P(OH)₄⁺.¹³

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