Some reactions of phosphorus compounds as studied by 31p nmr techniques

M. P. Nisbet

To Mum, Dad, and Steven

Everything in this universe is made of one element which is a note, a single note.

Atoms are really vibrations, you know, which are extensions of the BIG note.

Everything is one note, even the ponies.

Francis Vincent Zappa

1967

Declaration

The work described in this thesis was carried out in the University of Durham between September 1972 and July 1975. This work has not been submitted, either completely or in part, for a degree in this or any other university and is the original work of the author except where acknowledged by reference.

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Abstract

The solution chemistry of some simple phosphorus halides has been investigated in sulphuric acid, oleums, and halo-substituted sulphuric acids by ^{31}P n.m.r. spectroscopy. Solution of phosphorus (III) compounds was accompanied by oxidation to the phosphorus (V) state. The phosphorus (V) species so formed as well as those derived directly from phosphorus (V) halides and oxyhalides were stable over measurable periods of time. Solvolysis of phosphorus (V) - halogen bonds occurred in all the solvents, with some complications arising in the halo-substituted acids where halogen exchange was observed. Oxidation of some phosphorus (III) halides by halogens produced phosphorus (V) - halo species which were stabilized by solution in these highly acidic solvents. The ^{31}P n.m.r. solution spectrum of various phosphorus (V) - iodine species have been recorded for the first time with the help of a pulsed Fourier Transform instrument, capable of studying reacting systems.

The solution chemistry of a series of phenyl organophosphoryl compounds in these acid solvents has also been investigated by ^{31}P n.m.r. Protonation of the phosphoryl group takes place in all of the solvents, as well as sulphonation of the phenyl ring in 25% and 65% oleum, and to a lesser extent in $ClHSO_3$.

Mixed halo- and organohalo- phosphorus (V) compounds such as $[PCl_nBr_{4-n}]^+A^-$, R_nPX_{5-n}, $[R_nPX_{4-n}]^+A^-$, where X = Cl or Br and A^- is an anion, dissolve in 25% oleum with the formation of stable phosphonium cations.

An investigation of the solution chemistry of phenoxyhalophosphoranes indicates that the stable species in the system are the non halo-containing $(PhO)_4P^+$ cation and $(PhO)_5P$, neither of which show acceptor properties towards pyridine or chloride ions.

A limited investigation of the Lewis acid properties of PI_3 towards pyridines, and the Lewis base properties of PI_3 towards BBr_3 and BI_3 suggests that coordination complexes are formed in both systems.

Oxidation of PI_3 has been attempted by means of halogens and other halogen-containing oxidizing agents. No direct evidence for the formation of phosphorus (V)-iodine species was obtained, although reactions with $SbCl_5$ and PCl_5 produced unstable compounds which decomposed at low temperature liberating iodine.

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CHAPTER 1

INTRODUCTION

1) ^{31}P nuclear magnetic resonance spectroscopy

The phenomenon of nuclear magnetic resonance has been known for some time[1,2] and the first reported chemical shifts for phosphorus compounds were published in 1951.[3] In subsequent years the potential value of this type of measurement to chemists became apparent. As a result of the large chemical shifts and strong coupling constants, which were observable even with the early low-resolution instruments, data on ^{31}P n.m.r. spectroscopy has played an important role in the development of NMR theory in general.

Nuclei with odd atomic or mass numbers have magnetic moments, ^{1}H, ^{19}F and ^{31}P for example, while some even mass nuclei such as ^{14}N and ^{18}O also have magnetic moments. In a magnetic field these nuclei precess about the direction of the field with a frequency proportional to the applied field strength. The resonance frequency is about 17.2 MHz for ^{31}P in a 10,000 gauss magnetic field. The precession can be perturbed by the application of electromagnetic radiation of the resonance frequency.

The ratio of applied field strength to frequency is not quite the same for all nuclei of a particular isotope since the electron cloud shields the nucleus from the applied field. The distribution of the electron cloud about the nucleus will depend on the nature of the compound concerned, and thus the resonance frequency of two nuclei of the same type, but in different chemical environments, will differ. This difference is usually measured in parts per million of the

applied field or frequency and is called the chemical shift.

If two different nuclei both having magnetic moments or two similar nuclei in different chemical environments are present in the same molecule, there will be an interaction between their magnetic fields which may lead to splitting of the resonance peaks into multiplets. The degree of splitting depends on the nature of the nuclei involved, and on their proximity to each other. In phosphorus compounds splitting of the ^{31}P n.m.r. resonance by spin-spin interactions with ^{1}H, ^{19}F or other ^{31}P nuclei is frequently observed. A resonance peak split by n equivalent hydrogen or fluorine nuclei will give a multiplet of n + 1 peaks where the intensities will be proportional to the binomial coefficients.

The $P-CH_3$ group, for example, will exhibit four ^{31}P n.m.r. peaks with a 1:3:3:1 intensity while in general, two dissimilar phosphorus nuclei in the same molecule will give two doublets which may be further split by other magnetically active nuclei. It is worth noting that spin-spin splitting is not observable in every possible case. Any process which affects the lifetime of a spin state may cause the splitting to vanish. In P-Cl, P-Br, and P-I compounds, for example, where there is rapid quadrupolar relaxation of the halogen nucleus, no coupling is found.

^{31}P n.m.r. spectroscopy provides direct information about the phosphorus nucleus itself. ^{31}P chemical shifts cover a range greater than 700 ppm.[4] Usually changes in ^{31}P shifts on change of coordination are large and a rapid assignment can often be made on this basis. Although three-coordinate compounds span the whole range of shifts, species with higher coordination numbers usually fall within

specific ranges. In general the greater the coordination number of the phosphorus, the greater is the nuclear shielding and so the higher is the chemical shift. An increase of the formal negative charge on phosphorus also increases the chemical shift. The following shifts (relative to 85% H_3PO_4) in the series PCl_3 through to PCl_6^- show the magnitude of these effects.[4]

PCl_3	PCl_4^+	$POCl_3$	PCl_5	PCl_6^-	
- 219	- 86	- 2.5	+ 83	+ 296	ppm

The main drawback of ^{31}P n.m.r. is that although the ^{31}P isotope is present in 100% natural abundance, its nuclear properties make the technique only 6.6% as sensitive as ^{1}H n.m.r. for equal numbers of nuclei at constant magnetic field. This low sensitivity is offset to some extent by the large range over which ^{31}P n.m.r. chemical shifts extend, which allows operation under conditions favouring high sensitivity at the expense of resolution. Signal enhancement can be conveniently achieved by signal averaging using a computer of average transients (C.A.T.). The technique requires that the spectrum be scanned many times in a synchronous fashion. The repetitive scans then synchronize the averaging process with the result that the desired signal is reinforced because all additions of a positive signal are in phase. Noise signals will add out of phase and thus be averaged out. The noise accumulates as a root mean square thus giving a signal to noise improvement by a factor of $\sqrt{n}$ where n is the number of scans performed.

The use of Pulse-Fourier Transform n.m.r. for enhancement has a number of advantages over continuous wave n.m.r. with spectrum accumulation. The most important benefit of the F.T. method is the large increase in sensitivity which can be achieved. The sample is subjected to a short pulse of R.F. energy which provides uniform irradiation across the spectrum. In the resulting free induction decay all the frequencies in the spectrum are observed simultaneously as a function of time. Fourier transformation then gives the normal frequency spectrum. This produces a great saving in time compared with the continuous wave method where the spectrum is obtained by constant R.F. irradiation at a set frequency, with a magnetic field sweep to observe the different signals successively.

Further advantages stem from the data handling capabilities of the computer used with the F.T. spectrometer, which allows the optimum compromise between resolution and signal-to-noise ratio to be reached. Unfortunately there are a number of limitations to the F.T. method. The spectrum is recorded in a discontinuous digital form and as a consequence the resolution is limited by the number of data points available. Because of the limited number of these, very sharp signals may be defined by only two or three points so that areas cannot be measured accurately. These two drawbacks are inherent to both F.T. n.m.r. and normal C.A.T. techniques. A more serious drawback of F.T. n.m.r. in this respect is that false intensities may be produced when nuclei in different magnetic environments have different relaxation times. For example in ^{13}C n.m.r. spectroscopy, the long relaxation times of ^{13}C in C-Cl and C-Br systems leads to their signals appearing to be less intense in the spectra. This drawback can sometimes be

overcome by varying the pulse rate, but in general, peak intensities are more reliable from C.A.T. methods than from F.T. n.m.r.

In this work, the main advantage of F.T. n.m.r. over continuous wave n.m.r. was the speed of the method. A stable initial system is not necessary and this allows samples to be investigated in which reaction is rapid and attempts at investigation of some samples by continuous wave n.m.r. failed because of a rapid drift in the balence of the spectrometer bridge during the run. This was due to reaction and/or precipitation taking place during the investigation. Use of the F.T. spectrometer and its pulsed sampling helped overcome these problems.

2) Outline of Present Work.

The purpose of the present work was to extend and clarify the solution investigations of a number of previous workers, using ^{31}P n.m.r. spectroscopy as the main technique. A secondary aim was to try to extend the limited knowledge of phosphorus (V) systems containing P-I bonds. Few stable examples of phosphorus (V) iodo-compounds are known. Oxidation of triphenylphosphine by iodine[5] gives Ph_3PI_2 which has been shown to have the ionic formulation $Ph_3PI^+I^-$ in the solid by ^{31}P n.m.r. spectroscopy.[6] The compounds Ph_3PIBr and Ph_3PICl have also been shown to contain the Ph_3PI^+ ion in the solid state.[7] By mixing iodine with trialkylphosphines, R_3P (R = Et, Pr, Bu, iso-amyl and cyclohexyl) compounds of the form R_3PI_2 have been prepared and the

formulation $R_3PI^+I^-$ proposed, based on solubility behaviour and adduct formation with HgI_2.[8] POI_3 has been reported as a product of the reaction between alkyl phosphorodiiodites, $ROPI_2$, with iodine in CCl_4 or hexane[9] via an unstable intermediate $ROPI_4$.

$$ROPI_2 + I_2 \rightarrow [ROPI_4] \rightarrow RI + POI_3$$

PSI_3 is made by the slow reaction of PI_3 and sulphur in carbon disulphide, or from phosphorus, sulphur and iodine in the same solvent,[10] while the related diphosphorus dithiotetraiodide $P_2S_2I_4$ and diphosphorus thiotetraiodide P_2SI_4, are made by interaction of the elements in CS_2 with the exclusion of light.[11] The analogous selenium compounds have also been reported[12]. On the whole little work has been carried out in the field of phosphorus (V) - iodine compounds, so in conjunction with the main investigation, special interest was focussed on reactions likely to involve the formation of phosphorus (V)-iodine bonds.

The solution chemistry of phosphorus and phosphoryl halides in liquid HCl has been studied previously by ^{31}P n.m.r.[13] Oxidation reactions between phosphorus (III) compounds and halogens have been followed in liquid HCl at low temperature by conductimetric titrations.[14] Oxidation of some phosphorus compounds from the + 3 to the + 5 oxidation state was observed and the PCl_3Br^+ ion was characterized in the form of its BCl_4^- salt.[14] At room temperature similar oxidation reactions have been investigated by ^{31}P n.m.r.[13] Limited work on the solution chemistry of phosphorus and phosphoryl halides in sulphuric acid and related solvents,[15-19] coupled with oxidation studies by Paul et al[20]

in $FHSO_3$, suggested that a systematic ^{31}P n.m.r. investigation of these systems could prove interesting. The solvents used were 100% sulphuric acid, 25% and 65% oleums, and chloro- and fluoro-sulphuric acids. Previous studies of phosphorus compounds in these acids are reviewed in Chapter 3B section 1. The relative acidities of the various solvents have been deduced from comparison of chemical shift values for the protonated species derived from the phosphoryl halides. Oxidation of phosphorus (III) halides by various halogens has been attempted and the products of reaction dissolved in various sulphuric acids. The ^{31}P n.m.r. chemical shifts of a number of mixed halogeno-phosphorus (V) species have been obtained in this manner.

Previous work by Dillon and Waddington[18] on some aryl-substituted phosphoryl compounds in sulphuric acid solvents indicated that in addition to the expected protonation of the phosphoryl group, sulphonation of the ring took place. In the light of these results, the behaviour of some phenyl-substituted phosphoryl chlorides and related acids in various sulphuric acid solvents has been elucidated by ^{31}P n.m.r.

In addition to solution work in sulphuric acid, some aspects of the chemistry and structure of phosphorus (V) phenoxy halide species were investigated. Previous data on these compounds has been interpreted in terms of structures containing mixed halophenoxy phosphorus (V) anions and cations.[21-24]

^{31}P n.m.r. is the perfect tool to investigate such species, so the reaction between $(PhO)_3P$ and halogens, together with the reaction between phenol and PCl_5, was studied. In the course of this work $(PhO)_4P^+Cl^-$ and $(PhO)_5P$ were prepared. The acceptor properties

of these two compounds towards pyridine and chloride ions were also investigated as an extension of the work of Reeve.[25]

A limited investigation of the Lewis acid-Lewis base properties of PI_3 with respect to pyridine, boron tribromide and boron triiodide has been carried out. Oxidation of PI_3 by halogen and halogen-containing inorganic oxidizing agents has also been attempted.

CHAPTER 2

EXPERIMENTAL

1) The Dry Box.

Because of the great sensitivity of most of the compounds used to moisture, all reactions were carried out under an atmosphere of dry nitrogen. Manipulations were usually performed in a dry box continuously purged with dry nitrogen, and the moisture-sensitive reactants and products were stored under nitrogen in closed containers.

The glove box was equipped with two entry ports, a large port which was purged with nitrogen for at least 30 minutes before entry into the box, and a smaller quick entry port which was purged by means of excess pressure in the box. Phosphoric oxide was exposed inside the box to remove any traces of moisture. The skin formed in this process was removed to give a fresh P_2O_5 surface at periodic intervals. An external water pump was fitted via a liquid air cold trap so that reaction products could be freed from solvent inside the box. Final drying of products was usually carried out on a short vacuum line equipped with a rotary pump.

Apparatus constructed specially for preparations outside the dry box is described in the appropriate sections.

2) ^{31}P n.m.r. spectroscopy

During the course of these investigations two n.m.r. spectrometers were used

i) Perkin-Elmer R10 n.m.r. spectrometer

^{31}P n.m.r. spectra were obtained using this high resolution

spectrometer operating at 24.29 MHz, fitted with a Digiac computer of average transients (C.A.T.). The instrument uses a permanent magnet of field 14,000 gauss, 1.4 tesla. Samples were enclosed in 8.4 mm o.d. non-spinning tubes, closed with neoprene bungs covered with paraffin film (parafilm tape).

The maximum field-sweep width available on a conventional R10 is 200 ppm, but in order to scan larger fields a modification had been introduced which extended the maximum sweep width to 367 ppm. The sweep width with this modification was linear for about 70% of the range and then departed progressively from linearity. Allowance was made for this non-linearity by recording reference signals on either side of the experimental peak using the spectrometer field shift controls. The shift was then calculated from the distance of the experimental peak from the references, and the known separation of the reference peaks.

Signal enhancement was achieved by use of the C.A.T. Accumulation was triggered by the revolving recorder drum at the beginning of each sweep. The signal from the output amplifier was fed into an analogue/digital converter and was accumulated in the computer. After processing the accumulated spectrum was fed back into the R10 and could be plotted on the chart recorder.

On this instrument P_4O_6 was used as an external reference,[26] but shifts have been quoted relative to 85% H_3PO_4 to facilitate comparison with literature data.

The operating temperature of the R10 is 307.2 K.

ii) Fourier Transform n.m.r. spectrometer

The Fourier Transform n.m.r. spectrometer used in this work was constructed in this department by Dr A. Royston. The spectrometer is centred on a Varian 620/L minicomputer having 20K 16 bit words. Attached to the computer are these devices:

a) fast paper tape reader for reading in the F.T./n.m.r.program;
b) chart recorder for output spectra;
c) oscilloscope for displaying data held in computer;
d) pulse programmer to control timing functions in the system;
e) teletype to control system.

The aim of the system is to store the free induction decay n.m.r. signal induced by a powerful R.F. burst applied to a sample containing ^{31}P. If a burst of R.F. energy is Fourier analysed its power spectrum consists of a comb of frequencies centred on the original carrier frequency. For instance a 10 μsec burst repeated every second has components separated by 1 Hz, and as the displacement increases the amplitude gradually falls, with the first zero at 50 KHz offset. The component at 10 KHz is only 2% weaker than the centre frequency so n.m.r. frequencies at both ends of the 10 KHz range are irradiated equally well. At the end of the burst the different ^{31}P nuclei in the sample relax at their characteristic n.m.r. frequency, inducing a small voltage in the sample coil.

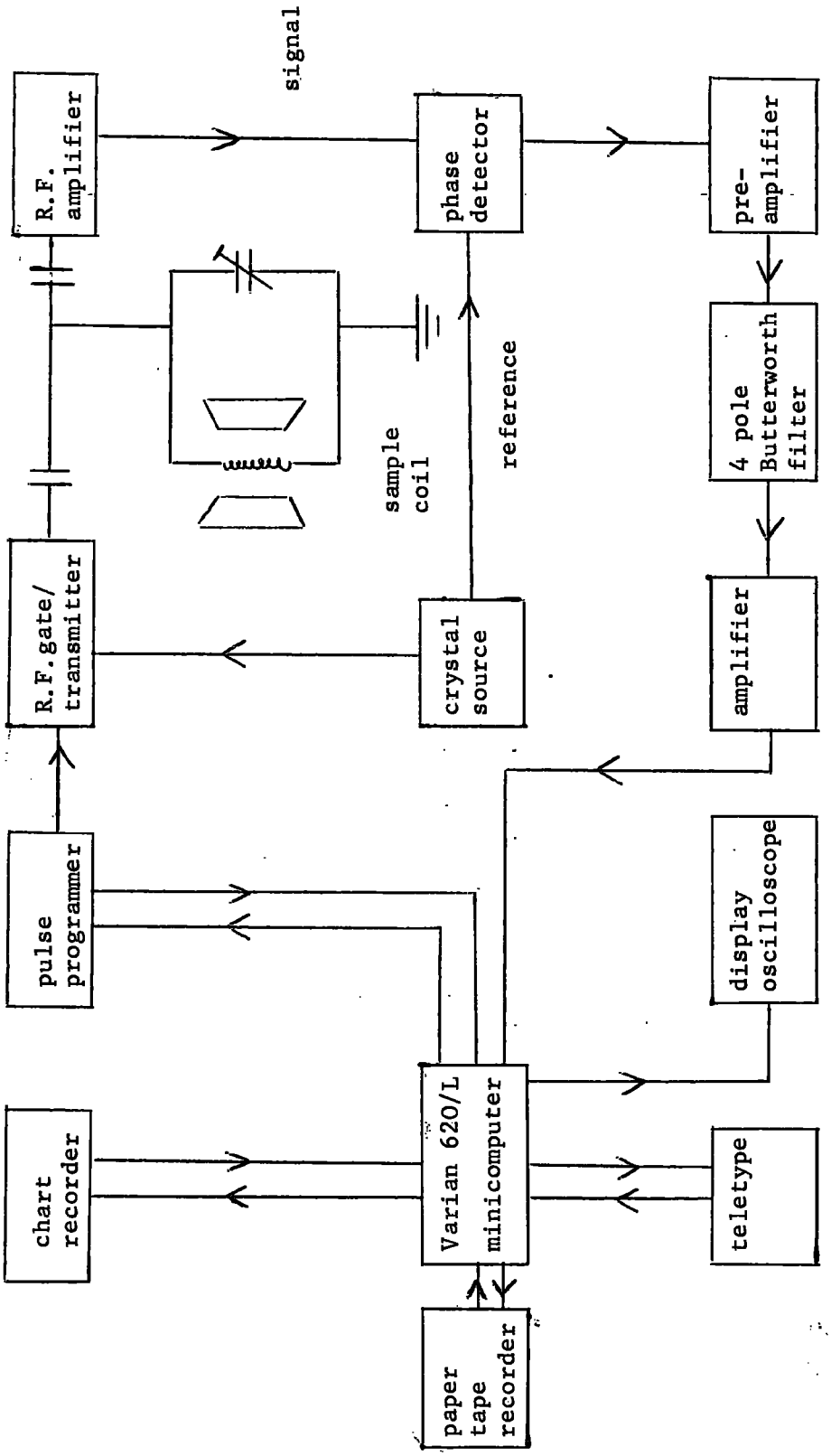
The timing of the R.F. burst (centred on 24.29 MHz) is controlled by a pulse programmer which in turn is operated entirely by software. Pulse sequence parameters are entered from the teletype.

There can be up to seven pulses, with lengths of 0.5 to 8191.75 μsec in 0.25 μsec steps, in the cycle, with any interval in the range of 20 msec to 327.67 secs between each one. Additionally the phase of each pulse relative to the phase detector reference of the receiver can be chosen.

The output of a crystal oscillator is directed to two parts of the apparatus; firstly to a switch operated by the pulse programmer, and thence to a 200W power amplifier connected to the sample probe; secondly to a phase detector which is part of the signal detection system.

Essentially the sample probe consists of a circuit tuned to the ^{31}P n.m.r. frequency, with the sample contained within an inductor placed in the pole gap of a Perkin-Elmer R10 permanent magnet (14,000 gauss). Following a 1000V R.F. burst across the inductance to cause the ^{31}P nuclei to precess in the manner described previously, relaxation induces a small R.F. voltage ($< 100\mu V$) across the coil. After amplification by a factor of up to 2000 times these n.m.r. frequencies are mixed with the original input to the R.F. gate to give an interferogram with a frequency of up to about 10 KHz. After passing through a low-pass filter, which reduces noise and spurious signals, and further amplification by 500 times, the signal is digitized into up to 2048 regularly spaced samples before being stored in the computer memory. So that many such interferograms can be added coherently, the hardware in the pulse programmer and the program ensure that the time at which each sample is taken is always accurate to within 0.5 μsec. For an improvement of the signal-to-noise ratio the results of up to half a million pulses can be added before

presentation on the display oscilloscope. The layout of the spectrometer circuits is shown schematically in the following block diagram.



After any necessary manipulations of the interferograms, Fourier Transform gives the real and complex components of the spectrum. From these can be derived either the power or phase-corrected spectrum.

The sweep width of the spectrum is related to the time interval between the samples of the free induction decay signal, and the resolution is affected by the time taken to accumulate all the samples. For example the sweep width can be from 40 to 400 ppm with a resolution of 0.04 to 0.8 ppm. Normally 1024 samples are taken, but the number can be varied from 32 to 2048. By shifting the magnetic field with sweep coils, ^{31}P resonances could be observed in the range -250 to + 750 ppm (relative to 85% H_3PO_4).

On this instrument 85% H_3PO_4 was used as an external reference and the operating temperature of the spectrometer was 307.2 K. Samples were enclosed in 5 mm non-spinning tubes, closed with plastic caps covered with paraffin film.

3) ^{11}B n.m.r. spectroscopy.

^{11}B n.m.r. spectra were recorded on the R10 spectrometer tuned to 19.25 MHz. Shifts were measured relative to external trimethyl borate and results have been expressed relative to this standard. The ^{11}B chemical shift of $BF_3.Et_2O$, the other main ^{11}B reference material, has been reported as + 18.75 ppm relative to $(MeO)_3B$.[13]

4) Analyses.

C, H and N were determined by microcombustion with a Perkin-Elmer 240 elemental analyser as a laboratory service. The reliability of

this instrument was variable and in general a greater reliance was placed upon phosphorus and halogen analyses.

The phosphorus and halogen analyses were carried out by R. Coult. In the case of phosphorus and chlorine, a sample (about 40 mgms) weighed in a gelatin capsule was decomposed by heating with sodium peroxide in a nickel Parr bomb. The residue was washed out, acidified with concentrated nitric acid and made up to 100 mls with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate/ammonium vanadate reagent and the absorbance measured at 420 μ using a Unicam SP500 spectrophotometer. Chlorine was determined by potentiometric titration, a suitable aliquot being titrated against N/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

Bromine and iodine were determined iodometrically following a Schoniger oxygen flask combustion of the compound as described by Ingram.[27]

5) Preparation of starting materials.

i) Phenyldichlorodibromophosphorane

$PhPCl_2Br_2$ was prepared by J. Lincoln according to the procedure used by Meisenheimer.[28]

2 mls (38.75 mmoles) of bromine dissolved in CCl_4 were slowly run into 5 mls (38.41 mmoles) $PhPCl_2$ also in CCl_4. A bright yellow precipitate formed and after complete addition, the mixture was stirred for several minutes. The solid was filtered, washed with pet ether (30-40) and dried under vacuum. The analysis figures for this

prep are given below:

	C	H	P	Br	Cl
% Theoretical $PhPCl_2Br_2$	21.24	1.48	9.14	47.20	20.94
% Found	19.13	1.63	9.06	47.60	20.10

ii) Diphenylchlorodibromophosphorane

Ph_2PClBr_2 was prepared by J. Lincoln.

2 mls (38.75 mmoles) of bromine dissolved in CH_2Cl_2 were slowly run into 6.10 mls (38.11 mmoles) Ph_2PCl also in CH_2Cl_2. A bright yellow precipitate formed and after complete addition the mixture was stirred for several minutes. The solid was filtered off, washed with pet ether (30-40) and dried under vacuum. The analysis figures for this compound are given below:

	C	H	P	Br	Cl
% Theoretical Ph_2PClBr_2	37.84	2.63	8.15	42.05	9.33
% Found	37.88	2.68	8.22	41.75	8.5

iii) Tetrabromophenylphosphorane

$PhPBr_4$ was prepared by J. Lincoln.

A solution of 1.2 mls (23.25 mmoles) of bromine in CH_2Cl_2 was added to 6.3 gms (23.51 mmoles) of $PhPBr_2$ in CH_2Cl_2. An orange precipitate formed and after complete addition, the mixture was stirred for a few moments. The solid was filtered, washed with pet ether (30-40) and dried under vacuum. The analysis figures are given below:

	C	H	P	Br
% Theoretical $PhPBr_4$	16.83	1.18	7.23	74.76
% Found	15.37	1.67	6.08	75.4

iv) Diphenylphosphinic chloride

Ph_2POCl was prepared by J. Lincoln.

A solution of Ph_2PCl_3 in $CHCl_3$ was saturated with SO_2. The resulting solution was fractionally distilled and the fraction boiling at 433-8 K (1 mm Hg)[29] was collected. The analysis figures for the product are given below:

	C	H	P	Cl
% Theoretical Ph_2POCl	60.89	4.29	13.08	15.01
% Found	58.36	2.78	12.96	15.52

v) Diphosphorus Tetraiodide

P_2I_4 was prepared following the procedure of Baudler.[30]

20.19 gms (79.49 mmoles) of iodine dissolved in CS_2 were added slowly to 2.47 gms (79.68 mmoles) white phosphorus in CS_2. The resulting clear orange-red solution was allowed to stand for 15 hours in the dark. The solution was concentrated on a vacuum line and the resulting red crystals filtered off. The crystals were recrystallised from a CS_2 solution containing white phosphorus. The analysis figures for this prep are given below:

	P	I
% Theoretical P_2I_4	10.9	89.1
% Found	13.4	85.6

These figures suggest the presence of elemental phosphorus in small amounts. No further purification was attempted since the excess phosphorus would not interfer in the use for which the P_2I_4 was intended - solid state ^{31}P n.m.r. spectral analysis [see Appendix 1].

A CS_2 solution of the solid showed a single ^{31}P n.m.r. resonance at -102 ppm assignable to P_2I_4.[31]

6) Purification of other materials used.

PI_3	recrystallised from CH_2Cl_2
AlI_3	sublimed under vacuum
PhOH	stored under reduced pressure in a vacuum dessicator over $CaSO_4$.
C_5H_5N	redistilled from KOH on to fused KOH and stored under nitrogen
$(C_5H_{11})_4N^+Cl^-$	dried under vacuum for several hours at 373 K and then stored under nitrogen
CH_2Cl_2	redistilled grade CH_2Cl_2 was dried and stored over mesh 4A molecular sieve under nitrogen.
$PhNO_2$	analar nitrobenzene was distilled from P_2O_5 and stored over molecular sieve under nitrogen.
C_6H_6	dried over sodium wire
CH_2ClCH_2Cl	distilled from P_2O_5
CCl_4	stored over P_2O_5

Other starting materials were either purchased in their highest available purity grade, or were donated, and used without further purification. Details of samples donated by Dr P.N. Gates of Royal Holloway College, London and Dr R.N. Reeve of Durham University, can be found in Chapter 3B, section 2(viii), Table 9.

CHAPTER 3A

THE SULPHURIC ACID SOLVENT SYSTEM

1) Introduction.

Interest in anhydrous sulphuric acid, oleums and substituted sulphuric acids as solvents is the result of a combination of several significant chemical features. These strongly acidic solvents undergo relatively extensive ionic self-dissociation, so that the pure acids have quite high specific conductances; electrolyte solutions in these solvents are therefore of high ionic strength. Many of the physical properties of the anhydrous acids indicate extensive association in the liquid. The interactions of various types of molecules, both inorganic and organic, with these acids are important in the development of general acid-base theory. The chemistry of sulphuric acid - oleum - substituted sulphuric acids solvent systems has not yet been extensively studied, but a sufficient variety of certain classes of compounds has now been investigated for a reasonably systematic account of their behaviour to be given.[32-36]

2) Sulphuric acid and the oleums.

100% H_2SO_4 and the oleums are most easily prepared by distilling SO_3 into 98% analytical reagent grade H_2SO_4 at room temperature, and adding slightly aqueous sulphuric acid until the required position on the freezing point curve for the H_2O-SO_3 system is reached. The maximum on the freezing point curve at 283.371 K corresponds to 100% H_2SO_4.[37]

Some of the physical properties of 100% sulphuric acid[33] are tabulated in Table 1.

Table 1 Some physical constants of sulphuric acid

Freezing point (K)		283.371
Boiling point (K)		563-590
Viscosity (centipoise)	at 298 K	24.54
Density (d_4^{25})		1.8269
Dielectric constant		100
Specific conductance ($ohm^{-1}cm^{-1}$)		1.0439×10^{-2}
Heat capacity ($cal\ deg^{-1}gm^{-1}$)		0.3373
Heat of Fusion ($cal\ mole^{-1}$)	at 283.37 K	2560

The high values of the boiling point and viscosity indicate that it is a highly associated liquid, presumably because of very strong intermolecular hydrogen bonding. As it has a rather high dielectric constant, it is generally a good solvent for electrolytes, but because of its highly associated nature it tends to be a rather poor solvent for non-electrolytes. This does not necessarily mean that it is a poor solvent for organic compounds, since many of these are protonated or form strongly hydrogen-bonded complexes with sulphuric acid, and are therefore soluble. The freezing point of sulphuric acid is convenient for cryoscopic measurements. The high specific conductance of sulphuric acid shows that it is rather extensively self-ionized,

the major part of this conductivity being due to $H_3SO_4^+$ and HSO_4^- ions formed by autoprotolysis

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

This extensive autoprotolysis shows that despite its high acidity sulphuric acid is also appreciably basic. The ions produced are of fundamental importance in the chemistry of any protonic solvent, primarily because they determine acid-base behaviour and, in particular, because they limit the acid-base range that is accessible in the solvent. In sulphuric acid any solute that produces HSO_4^- ions may be regarded as a base, and any solute that produces $H_3SO_4^+$ ions is an acid. The $H_3SO_4^+$ ion is the strongest possible acid and the HSO_4^- ion is the strongest possible base of the sulphuric acid solvent system.

Sulphuric acid is also slightly self-dissociated into SO_3 and water

$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

Water is almost completely ionized as a base

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

while SO_3 is completely converted to disulphuric acid, $H_2S_2O_7$, in dilute solutions, and perhaps to small amounts of higher polysulphuric

acids, such as $H_2S_3O_{10}$. Disulphuric acid itself is ionized as a moderately weak acid

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons HS_2O_7^- + H_3SO_4^+$$

Thus since the ions $H_3SO_4^+$ and HSO_4^- are in equilibrium as a consequence of the autoprotolysis reaction it follows that the ions H_3O^+ and $HS_2O_7^-$ must also be in equilibrium.

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$

This is called the ionic self-dissociation reaction. The complete self-dissociation reaction in the sulphuric acid solvent system can be described by the preceeding equations, the equilibrium constants being at 298 K[38]

K_1	$= [H_3SO_4^+][HSO_4^-]$	2.7×10^{-4}
K_2	$= [H_3O^+]\ [HS_2O_7^-]$	5.1×10^{-5}
K_3	$= [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7]$	1.4×10^{-2}
K_4	$= [H_3O^+][HSO_4^-]/[H_2O]$	1

The constitution of oleum solutions is somewhat disputed. $H_2S_2O_7$ is known to be present, and it seems likely that in oleum solutions more concentrated that 12% SO_3, $H_2S_3O_{10}$ is also present together with smaller quantities of higher polysulphuric acids.[39] In moderately strong oleums the monomer SO_3 is formed and in very strong oleums some of the trimer $(SO_3)_3$ is present.[32]

These solvents are closely related to H_2SO_4 and will influence the self-dissociation reactions which take place in much the same way as in 100% H_2SO_4.

The main experimental methods for the investigation of solutions of H_2SO_4 and oleums are cryoscopy and electrical conductivity together with Raman, I.R., U.V., visible absorption and N.M.R. spectroscopy.[33]

Sulphuric acid is a good solvent for compounds which ionize as electrolytes, as might be expected from its high dielectric constant, the polarity of its molecules and their ability to form strong hydrogen bonds. Electrolytes may be classified in the usual way according to the solvo-system definition of acids and bases. Acids give the sulphuric acidium ion, $H_3SO_4^+$

$$HA + H_2SO_4 \rightleftharpoons H_3SO_4^+ + A^-$$

and bases give the hydrogen sulphate ion, HSO_4^-

$$B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-$$

Because of the high acidity of sulphuric acid, bases are the largest class of electrolytes. Sulphuric acid has a levelling effect on the strengths of bases in the same way that water has a levelling effect on the strengths of acids. Acids of the sulphuric acid system are rarer but several examples are known.

i) Bases in sulphuric acid[32-4]

Basic solutions may be formed in various ways.

a) From metal sulphates. Hydrogen sulphates are fully ionized strong bases and are the direct analogues of the hydroxides in water. Solutions of hydrogen sulphates are often prepared more conveniently from the parent sulphate

$$KHSO_4 \rightarrow K^+ + HSO_4^-$$

$$K_2SO_4 + H_2SO_4 \rightarrow 2K^+ + 2HSO_4^-$$

b) solvolysis of salts of weak acids. Several salts of other acids (if they are not insoluble as, for example, AgCl, $CuBr_2$, $AlCl_3$ and $AlPO_4$) undergo complete solvolysis and thus give rise to strongly basic solutions. Solvolysis occurs because the other acids in sulphuric acid are either exceedingly weak (e.g. $HClO_4$) or do not behave as acids at all but react as bases (eg H_3PO_4 and HNO_3)

$$NH_4ClO_4 + H_2SO_4 \rightarrow NH_4^+ + HSO_4^- + HClO_4$$

$$KNO_3 + H_2SO_4 \rightarrow K^+ + HSO_4^- + HNO_3$$

$$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$$

$$\downarrow H_2SO_4$$

$$H_3O^+ + NO_2^+ + HSO_4^-$$

c) Protonation. A very large number of substances behave as bases, forming their conjugate acids by addition of a proton.[40] Thus almost any organic molecule with a potentially basic site, such as a lone pair of electrons, or an unsaturated system, dissolves in sulphuric acid with the formation of its conjugate acid. Many ketones, carboxylic acids, esters, amines and amides dissolve in sulphuric acid in this manner.[40]

$$Me_2CO + H_2SO_4 \rightarrow Me_2COH^+ + HSO_4^-$$
$$MeCOOH + H_2SO_4 \rightarrow MeCOOH_2^+ + HSO_4^-$$

Even triphenylamine and triphenylphosphine behave as strong bases in sulphuric acid.[32] Water provides an example of an inorganic substance that acts as a strong base

$$H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^-$$

d) Complex bases. Many oxy- and hydroxy- compounds behave as bases because they are dehydrated by the solvent. The simplest examples of this type of behaviour are illustrated by[41-43]

$$EtOH + 2H_2SO_4 \rightarrow EtSO_4H + H_3O^+ + HSO_4^-$$
$$(Me_3Si)_2O + 3H_2SO_4 \rightarrow 2Me_3SiSO_4H + H_3O^+ + HSO_4^-$$
$$HIO_3 + 2H_2SO_4 \rightarrow IO_2HSO_4 + H_3O^+ + HSO_4^-$$

In addition the hydrogen sulphate itself sometimes acts as a base either by forming its conjugate acid or by auto-ionization.[44,45]

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$
$$Ph_3COH + 2H_2SO_4 \rightarrow Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

ii) Acids in sulphuric acid[32-4]

The majority of substances which behave as acids in aqueous solution do not exhibit acidic properties in sulphuric acid, but behave as bases. Even $HClO_4$ which is often regarded as the strongest known mineral acid is only very slightly ionized in sulphuric acid,[46] while perchlorates undergo complete solvolysis[47]

$$MClO_4 + H_2SO_4 \rightarrow M^+ + HSO_4^- + HClO_4$$

The first acids of the sulphuric acid system to be recognized were disulphuric acid, $H_2S_2O_7$ and the higher polysulphuric acids $H_2S_3O_{10}$ etc, which are present in oleums.[39] These are weak acids of the sulphuric acid system as are $FHSO_3$[46] and $ClHSO_3$.[46]

The first strong acid of the sulphuric acid solvent system to be recognized was the complex tetra(hydrogen sulphato) boric acid, $HB(HSO_4)_4$.[48] Solutions of this compound can be obtained by dissolving boric acid in oleum.

$$H_3BO_3 + 3H_2S_2O_7 \rightarrow H_3SO_4^+ + H_2SO_4 + B(HSO_4)_4^-$$

Cryoscopic and conductimetric measurements confirm these reactions and show that the acid $HB(HSO_4)_4$ is extensively ionized, i.e. that it is a strong acid. Solutions of other complex sulphato-acids such as $H_2Sn(HSO_4)_6$ and $H_2Pb(HSO_4)_6$ have also been prepared, but they do not appear to be as strong as $HB(HSO_4)_4$.[49]

iii) Oxidation Reactions of H_2SO_4

At low temperatures 100% H_2SO_4 is only a moderately strong oxidizing agent. In the oxidation process, sulphuric acid is reduced to SO_2 according to the electronic equation

$$5H_2SO_4 + 2e^- \rightarrow SO_2 + 2H_3O^+ + 4HSO_4^-$$

E.S.R. measurements have shown that radical cations are formed by the oxidation of hydrocarbons such as anthracene.[50] Iodine is only slightly soluble in sulphuric acid and gives a pale violet solution. A slow reaction with the formation of I_3^+ and I_5^+ seems to take place. In dilute oleum iodine is much more soluble and gives a brown solution due to the presence of the I_3^+ ion.[51] Selenium and tellurium dissolve in H_2SO_4 to give green and red solutions respectively ascribed to the formation of Se_8^{2+} and Te_4^{2+} species.[52] Stable solutions of the cations S_4^{2+}, S_8^{2+} and S_{16}^{2+} have been obtained by oxidizing sulphur with SO_3 in oleum,[53] and solution of yellow phosphorus in disulphuric acid is reported to yield P_4^{2+} and P_8^{2+} ions.[54]

iv) Sulphonation

Very many organic compounds give stable solutions in sulphuric acid from which they can often be quantitatively recovered by pouring the solution on to ice. This is at least partly because they are usually protonated and the protonated group deactivates the rest of the molecule towards sulphonation. If an aromatic molecule contains non-basic

or very weakly basic activating groups, in addition to the protonated group, however, or if the protonated group is sufficiently separated from the aromatic ring, the compound will also rapidly sulphonate in the aromatic ring. For example PhCOOH in the protonated form is quite stable in 100% H_2SO_4, but m-$CH_3C_6H_4COOH$ is sulphonated completely in one hour.[55]

The active reagent in sulphonation is thought to be either SO_3 or HSO_3^+. 100% H_2SO_4 which contains only a very small equilibrium amount of SO_3 is, therefore, not a powerful sulphonating agent but oleums which contain an excess of SO_3 are much more efficient.[56]

v) Hydrolysis.

It is at first sight somewhat surprising that, despite the strongly dehydrating properties of sulphuric acid, hydration occasionally occurs in which a solute extracts water from the solvent leaving an excess of SO_3. Examples are provided by solutions of acetic anhydride[57] and nitriles.[58]

$$(MeCO)_2O + 3H_2SO_4 \rightarrow 2MeCOOH_2^+ + HS_2O_7^- + HSO_4^-$$

$$RCN + 2H_2SO_4 \rightarrow RCONH_2 + H_2S_2O_7.$$

This brief summary of the properties of sulphuric acid shows that a variety of interesting reactions can be carried out in this medium. The chemistry of the related oleum solvents is on the whole an extension of the chemistry of 100% H_2SO_4, where the effect of the added SO_3 on the reacting system is taken into account. More extensive reviews of these systems are available which amplify the comments given here.[32-4]

3) Fluorosulphuric acid[34-6]

This acid is obtained by distillation of concentrated oleum (60% SO_3) with calcium fluoride or by the general reaction of SO_3 with a metal fluoride.

$$SO_3 + MF \rightarrow MSO_3F \xrightarrow[\text{acid}]{\text{strong}} FHSO_3$$

In contrast with sulphuric acid, $FHSO_3$ shows very limited self-dissociation which affects its properties to only a minor extent. Autoprotolysis is the only mode of self-dissociation for which definite data has been obtained.[59]

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$$

The autoprotolysis constant,[59] $K = [SO_3F^-][H_2SO_3F^+]$ is 3.8×10^{-8} which is considerably smaller than the corresponding constant for H_2SO_4,[38] 2.7×10^{-4}.

Electrolytes may be divided into acids and bases whereby acids give the fluorosulphuric acidium ion, $H_2SO_3F^+$ and bases the fluorosulphate ion, SO_3F^-.

$$HA + FHSO_3 \rightarrow A^- + H_2SO_3F^+$$
$$B + FHSO_3 \rightarrow BH^+ + SO_3F^-$$

Simple base behaviour arises in a similar way to H_2SO_4. The alkali and alkaline earth fluorosulphates dissolve as fully dissociated

electrolytes in $FHSO_3$, behaving as strong bases in this solvent analogous to the corresponding hydrogen sulphates in sulphuric acid and the hydroxides in water. Since $FHSO_3$ is such a strong acid, salts of other inorganic acids undergo complete solvolysis and yield the FSO_3^- ion. Many compounds when dissolved in $FHSO_3$ undergo protonation thereby acting as bases. Inorganic compounds of this type include H_2SO_4, HF, and $HClO_4$.[60] Organic molecules which have an unsaturated system or in which there are lone pairs of electrons on atoms such as oxygen, nitrogen, or sulphur, are protonated in $FHSO_3$. This is similar to the situation in H_2SO_4 except that because of the higher acidity of $FHSO_3$, organic bases are in general protonated to a greater extent in this solvent.

Some compounds undergo more complex reactions resulting in base behaviour. Water undergoes both protonation and solvolysis in $FHSO_3$.[61]

$$FHSO_3 + H_2O \rightarrow H_3O^+ + FSO_3^- \rightleftharpoons HF + H_2SO_4$$

while solutions of KNO_3 in $FHSO_3$ contain the nitronium ion[61]

$$KNO_3 + 3HSO_3F \rightarrow K^+ + NO_2^+ + H_3O^+ + 3FSO_3^-$$

The very high acid strength of $FHSO_3$ which leads to the formation of many bases in this system makes it extremely difficult to find acids. Although SO_3 dissolves in $FHSO_3$ forming fluorodisulphuric acid, this acid is not sufficiently strong to ionize in $FHSO_3$, in contrast with $H_2S_2O_7$ which is a moderately strong acid of the sulphuric acid solvent

system.[62] SbF_5 acts as a weak acid in $FHSO_3$ but its ionization is not simple. A detailed interpretation of the conductivity data for this system suggests that there are two acid species present, $H[SbF_5(SO_3F)]$ which is a weak acid, and $H[(SbF_5)_2(SO_3F)]$ which is a strong fully dissociated acid.[63] $H[SbF_5(SO_3F)]$ is just one of a series of acids of general formula $H[SbF_{5-x}(SO_3F)_{x+1}]$, where $x = 0, 1, 2, 3$, formed by addition of mixtures of SO_3 and SbF_5 to $FHSO_3$.[63]

Fluorosulphuric acid is an excellent fluorinating agent, reacting with many oxides, oxyacids and their salts. Oxyfluorides are the usual products of these reactions but occasionally a fully fluorinated product is obtained[64,65]

$$As_2O_3 + 9FHSO_3 \rightarrow 2AsF_3 + 3H_3O^+ + 6SO_3 + 3FSO_3^-$$

$$P_4O_{10} + 18FHSO_3 \rightarrow 4POF_3 + 6H_3O^+ + 12SO_3 + 6FSO_3^-$$

Fluorosulphuric acid has found extensive use as a catalyst and reagent in the field of organic chemistry and many processes have been patented. Examples of its use are as a catalyst in alkylation reactions, polymerization reactions, isomerization of hydrocarbons, condensation reactions, and the preparation of organofluorine derivatives.[36]

4) Chlorosulphuric acid.

Little interest has been shown in the properties of $ClHSO_3$ as a non-aqueous solvent. Since sulphuric acid and fluorosulphuric acid are known to be good solvents for a wide variety of inorganic

and organic solutes, however, $ClHSO_3$ might be equally useful. The acid is usually prepared from oleum and an alkali metal chloride

$$NaCl + H_2S_2O_7 \rightarrow ClHSO_3 + NaHSO_4$$

Paul and co-workers[66] from studies of the electrical conductivities of solutions of some tertiary bases and alkali chlorosulphates concluded that the mode of solvent dissociation was

$$2HSO_3Cl \rightleftharpoons H_2SO_3Cl^+ + SO_3Cl^-$$

The alternative ionization path

$$HSO_3Cl \rightleftharpoons HSO_3^+ + Cl^-$$

appears to be of little importance since the conductivities of solutions of the Lewis acids $AlCl_3$, $SbCl_3$, $SnCl_4$, $TiCl_4$ and SO_3 show that they behave as non-electrolytes.[66] The alkali metal chlorosulphates appear to behave as fully dissociated electrolytes in $ClHSO_3$, whereas alkaline earth chlorosulphates are incompletely dissociated. Acetic and benzoic acids are fully protonated in both sulphuric acid and $ClHSO_3$.[67] Alkali metal chlorides react quantitatively with $ClHSO_3$ to give HCl which behaves as a very weak base of the $ClHSO_3$ solvent system.[67]

$$MCl + ClHSO_3 \rightarrow M^+ + SO_3Cl^- + HCl$$
$$HCl + ClHSO_3 \rightleftharpoons H_2Cl^+ + SO_3Cl^-$$

Solutions of $SeCl_4$ and $TeCl_4$ act similarly to give the $SeCl_3^+$ and $TeCl_3^+$ cations.[68]

$ClHSO_3$ appears to be about 70 times as strongly acidic as sulphuric acid.[69] This greater acidity as compared with H_2SO_4 and its relatively high dielectric constant suggest that it is a potentially useful solvent for both inorganic and organic species, despite the lack of attention it has so far received.

CHAPTER 3B

PHOSPHORUS HALIDES IN SULPHURIC ACID, OLEUMS, AND HALOSUBSTITUTED SULPHURIC ACIDS.

1) Introduction.

Gillespie et al[32] concluded from cryoscopic and conductimetric measurements that potassium dihydrogen phosphate is completely protonated in 100% sulphuric acid. They also deduced[70] that sulphuric acid is dehydrated by disodium dihydrogen pyrophosphate and pentasodiumtripolyphosphate. In all cases the phosphorus species present was reported to be the $P(OH)_4^+$ ion.

Dillon and Waddington[71] have studied by ^{31}P n.m.r. the behaviour of several inorganic phosphates in sulphuric acid, chlorosulphuric acid, and oleum solutions of varying sulphur trioxide content. In 100% sulphuric acid only one ^{31}P n.m.r. signal identified as $P(OH)_4^+$, was seen. In oleums containing more than 12.5% SO_3 two signals were always observed, the chemical shifts of which moved to higher field with increasing SO_3 concentration. The causes of this variation in chemical shift were discussed in terms of rapid equilibria between condensed phosphate species.

Olah and McFarland[60,72] have examined the protonation of several phosphorus compounds in fluorosulphuric acid and in fluorosulphuric acid-antimony pentafluoride ('Magic acid') solutions using ^1H, ^{19}F and ^{31}P n.m.r. Their evidence suggests that phosphoric acid is fully protonated in $FHSO_3$ solution[72] as the $P(OH)_4^+$ ion, but that for the fluorine-substituted phosphoric acids,[60] the degree of protonation decreases with successive replacement of OH by F. Monofluorophosphoric

acid is almost completely protonated in $FHSO_3$ while difluorophosphoric acid is also substantially protonated. POF_3 and PF_3 give little indication of protonation in $FHSO_3$, but more complete protonation of difluorophosphoric acid and POF_3 is indicated in 'Magic acid'. The conclusions of these workers were based on changes in both chemical shift and P-F coupling constants. It is interesting to note that at 273 K in a large excess of $FHSO_3$, hydroxyl replacement by fluorine from the solvent was observed in the case of difluorophosphoric acid, POF_3 being produced.[60] $FHSO_3$ has for some time been used as a fluorinating agent for many substances at ambient temperatures[64,65] (see also Chapter 3A section 3).

The solution chemistry of the phosphoryl halides in some strongly acidic solvents has been studied by Paul and co-workers.[15-17] The results are interpreted as incomplete protonation of phosphoryl chloride and bromide in 100% H_2SO_4 and $FHSO_3$ but complete protonation in disulphuric acid to form PX_3OH^+ (X = Cl or Br). No evidence was found for protonation of POF_3. ^{31}P n.m.r. investigations of the behaviour of some phosphoryl compounds in 100% H_2SO_4, 20% oleum, chlorosulphuric acid and 65% oleum by Dillon and Waddington[18] also suggest that phosphoryl chloride is a weak base in the solvents, and that its degree of protonation as shown by the down-field chemical shift increases as the acid strength increases. Paul et al also reported[15,17] that thiophosphoryl halides are basic enough to be protonated on the sulphur to give PX_3SH^+ (X = Cl, Br) in disulphuric and fluorosulphuric acids, but that the P = S group is less basic than the P = O group.

In addition this group studied the solution behaviour of simple

phosphorus (III) and phosphorus (V) halides in disulphuric acid[19] and fluorosulphuric acid[17] by cryoscopy and conductance methods. Phosphorus (V) chloride was reported to act as a chloride ion donor in disulphuric acid yielding the PCl_4^+ ion and chlorosulphuric acid, while phosphorus pentabromide dissociated to phosphorus tribromide and bromine. The PBr_3 was then oxidized to phosphoryl bromide which was in turn protonated. Solutions of phosphorus trichloride and tribromide in disulphuric acid are highly conducting and this behaviour was explained by oxidation to give the protonated phosphoryl halides.

In fluorosulphuric acid[17] Paul et al suggested that phosphorus pentachloride dissolves to give the PCl_4^+ ion. These workers also found that addition of phosphorus trichloride and phosphorus tribromide to fluorosulphuric acid produced no change in the conductance of the solution. The rationalization of this data was that the PX_3 species might have undergone solvolysis to form phosphorus trifluorosulphate $P(SO_3F)_3$ which then behaves as a non-electrolyte.

Paul and co-workers also attempted some redox reactions in $FHSO_3$ by taking phosphorus (III) compounds with a number of oxidizing agents.[20] Oxidation of phosphorus trichloride by chlorine, nitrosyl chloride, and iodine monochloride yielded $PCl_4^+ SO_3F^-$ while reaction with bromine was reported to produce $PCl_3Br^+SO_3F^-$. Similar reactions were carried out with phosphorus tribromide, and products of the form $PBr_3Cl^+SO_3F^-$ and $PBr_4^+SO_3F^-$ were postulated although isolation proved difficult. Very recently analogous reactions have been reported in acetic anhydride which are in general agreement with these results[73].

Paul et al[54] have also studied the solutions formed when yellow phosphorus is dissolved in disulphuric acid. Spectrophotometric, cryoscopic and conductance measurements on these solutions were interpreted in terms of the formation of the P_4^{2+} and P_8^{2+} ions.

This brief review of the chemistry of inorganic phosphorus compounds in sulphuric and related acids shows that various types of reaction are possible in these solvents. In an attempt to rationalize and extend some of this work a ^{31}P n.m.r. spectroscopic study was undertaken on solutions of phosphorus (III), phosphorus (V) and phosphoryl halides in 100% H_2SO_4, 25% and 65% oleums, chloro- and fluorosulphuric acids. Previous workers have for the most part used cryoscopic and conductimetric techniques which yield information on the bulk properties of the system rather than on the specific reactions and species formed therein. By the use of n.m.r. spectroscopy it was hoped to gain more information on the nature of the phosphorus species present in solution.

The approach used in these investigations was to make up solutions of the respective phosphorus and phosphoryl halides in a particular solvent and then to monitor the system over a period of time by means of ^{31}P n.m.r. The length of time required depended on the speed of reaction, and was continued until no further changes could be detected.

2) Present Work

i) Phosphoryl bromide

Solution of $POBr_3$ in 100% sulphuric acid occurred without any obvious reaction to yield a colourless liquid. The ^{31}P n.m.r. spectrum

of the solution showed a single signal at + 80 ppm. This compares with a reported shift of + 103.4 ppm[74] for $POBr_3$. The downfield shift of 23.4 ppm is consistent with protonation of the phosphoryl oxygen (Chapter 3B section 2 (iv)). After a period of 10 days the ^{31}P n.m.r. spectrum showed three signals at -2, + 26 and + 80 ppm, the two downfield signals being comparatively weak. The signal at + 26 ppm had disappeared after 24 days and the peak at -2 ppm had increased relative in intensity to the signal at + 80 ppm. Over a period of a further 7 months no new signals were detected in the spectrum although the -2 ppm signal grew in intensity, a ratio of approximately 3:2 relative to the resonance at + 80 ppm being reached after 8 months.

The peak at -2 ppm is very close to the reported shift of protonated phosphoric acid in 100% H_2SO_4.[71] Over the period of investigation the solution darkened to a colour which suggested bromine liberation and the shift values obtained are consistent with solvolysis of $POBr_3$.

$$P\text{-}Br + H_2SO_4 \rightarrow P\text{-}OH + HBr + SO_3$$
$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

The overall reaction is

$$PBr_3OH^+ \rightarrow P(OH)_4^+.$$

Under these circumstances the signal found in the early stages of the reaction at + 26 ppm could be due to an intermediate bromohydroxyphosphonium species. Later work (Chapter 3B section 2(i)) which

assigns signals at -2 and + 10 ppm in a 25% oleum solution of $POBr_3$ to $PBr(OH)_3^+$ and $PBr_2(OH)_2^+$ respectively suggests that the +26 ppm peak in this solution is due to $PBr_2(OH)_2^+$. A downfield shift for this species of 16 ppm in going from 100% H_2SO_4 to 25% oleum is not unreasonable since the degree of protonation will depend on the acid strength of the solution. It has been found[71] that the shift differences on protonation of a phosphoryl group in which the phosphorus is attached to several oxygens are small since extensive delocalization of the positive charge is possible. This phenomenon would tend to rule out the + 26 ppm peak as being due to $PBr(OH)_3^+$ since its signal position in 25% oleum appears to be at -2 ppm. The non-appearance of a signal assignable to the $PBr(OH)_3^+$ species is probably because it is never present in high enough concentrations for the expected peak to be observed.

The ^{31}P n.m.r. spectrum of a solution of $POBr_3$ in 25% oleum showed a single resonance at + 66 ppm. The downfield shift from $POBr_3$ of 37.4 ppm is consistent with more extensive protonation of the phosphoryl oxygen than in 100% sulphuric acid, as found also for $POCl_3$ (Chapter 3B section 2(iv)). No change in the spectrum was found after one month although the previously colourless solution had taken on a faint bromine colouration. After 8 months the solution was darker and the ^{31}P n.m.r. spectrum contained weak peaks at -2, + 6, and + 10 ppm in addition to a very intense peak at + 64 ppm.

From a consideration of the relative peak intensities (Fig. 1) and the shift value of + 6.6 ppm for the $P(OH)_4^+$-protonated pyrophosphate equilibrium in 25% oleum,[71] a reasonable signal assignment and solvolysis path is

$$PBr_3OH^+ \rightarrow PBr_2(OH)_2^+ \rightarrow PBr(OH)_3^+ \rightarrow P(OH)_4^+$$

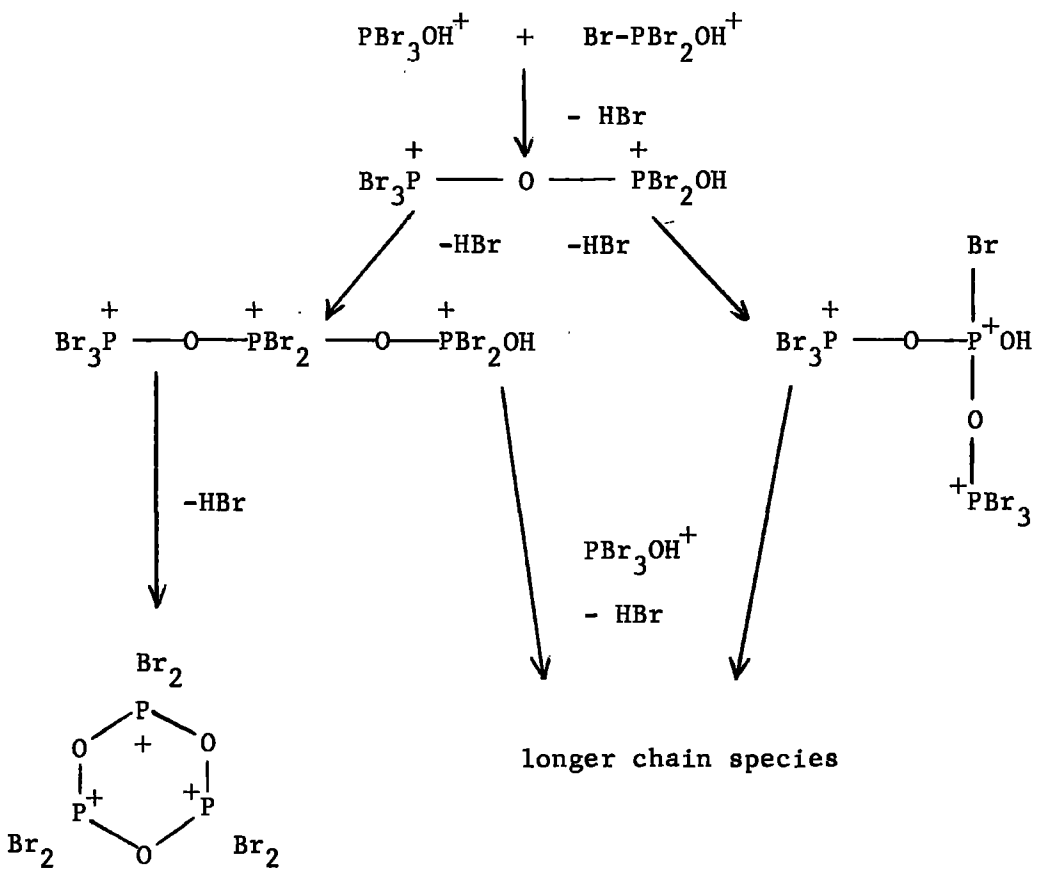
shift +64ppm +10 ppm - 2 ppm + 6 ppm

The rate of solvolysis of $POBr_3$ in 25% oleum appears to be much slower than in 100% H_2SO_4 and this probably explains the appearance of the resonances of the two intermediate species in the ^{31}P n.m.r. spectrum, since these will be relatively more stable and may thus form in measurable concentrations. The downfield shift of the postulated $PBr_2(OH)_2^+$ species in 25% oleum compared with 100% H_2SO_4 is again consistent with an increased degree of protonation in the stronger acid medium.

In contrast with the results obtained from 100% sulphuric acid and 25% oleum where bromine liberation was slow, the solution obtained from $POBr_3$ in 65% oleum darkened very rapidly and after 2 days contained a large amount of liquid bromine. The initial spectrum showed a single peak at + 57 ppm. while after 7 hours the ^{31}P n.m.r. spectrum showed the same broad signal at + 57 ppm with two weak signals at + 17 and + 26 ppm. After one day the ^{31}P n.m.r. spectrum showed weak signals at + 17 and + 42 ppm, and strong signals at + 26, + 35 and + 55 ppm. After 2 days the signal at + 17 ppm had disappeared, the peaks at + 25, + 33 and + 41 ppm had increased in intensity while the + 55 ppm resonance had moved downfield to + 47 ppm and was reduced in intensity. The ^{31}P n.m.r. spectrum of this solution after 3 days showed signals at + 25, + 34 and + 43 ppm in the ratio of approximately 4:5:2. The spectrum of the one month old solution showed no further peaks but the signal intensity ratio had changed to approximately 5:4:2 (Fig. 2). Assignment of the signals obtained in this reaction is not easy. The signal found between + 57 and + 47 ppm is probably due to protonated phosphoryl bromide. The shift values are lower than those found in 25% oleum which is consistent with a higher degree of protonation in a strong acid medium. The variation of the shift with time is not unreasonable, since a decrease in the concentration of the phosphoryl bromide will lead to an increasing downfield movement of its peak position as the acid strength will be effectively constant.

The four signals found in the region + 17 to + 43 ppm are less readily assignable. The relative intensities and signal positions of the peaks are not consistent with phosphoric acid production via monomeric $PBr_2(OH)_2^+$ and $PBr(OH)_3^+$ species. Solvolysis has been shown to be slow in both 100% H_2SO_4 and 25% oleum, and hence would not be expected to occur rapidly in such a strongly acidic medium as 65% oleum. The reaction proceeds with a copious and fairly rapid production of bromine, however, so clearly P-Br bonds are being broken.

65% oleum is a very powerful dehydrating agent but such a mode of reaction would not account for the production of bromine. As the acid strength of 65% oleum is so high the protonation of phosphoryl bromide is expected to be extensive. Under these circumstances, it is not unreasonable to postulate condensation of the protonated phosphoryl bromide species by hydrogen bromide elimination. A possible reaction sequence is

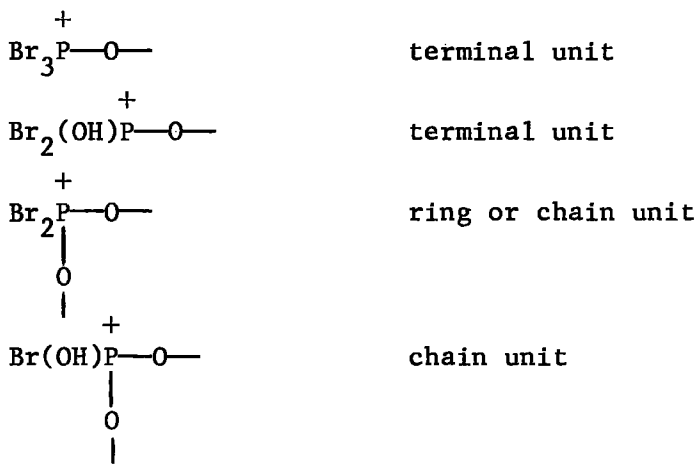


HBr is not expected to exist as such in 65% oleum solution, since the following reaction has been reported in disulphuric acid[19]

$$2HBr + 2H_2S_2O_7 \rightarrow Br_2 + SO_2 + 3H_2SO_4$$

Strong oleums contain disulphuric and higher polysulphuric acids[39] so a similar reaction is expected if hydrogen bromide is produced in 65% oleum. The removal of HBr by such a reaction could provide a driving force for the condensation.

The suggested reaction scheme contains species of the form,



On the assumption that attack is preferential at chain ends leading to elongation rather than at middle units which would lead to branching, these are the only species that could be formed.

^{31}P n.m.r. spectra of compounds which contain unsymmetrical P-O-P units would be expected to give multiplet structure because of P-O-P coupling. In the very high acidic media employed, however, proton exchange at the OH groups in the poly-species will be rapid and this will serve to decouple the phosphorus nuclei to which they are attached,

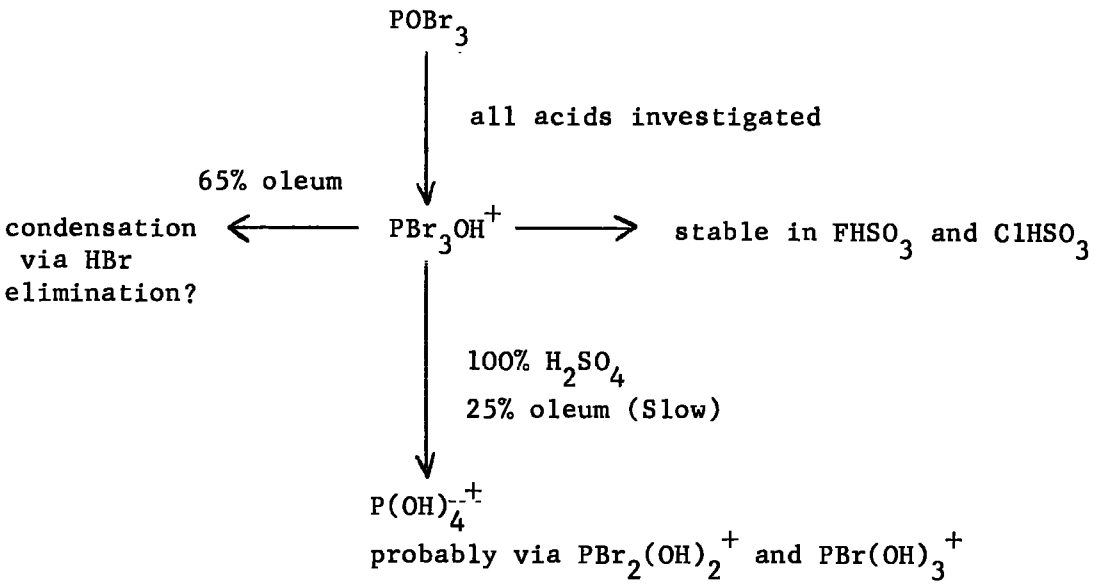
thus destroying the splitting.

^{31}P n.m.r. spectra of ATP and ADP salts run in dilute acid media show line broadening and loss of the multiplicity found in alkaline solutions.[75] An exact assignment of the peaks found in the 65% oleum spectrum is very difficult. Usually terminal units have lower shifts than ring or chain units[4,71] while the units containing bromine atoms would be expected to have higher shifts than the related hydroxy species. On this basis the following tentative assignment can be made taking into account the spectral intensity changes with time (Fig. 2).

$Br_3\overset{+}{P}—O—$	terminal unit	+ 26 ppm
$Br_2(OH)\overset{+}{P}—O—$	terminal unit	+ 17 ppm
$Br_2\overset{+}{P}(=O)—O—$	ring or chain unit	+ 42 ppm
$Br(OH)\overset{+}{P}(=O)—O—$	chain unit	+ 35 ppm

The ^{31}P n.m.r. spectra of phosphoryl bromide solutions in chloro- and fluorosulphuric acid both showed one signal at + 76 and + 74 ppm respectively. No other peaks were found when the samples were re-run some time after being made up. The solutions were monitored for 4 months in each case. These signals are consistent with protonation of the phosphoryl oxygen in both solvents.

The overall results obtained for solutions of phosphoryl bromide in the acids considered can be summarized as follows



These results on the whole agree with the conclusions of Paul and co-workers[15-17] where they overlap, although the shift values obtained for the solutions in 65% oleum initially suggest that their deduction of complete protonation of phosphoryl bromide by disulphuric acid may be incorrect. The low concentrations of solute used by Paul et al,[15-17] however, could mean that their measurements were carried out on essentially fully protonated phosphoryl bromide. The longer term studies suggest that slow solvolysis of $POBr_3$ occurs in 100% H_2SO_4 and 25% oleum but not in $FHSO_3$ and $ClHSO_3$.

The apparent absence of condensation products from $POBr_3$ solutions in the acids other than 65% oleum suggests that either no condensation occurs or that the condensed products are unstable and decompose to monomers. The formation of HBr in the condensation process acts as a driving force for further condensation since it is removed from the reaction medium as elemental bromine. This could take place in the lower strength acids as well as in 65% oleum. The lack of further

reaction of the PBr_3OH^+ ion in $FHSO_3$ and $ClHSO_3$ suggests that it does not condense. The production of bromohydroxyphosphonium species in the 100% H_2SO_4 and 25% oleum solutions of $POBr_3$ could be explained by rapid cleavage of the P-O-P units formed by dehydration of the solvent, so the possibility of condensation in these two solvents cannot be entirely eliminated. In view of the lack of condensation in $FHSO_3$ and $ClHSO_3$, the alternative route to bromohydroxyphosphonium species by straightforward solvolysis seems the more likely course especially in 100% H_2SO_4.

ii) Phosphorus (V) bromide

Dissolution of solid PBr_5 in 100% H_2SO_4 gave rise to a vigorous reaction and much evolution of heat. The orange-brown solution contained a small amount of an oily dark brown liquid, presumably elemental bromine. The ^{31}P n.m.r. spectrum of the solution initially showed two signals at + 80 and + 84 ppm of approximate intensity 1:4. Over a period of $5\frac{1}{2}$ hours this intensity ratio was reversed and after one day the only signal present was at + 80 ppm. Reinvestigation of this sample after 17 days showed no change in the spectrum but after 40 days a weak peak had appeared at 0 ppm. After 4 months the ^{31}P n.m.r. spectrum showed two signals at -3 and + 81 ppm of approximate intensity ratio 2:3. As the reaction proceeded a large amount of liquid bromine was formed in the n.m.r. tube.

The ^{31}P n.m.r. spectral results are consistent with the following reaction sequence.

Initial Solution

$$PBr_4^+Br^- + H_2SO_4 \rightarrow PBr_4^+ + HSO_4^- + HBr$$

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$$

solvolysis

$$PBr_4^+ \xrightarrow{\text{Fast}} PBr_3OH^+ \xrightarrow{\text{Slow}} P(OH)_4^+$$

+ 84 ppm + 80 ppm - 3 ppm

The assignment of the peak at + 84 ppm to PBr_4^+ agrees with a reported shift of + 81 ppm in liquid HCl,[76] while the assignment of the other peaks agrees well with data obtained for $POBr_3$ in 100% H_2SO_4 (Chapter 3B section 2(i)).

Solution of PBr_5 in both 25% oleum and 65% oleum was accompanied by a vigorous reaction with heat evolution and bromine formation. The ^{31}P n.m.r. spectra of both solutions, which contained liquid bromine, showed a single peak at + 84 and + 86 ppm in 25% and 65% oleums respectively. Investigation of the solution in 25% oleum over a period of $4\frac{1}{2}$ months showed that a weak peak appeared very slowly at + 70 ppm. The 65% oleum solution showed no peaks other than the one at + 86 ppm over a period of 5 months.

These results are consistent with solution of PBr_5 in these solvents yielding PBr_4^+ and bromine via oxidation of bromide ion. Slow solvolysis of PBr_4^+ to PBr_3OH^+ appears to occur in 25% oleum since the peak at + 70 ppm agrees well with the peak at + 66 ppm found for solution of $POBr_3$ in 25% oleum (Chapter 3B section 2(i)). The exact shift will in any case be concentration-dependent. The PBr_4^+ ion appears to be quite stable in 65% oleum over a long period of time.

The pale orange solution formed when PBr_5 dissolves in chlorosulphuric acid showed only one ^{31}P n.m.r. signal at + 85 ppm when investigated over a 20 day period. This peak is assignable to PBr_4^+ and the pale colour of the solution suggests that the bromide ion is rather more stable in chlorosulphuric acid than in sulphuric acid or oleums. After a period of 10 months, the solution had darkened slightly in colour and re-investigation of the ^{31}P n.m.r. spectrum yielded a complex picture (Fig. 3). The peaks present are readily assignable to species of the form $[PCl_nBr_{4-n}]^+$ and $[PCl_mBr_{3-m}OH]^+$ where $(0 \leq n \leq 2)$ and $(0 \leq m \leq 3)$ (Table 2).

These results show that $ClHSO_3$ is acting as both a solvolysing agent and a source of chlorine. The latter action is a little surprising in view of the result obtained from solution of $POBr_3$ in chlorosulphuric acid (Chapter 3B section 2(i)), where no reaction other than protonation was observed over a period of 4 months. A possible explanation is that the $ClHSO_3$ is acting as an indirect source of chloride ion by the following route.

$$Br^- + ClHSO_3 \rightarrow HBr + ClSO_3^-$$

$$2HBr + ClHSO_3 \rightarrow Br_2 + SO_2 + HCl + H_2O$$

$$ClHSO_3 + H_2O \rightarrow HCl + H_2SO_4.$$

The HCl produced could then act as a source of the exchanging chlorine. The observation that the PBr_5 solution in chlorosulphuric acid darkens slowly with time and the lack of liquid bromine formation suggests that the bromide ion only reacts slowly in $ClHSO_3$. Hence the proposed reaction

Table 2. ^{31}P n.m.r. chemical shift values for species derived from phosphorus (V) bromide in chlorosulphuric acid

Species	chemical shift (ppm)	
	Observed	Literature
$PCl_2Br_2^+$	-9	-9.7 in liquid HCl[76]
$PClBr_3^+$	+35	+34.6 in liquid HCl[76]
PBr_4^+	+84	+81 in liquid HCl[76]
PCl_3OH^+	-22	-24.4 in $ClHSO_3$[18]
PCl_2BrOH^+	+ 7	+ 8 in $ClHSO_3$*
$PClBr_2OH^+$	+40	+39 in $ClHSO_3$*
PBr_3OH^+	+76	+76 in $ClHSO_3$*

* This work, see Chapter 3B section 2(viii)

scheme would account satisfactorily for slow but steady production of chlorine available for exchange with the P-Br species present.

PBr_5 dissolves in fluorosulphuric acid with vigorous reaction and evolution of heat to yield a brown solution consistent with bromine formation. The solution darkened on standing. The initial ^{31}P n.m.r. solution spectrum consisted of a strong signal at + 86 ppm assignable to PBr_4^+ and a weak 1:3:3:1 quartet centred at + 38 ppm ($^1J_{PF}$= 1070 Hz). The appearance of a quartet is indicative of the formation of P-F bonds in this reaction and the n.m.r. parameters obtained are compatible with POF_3 (^{31}P n.m.r. shift + 36.6 ppm, $^1J_{PF}$= 1060 Hz).[60] After 2 days the spectrum consisted of a peak at + 84 ppm, a quartet at + 37 ppm and a 1:2:1 triplet at + 22 ppm ($^1J_{PF}$ = 997 Hz). The triplet appears to be due to protonated difluorophosphoric acid (^{31}P n.m.r. shift + 22.6, $^1J_{PF}$= 1002Hz).[60] No new signals were found in the ^{31}P n.m.r. spectrum after 9 days but the signal at + 84 ppm was considerably reduced in intensity while the two downfield signals were much stronger.

These results are consistent with reaction of the PBr_4^+ ion initially formed with excess fluorosulphuric acid to form POF_3. The lack of signals due to intermediate species is probably due to their low concentration during the course of reaction. The slow darkening of the solution suggests a gradual liberation of bromine. A possible reaction sequence being

$$PBr_4^+Br^- + FHSO_3 \rightarrow PBr_4^+ + FSO_3^- + HBr$$

$$2HBr + FHSO_3 \rightarrow Br_2 + HF + H_2O + SO_2$$

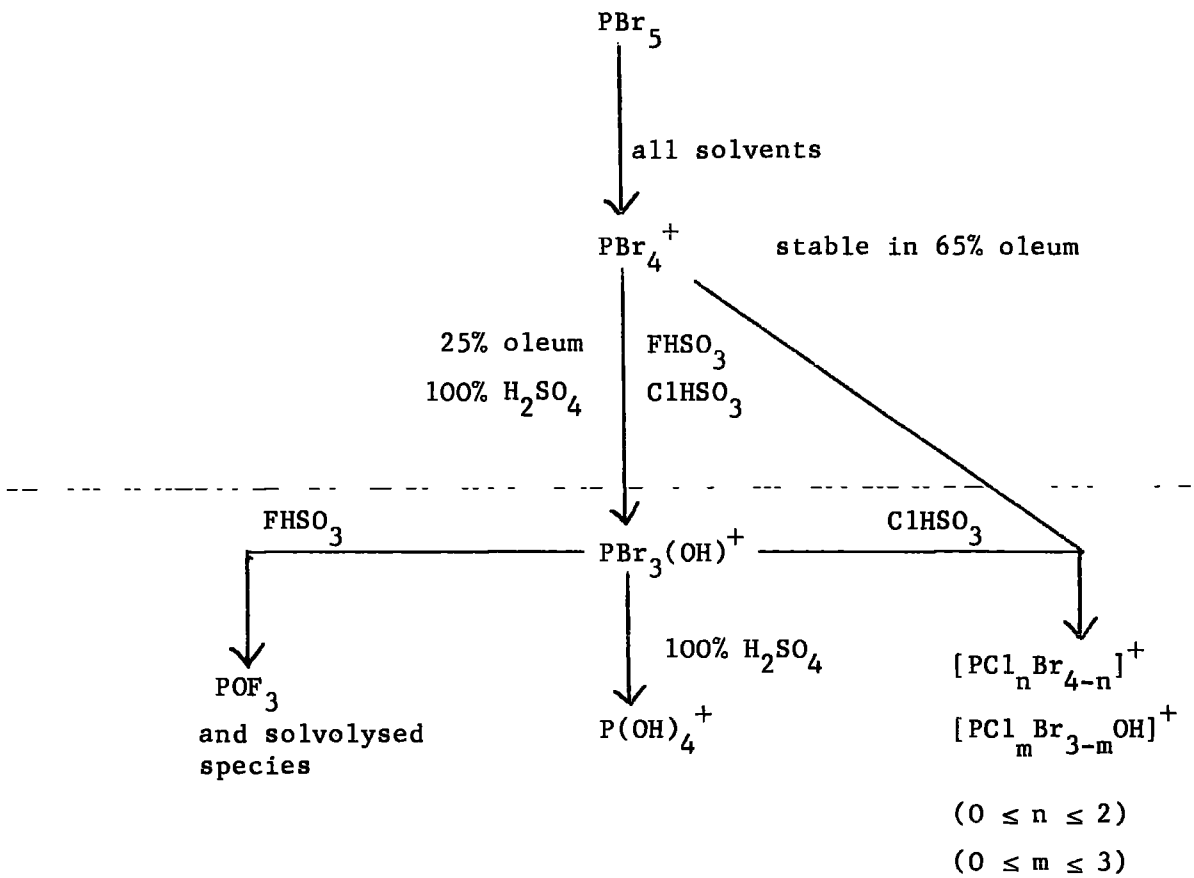
$$PBr_4^+ \longrightarrow PBr_3OH^+ \longrightarrow POF_3$$

Although the PBr_3OH^+ signal was not found, its presence in the reaction sequence is supported by the observation that a solution of $PBr_4^+BBr_4^-$ in $FHSO_3$ showed a weak signal at + 71 ppm in addition to a strong peak at + 85 ppm when the solution was 9 days old (Chapter 3B section 2(viii)). The occurence of fluorine substitution in this system is interesting since a solution of $POBr_3$ in fluorosulphuric acid (Chapter 3B section 2(i)) showed no signs of reaction other than protonation. As for PBr_5 in $ClHSO_3$, this may be because the acid acts as an indirect source of fluorine via fluoride ion formation as suggested in the possible reaction scheme.

The production of protonated difluorophosphoric acid indicates that solvolysis of the POF_3 takes place. Bromine formation would not only lead to direct degradation of the $FHSO_3$ but also to water production. Hence during the reaction the fluorosulphuric acid will be reduced in strength, thus promoting solvolysis of phosphorus-halogen bonds.

The lack of signals due to intermediates between PBr_4^+ and POF_3 makes it difficult to elucidate the exact course of the reaction. The results obtained from PBr_3 in $FHSO_3$ (Chapter 3B section 2(iii)) suggest that reaction occurs via PBr_4^+ degradation to PBr_3OH^+ followed by F-Br exchange to yield POF_3. This course of events so reduces the acidity of the medium that solvolysis of POF_3 to $PF_2(OH)_2^+$ is then possible.

The overall reactions of PBr_5 in the acidic media considered can be summarized as follows.



The data shows quite a varied reaction scheme which is highly dependent on the acid used. The conclusion of Paul et al[19] that PBr_5 dissolves in disulphuric acid with dissociation to PBr_3 and Br_2, followed by subsequent oxidation to protonated phosphoryl bromide is not substantiated. In the present work, PBr_5 was found to dissolve in 25% oleum to give PBr_4^+ which only solvolysed slowly. Since disulphuric acid is equivalent to 33% oleum, it is reasonable to expect PBr_5 to act in a similar manner to produce PBr_4^+, particularly in view of the stability of this ion in 65% oleum.

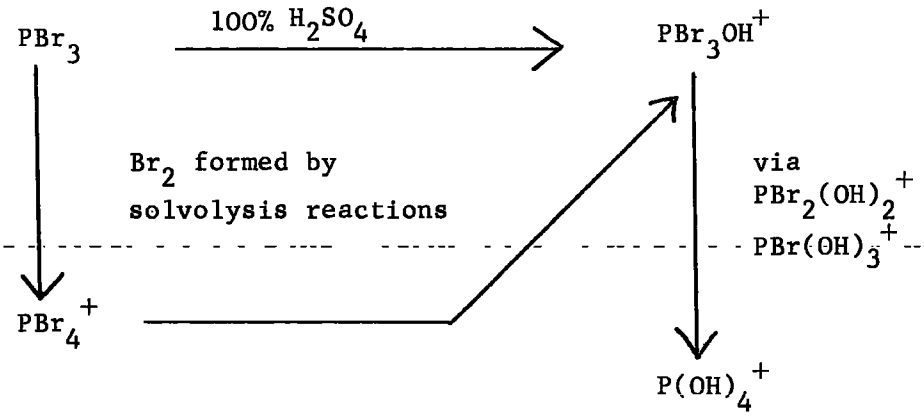
iii) Phosphorus (III) bromide.

Addition of 100% H_2SO_4 to PBr_3 caused no sign of reaction, and the two liquids appeared to be immiscible. The mixture was shaken over a period of 6 hours but two layers were still present, although a yellow colouration had appeared in both. The mixture was left standing and on shaking, 11 hours after being made up, a violent reaction occured. Much heat was evolved and a red-brown solution was formed. The mixture was allowed to stand overnight and a brown liquid then formed at the bottom of the n.m.r. tube, presumably elemental bromine.

Initial spectra run on the two-phase sample showed a very intense signal at -228 ppm and weak signals at + 20, + 78 and + 83 ppm. The peak at -228 ppm agrees well with the shift value of -227 ppm for PBr_3.[77] The weak peaks at + 20, + 78 and + 83 are assignable to $PBr_2(OH)_2^+$, PBr_3OH^+ and PBr_4^+ respectively and agree with data reported elsewhere in this work.

The ^{31}P n.m.r. spectrum run after reaction had occurred to give a one-phase sample showed three signals at -3, + 28 and + 80 ppm, the latter being much more intense than the two downfield signals. Over a period of 20 days the + 28 ppm signal disappeared while the -3 ppm peak grew relative to the + 80 ppm signal, reaching approximately equal intensity after 27 days. Spectra taken at 57 and 80 days confirmed the increase in size of the -3 ppm signal relative to the + 80 ppm signal and reinvestigation of the tube after 9 months showed only one peak at -2 ppm. The signals at -3, + 28 and + 80 are in agreement with data obtained from the solvolysis of $POBr_3$ in 100% H_2SO_4 (Chapter 3B section 2(i)) and are assignable to $P(OH)_4^+$, $PBr_2(OH)_2^+$ and PBr_3OH^+

respectively. The lack of a signal assignable to $PBr(OH)_3^+$ is probably due to its low concentration during the reaction. A possible reaction scheme is



The presence of PBr_4^+ initially in the spectrum is interesting. The reason for its production is probably as follows. Initial reaction at the interface of the two-phase system produces PBr_3OH^+. Some solvolysis of the PBr_3OH^+ then takes place yielding $PBr_2(OH)_2^+$ etc. and bromine, because the reaction is occurring over a limited area and the acid strength in this region will be much reduced. The bromine so formed reacts with PBr_3 present at the interface to form PBr_5 which in turn dissolves in the 100% H_2SO_4 to give PBr_4^+. This solution will regenerate bromine, weaken the strength of the acid at the interface and promote further solvolysis, thus propagating the reaction. The rapid solvolysis of the PBr_4^+ ion so formed is not surprising in view of the observation that solutions of PBr_5 in 100% H_2SO_4 produced PBr_3OH^+ exclusively from PBr_4^+ after approximately 7 hours.

The ^{31}P n.m.r. data obtained from this solution suggests that although the main reaction of PBr_3 in 100% H_2SO_4 is oxidation to yield PBr_3OH^+, the process is complicated by the initial immiscibility of the

reactants, which leads to further reactions involving the formation of PBr_4^+ and solvolysis products of PBr_3OH^+. After a one-phase system containing mainly PBr_3OH^+ is formed, the expected solvolysis path is followed to give $P(OH)_4^+$.

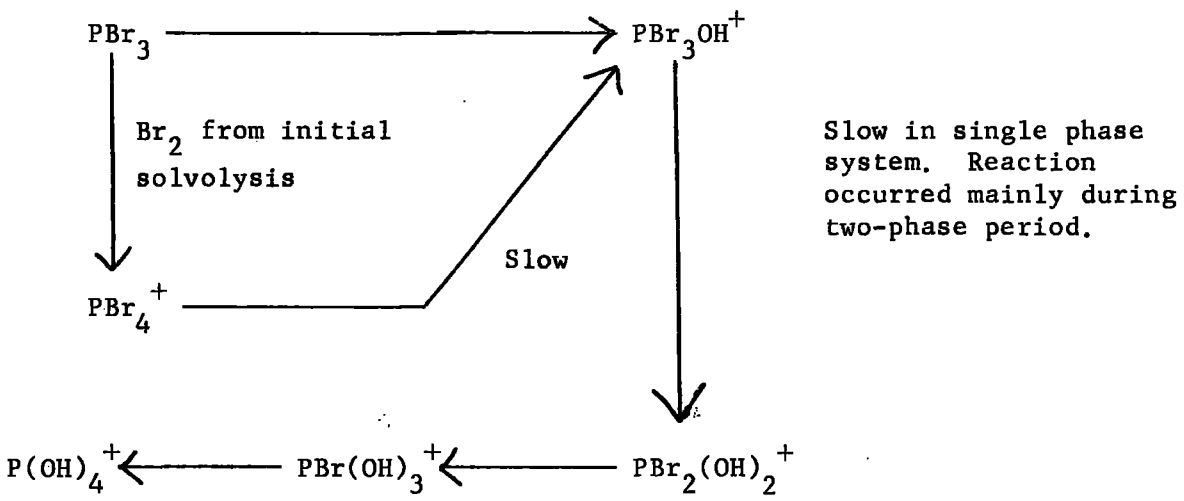
As with 100% H_2SO_4, addition of 25% oleum to PBr_3 produced a two-phase system and no obvious reaction occurred. The mixture was shaken continually and over a period of a few hours both layers turned through yellow to brown. Four hours after the mixture was made up a vigorous reaction takes place with much heat being evolved. The single phase produced was dark brown, suggesting the formation of bromine, and on further standing liquid bromine formed at the bottom of the tube. Attempts to run ^{31}P spectra were unsuccessful initially but on the following day spectra were successfully obtained and the tube was monitored for seven months (Fig. 4).

Over this period there was little sign of decomposition of the species giving peaks at + 72 and + 84 ppm. The main reactions appeared to involve peaks in the -3 to + 15 ppm region. The ^{31}P n.m.r. peaks in these spectra are assignable as shown in Table 3.

Table 3. ^{31}P n.m.r. chemical shift values for species derived from phosphorus (III) bromide in 25% oleum

Chemical shift (ppm)	Assignment
+ 84	PBr_4^+
+ 72	PBr_3OH^+
+ 12	$PBr_2(OH)_2^+$
- 3	$PBr(OH)_3^+$
+ 4 and + 15	$P(OH)_4^+$ and polyphosphate equilibria [71]

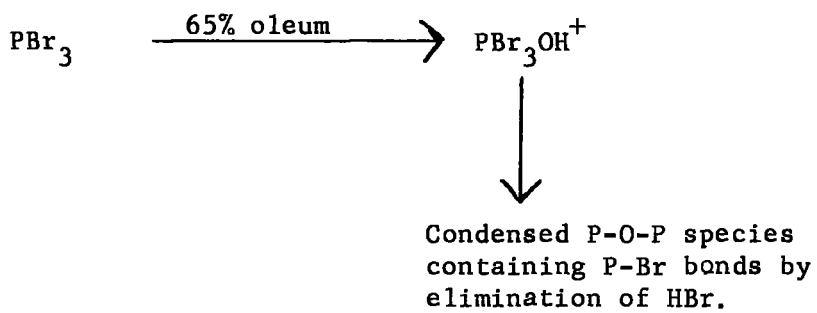
The peaks at + 84 and + 72 ppm are consistent with data obtained from PBr_5 and $POBr_3$ respectively in 25% oleum (Chapter 3B sections 2(ii) and 2(i)), and those at + 4 and + 15 ppm with results from some inorganic phosphates in oleum solutions.[71] The assignment of the + 12 and -3 peaks to $PBr_2(OH)_2^+$ and $PBr(OH)_3^+$ seems reasonable since the reactions involved are oxidation of PBr_3 followed by solvolysis. The order of appearance of the respective peaks and their relative changes in intensity with time are consistent with a stepwise solvolysis of $PBr_2(OH)_2^+$ to $P(OH)_4^+$ via $PBr(OH)_3^+$, and the shifts agree with data from solutions of $POBr_3$ in 25% oleum (Chapter 3B section 2(i)). The apparent stability of PBr_3OH^+ and PBr_4^+ in this system is in agreement with independent data obtained from the parent compounds in 25% oleum. The proposed reaction scheme is thus



As in the case of the 100% H_2SO_4 solution of PBr_3, the appearance of PBr_4^+ and $PBr_2(OH)_2^+$ in addition to PBr_3OH^+ is probably because the initial reaction takes place at a liquid junction interface. After the formation of a homogeneous mixture, the rate of solvolysis of PBr_3OH^+ and PBr_4^+ is slow, the main solvolysis happening from $PBr_2(OH)_2^+$ down to $P(OH)_4^+$.

In contrast with the 100% H_2SO_4 and 25% oleum solvents, addition of 65% oleum to PBr_3 gave rise to an immediate violent reaction. Much heat was evolved and a bromine-coloured solution was formed. On standing overnight a large amount of liquid bromine had collected at the bottom of the tube. The initial ^{31}P n.m.r. spectrum showed a single peak at + 50 ppm while after 6 hours two weak signals at + 18 and + 25 ppm had appeared. After one day the ^{31}P n.m.r. spectrum showed weak signals at + 17 and + 49 ppm, and strong signals at + 20, + 35 and + 42 ppm. The spectrum taken after 2 days showed 3 signals at + 25, + 33 and + 43 ppm respectively of approximate intensity 3:5:2. No further signals were found after 2 months although the signal intensity had changed to approximately 5:4:2.

The results of this experiment are remarkably similar to those obtained from $POBr_3$ in 65% oleum and suggest the following reaction sequence



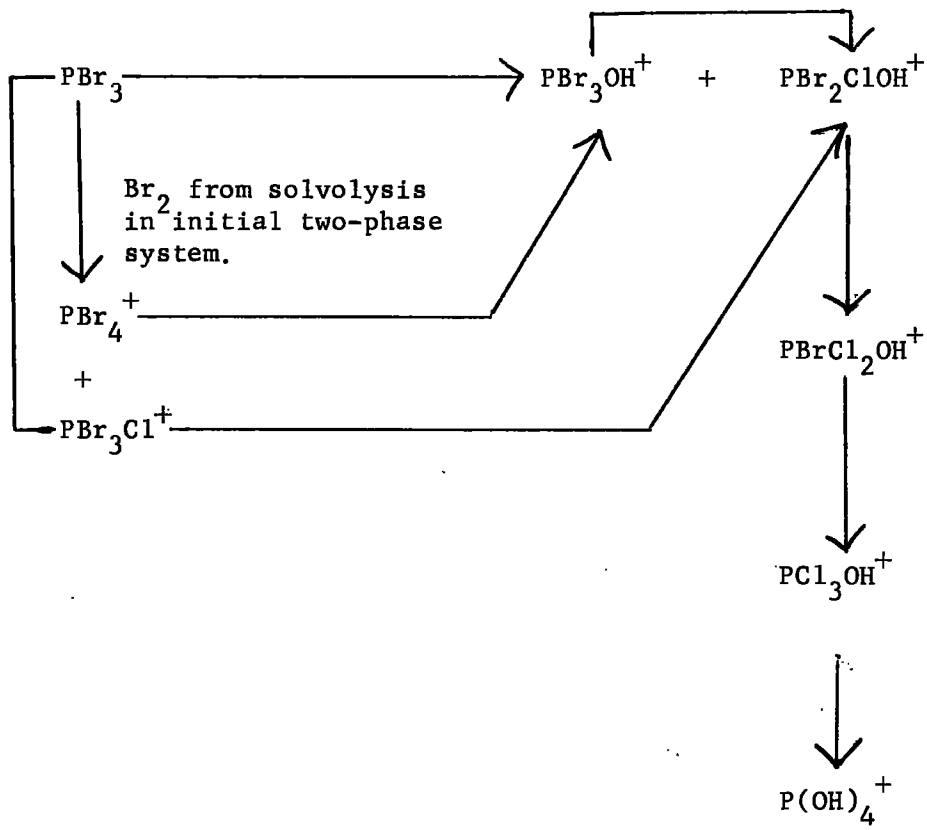
The lack of a signal assignable to PBr_3OH^+ after 2 days is in agreement with its decomposition in 2 days when formed from $POBr_3$ in 65% oleum (Chapter 3B section 2(i)). The lack of a signal at + 84 ppm shows that no PBr_4^+ was formed during the reaction. This supports the hypothesis that PBr_4^+ found in the 100% H_2SO_4 and 25% oleum was a consequence of PBr_3 - Br_2 oxidation at the liquid interface in the original two-phase systems, since PBr_4^+ is a stable entity in 65% oleum (Chapter 3B section 2(ii)).

Addition of chlorosulphuric acid to PBr_3 gave a two-phase system but reaction was observed at the interface. Immediate shaking of this mixture gave rise to a vigorous reaction with evolution of heat, forming a pale orange solution. The ^{31}P n.m.r. spectrum of this solution showed one strong signal at + 82 ppm and three weak signals at + 36, + 43 and + 84 ppm. No change in the spectrum was found after 5 days and the signals are readily assignable to

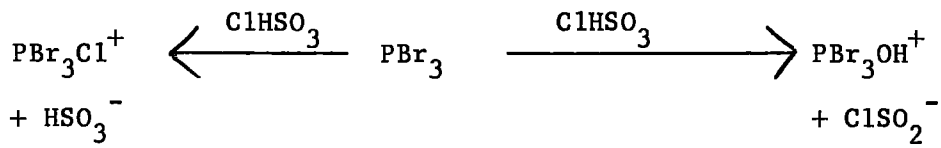
PBr_3Cl^+	+ 36 ppm
PBr_2ClOH^+	+ 43 ppm
PBr_3OH^+	+ 82 ppm
PBr_4^+	+ 84 ppm

After 23 days the ^{31}P n.m.r. solution spectrum consisted of a strong signal at + 82 ppm and a weaker signal at + 44 ppm assignable to PBr_3OH^+ and PBr_2ClOH^+ respectively, plus two weak signals at - 19 and + 11 ppm. The signal at - 19 ppm is compatible with production of PCl_3OH^+ [18] and the signal at + 11 is probably due to the intermediate

species PCl_2BrOH^+ (Chapter 3B section 2(viii)). Little change could be seen in the spectrum after 35 days, although the - 19 ppm peak appeared to be increasing in intensity. After $7\frac{1}{2}$ months the ^{31}P n.m.r. spectrum still showed little change with peaks at + 82, + 45, + 10 and - 19 ppm. The - 19 ppm peak had decreased in intensity, however, and a new peak at -2 ppm could be seen. The new peak may be assigned to $P(OH)_4^+$ [18] and suggests that the hydroxy-species are slowly solvolysed. A probable reaction sequence is



The data suggests that $ClHSO_3$ can act as an oxidizing agent by two modes



As with PBr_5, chlorosulphuric acid thus acts as a chlorinating agent as well as a solvolysing agent. Since $POBr_3$ does not appear to exchange with $ClHSO_3$ (Chapter 3B section 2(i)) it seems likely that $ClHSO_3$ is again acting as an indirect source of chlorine. A possible reaction sequence is

$$PBr_3 + ClHSO_3 \rightarrow PBr_3OH^+ + SO_2Cl^-$$
$$SO_2Cl^- + ClHSO_3 \rightarrow HCl + SO_2 + ClSO_3^-$$

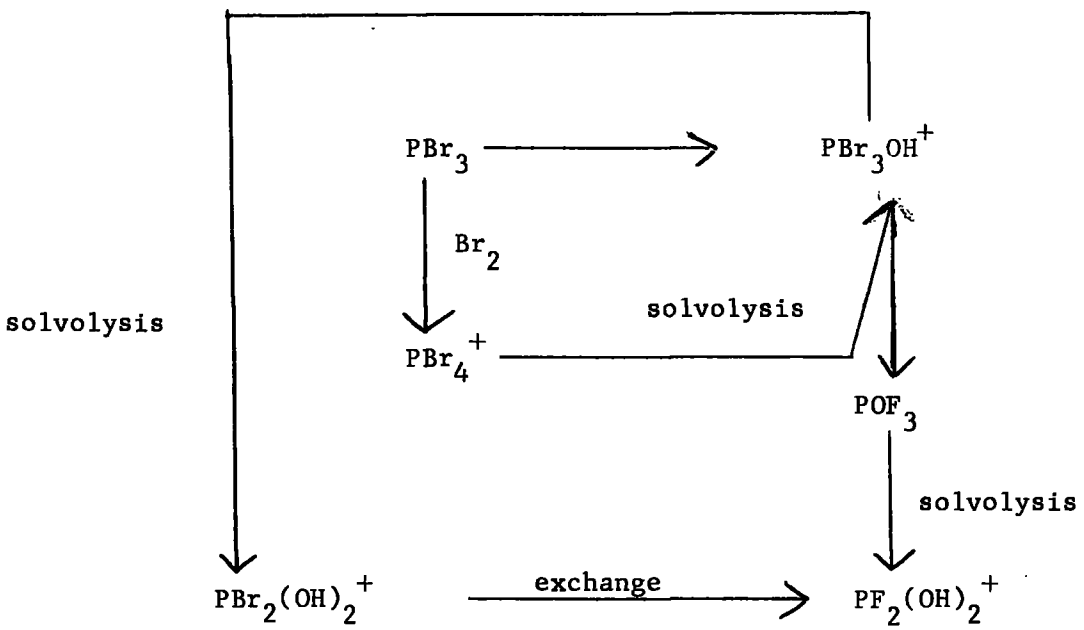
Although numerous salts of the chlorosulphite anion, $ClSO_2^-$ are known,[78] the parent acid is not so this decomposition path to produce HCl is quite probable. Hence there is an alternative source of chlorine which may give rise to the exchange species observed. A more detailed discussion of this possibility is given later in this section where similar reactions in the $PBr_3/FHSO_3$ system are considered.

Addition of fluorosulphuric acid to PBr_3 gave a two-phase liquid system and even on shaking there appeared to be little reaction. The mixture was shaken over a period of 2 hours and then left. Approximately 3 hours after mixing up an extremely violent reaction occurred with the liberation of heat to give a dark brown solution suggesting bromine formation.

The initial ^{31}P n.m.r. solution spectrum taken 15 minutes after the violent reaction showed two strong signals at + 78 and + 83 ppm, a weak quartet at + 36 ppm ($^1J_{PF}$ = 1070 Hz) and a weak triplet at + 20 ppm ($^1J_{PF}$= 1010 Hz). After 30 minutes, the same four peaks were apparent but the signal at + 83 ppm was much reduced in strength while the signal

at + 78 ppm had broadened considerably. After one hour only two signals were present, a broad strong signal at + 80 ppm and a weak triplet at + 22 ppm. Over the next 14 days, no new signals were seen but the intensity of the + 22 ppm triplet increased with respect to the broad peak at + 80 ppm.

The assignment of the peaks found in this system is relatively easy. The signal at + 83 ppm is almost certainly due to PBr_4^+ while the broad signal between + 78 and + 80 ppm is due to PBr_3OH^+. The appearance of multiplet signals is consistent with the formation of P-F bonds and the shift data agrees with published values for POF_3 (+ 36 ppm quartet) and $PF_2(OH)_2^+$ (+ 20 to + 22 ppm triplet).[60] A probable reaction scheme is



A number of interesting points arise from these results.

a) a solution of $POBr_3$ in $FHSO_3$ showed no sign of exchange whereas with PBr_3 in this solvent exchange was quite rapid and extensive

b) PBr_4^+ was produced but was solvolysed rapidly to PBr_3OH^+ unlike the PBr_4^+ formed from PBr_5 in $FHSO_3$ which was solvolysed slowly

c) the fleeting appearance of a weak POF_3 signal followed by a marked increase in concentration of $PF_2(OH)_2^+$ seems strange at first glance.

The main difference between solutions of phosphorus (III) and (V) compounds in sulphuric acids is that the phosphorus (III) compounds are likely to be oxidized to phosphorus (V). For inorganic phosphorus (V) species the only probable reactions are protonation, with condensation possible in the stronger acid solvents, and/or solvolysis. Thus the phosphorus (III) reactions involve a more complex system and points a) to c) raised previously can be explained from a consideration of the following equations

A $PBr_3 + FHSO_3 \rightarrow PBr_3OH^+ + FSO_2^-$

B $FSO_2^- + FHSO_3 \rightarrow SO_2 + HF + FSO_3^-$

C $3HF + PBr_3OH^+ \rightarrow POF_3 + 3HBr + H^+$

D $2HBr + FHSO_3 \rightarrow Br_2 + HF + H_2O + SO_2$

E $H_2O + FHSO_3 \rightarrow HF + H_2SO_4$

In equation A, PBr_3 is oxidized and the solvent reduced to give the fluorosulphite anion. Fluorosulphurous acid is not known[79] and equation B, therefore seems a reasonable course of reaction. Thus a new source of fluorine in the form of HF is produced and may take part in equation C to yield POF_3, which is not protonated in this medium.[60] Equation D explains the appearance of bromine in the solution as well as providing a further source of HF and more importantly, H_2O. In equation E the parent acid is hydrolysed to yield more HF and sulphuric acid.

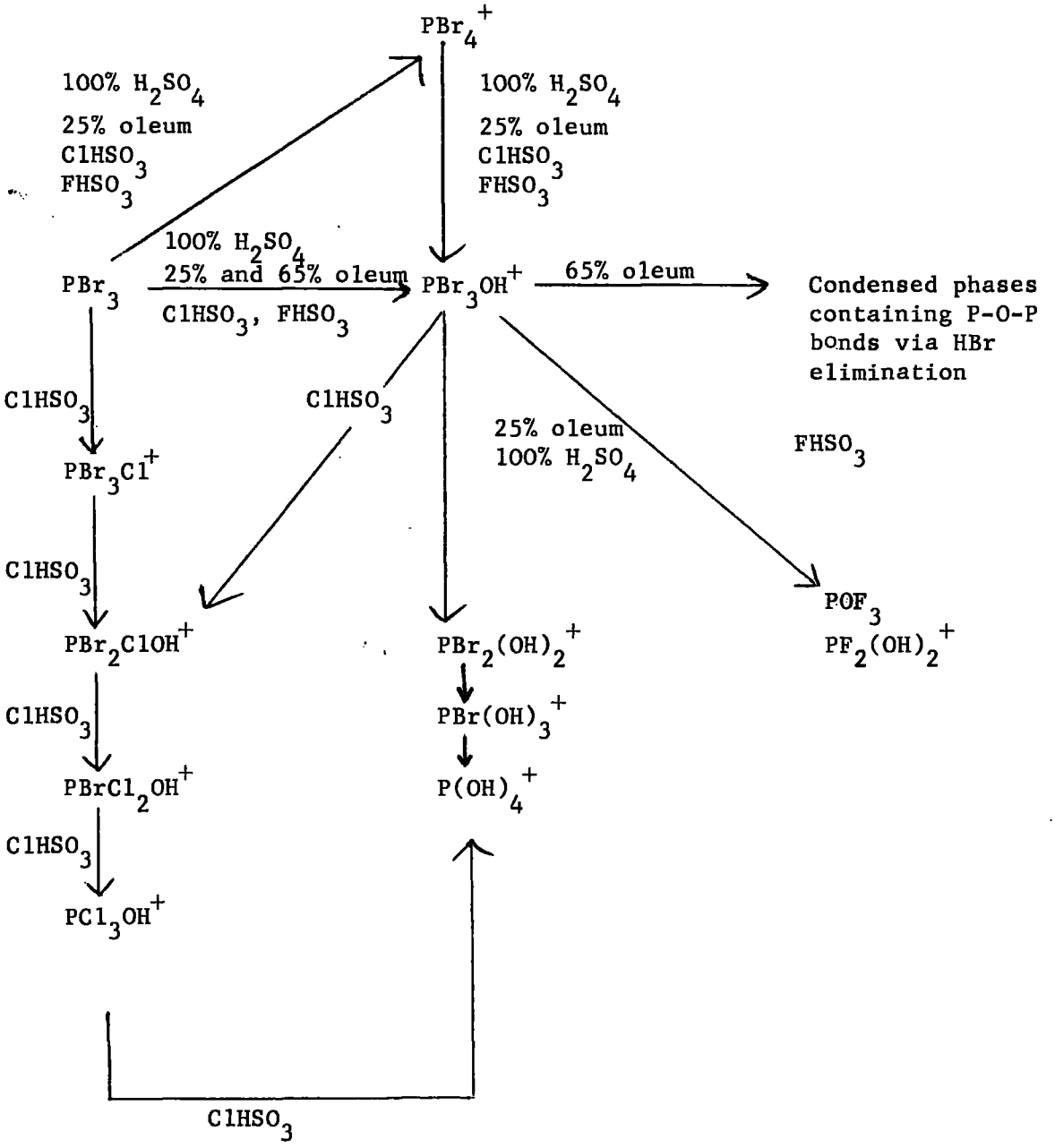
These five equations thus account for all the points raised previously as well as the solution species observed.

a) Exchange of the PBr_3OH^+ is probably due indirectly to fluorosulphuric acid. In a solution of $POBr_3$ in $FHSO_3$ alone, PBr_3OH^+ and $FHSO_3^-$ are formed exclusively. The HF from some or all of reactions B, D and E is probably the agent for Br - F exchange when PBr_3 is the solute.

b) Bromine is produced in equation D and this probably reacts at the interface with liquid PBr_3 to yield PBr_4^+. The rapid solvolysis of PBr_4^+ in this system may well be due to the formation of H_2SO_4 in equation E since PBr_4^+ has been observed to decompose rapidly in 100% H_2SO_4 giving PBr_3OH^+. In addition, general degradation of the solvent $FHSO_3$ is occuring, which will reduce the acid strength and accelerate the solvolysis of PBr_4^+.

c) The low concentration of POF_3 and high concentration of $PF_2(OH)_2^+$ found is probably due to the same causes as the solvolysis of PBr_4^+. The reaction which produces HF and H_2SO_4 gives the solution fluorinating and solvolysing properties. The PBr_3OH^+ formed initially could well exchange to give POF_3 directly which is then rapidly solvolysed in the degraded solvent, or the PBr_3OH^+ could be solvolysed to $PBr_2(OH)_2^+$ which subsequently is fluorinated to give $PF_2(OH)_2^+$. Both courses are possible, but it is difficult to say which is followed.

The equations A to E quoted for $FHSO_3$ are equally applicable to $ClHSO_3$. Solutions of PBr_3 in $ClHSO_3$ followed generally the same route as $PBr_3/FHSO_3$, with halogen exchange and solvolysis of the phosphorus (V) species formed by the oxidation of the starting compound. The only apparent difference is the non-detection of a resonance assignable to the PBr_3F^+ ion, whereas PBr_3Cl^+ was found in $ClHSO_3$. The results obtained for dissolution of PBr_3 in the various acids can be summarized as follows



The data obtained for solutions of PBr_3 in 100% H_2SO_4 and 25% oleum is in general agreement with that of Paul et al for solutions in disulphuric acid[19] in so far as the initial oxidation reaction is concerned.

The ^{31}P n.m.r. data suggests, however, that the initial immiscibility of the reactants complicates the product composition, and that further reaction occurs in which the phosphorus (V) products are solvolysed. No evidence was found to support Paul's suggestion that solution of PBr_3 in fluorosulphuric acid might proceed via solvolysis to yield $P(SO_3F)_3$,[17] and the results support oxidation of PBr_3 as the prefered reaction.

iv) Phosphoryl chloride.

Solutions of $POCl_3$ have been prepared in various acidic media and the ^{31}P n.m.r. spectra recorded. Table 4 summarizes the shift data obtained here and by previous investigations.

Table 4. ^{31}P n.m.r. chemical shift values (ppm) for phosphoryl chloride in acidic solvents.

Source	HCl	100% H_2SO_4	20% oleum	25% oleum	65% oleum	$ClHSO_3$	$FHSO_3$
All[18] except HCl which is[13]	-6.9	- 20.2	-34.8		- 43	- 22	
This work		- 20		- 35.3	- 55.9	- 25	- 23

The reported chemical shift of liquid $POCl_3$ is - 2.2 ppm[74] and all the shifts given are downfield from the parent species. This is consistent with protonation of the phosphoryl oxygen of $POCl_3$, the increasing downfield shift indicating more extensive protonation as the acid strength increases.

$POCl_3$ dissolved in 100% H_2SO_4, 25% and 65% oleums, $ClHSO_3$ and $FHSO_3$ to give colourless solutions which showed no sign of reaction when monitored by ^{31}P n.m.r. All that appears to happen is protonation of the phosphoryl oxygen to yield PCl_3OH^+ which is then stable even over a period of a few months.

These results are in agreement with Paul's conductimetric work on $POCl_3$ in disulphuric acid[15] and fluorosulphuric acid[17] which was interpreted as solution of the $POCl_3$ with protonation and no further reaction. The only difference from Paul's conclusions is his assertion that $POCl_3$ is completely protonated in disulphuric acid,[15] but since the degree of protonation of $POCl_3$ is concentration-dependent, it is not possible to be categoric on this point.

Coordination to phosphorus via the oxygen of the phosphoryl group has been shown to cause a downfield shift in the ^{31}P n.m.r. resonance[80] of a number of $POCl_3$ adducts. The magnitude of this shift will depend on the strength of coordination since this will cause a reduction in electron density in the P=O bond and hence a decrease in the shielding of the phosphorus nucleus from an external magnetic field. In the protonation of $POCl_3$, the larger the downfield shift, the higher the degree of protonation of the phosphoryl oxygen, since $POCl_3$ functions as a weak base. Hence it is easy to see that the downfield shift of the

^{31}P n.m.r. resonance of protonated $POCl_3$ will depend on the concentration of the solute as well as the strength of the acid. This concentration factor is the probable reason for the difference of 13 ppm between the reported shift for $POCl_3$ in 65% oleum,[18] and that found in the present work, different concentrations having been used. This concentration-dependence could also explain Paul's statement[15] that $POCl_3$ is completely protonated in disulphuric acid. If his solutions were very dilute he may indeed have carried out conductance measurements on fully-protonated $POCl_3$.

These results are in fairly good agreement with those from $POBr_3$ in the same solvents although evidence was found for slow solvolysis of PBr_3OH^+ in 25% oleum and 100% sulphuric acid. The only really startling difference is between solutions of $POBr_3$ and $POCl_3$ in 65% oleum. PBr_3OH^+ rapidly reacts with this solvent to yield bromine and new phosphorus (V) species, and a condensation mechanism via HBr elimination has been postulated to explain these results. The only reaction between $POCl_3$ and 65% oleum appears to be protonation to yield PCl_3OH^+. A possible explanation of this difference is given below in terms of the proposed condensation via hydrogen halide elimination

$$P^+—X \quad + \quad HO - P^+ \longrightarrow P^+—O—P^+ \quad + \quad HX$$

X = Br HBr is unstable in sulphuric acids and yields Br_2 according to the equation[19]

$$2HBr + 2H_2S_2O_7 \longrightarrow Br_2 + 3H_2SO_4 + SO_2$$

X = Cl HCl is not oxidized to chlorine. The only possible reaction is the formation of $ClHSO_3$[109]

$$HCl + H_2S_2O_7 \longrightarrow ClHSO_3 + H_2S\,O_4$$

Formation of bromine probably acts as a driving force for the condensation from $POBr_3$, whereas in the $POCl_3$ case, the formation of $ClHSO_3$ leaves the chlorine still available in solution for re-reaction and condensation is not favoured.

v) Phosphorus (V) chloride.

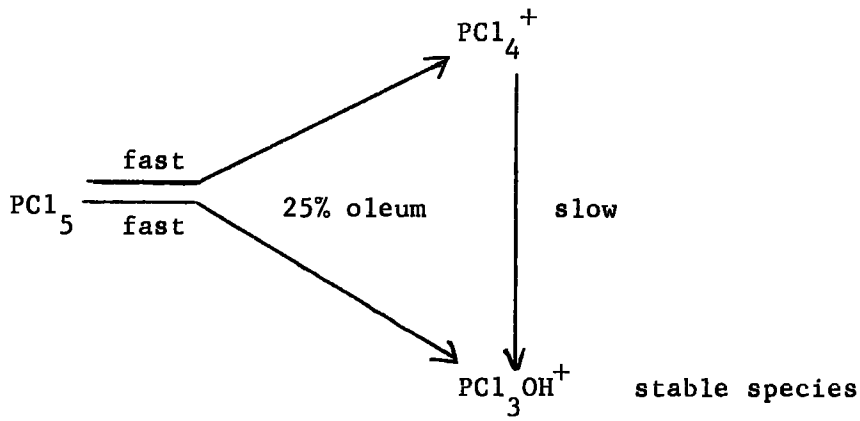
Addition of 100% sulphuric acid to PCl_5 caused a vigorous reaction and yielded a pale brown solution which darkened on standing. The ^{31}P n.m.r. solution spectrum showed only one signal at - 20 ppm which is immediately assignable to PCl_3OH^+.[18] Continued investigation of the sample over a period of 70 days showed no change in the spectrum. After 6 months a small peak had appeared at -1 ppm and the 10 month spectrum showed two peaks at -20 and -2 ppm of approximate intensity 3:1. The new peak at -2 ppm is immediately assignable to $P(OH)_4^+$ and suggests the reaction sequence

$$PCl_5 \xrightarrow[\text{Fast}]{100\%\ H_2SO_4} PCl_3OH^+ \xrightarrow[\text{Slow}]{\text{via } PCl_2(OH)_2^+ \text{ via } PCl(OH)_3^+} P(OH)_4^+$$

The lack of signals assignable to $PCl_2(OH)_2^+$ and $PCl(OH)_3^+$ is probably due to their low concentration during the reaction.

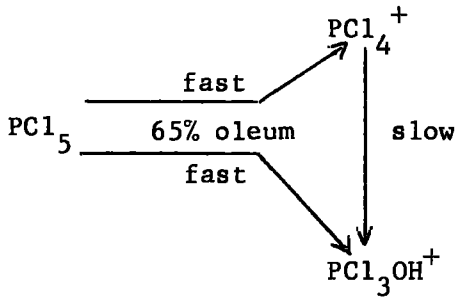
Addition of 25% oleum to PCl_5 produced a vigorous reaction, yielding a pale brown solution which turned dark brown over a period of 2 days. The initial ^{31}P n.m.r. solution spectrum showed a very strong signal at -24 ppm and a weak signal at -89 ppm. No change in the spectrum could be seen after 16 days, but after 35 days only the

signal at - 24 ppm was present. Continued investigation of the spectrum over a period of $10\frac{1}{2}$ months showed no further changes. The signal at -89 ppm is assignable to PCl_4^+ and agrees with a solution shift in liquid HCl of - 87.3 ppm.[76] The signal at - 24 ppm is probably due to PCl_3OH^+. This is 11 ppm higher than the shift found previously for $POCl_3$ in 25% oleum (Table 3). The difference is probably caused by concentration effects, and by degradation of the solvent during the reaction which reduces the extent of protonation of the phosphoryl oxygen. The reaction sequence thus appears to be



Addition of 65% oleum to PCl_5 gave a very dark brown solution after a vigorous reaction. The initial ^{31}P n.m.r. spectrum showed two signals at - 86 and - 21 ppm which are immediately assignable to PCl_4^+ and PCl_3OH^+ respectively. No change in the spectrum was found after 68 days although the intensity of the signal at - 86 ppm seemed to have decreased. After 10 months the solution spectrum showed a single peak at - 22 ppm from PCl_3OH^+. As for PCl_5 in 25% oleum, the peak assigned to PCl_3OH^+ occurs at higher field than the resonance ascribed to this ion from the spectrum of $POCl_3$ in 65% oleum (Table 3). In this case, the

difference is 34 ppm. As the signal position is very concentration-dependent, however, solutions of $POCl_3$ itself in 65% oleum showing shift differences of 13 ppm (Table 3), this assignment seems reasonable when the probable reaction course is considered. Degradation of the solvent will take place during the reaction because PCl_6^- which is present in PCl_5[81] appears to be unstable in these acidic solvents (see data on $Et_4N^+PCl_6^-$ in this section). This will alter the shift of any protonated species dissolved in it. A probable reaction sequence is



stable species

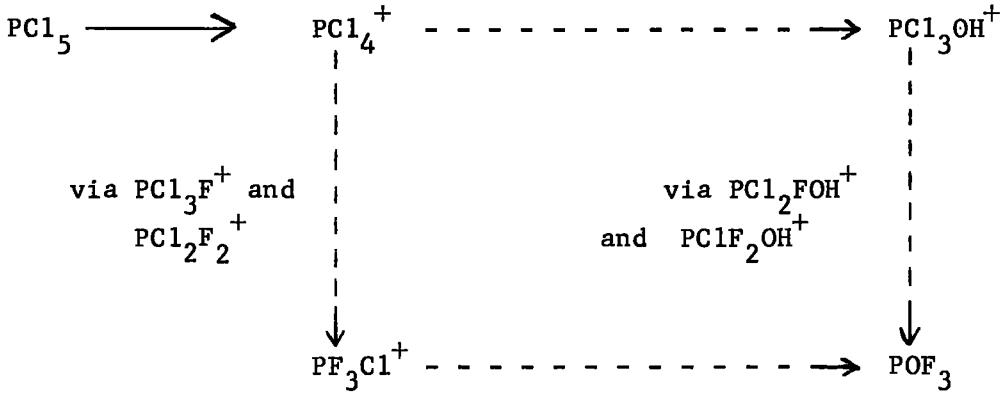
Addition of $ClHSO_3$ to PCl_5 yielded a colourless solution after a vigorous reaction. The initial ^{31}P n.m.r. spectrum showed one peak at - 87 ppm and no further peaks were apparent after 20 days. After 10 months the spectrum showed two peaks of approximately equal intensity at - 88 and - 22 ppm. The peaks are consistent with formation of PCl_4^+ followed by slow solvolysis to yield PCl_3OH^+. The most interesting point from this reaction is that PCl_5 dissolves in $ClHSO_3$ to yield exclusively PCl_4^+ initially while PCl_5 solutions in 100% H_2SO_4 and oleums showed the presence of PCl_3OH^+ after the initial reaction.

This point is discussed more fully later in this section.

The reaction sequence appears to be

$$PCl_5 \xrightarrow{\text{fast}} PCl_4^+ \xrightarrow{\text{slow}} PCl_3OH^+$$

Addition of $FHSO_3$ to PCl_5 produced a vigorous reaction to yield a pale brown solution. The initial ^{31}P n.m.r. solution spectrum showed a single peak at - 87 ppm. After two days the -_87 ppm peak was much reduced in strength and a quartet had appeared at + 38 ppm ($^1J_{PF}$ = 1070 Hz). The nine days old sample showed little change in the peak strengths. These resonances are consistent with initial production of PCl_4^+ followed by solvolysis and Cl-F exchange to yield POF_3. As in a number of other systems involving $FHSO_3$ (and $ClHSO_3$), there is thus evidence for halogen exchange. Although no intermediates were detected between PCl_4^+ and POF_3 probably because they were not formed in high enough concentration to be observed, possible reaction sequences are



These are based on the formation of POF_3 as the final product.

It is not easy to decide which reaction course is followed, but since

PBr_4^+ appeared to react via PBr_3OH^+ to POF_3 in $FHSO_3$, the route via PCl_3OH^+ is perhaps more probable. $POCl_3$ has been shown to dissolve in $FHSO_3$ with protonation but no other apparent reaction. This suggests that $FHSO_3$ does not act as a direct fluorinating agent towards PCl_3OH^+, so an alternative fluorine source must be generated in the reaction. In the analogous $PBr_5/FHSO_3$ systems it was comparatively easy to see a route by which HF could be produced, but in this case the mechanism is less obvious. Evidence from a $POBr_3$/NaCl mixture in $FHSO_3$ suggests that Cl^- can interact with the solvent to provide a source of fluorine for exchange (Chapter 3B section 2(viii)). Hence solution of PCl_5 as $PCl_4^+Cl^-$ or as $PCl_4^+PCl_6^-$ could well produce chloride ions which in their turn may generate the fluorine required for formation of POF_3. The instability of the PCl_6^- entity is discussed later in this section. A possible reaction by which the fluorine for exchange is generated is given below

$$HCl + FHSO_3 \rightleftharpoons HF + ClHSO_3$$

The equilibrium would be expected to be over to the left, but protonation of HF which is a stronger base than HCl will remove HF from the system

$$HF + HFSO_3 \rightleftharpoons H_2F^+ + FSO_3^-$$

This reaction will tend to pull the halogen-exchange equilibrium over to the right, thus increasing the amount of HF available for exchange.

Paul et al have studied the behaviour of PCl_5 in disulphuric acid[19] and fluorosulphuric acid[17]. In both solvents they report the detection of the PCl_4^+ ion only. The results of this work show that a rather more complex reaction occurs. In 100% H_2SO_4, PCl_5 yields PCl_3OH^+ exclusively which slowly solvolyses, but in 25% and 65% oleums, although PCl_3OH^+ is the main product, some evidence for PCl_4^+ formation was found. The rate of solvolysis of PCl_3OH^+ appears to be negligible in the oleum solvents. In the halosubstituted sulphuric acids, the main product of solution of PCl_5 is initially PCl_4^+ which is then solvolysed. Further reaction takes place with $FHSO_3$ to yield POF_3.

Since PCl_5 exists as $PCl_4^+PCl_6^-$ in the solid state,[81] it was decided to study the behaviour of $Et_4N^+PCl_6^-$ in a number of the solvents used, in an attempt to rationalize the apparent differences.

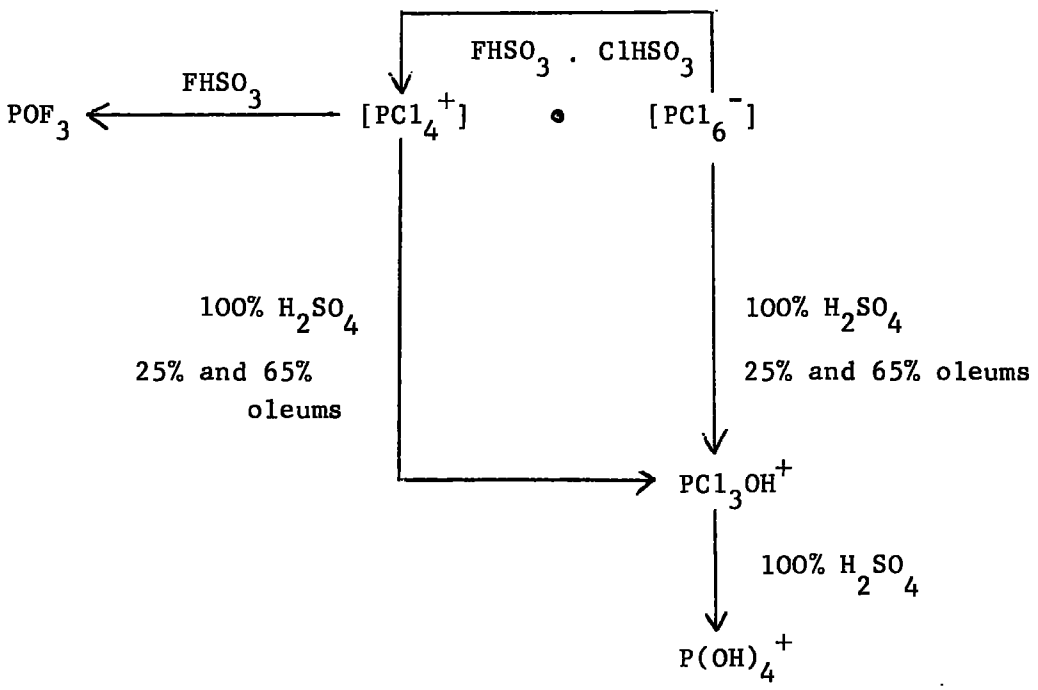
Table 5. ^{31}P n.m.r. chemical shift values (ppm) for $Et_4N^+PCl_6^-$ in acidic solvents.

Solvent	Main peak and assignment		Other peaks
100% H_2SO_4	-20	PCl_3OH^+	NONE
25% oleum	-26	PCl_3OH^+	NONE
65% oleum	-52	PCl_3OH^+	NONE
$ClHSO_3$	-90	PCl_4^+	NONE
$FHSO_3$	-88	PCl_4^+	weak quartet POF_3 + 38 ($^1J_{PF}$=1070Hz)

The data indicates that PCl_6^- is probably the main source of PCl_3OH^+ formed initially from PCl_5 in sulphuric acid and oleum. The production of this species leads to degradation of the solvent and some solvolysis of the PCl_4^+ ion, to the extent that in 100% H_2SO_4 this ion was not detected. PCl_6^- yields predominantly PCl_4^+ in the halosubstituted acids and further reaction starts from this species.

This apparent instability of 6 coordinate phosphorus (V) halospecies was also found for solution of $K^+PF_6^-$ in 25% oleum. The compound dissolved with a vigorous reaction to yield a colourless solution. The initial ^{31}P n.m.r. spectrum showed a strong quartet at + 35 ppm ($^1J_{PF}$ = 1070 Hz) and a weak triplet at +21 ppm ($^1J_{PF}$= 1000Hz). On standing for 8 days the intensities were approximately reversed. This data suggests that the PF_6^- anion dissolves in 25%oleum with decomposition to produce POF_3 (+ 35 ppm quartet)[60] but that the simultaneous degradation of the solvent reduces the acid strength, thus leading to solvolysis and production of $PF_2(OH)_2^+$ (+ 21 ppm triplet).[60]

When these results for PCl_6^- and PF_6^- are taken into account, a rather more meaningful summary of the PCl_5 solution data can be made.



vi) Phosphorus (III) chloride.

Addition of 100% H_2SO_4 to PCl_3 caused no immediate sign of reaction, two immiscible layers being produced. Even on shaking over a period of 2 hours, little solution seemed to take place. The mixture was left standing and after 8 hours a violent reaction occurred with evolution of heat to give a single-phase colourless solution.

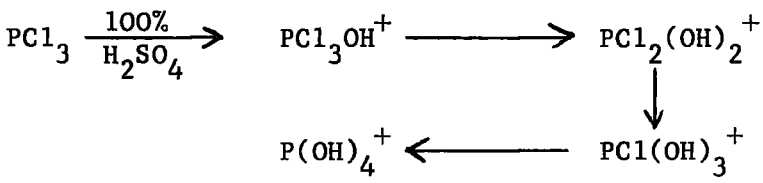
The initial spectra run on this reacted sample showed a single peak at - 19 ppm. After 2 days a new peak had appeared at - 15 ppm and two days later a further peak at -1 ppm was present. The peak intensity ratio after 4 days for the -18:-15:-1 ppm peaks was approximately 3:1:2. After 23 days only one peak at -1 ppm could be seen but a weak signal at + 15 ppm was present after 66 days, no change occurring over the next 8 months.

The peak assignment in this system is comparatively straightforward. The signal at - 19 ppm is in close agreement with the peak found for $POCl_3$ in 100% H_2SO_4 and must therefore be due to PCl_3OH^+. The peak at -1 ppm is easily assigned to $P(OH)_4^+$ [71] while the weak signal at + 15 ppm found later on in the reaction is ascribed to protonated trimetaphosphate.[71] The occurrence of two signals in this region for phosphate species would not be expected for 100% H_2SO_4 but is consistent with data found for phosphate solutions in $ClHSO_3$.[71] The resonance at + 15 ppm only appears late in the reaction and supports the formation of $ClHSO_3$ during the solvolysis

$$P^+ - Cl + H_2SO_4 \rightarrow P^+ - OH + ClHSO_3$$

All of the peaks have now been assigned except for the one at - 15 ppm found in the early stages of the reaction. Since solvolysis

of PCl_3OH^+ to $P(OH)_4^+$ takes place, it is reasonable to assign this peak to either $PCl_2(OH)_2^+$ or $PCl(OH)_3^+$. Later work (this section) indicates that the signal is due to $PCl_2(OH)_2^+$. The lack of a signal from $PCl(OH)_3^+$ is probably because its concentration remains low throughout the reaction. Hence a reasonable reaction sequence is



The solvolysis of PCl_3OH^+ in this system, whereas no reaction was observed for $POCl_3$ in 100% H_2SO_4 other than protonation, is probably due to degradation of the solvent in the initial oxidation which then promotes further reaction.

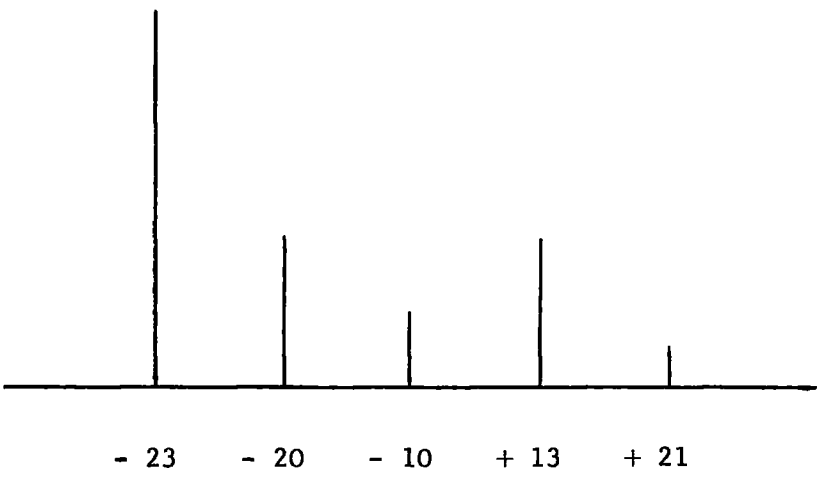
As with 100% H_2SO_4, addition of 25% oleum to PCl_3 yielded a two-phase system. The mixture was shaken and after 30 minutes a violent reaction occurred to yield a colourless solution.

The course of the subsequent reaction as followed by ^{31}P n.m.r. was very similar to the 100% H_2SO_4 system. The initial spectrum showed a single peak at - 21 ppm and two days later a new peak at - 14 ppm could be seen. After 25 days the spectrum consisted of three signals at - 20, - 14 and + 2 ppm of intensity 5:1:3. The - 14 ppm peak had disappeared after 68 days while a new one at + 15 could be seen. After 10 months the spectrum showed three signals at - 20, 0 and + 15 ppm of intensity ratio 2:5:1. The signals at - 20, - 14, 0 to + 2, and + 15 ppm are assignable to PCl_3OH^+, $PCl_2(OH)_2^+$, $P(OH)_4^+$,[71] and a further

polyphosphate equilibrium[71] peak respectively. The assignment of the - 14 ppm resonance to $PCl_2(OH)_2^+$ and not $PCl(OH)_3^+$ is supported by evidence given later in this section. It is worth noting that the shift values obtained in the 25% oleum and 100% H_2SO_4 solutions of PCl_3 are quite similar. This is due to concentration effects which affect the peak positions as well as to degradation of the solvent. The reaction scheme is presumably the same as in 100% H_2SO_4.

$$PCl_3 \xrightarrow[\text{oleum}]{25\%} PCl_3OH^+ \xrightarrow[\text{and } PCl(OH)_3^+]{\text{via } PCl_2(OH)_2^+} P(OH)_4^+$$

In contrast with the two previous reactions, addition of 65% oleum to PCl_3 caused an immediate violent reaction to yield a pale brown solution. The initial ^{31}P n.m.r. solution spectrum showed signals at - 28 and - 19 ppm. Little change was found after 64 days, but after 10 months the system gave the following complex spectra



The signals in these spectra are assignable as follows

- 28 to - 23 ppm		PCl_3OH^+
- 20 to - 19 ppm		$PCl_2(OH)_2^+$
- 10 ppm		$PCl(OH)_3^+$
+ 13 ppm	}	phosphate
+ 21 ppm	}	equilibrium[71]

The variation in shift positions is not unexpected since the position of any particular resonance will be very concentration-dependent, the species all being weak bases. Another important factor is the degradation of the solvent as reaction takes place.

The high field position of the PCl_3OH^+ peak compared with $POCl_3$ in 65% oleum (Table 3) is due to these concentration effects. The assignment of the peaks at - 20 and -10 ppm to $PCl_2(OH)_2^+$ and $PCl(OH)_3^+$ respectively are quite reasonable especially when the parent acid HPO_2Cl_2, dichlorophosphoric acid, has a reported ^{31}P n.m.r. shift of - 9.3 ppm[82]. This data seems to confirm the identity of the - 15 ppm peak in 100% H_2SO_4 and 25% oleum as $PCl_2(OH)_2^+$. An upfield movement of this order of magnitude from 65% oleum to these solvents would be expected for a partially protonated species. $PCl(OH)_3^+$ would not be expected to give a signal at - 15 ppm in 25% oleum and 100% H_2SO_4 when it appears at - 10 ppm in this 65% oleum solution.

The appearance of the - 19 ppm peak assigned to $PCl_2(OH)_2^+$ in the initial spectrum is a little surprising at first glance since no peak from this species was found initially in 100% H_2SO_4 or 25% oleum. A probable explanation is that the initial reaction occurred so quickly that a local reduction of the acid strength gave rise to some solvolysis

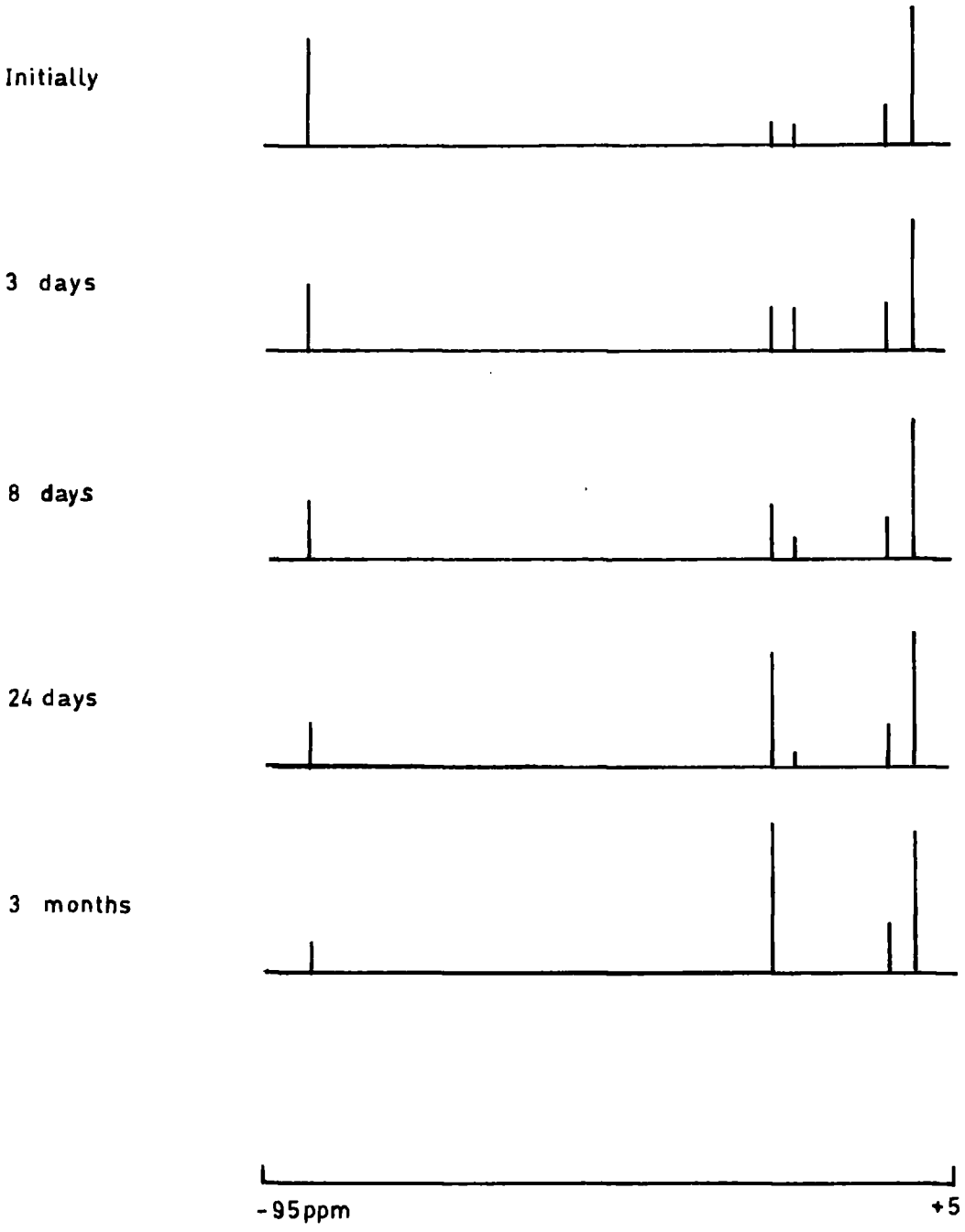


Figure 5

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) chloride in chlorosulphuric acid.

of the PCl_3OH^+ formed. When the solution was properly mixed, solvolysis was retarded by the high acid strength, hence leading to a time lag before peaks from species further in the reaction sequence appeared. The spectral data obtained is consistent with the following reaction scheme,

$$PCl_3 \xrightarrow[\text{oleum}]{65\%} PCl_3OH^+ \longrightarrow PCl_2(OH)_2^+ \longrightarrow PCl(OH)_3^+ \longrightarrow P(OH)_4^+$$

Initially PCl_3 appeared immiscible with $ClHSO_3$, but on shaking it dissolved to give a colourless solution. After approximately 10 minutes the solution began to bubble and a vigorous reaction occurred to give a pale green solution after 30 minutes. The ^{31}P n.m.r. spectrum of this solution showed quite a complex pattern (Figure 5).

Although the exact peak positions are variable with time because of changes in acid strength, comparison of this spectrum with the one obtained from 65% oleum suggests that the high-field peaks are due to PCl_3OH^+ and more extensively solvolysed species. The low field resonance is probably from PCl_4^+ and is in good agreement with data obtained from PCl_5 in $ClHSO_3$. The peak assignments appear to be

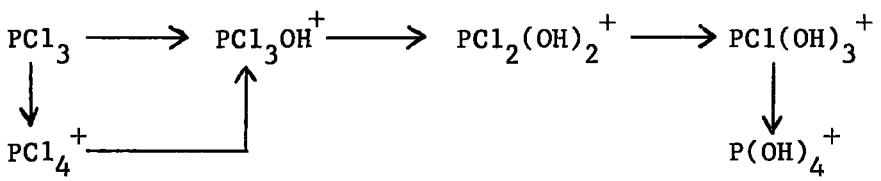
- 88 ppm	PCl_4^+
- 20 to - 18 ppm	PCl_3OH^+
- 18 to - 15 ppm	$PCl_2(OH)_2^+$
- 2 to - 4 ppm	$PCl(OH)_3^+$
0 to + 2 ppm	$P(OH)_4^+$ [71]

The data for this system supports the assignment of the signal at - 15 ppm in the 100% H_2SO_4 and 25% oleum solutions, since $PCl(OH)_3^+$ appears at approximately - 3 ppm while $PCl_2(OH)_2^+$ lies at about - 16 ppm. The presence of the PCl_4^+ signal at - 88 ppm is interesting in that it shows $ClHSO_3$ acting as an oxidizing agent in two ways. This result agrees with the $PBr_3/ClHSO_3$ system where some PBr_3Cl^+ was formed.

$$PCl_4^+HSO_3^- \xleftarrow[ClHSO_3]{} PCl_3 \xrightarrow[ClHSO_3]{} PCl_3OH^+ClSO_2^-$$

anion unstable, yields SO_2 and Cl^-.

The complex nature of the initial spectrum indicates quite a complicated reaction path. Visual observation suggested that early miscibility of PCl_3 and $ClHSO_3$ was followed by reaction. The spectroscopic evidence confirms that PCl_3 must dissolve in $ClHSO_3$ before reaction commences, but that once reaction has started, the heat generated accelerates the process and makes it less selective. It seems probable that local attack gives the oxidized product but that the solvent is degraded to such an extent that solvolysis can also occur. After this initial non-selective reaction, mixing of the medium gives a homogeneous solution in which solvolysis is slow. A reasonable reaction scheme is therefore



Addition of $FHSO_3$ to PCl_3 gave a two-phase liquid system. No apparent reaction occurred on shaking. After standing for one hour a violent reaction took place with the liberation of heat to give a pale brown solution.

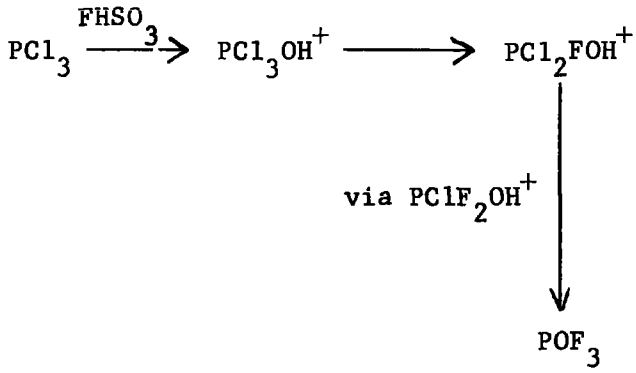
The initial ^{31}P n.m.r. solution spectrum showed a strong signal at - 29 ppm and a weak doublet at - 12 ppm ($^1J_{PF}$= 1200 Hz). After 30 minutes the spectrum was little changed but a weak quartet had appeared at + 37 ppm ($^1J_{PF}$ = 1070 Hz). Over the next 3 hours no new signals were found, but the doublet and quartet grew in intensity. Over a period of 14 days, the same signals were present in solution but the intensity of the doublet decreased while that of the quartet increased relative to the - 29 ppm peak.

Assignment of the peaks is relatively facile. The signal at - 29 ppm is almost certainly due to PCl_3OH^+ and the appearence of the quartet at + 37 ppm is consistent with POF_3.[60] The earlier evidence that PCl_3OH^+ was stable in $FHSO_3$ solutions over a period of 4 months suggests, as in previous instances, that an alternative source of fluorine must be present to account for the formation of POF_3. A reasonable reaction sequence is

$$PCl_3 + FHSO_3 \longrightarrow PCl_3OH^+ + FSO_2^-$$
$$FSO_2^- + FHSO_3 \longrightarrow HF + SO_2 + FSO_3^-$$
$$PCl_3OH^+ + 3HF \longrightarrow POF_3 + 3HCl + H^+$$

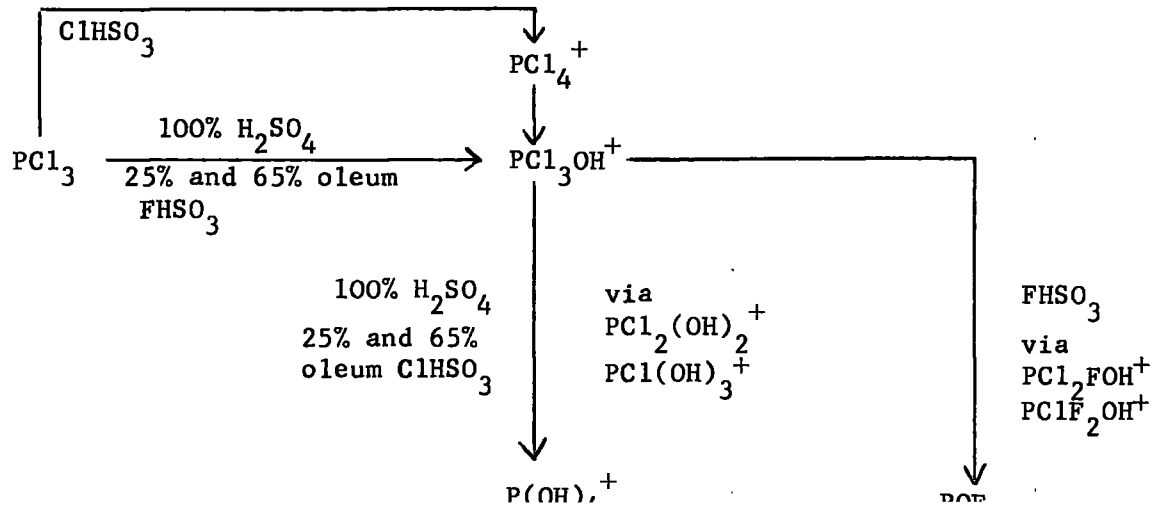
The appearence of a doublet at - 12 ppm is interesting and is consistent with the species PCl_2FOH^+ which is a probable intermediate in the formation of POF_3. The $^1J_{PF}$ value of 1200 Hz is compatible with formation of a phosphorus (V) cation containing a P-F bond, and may be

compared with the $^1J_{PF}$ value of 1296 Hz reported for PCl_3F^+.[83] The magnitude of the $^1J_{PF}$ coupling constants decreases substantially from PF_3 ($^1J_{PF}$= 1441 Hz) via PF_5 ($^1J_{PF}$= 916 Hz) to PF_6^-($^1J_{PF}$= 710 Hz), and corresponds to a decrease of the s orbital character in the hybridization.[84] The value of 1200 Hz for the observed coupling constant supports tetrahedral (sp^3) hybridization for the phosphorus, as expected in PCl_2FOH^+. The presence of this doublet in the spectrum along with the POF_3 quartet suggests a reaction scheme of the form



The lack of a signal due to $PClF_2OH^+$ is probably because it is never present in high enough concentrations for the expected triplet to be observed.

The results obtained for PCl_3 in the various acids may be summarized as follows



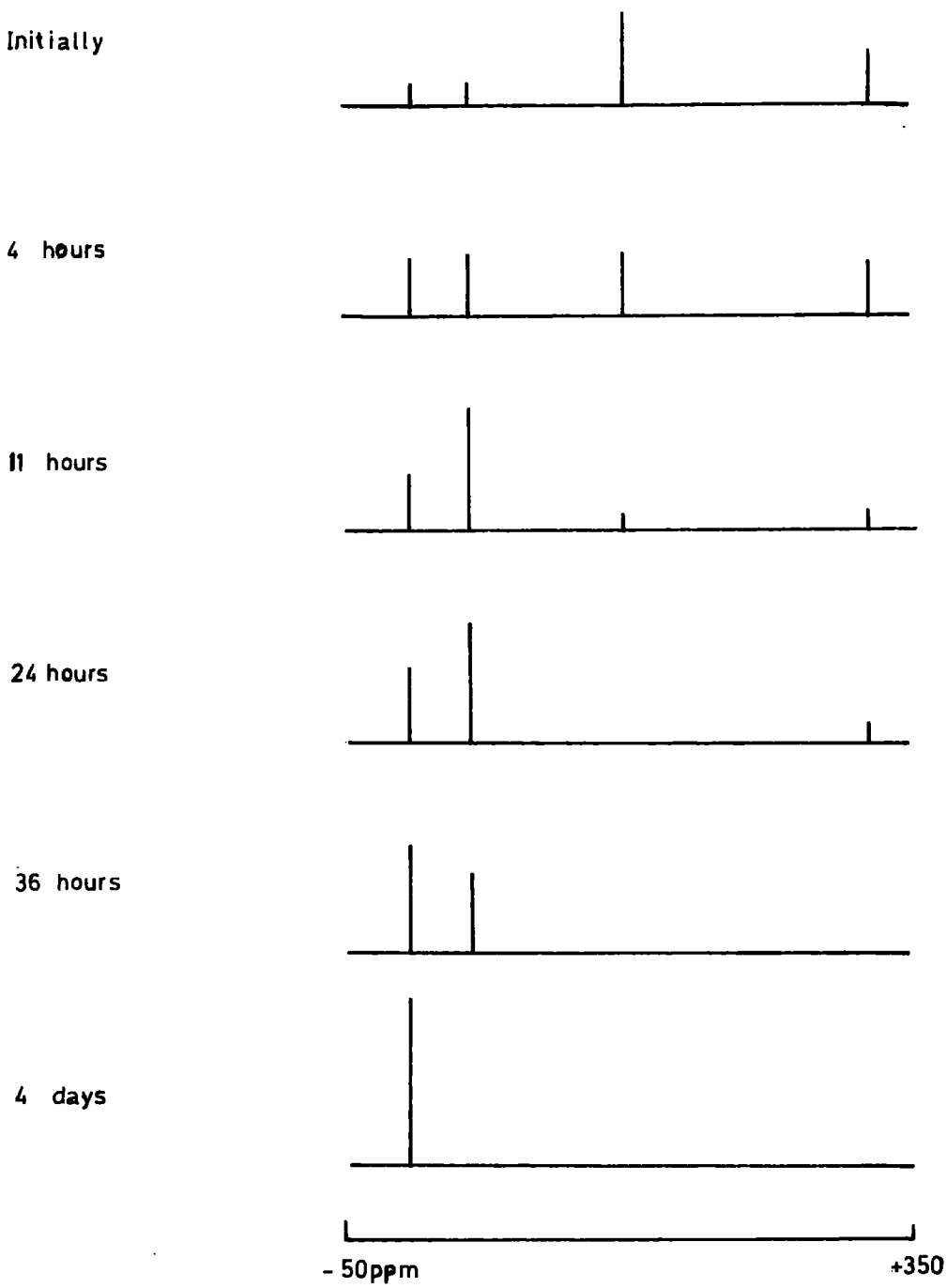


Figure 6

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide in 100% sulphuric acid.

The data obtained is in general agreement with the work of Paul et al in disulphuric acid[19] insofar as the initial reaction is concerned. The longer-term aspects of the present work show that further reaction can occur in the degraded solvent but that solvolysis is usually slow. No evidence was found to support Paul's suggestions[17] that solution of PCl_3 in fluorosulphuric acid might proceed via solvolysis of PCl_3 to yield $P(SO_3F)_3$. The results indicate that oxidation of PCl_3 to PCl_3OH^+ is followed by further reaction.

vii) Phosphorus (III) iodide.

On shaking a mixture of PI_3 and 100% H_2SO_4, slow dissolution of the solid seemed to occur and the sulphuric acid darkened. Over a period of one day the solid and solution both darkened and it soon became apparent that iodine was being produced in the form of long thin lustrous needles. As the reaction proceeded the solution was monitored by ^{31}P n.m.r.

The initial spectra run on the reacting sample showed 4 signals at -4, + 41, + 149, and + 325 ppm. The reaction proceeded as shown diagramatically in Figure 6, yielding finally a single peak at - 4 ppm.

The peak assignment in this system is straightforward if the mode of reaction of PCl_3 and PBr_3 in 100% H_2SO_4 is considered, as discussed previously. In both these systems initial oxidation of the phosphorus (III) halide to the corresponding protonated phosphoryl compound took place, followed by solvolysis to give $P(OH)_4^+$, as shown

$$PX_3 \xrightarrow[H_2SO_4]{100\%} PX_3OH^+ \longrightarrow PX_2(OH)_2^+ \longrightarrow PX(OH)_3^+ \longrightarrow P(OH)_4^+$$

It is reasonable to assume that PI_3 will follow a similar course, and taking into account the relative signal intensities and positions, the following peak assignment is suggested

- 4 ppm	$P(OH)_4^+$
+ 41 ppm	$PI(OH)_3^+$
+149 ppm	$PI_2(OH)_2^+$
+325 ppm	PI_3OH^+

The assignment of the - 4 ppm peak to $P(OH)_4^+$ is consistent with the data of Dillon and Waddington.[71] The appearance of solid iodine during the reaction and formation of $P(OH)_4^+$ as the final product may be explained by the following equations

$$P^+ \text{---} I + 2H_2SO_4 \longrightarrow \overset{+}{P}\text{-}OH + HI + H_2S_2O_7$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

These reactions are analogous to the reactions in the corresponding bromine system, and lead to a probable sequence

$$PI_3 \xrightarrow[H_2SO_4]{100\%} PI_3OH^+ \longrightarrow PI_2(OH)_2^+ \downarrow PI(OH)_3^+ \longrightarrow P(OH)_4^+$$

The shift of + 325 ppm for PI_3OH^+ is higher than expected from the reported value for POI_3 in ethyl iodide of + 273.4 ppm,[9] since protonation of the phosphoryl group should cause a downfield movement.

The comparable order of magnitude of the shifts however, tends to support the proposed reaction scheme. The high shift value obtained for the proposed PI_3OH^+ ion indicates that iodine must be present, since the presence of six-coordinate species may be discounted in view of the instability of PCl_6^- and PF_6^- in strongly acidic media. The possible formation of PI_4^+ cannot be immediately ruled out, but this seems unlikely since the shift of the species formed varies with acid strength, suggesting that hydroxy-groups are present in the species. This assignment is further supported by the results in $ClHSO_3$ and $FHSO_3$ (see later in this section).

Solution of PI_3 in both 25% and 65% oleum gave rise to very violent exothermic reactions with the immediate production of iodine. The dark brown 25% oleum solution showed a simple ^{31}P n.m.r. spectrum of a strong peak at + 5 ppm and a weak peak at + 15 ppm. No change in the spectrum was observed with time. The dark blue 65% oleum solution showed initially two strong signals at + 20 and + 28 ppm and a weak signal at + 40 ppm. Over a period of 11 days the + 20 ppm signal grew in intensity with respect to the other signals, and after 40 days the spectrum consisted of a strong peak at + 23 ppm and a weak peak at + 31 ppm.

A reasonable peak assignment is therefore

25% oleum	65% oleum	
+ 5 ppm	+ 20 to + 23	$P(OH)_4^+$ equilibrium
+15 ppm	+ 28 to + 31	trimetaphosphate equilibrium
———	+ 40	?

The assignment for the 25% oleum solution is straightforward, but the 65% oleum case is less so. The final spectrum of a strong peak at + 23 ppm and a weak signal at + 31 ppm corresponds well with the various phosphate equilibria.[71] The extra signal at + 40 ppm could arise from condensation of iodine containing species via hydrogen iodide elimination to give condensed phases still containing P-I bonds. Slow solvolysis of the P-I bonds would lead to ring or chain phosphates which would then react in 65% oleum to give the two final peaks.[71] The movement of the two signals ascribed to the phosphate equilibrium from + 20 to + 23 ppm, and + 28 to 31 ppm respectively is in agreement with the reaction scheme proposed since slow solvolysis of P-I bonds would lead to a change of the acid strength of the medium. This explanation is analogous to the HBr elimination - condensation proposed in the $POBr_3$/65% oleum reaction system.

The main point of interest which arises from these solutions is the apparent stability of the phosphorus (V) - iodine species in 100% H_2SO_4 when compared with 25% and 65% oleums. Since 100% H_2SO_4 is a much weaker acid than the two oleums, more rapid solvolysis of the P-I bonds might be expected in this medium. The higher oxidizing power of the oleums is probably the key to this apparent anomaly. Rapid initial oxidation coupled with degradation of the solvent on addition of the oleums to PI_3 leads to a localized more weakly acid region which causes extensive solvolysis of the P-I bonds before stabilization can occur in the bulk medium. In 65% oleum hydrogen iodide elimination reactions may also be favoured and again complicate

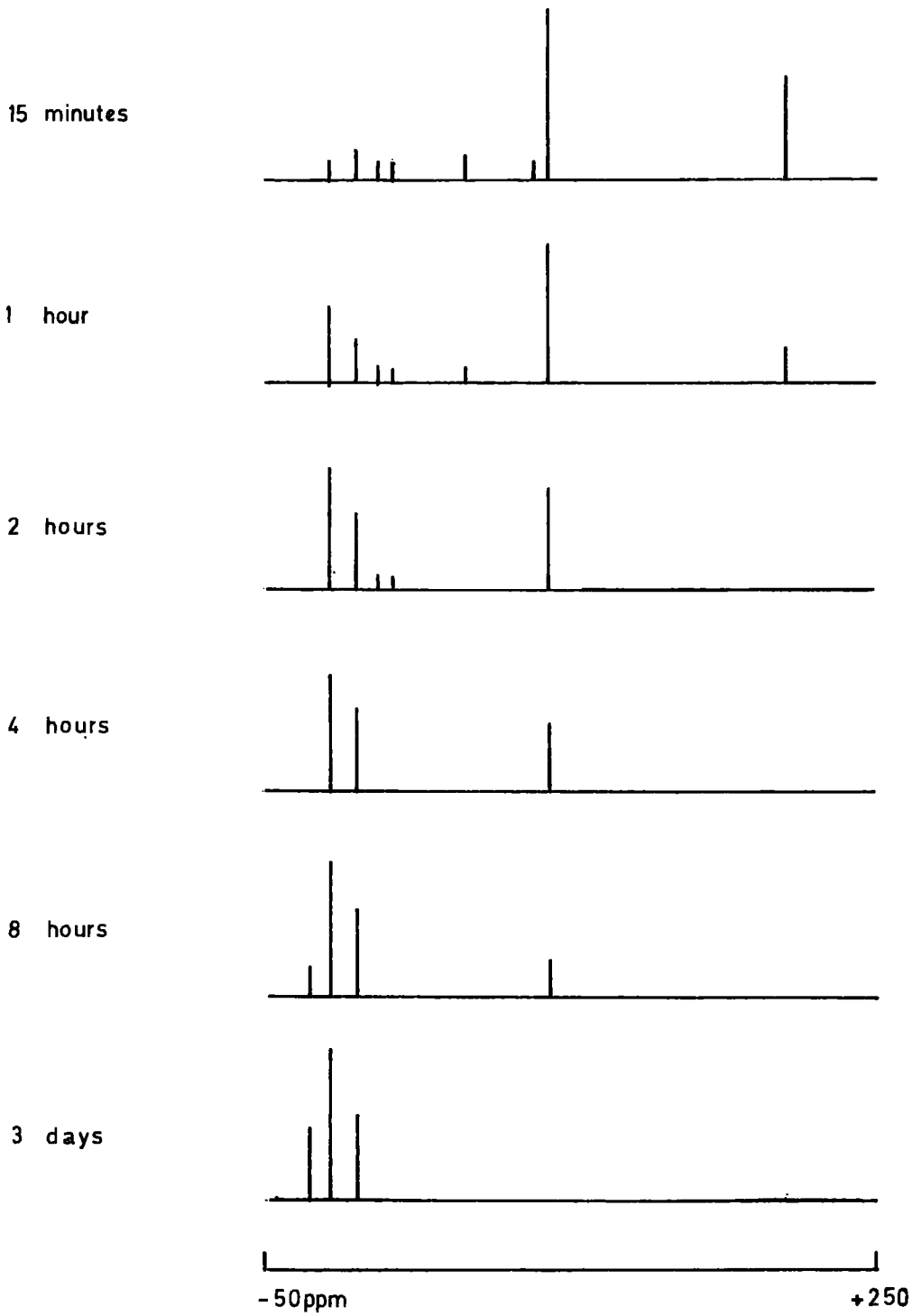


Figure 7

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide in chlorosulphuric acid.

the system. When PI_3 reacts with 100% H_2SO_4, solution and reaction are comparatively slow, so that diffusion of the low-concentration species formed through the bulk of the solvent allows stabilization to take place.

Addition of $ClHSO_3$ to solid PI_3 caused a vigorous reaction to give a dark brown solution and a black oily material. Reaction between the black oil and the solvent then occurred to yield after approximately 10 minutes a dark brown solution. Fifteen minutes after the solution was made up, a large amount of iodine precipitated out and precipitation continued for 2 days. On further standing, however, the iodine re-dissolved to give a clear dark brown solution. During the period of the reaction the solution was monitored by ^{31}P n.m.r. The results are summarized diagramatically in Figure 7, and a spectrum is shown in Figure 8.

The complexity of the spectra suggests that more than a simple oxidation-solvolysis sequence takes place. A possible reaction scheme can be proposed, based on the following assumptions:

a) In $ClHSO_3$ phosphorus (III) halides are oxidized to phosphorus (V) by formation predominantly of a phosphoryl group, but oxidation can also occur by formation of a P-Cl bond. Evidence supporting this has been found for solution of PCl_3 (Chapter 3B section 2(vi)) and PBr_3 (Chapter 3B section 2(iii)) in $ClHSO_3$.

b) Exchange of halogens can occur in phosphorus (III) halide/$ClHSO_3$ systems resulting in the formation of a P-Cl bond. The results for solutions of PBr_3 in $ClHSO_3$ (Chapter 3B section 2(iii)) support this hypothesis.

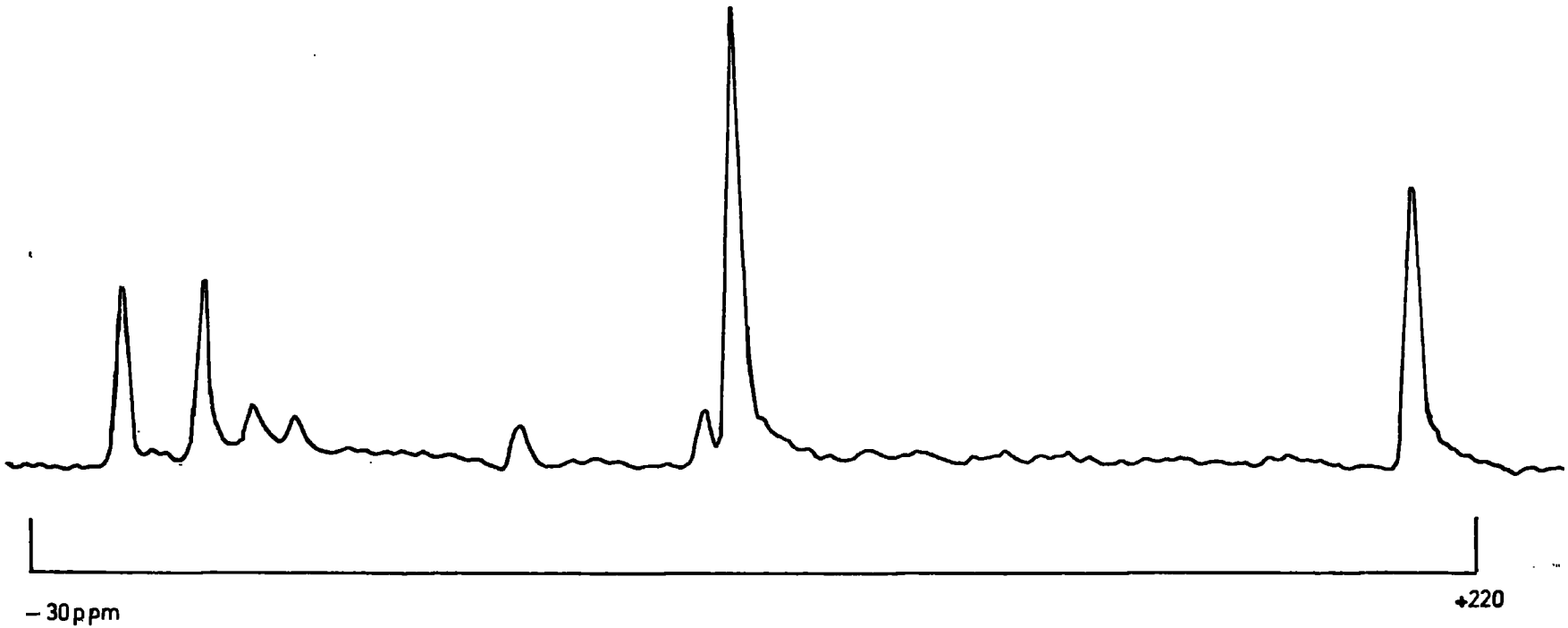
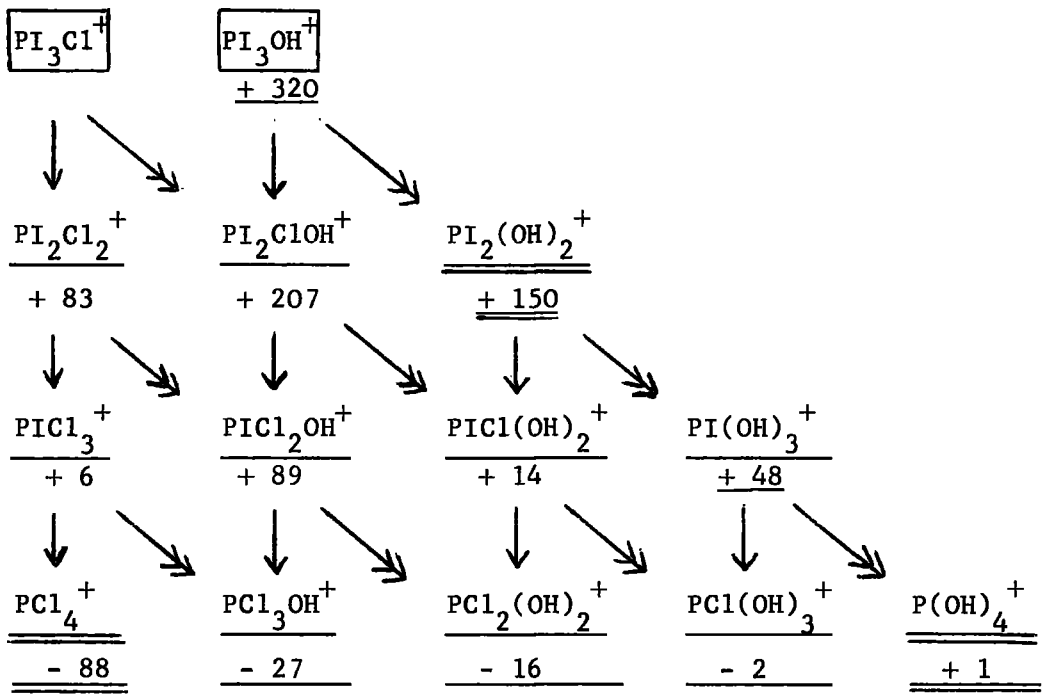


Figure 8

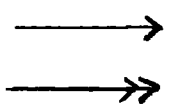
The ^{31}P n.m.r. spectrum of phosphorus (III) iodide in chlorosulphuric acid, 15 minutes after preparation of the sample.

The suggested reaction scheme is shown below:



P	species postulated as being formed in course of reaction, but not observed during study of system
P	species postulated as being formed during course of reaction in measurable quantities
P	possible species but lack of evidence for formation together with known stability in $ClHSO_3$ suggests that they will not be present in appreciable concentrations.

Numbers refer to shift values (ppm) and when underlined result is in agreement with independent data.



Cl for I

OH for I

The data for the PCl_4^+----$P(OH)_4^+$ series is consistent with results obtained from solutions of PCl_5, $POCl_3$ and PCl_3 in $ClHSO_3$, after allowing for concentration effects on the exact peak positions for the protonated species. Similarly, the data for the PI_3OH^+----$PI(OH)_3^+$ series compares well with results obtained for solution of PI_3 in 100% H_2SO_4, allowing for concentration effects.

The reaction scheme covers all the possible species formed in a $PI_3/ClHSO_3$ system based on the assumptions given previously. The peak assignments are supported by independent data in all instances except for

$PI_2Cl_2^+$	+ 83 ppm
PI_2ClOH^+	+207 ppm
$PICl_2OH^+$	+ 89 ppm
$PICl(OH)_2^+$	+ 14 ppm
$PICl_3^+$	+ 6 ppm

The assignment of these peaks is based on their relative intensities and chemical shifts with respect to the other species formed, taking into account the course of reaction suggested by the appearance of known peaks. The assignment of the + 207 and + 89 signals to OH-containing species is supported by results from a second tube which gave similar peaks at + 196 and + 87 ppm respectively, showing that the shifts of these two species are concentration-dependent and that they cannot be due to tetrahalophosphonium ions.

The evidence obtained is consistent with initial oxidation of PI_3 to PI_3OH^+, followed by rapid cleavage of the P-I bonds. Two courses of

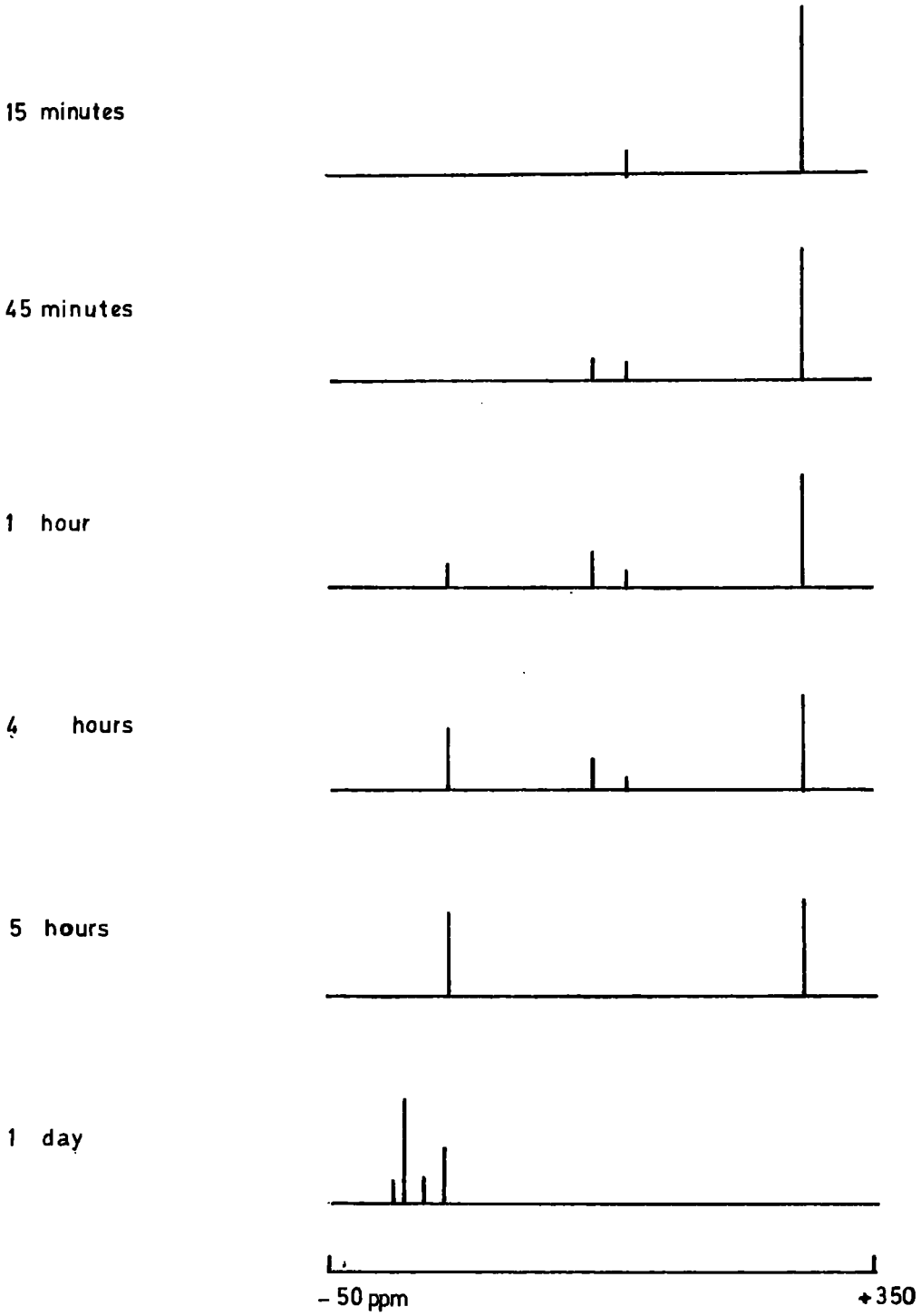


Figure 9

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide in fluorosulphuric acid.

reaction are possible in which P-I bonds are replaced by either P-OH or P-Cl. The final products of the reaction suggest that formation of the P-Cl or P-OH bonds gives a stable system in which further reaction is slow. This agrees with the data obtained for solution of phosphorus (III) and phosphorus (V) halides in $ClHSO_3$.

Solid PI_3 dissolved in $FHSO_3$ with effervesence and yielded a dark brown solution. After about 30 minutes iodine crystals started to precipitate and this continued for one day. The course of the reaction as followed by ^{31}P n.m.r. spectroscopy is represented diagramatically in Figure 9.

The results from solutions of PBr_3 (Chapter 3B section 2(iii)) and PCl_3 (Chapter 3B section 2(vi)) in $FHSO_3$ show that the phosphorus (III) halide is oxidized to the corresponding phosphoryl halide which then undergoes fluorine exchange to yield POF_3. The course of these reactions involves degradation of the solvent followed by solvolysis of POF_3 to $P(OH)_4^+$.

When these points are taken into consideration, it is quite facile to assign the peaks in this system (Table 6).

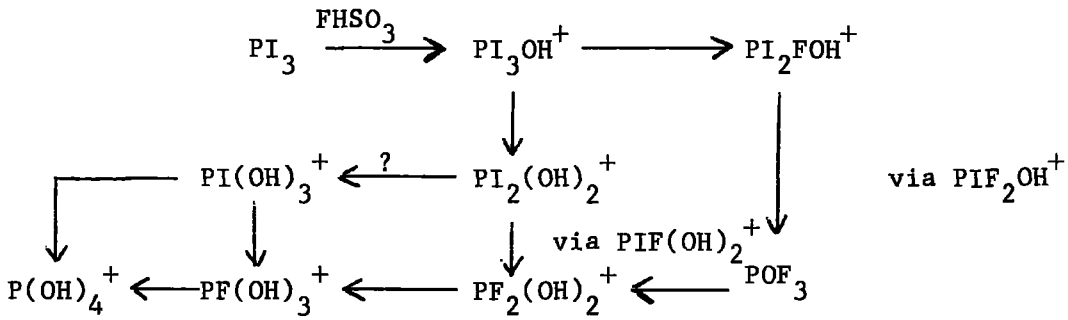
The signals ascribed to POF_3 and the related solvolysed species are in good agreement with literature reports,[60,72] and add some weight to the assignments of the three other signals. The peak at + 308 ppm is assigned to PI_3OH^+ and compares with a shift of + 325 ppm found in 100% H_2SO_4. The downfield shift of 17 ppm is consistent with more extensive protonation in the stronger acid $FHSO_3$. The peak at + 144 ppm agrees with a shift of + 149 for $PI_2(OH)_2^+$ in 100% H_2SO_4, the downfield shift again indicating increased protonation.

Table 6. ^{31}P n.m.r. chemical shift values (ppm) for species derived from phosphorus (III) iodide in fluorosulphuric acid.

Chemical Shift		J	Assignment
-1			$P(OH)_4^+$ 72
+7	Doublet	$^1J_{PF}$= 1000Hz	$PF(OH)_3^+$ 60
+ 22	Triplet	$^1J_{PF}$= 1010Hz	$PF_2(OH)_2^+$ 60
+ 37	Quartet	$^1J_{PF}$= 1070Hz	POF_3 60
+144			$PI_2(OH)_2^+$
+167	Doublet	$^1J_{PF}$= 1290Hz	PI_2FOH^+
+308			PI_3OH^+

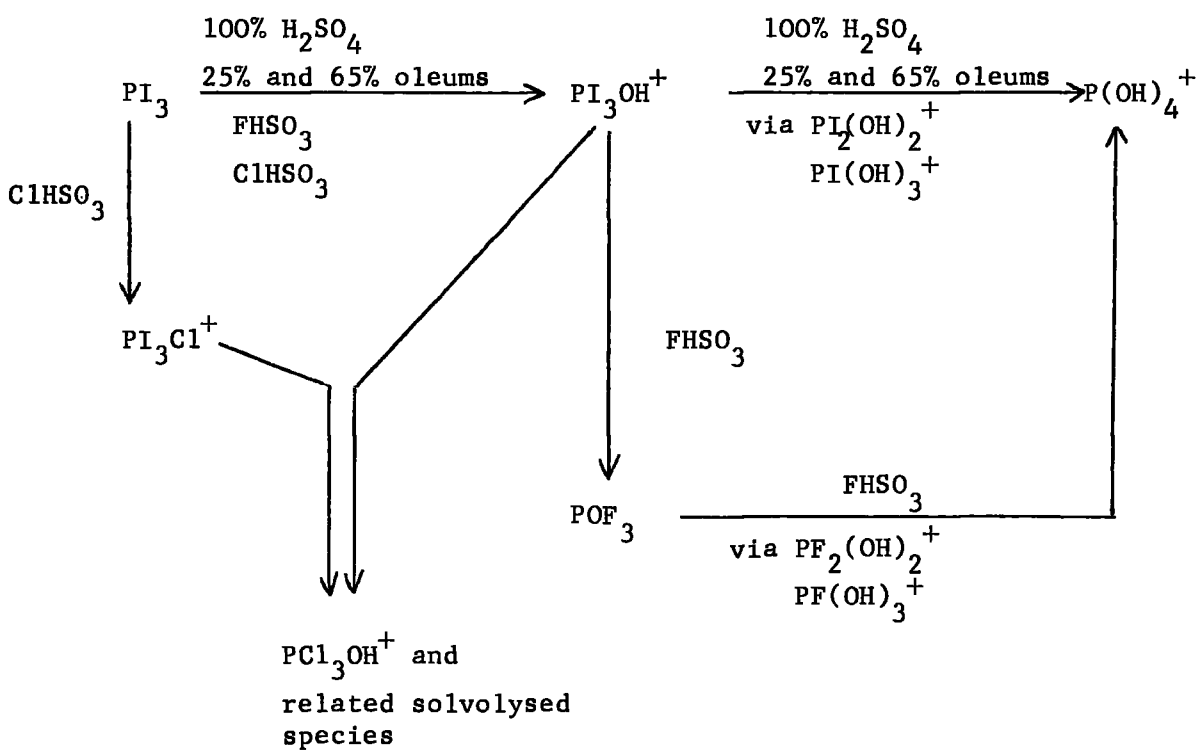
The appearance of a doublet at + 167 ppm ($^1J_{PF}$= 1290 Hz) is compatible with the species PI_2FOH^+ which is a probable intermediate in the formation of POF_3. The $^1J_{PF}$ value of 1290 Hz seems reasonable for formation of a phosphorus (V) cation and may be compared with the $^1J_{PF}$ value of 1296 Hz reported for PCl_3F^+.[83] A similar doublet found in the $PCl_3/FHSO_3$ system at - 12 ppm ($^1J_{PF}$= 1200 Hz) was assigned to PCl_2FOH^+ (Chapter 3B section 2(vi)). The presence of this doublet in the spectrum along with the quartet due to POF_3 suggests a reaction

scheme of the form



The lack of signals assignable to PIF_2OH^+, $PIF(OH)_2^+$ or $PI(OH)_3^+$ is probably because they are never present in high enough concentrations to be observed. In the case of the missing fluorine-containing species, the expected multiplet structures of the signals will not help in their observation if they are of low intensity.

The result for PI_3 in the various acids may be summarized as follows:



viii) Mixed halide systems.

a) Halide mixtures.

In previous sections of this chapter some evidence for halogen exchange in halosulphuric acid solutions of PX_3 and PX_5 species was obtained. The basic source of exchanging halogen is of course the solvent, but the data does not eliminate the possibility of further exchange between the phosphorus species present in solution after the initial reaction with the solvent. Since phosphorus (III) halides are oxidized predominantly to phosphoryl species in these acids, it was decided to investigate the behaviour of some phosphorus (V) halide mixtures in a number of the solvents to try to clarify this point. The solutions were monitored by ^{31}P n.m.r., and the results are summarized in Table 7.

Table 7. ^{31}P n.m.r. chemical shift values (ppm) for phosphorus halide mixtures in acidic solvents.

System \ Peaks found	PCl_4^+	PCl_3OH^+	PBr_3OH^+	PBr_4^+	Comments
$POBr_3 + POCl_3$ in 25% oleum		-25	+65		No change after 42 days, but new weak signals at +4 and +15 ppm after 10 months, suggest slow solvolysis to $P(OH)_4^+$ 71
$PBr_5 + PCl_5$ in 25% oleum	-88	-27		+85	No change after 7 days but new weak signal at +60 ppm after 42 days, assignable to PBr_3OH^+ and increased intensity of - 27 ppm signal indicate slow solvolysis
$PBr_5 + PCl_5$ in 65% oleum	-88	-23	+75	+85	No change after 50 days but increased intensity of -23 and +75 ppm peaks after 10 months suggests slow solvolysis.

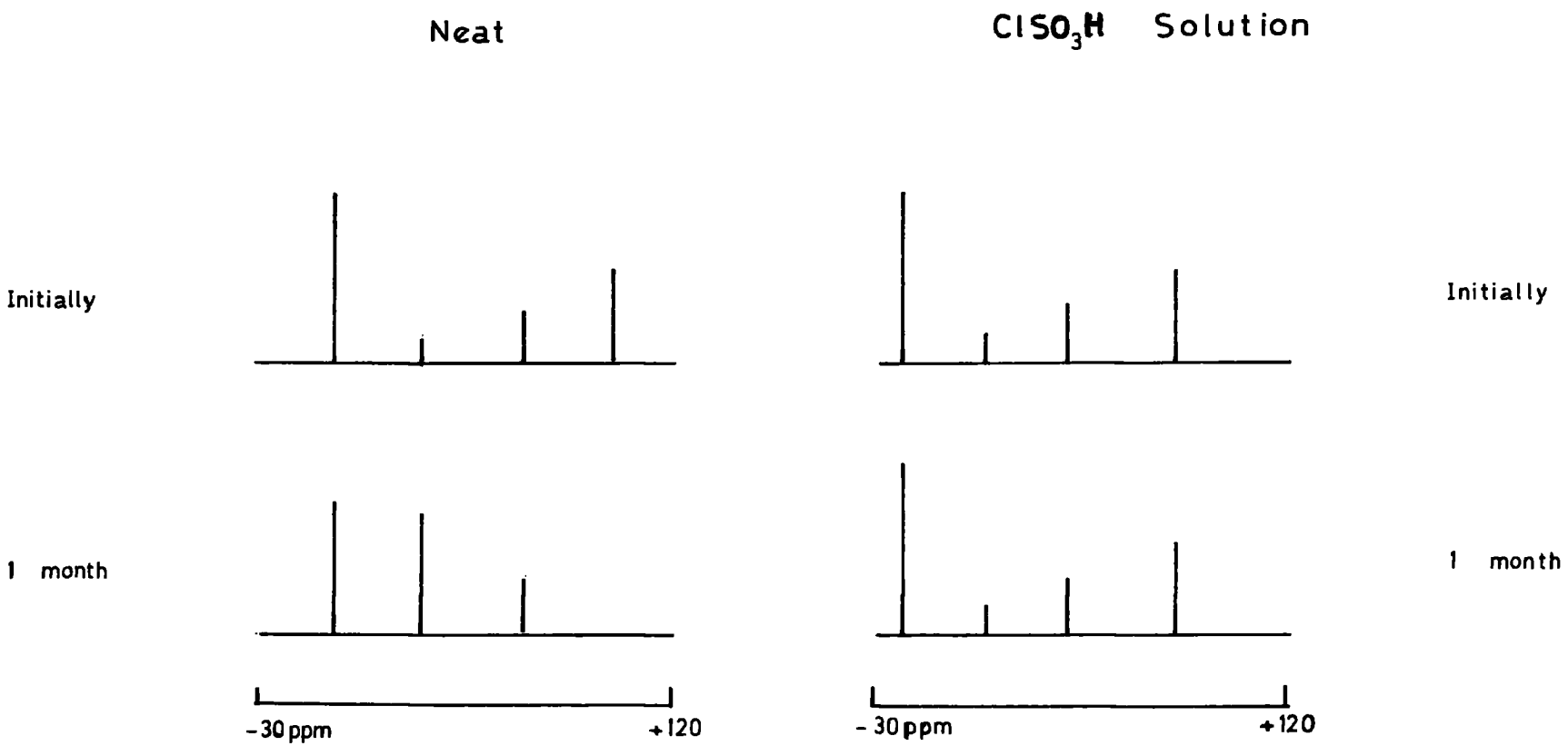


Figure 10

Relative peak heights for the ^{31}P n.m.r. spectrum of a mixture of phosphoryl chloride and bromide with $Eu(fod)_3$.

The results are in close agreement with data obtained from the parent species separately. The differences in peak positions of the protonated phosphoryl species are not unexpected since solution of the halides is accompanied by solvent degradation as discussed previously. The apparent discrepancy between the results for the PCl_5-PBr_5 mixture and the components separately in 65% oleum is understandable in this light. Previous work (Chapter 3B section 2(ii)) has suggested that PBr_4^+ is stable in 65% oleum, but here it is slowly solvolysed. Ample evidence for degradation of the solvent is present in that the PCl_3OH^+ resonance occurs 30 ppm downfield from that reported for $POCl_3$ in 65% oleum (Table 4) and slow solvolysis of PBr_4^+ to PBr_3OH^+ in the medium may thus be expected. This data suggests that no halogen exchange occurs between phosphorus (V) halogen species in sulphuric acid solutions.

$POBr_3$ dissolves in $POCl_3$ quite readily and ^{31}P n.m.r. studies indicate that no halogen exchange occurs at 307.2 K,[99] but at higher temperatures (573 K) exchange takes place quite rapidly.[74] At room temperature addition of the shift reagent $Eu(fod)_3$ to the solution in catalytic amounts promotes halogen exchange, however, and the species $POCl_2Br$ and $POClBr_2$ are formed.[99] A solution of $POBr_3$ was made up in $POCl_3$ and a small amount of $Eu(fod)_3$ was added. After standing for one day, a portion of the neat liquid was placed in an n.m.r. tube while a similar portion was dissolved in $ClHSO_3$. The results are given diagramatically in Figure 10. The high intensity of the $POCl_3$ and PCl_3OH^+ peaks in the respective systems is due to the use of $POCl_3$ as solvent. The peaks in these solutions are thus readily assigned (Table 8).

Table 8. ^{31}P n.m.r. chemical shift values (ppm) for mixed phosphoryl bromo-chlorides

Species	$POCl_3$	$POCl_2Br$	$POClBr_2$	$POBr_3$
parent [74]	-2.2	+29.6	+64.8	+103.4
parent in $POCl_3$	-2	+30	+66	+103
protonated species in $ClHSO_3$	-22	+10	+41	+79

The values for the parent species are in agreement with literature reports[74] and the shifts assigned to the protonated species are consistent with the expected downfield movement on protonation. One interesting point is that while the slow exchange continues in the parent sample to give species with predominantly P-Cl bonds, no further exchange occurs after solution in $ClHSO_3$. It is quite probable that the $Eu(fod)_3$ reagent is destroyed in such a highly acidic medium and this presumably stops further exchange. This reaction adds further support to the conclusion that phsophorus (V) halide species do not exchange in sulphuric acid solutions.

Although halogen exchange appears to be possible between PX_3 or PX_5 species and $FHSO_3$ or $ClHSO_3$, the results from these POX_3 solutions show no evidence for exchange. This difference has been interpreted in terms of the halosubstituted acid acting as an indirect source of exchanging halogen via side reactions which produce halide ions. In an attempt to verify this hypothesis, solutions of $POBr_3$ in $FHSO_3$ and $ClHSO_3$ were

reacted with NaCl and KF respectively. Since $POBr_3$ is stable in $ClHSO_3$ and $FHSO_3$ (Chapter 3B section 2(i)), any difference in the reaction products can be directly attributed to the presence of the added halide ion. The alkali halide dissolved with effervescence, after which the sample was monitored by ^{31}P n.m.r. A summary of the results follows:

A. $POBr_3$ + NaCl in $ClHSO_3$:

Strong signal at + 83 ppm [PBr_3OH^+] together with weak signals at -2 [$P(OH)_4^+$],[71] + 15 [PCl_2BrOH^+] and + 36 ppm [$PClBr_2OH^+$]. Little change after 14 days although the signal at + 36 ppm had disappeared and had been replaced by a signal at - 15 ppm [PCl_3OH^+].

B. $POBr_3$ + KF in $ClHSO_3$:

Strong signal at + 83 ppm [PBr_3OH^+] plus weak signals at -2 [$P(OH)_4^+$][71] and + 8 ppm ($^1J_{PF}$ = 990 Hz, doublet)[$PF(OH)_3^+$].[60] After 14 days little change in the intensities of the original signals was found but new signals at + 23 ($^1J_{PF}$= 1000Hz, triplet)[$PF_2(OH)_2^+$] and + 36 ppm ($^1J_{PF}$ = 1060 Hz, quartet)[POF_3] were present.

C. $POBr_3$ + NaCl in $FHSO_3$:

Strong signal at + 83 ppm [PBr_3OH^+] plus a strong signal at - 2 ppm [$P(OH)_4^+$],[72] and a weak signal at + 8 ppm ($^1J_{PF}$ = 990 Hz doublet) [$PF(OH)_3^+$].[60] Little change was found after 14 days although a new signal at + 36 ppm [$PClBr_2OH^+$] could be seen.

D. $POBr_3$ + KF in $FHSO_3$:

Strong peak at - 2 ppm [$P(OH)_4^+$][72] and a weak signal at + 78 ppm [PBr_3OH^+]. After 14 days little change had occurred but a new weak signal at + 8 ppm ($^1J_{PF}$= 990 Hz, doublet)[$PF(OH)_3^+$][60] was present.

The shift values are all consistent with the assignments made and agree with literature values where known. The shift parameters assigned to the phosphoryl chloro-bromo species are in agreement with the results given previously in this section.

The data shows that NaCl can act as a source of exchanging chloride in both $ClHSO_3$ and $FHSO_3$, with the added property of being able to produce a source of exchanging fluorine when dissolved in $FHSO_3$. KF appears to be able to act as a source of exchanging fluorine when dissolved in $ClHSO_3$. The results of KF in the $POBr_3/FHSO_3$ solution are less convincing since extensive solvolysis of the $POBr_3$ was observed. The only fluorine substituted species found was $PF(OH)_3^+$. Since the course of reaction is similar to the initial reaction of KF in the $POBr_3/ClHSO_3$ system which later showed extensive fluorination it seems probable that KF also acts as a source of exchanging fluorine in the $POBr_3/FHSO_3$ system. In all cases quite appreciable amounts of $P(OH)_4^+$ were formed in the systems. This is probably due to the initial solid/liquid reaction leading to a local decrease in the acid strength and subsequent solvolysis of some of the PBr_3OH^+.

It thus appears that in solution of mixtures of phosphorus (V) halides no halogen exchange occurs, either between the phosphorus species or with the solvents themselves. When an alternative source of halide ion is present, however, exchange at phosphorus can yield mixed species.

b) Mixed halide compounds.

The data in section 2(viiia) of this chapter suggests that sulphuric acids may dissolve compounds thought to contain mixed phosphorus (V) halide species leading to stable solutions which can be monitored by

^{31}P n.m.r. $ClHSO_3$ and $FHSO_3$ will not be favourable as solvents for samples where an alternative source of halogen is present, however, since this may cause exchange. Since some complication had arisen in the use of 65% oleum in similar systems (Chapter 3B section 2(i)) and 100% H_2SO_4 is quite an active solvolysing agent, 25% oleum was chosen as the optimum medium to investigate some compounds thought to contain mixed halide derivatives of phosphorus (V).

Dissolution of the solids in 25% oleum was generally accompanied by effervesence which soon ceased to yield clear solutions. These were monitored by ^{31}P n.m.r. and even after a period of one month no further reaction was seen. Indeed one solution was monitored for 10 months without any further reaction occurring. The results are summarized in Table 9. The peak assignments are in good agreement with values obtained in liquid HCl[76] and with solid state data.[85,86] The solid state spectra[85,86] showed some variation in chemical shift for individual ions (12 ppm or more), reflecting a change of counter-ion. In 25% oleum individual ions show the same shift within experimental error since the counter-ion present in solution will be effectively constant. The shift values obtained for the individual species correspond to the presence of a large anion, probably HSO_4^- or $HS_2O_7^-$. Comparison of the intensities of the solution signals with the solid state results for the same sample suggests that the phosphorus cations dissolve in 25% oleum unchanged and that no further reaction occurs on standing.

The bulk of the samples show peaks assignable to $[PCl_nBr_{4-n}^+]$ ($0 \leq n \leq 4$) cations and require no further comment. Some samples, however gave signals due to PX_3OH^+ species and the reasons for their appearence should be considered.

Table 9. ^{31}P n.m.r. chemical shift values (ppm) for mixed phosphorus (V) halides in 25% oleum

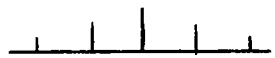
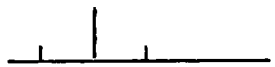
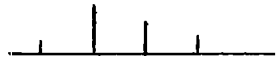
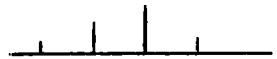
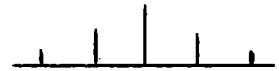
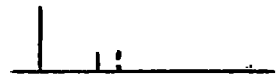
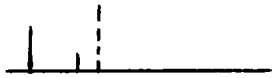
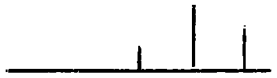
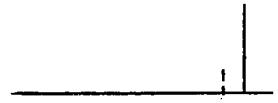
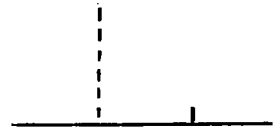
Sample	PCl_4^+	PCl_3Br^+	$PCl_2Br_2^+$	$PClBr_3^+$	PBr_4^+	Intensities	Comments
HCl solution[76]	-87.3	-50.1	-9.7	+36.4	+81.0		
P. Gates $PCl_3Br^+BCl_4^-$	-88	-50	-9				
P. Gates 116	-88	-50	-9				
P. Gates 133	-87	-50	-9	+37			
P. Gates 142	-87	-50	-9	+36			
P. Gates 146	-88	-51	-9	+36			
P. Gates 130	-88	-51	-10	+36			
P. Gates $PCl_{4-n}Br_n^+BCl_4^-$	-89	-51	-9	+36	+84		See Figure 11
HCl solution[76]	-87.3	-50.1	-9.7	+36.4	+81.0		
P. Gates $PCl_4^+SbCl_5Br^-$	-88	-51					Extra peak at =32 ppm assignable to PCl_3OH^+

Table 9. continued

Sample	PCl_4^+	PCl_3Br^+	$PCl_2Br_2^+$	$PClBr_3^+$	PBr_4^+	Intensities	Comments
P. Gates P_2Cl_9Br	-88	-51					Extra peak at -25 ppm assignable to PCl_3OH^+
P. Gates $PBr_4^+BBrCl_3^-$			-9	+36	+85		
P. Gates 136 $PBr_3Cl^+X^-$			-8	+36	+86		
R. Reeve $PCl_5 + BBr_3$	-88	-51	-10	+36			
R. Reeve PCl_3Br_4					+85		Extra peak at + 64 ppm assignable to PBr_3OH^+
R. Reeve $Bu_4N^+Br^- + PCl_5$				+35 ?			Extra peak at - 28 ppm assignable to PCl_3OH^+

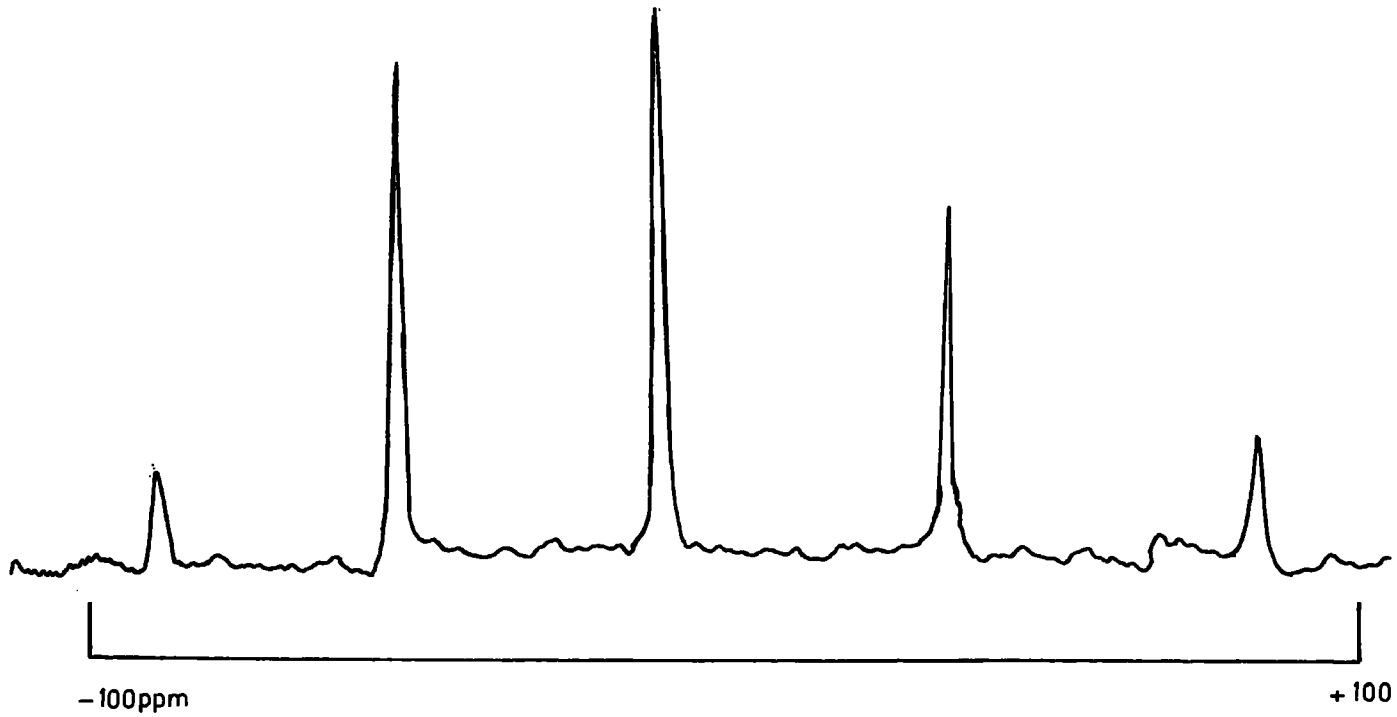


Figure 11

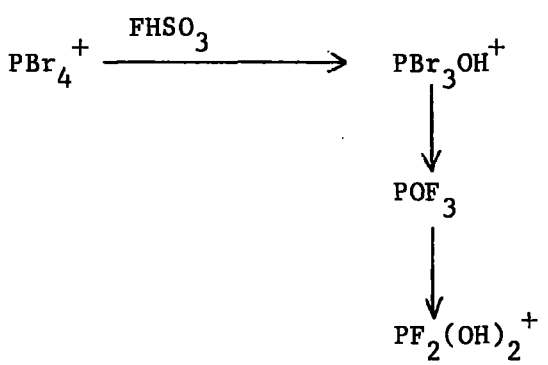
The ^{31}P n.m.r. spectrum of $[PCl_{4-n}Br_n^+][BCl_4^-]$ $(0 \leq n \leq 4)$ in 25% oleum.

For both $PCl_4^+SbCl_5Br^-$ (P. Gates) and PCl_3Br_4 (R. Reeve) the weak signals from PCl_3OH^+ and PBr_3OH^+ respectively are probably caused by hydrolysis of the sample prior to solution in 25% oleum. Thus unhydrolysed $PCl_4^+SbCl_5Br^-$ appears to contain predominantly PCl_4^+ with a little PCl_3Br^+ while PCl_3Br_4 has PBr_4^+ [25] as the only phosphorus-containing species.

The presence of a strong signal assignable to PCl_3OH^+ in the solution of P_2Cl_9Br is understandable in terms of the proposed formulation of this compound which contains PCl_6^-.[88] Previous results (Chapter 3B section 2(v)) have shown that the PCl_6^- anion gives only PCl_3OH^+ in 25% oleum. A sample of P_2Cl_9Br was dissolved in 65% oleum and gave a strong peak at - 88 ppm [PCl_4^+], and weak signals at - 51 [PCl_3Br^+] and - 44 ppm [PCl_3OH^+]. This result confirms that P_2Cl_9Br contains PCl_4^+, PCl_3Br^+ and PCl_6^- as the phosphorus constituents.[88]

The most difficult assignment is that of the signals of the solid obtained from the reaction of $Bu_4N^+Br^-$ and PCl_5.[25] The weak resonance at + 35 ppm could be due to either $PClBr_3^+$ or $PClBr_2OH^+$ while the peak at - 28 ppm is assignable to PCl_3OH^+. The lack of a PCl_4^+ signal at -88 ppm indicates that both PCl_5 and PCl_4^+ are absent since this ion is stable for some time in 25% oleum (see next part of this section). The signal at + 35 ppm suggests that there is a small amount of a P-Br containing species present. A possible explanation is some interaction between Br^- and PCl_5 to form PCl_5Br^- which decomposes in 25% oleum in a similar way to PCl_6^- yielding predominantly PCl_3OH^+ but with a little $PClBr_2OH^+$ as well.

In addition to the mixed phosphorus-halogen species investigated the ^{31}P n.m.r. spectra of solutions of $PCl_4^+BCl_4^-$ and $PBr_4^+BBr_4^-$ were recorded in both 25% oleum and $FHSO_3$. The 25% oleum and $FHSO_3$ solutions of $PCl_4^+BCl_4^-$ both showed a single peak at - 87 ppm assignable to PCl_4^+, while both $PBr_4^+BBr_4^-$ solutions showed peaks at + 85 ppm atributable to PBr_4^+. No further reaction was observed over a period of 30 days for the 25% oleum solutions, but after 2 days both $FHSO_3$ solutions showed a reduction in strength of the original signal and a new quartet had appeared at + 36 ppm ($^1J_{PF}$= 1070 Hz) which grew with time. After 11 days the same signals were apparent plus a triplet at + 22 ppm ($^1J_{PF}$ = 1006 Hz) and in the $PBr_4^+BBr_4^-$ solution a weak signal at + 71 ppm was present. The multiplet signals are easily assignable to POF_3 (+ 36 ppm)[6] and $PF_2(OH)_2^+$ (+ 22 ppm).[60] These results indicate that the PX_4^+ species investigated are stable in 25% oleum but undergo fluorination and solvolysis in $FHSO_3$. The weak signal found at + 71 ppm in the $PBr_4^+BBr_4^-$ solution in $FHSO_3$ after 11 days is assignable to PBr_3OH^+. The presence of PBr_3OH^+ in the system is compatible with a reaction scheme



Its late appearance in the ^{31}P n.m.r. spectrum could be because fluorination of the PBr_3OH^+ occurs at such a rate initially that its

concentration only becomes measurable when the fluorination process stops. The lack of signals for any intermediates however, leaves this interpretation open to question; the PBr_3OH^+ could be produced in a side reaction or at a later stage of the main reaction after fluorination. No signal for PCl_3OH^+ was found for the $PCl_4^+BCl_4^-$ solution in $FHSO_3$, but the fluorination of PCl_3OH^+ produced from PCl_3 in $FHSO_3$ (Chapter 3B section 2(vi)) appeared to proceed via PCl_2FOH^+. A reaction scheme involving solvolysis of the PX_4^+ cation before fluorination is thus not unreasonable. The apparent stability of the PCl_4^+ ion in 25% oleum is further evidence that its instability when generated from PCl_5 in sulphuric acids is caused by reaction of the PCl_6^- present, which leads to degradation of the solvent and an increase in its solvolysing properties.

The results in this section confirm that 25% oleum will be a useful solvent for compounds thought to contain mixed halogeno-phosphorus cations, since little decomposition of the species or halogen exchange seems to occur.

c) Halogen oxidation of phosphorus (III) halides.

Paul and his co-workers have attempted to oxidize phosphorus (III) compounds in $FHSO_3$ with a number of oxidizing agents,[20] and compounds of the form $PCl_4^+X^-$, $PCl_3Br^+X^-$, $PBr_4^+X^-$ and $PBr_3Cl^+X^-$ where X^- is $FHSO_3^-$ have been claimed. The evidence for these formulations was based on conductimetric and I.R. spectroscopic data, with some limited supporting analytical figures. The results are not conclusive, especially for the $PBr_4^+X^-$ and $PBr_3Cl^+X^-$ species. In the light of work discussed in

section 2(viiib) of this chapter which showed that several samples prepared by halogen oxidation of phosphorus (III) halides contained a mixture of phosphorus (V) cations, it is most unlikely that Paul et al prepared pure samples containing PCl_3Br^+ or $PClBr_3^+$. A ^{31}P n.m.r. investigation of PCl_5, PBr_5 and some systems of the form $PX_3 + Y_2 \pm BZ_3$ (X, Y, Z = Cl or Br) in liquid HCl[76] produced n.m.r. shift data for the complete series of ions $[PCl_nBr_{4-n}]^+$ $(0 \leq n \leq 4)$, and suggested that halogen oxidations of phosphorus (III) halides do not give simple products.

In order to clarify the data available some halogen oxidations of phosphorus (III) compounds were therefore attempted in both 25% oleum and $FHSO_3$ which are useful solvents for phosphorus (V) mixed halide species (Chapter 3B section 2(viiib)). A summary of the reactions investigated is given in Table 10.

The solutions were allowed to warm up from 233 K to room temperature after mixing and the required solvent added. In all cases, vigorous reaction occurred to yield clear solutions of varying shades of brown, which were then studied by ^{31}P n.m.r. The results are represented diagramatically in Figures 12, 13 and 14.

Comparison of the shift values determined in these reactions with data discussed in Section 2(viiib) of this chapter leads to the following assignments for the $PCl_3 + Br_2$ and $PBr_3 + Cl_2$ systems (Table 11) (Figures 12 and 13).

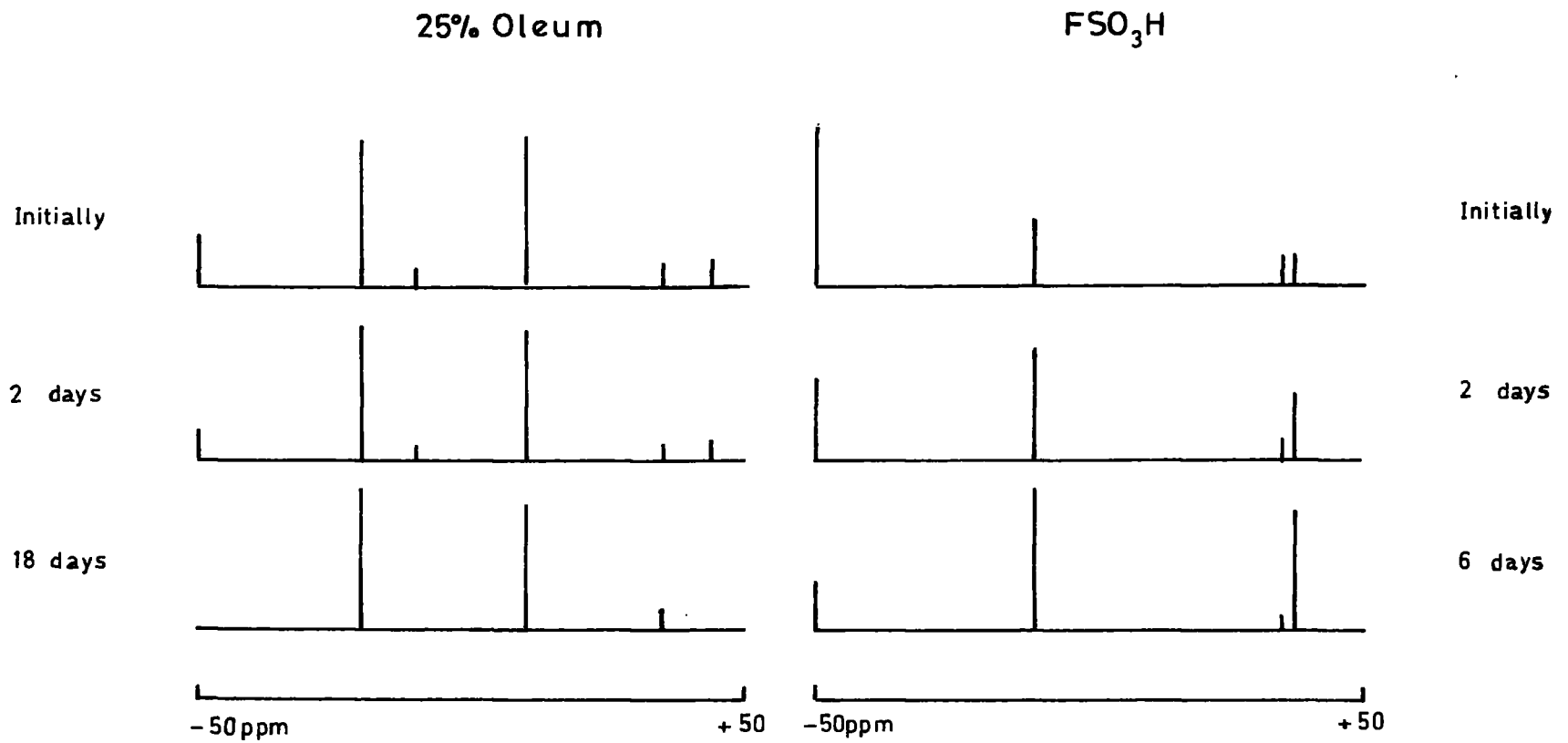


Figure 12

Relative peak heights for the ^{31}P n.m.r. spectra of phosphorus (III) chloride and bromine in acidic solvents.

Table 10. Solutions of phosphorus (III) halide-halogen mixtures in acidic media.

Reactants	Mode of addition	Observation	Solvents Studied
$PCl_3 + Br_2$ 1:1	Bromine (m.pt. 266 K) added to PCl_3 (m.pt 161K)	Vigorous reaction yielded yellow solid	25%oleum
			$FHSO_3$
$PBr_3 + Cl_2$ 1:1	PBr_3(m.pt 233 K) added to chlorine (b.pt 238 K)	Vigorous reaction yielded yellow-brown solid	25%oleum
			$FHSO_3$
$PI_3 + Br_2$ 1:1	Bromine (m.pt. 266K) added to PI_3 (m.pt 334 K)	No obvious reaction, bromine solidified	$FHSO_3$
$PI_3 + I_2$ 1:1	Solid PI_3 added to iodine and mixed	No obvious reaction	25%oleum

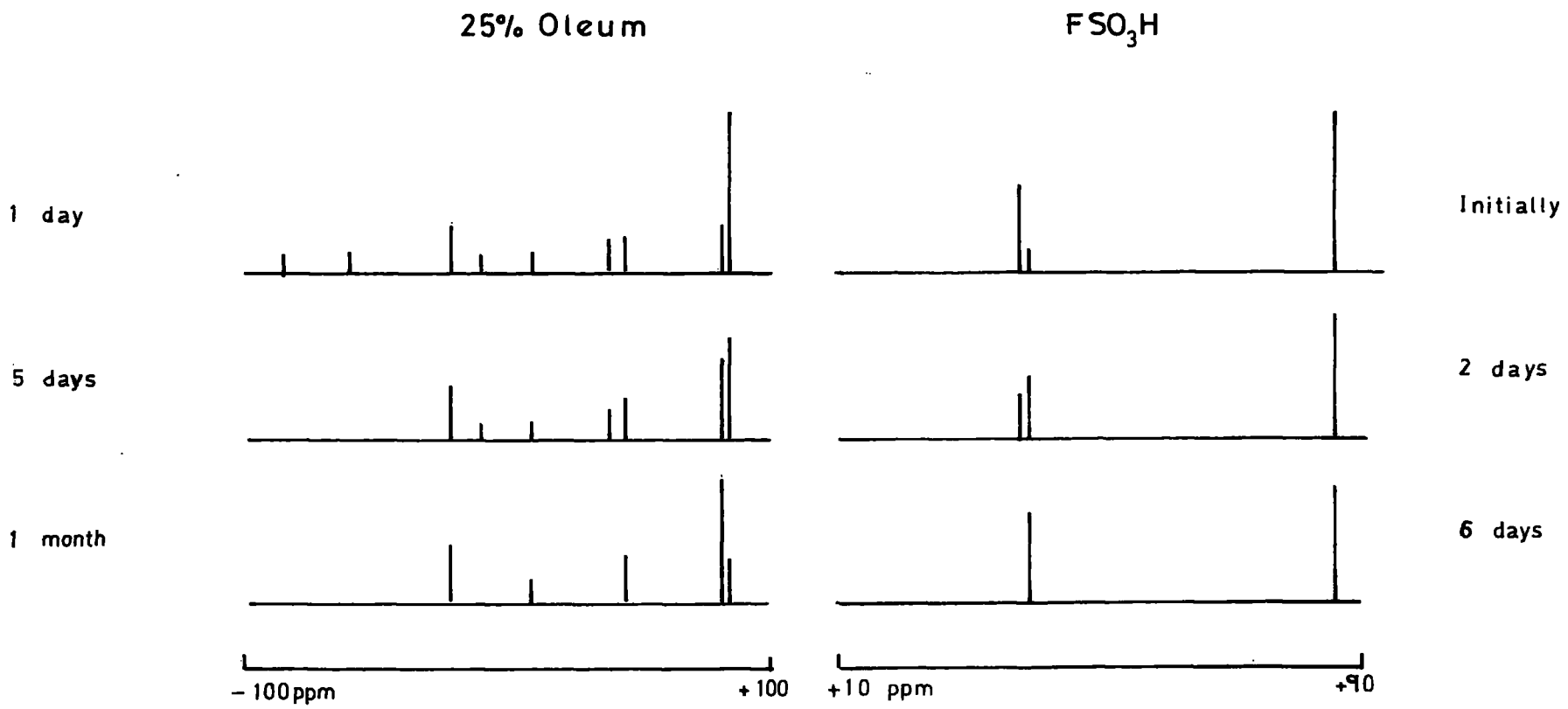


Figure 13

Relative peak heights for the ^{31}P n.m.r. spectra of phosphorus (III) bromide and chlorine in acidic solvents.

Table 11. ^{31}P n.m.r. chemical shift values (ppm) for solutions of phosphorus (III) halide - halogen mixtures in acid media

Peak / System	PCl_4^+	PCl_3Br^+	PCl_3OH^+	$PCl_2Br_2^+$	PCl_2BrOH^+	$PClBr_3^+$	$PClBr_2OH^+$	PBr_3OH^+	PBr_4^+
$PCl_3 + Br_2$ 1:1 in 25% oleum		-51	-21	-10	+ 10	+ 35	+ 43		
$PCl_3 + Br_2$ 1:1 in $FHSO_3$		-50		-9		+ 35			
$PBr_3 + Cl_2$ 1:1 in 25% oleum	-86	-50	-20	-9	+ 11	+ 37	+ 44	+ 81	+ 85
$PBr_3 + Cl_2$ 1:1 in $FHSO_3$				-10 ?		+ 35			+ 84

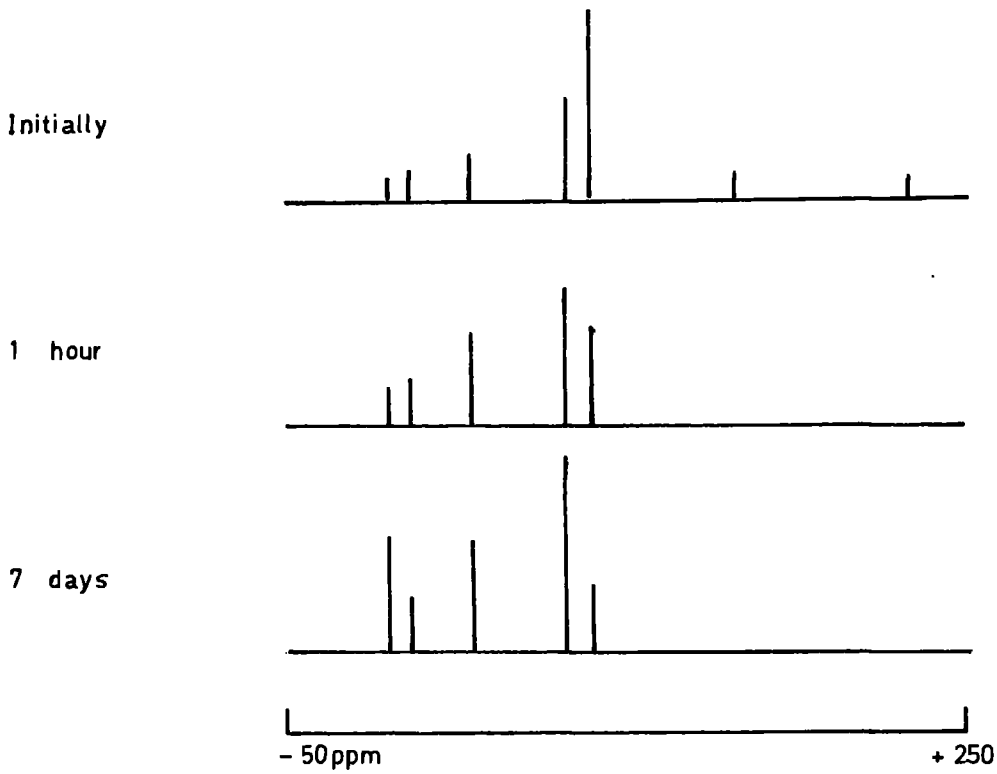
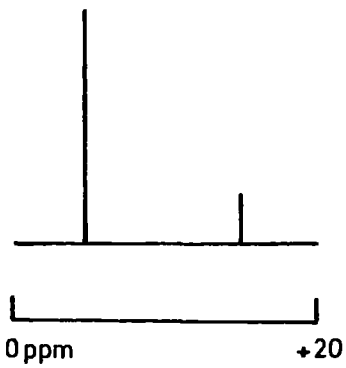


Figure 14

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide and bromine in fluorosulphuric acid.



Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide and iodine in 25% oleum.

In addition to the peaks tabulated, both solutions made up in $FHSO_3$ showed a quartet at + 36 ppm ($^1J_{PF}$ = 1080 Hz) assignable to POF_3.[60]

The signals found in the $FHSO_3$ solution of $PI_3 + Br_2$ (Figure 14) are for the most part easily explicable as shown in Table 12.

Table 12. ^{31}P n.m.r. chemical shift values for PI_3-Br_2 mixture in fluorosulphuric acid.

Chemical shift (ppm)	J	Assignment
- 4		$P(OH)_4^+$ [72]
+ 6	Doublet $^1J_{PF}$= 1000Hz	$PF(OH)_3^+$ [60]
+34	Quartet $^1J_{PF}$= 1080 Hz	POF_3 [60]
+74		PBr_3OH^+
+84		PBr_4^+
+149		$PI_2(OH)_2^+$
+222		PI_2BrOH^+

The assignments are in agreement with previously published data where available, and the other shifts are comparable with data obtained in independent reactions. The only difficult assignment is that of the signal at + 222 ppm. Since PI_3OH^+ and $PI_2(OH)_2^+$ give n.m.r. peaks at approximately + 300 and + 144 ppm respectively in $FHSO_3$ (Chapter 3B section 2(vii)), the assignment of the + 222 ppm resonance to PI_2BrOH^+ seems reasonable when the expected mode of reaction between PI_3 and bromine is considered. Further evidence to support this

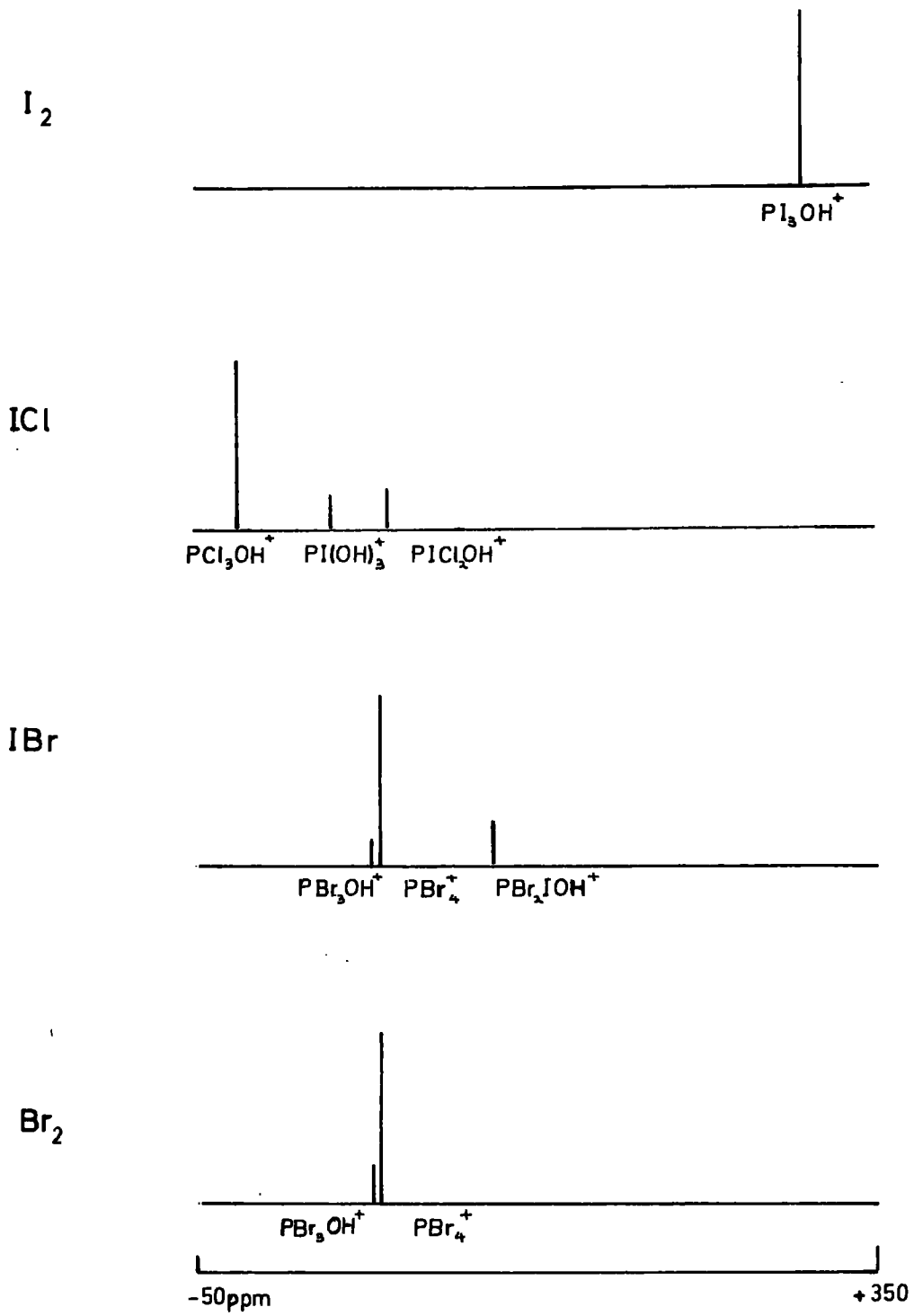


Figure 15

Relative peak heights for the ^{31}P n.m.r. spectra of phosphorus (III) iodide with halogens in 100% sulphuric acid.

assignment is given in the next section.

The solution of PI_3 and iodine in 25% oleum (Fig. 14) shows no evidence for the presence of phosphorus (V)-iodine species. The shift data is consistent with solvolysis of the phosphorus components to $P(OH)_4^+$.[71]

These attempts at PI_3-halogen oxidations using $FHSO_3$ and 25% oleum as solvents have given some useful data, but the presence of fluorine in $FHSO_3$ complicates the resultant spectra, while 25% oleum appears to solvolyse phosphorus (V)-iodine species quite rapidly, as found for PI_3 itself in this solvent. As described previously (Chapter 3B section 2(vii)) signals of PI_3OH^+, $PI_2(OH)_2^+$ and $PI(OH)_3^+$ were rather unexpectedly observed in the solution of PI_3 in 100% H_2SO_4. It was therefore decided to attempt halogen oxidations of PI_3 in 100% H_2SO_4, in the hope that other phosphorus (V)-iodine species might be stabilized.

PI_3 was covered with a layer of 100% H_2SO_4 at room temperature and IBr, ICl, Br_2 and I_2 respectively were added in the required amounts to give 1:1 mixtures. This mode of reaction was chosen because the slow solution of PI_3 in 100% H_2SO_4 would allow reaction of the halogen with the PI_3 but hopefully stabilize the phosphorus (V) product by rapid solution. The reactions are summarized in Table 13.
The ^{31}P n.m.r. spectral data is summarized in Figure 15 with peak assignments. All the assignments are in good agreement with data obtained previously, allowing for the shift dependence of species containing P-OH groupings dissolved in acidic media. The peak at + 169 ppm in the PI_3 + IBr solution has been assigned to PBr_2IOH^+.

Table 13. Solutions of phosphorus (III) iodide-halogen mixtures in 100% sulphuric acid.

Reaction	Observation
$PI_3 + I_2$ 1:1 in 100% H_2SO_4	No reaction obvious even on shaking. Not all PI_3 dissolved
PI_3 + IBr 1:1 in 100% H_2SO_4	No obvious reaction. Some iodine precipitation but not all PI_3 dissolved.
PI_3 + ICl 1:1 in 100% H_2SO_4	Vigorous reaction on shaking but not all PI_3 dissolved. Some iodine precipitation.
$PI_3 + Br_2$ 1:1 in 100% H_2SO_4	Vigorous reaction on shaking with some iodine precipitation. Not all PI_3 dissolved.

This is the only assignment not confirmed by previous data. In the solution of $PI_3 + Br_2$ in $FHSO_3$, a signal at + 222 ppm was assigned to PI_2BrOH^+, but no signal due to PBr_2IOH^+ was observed. In an attempt to verify these assignments the following solutions were prepared.

PI_3 was shaken with 100% H_2SO_4 until the liquid was a pale yellow colour. Previous investigation of this system (Chapter 3B section 2(vii)) suggests that the yellow colouration is due to PI_3OH^+ formed in the early stages of the reaction. To portions of this PI_3OH^+ solution were added small amounts of IBr, ICl and Br_2 in the hope that halogen exchange would give the mixed halogen species based on PI_3OH^+.

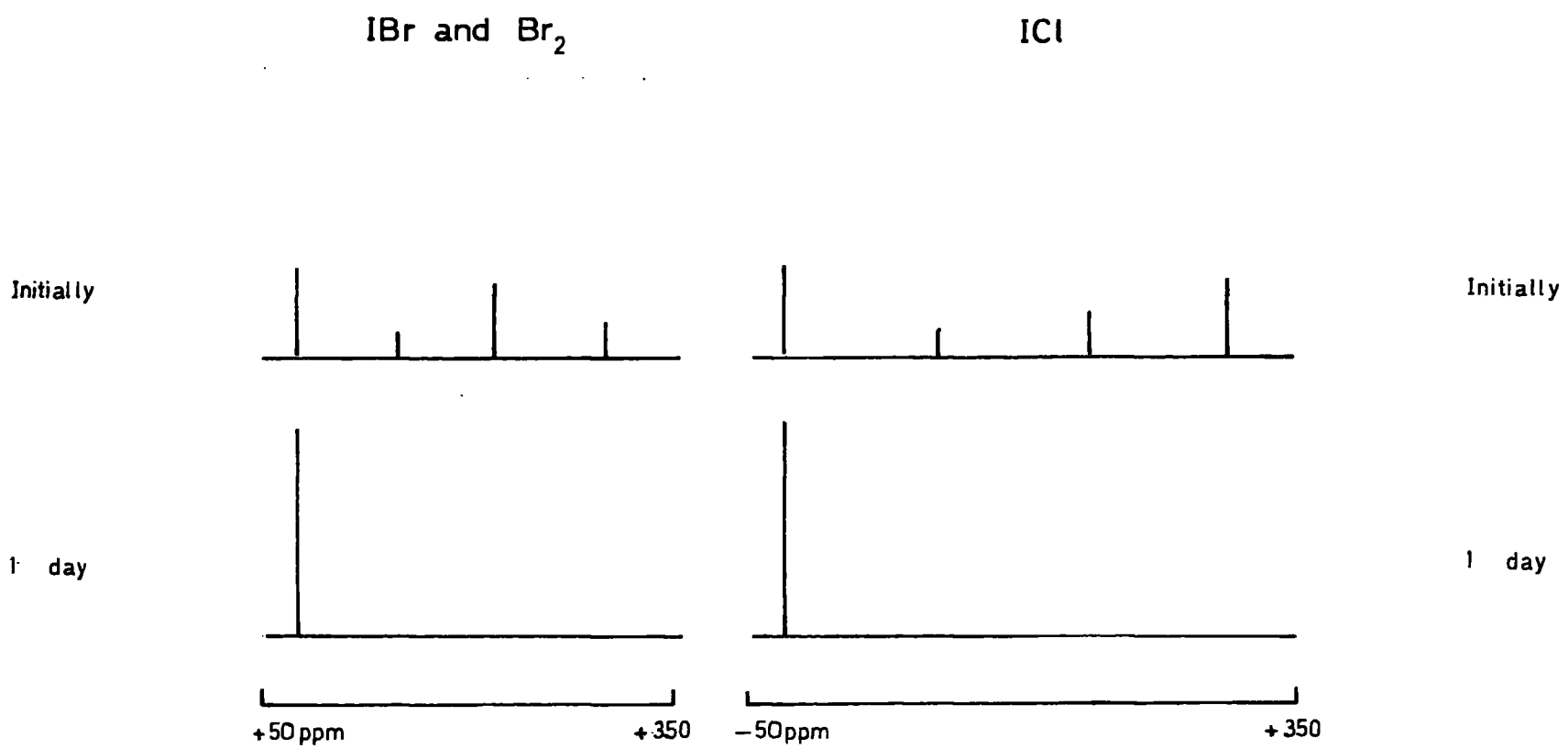


Figure 16

Relative peak heights for the ^{31}P n.m.r. spectra of PI_3OH^+ with halogens in 100% sulphuric acid.

The spectra obtained are represented diagramatically in Figure 16.

The final peaks found after 1 day at + 78 and - 20 ppm respectively are assignable to PBr_3OH^+ and PCl_3OH^+, while the initial peak in all solutions around + 307 ppm is assignable to PI_3OH^+. The other signals are probably due to species containing three halogens and one hydroxyl group formed by halogen exchange between the PI_3OH^+ species and the added halogen. On this basis the peaks may be readily assigned:

IBr and Br_2 solutions

+ 78 ppm	PBr_3OH^+
+ 150 ppm	PBr_2IOH^+
+ 223 ppm	$PBrI_2OH^+$
+ 307 ppm	PI_3OH^+

ICl solution

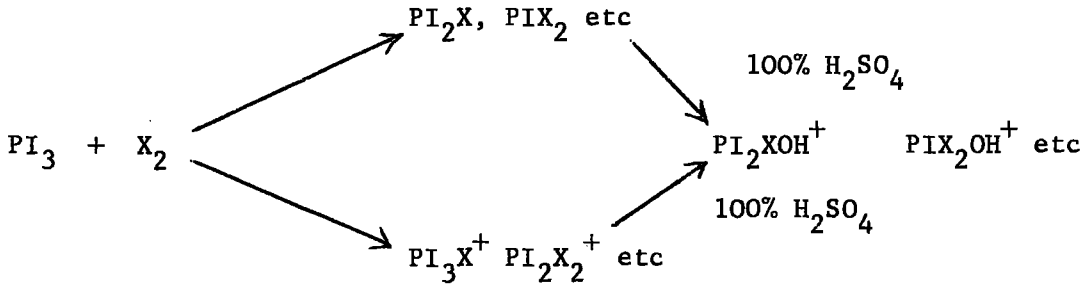
- 20 ppm	PCl_3OH^+
+ 91 ppm	PCl_2IOH^+
+ 198 ppm	$PClI_2OH^+$
+ 305 ppm	PI_3OH^+

These shifts are in good agreement with previous results, allowing for possible differences in position for the hydroxy species with acid strength.

These results indicate that although 100% H_2SO_4 is a good medium for stabilizing phosphorus (V) -iodine species, it is less suitable for attempting oxidation of PI_3, which because of its insolubility in the medium leads to inhomogeneous reaction. This is clearly

demonstrated by the attempted 1:1 reaction between PI_3 and a halogen, where no evidence for iodine-containing tetrahalophosphonium ions was found. The most probable course of reaction appears to be exchange of PI_3 with the added halogen, followed by oxidation to $PX_nY_{3-n}OH^+$ species on dissolution in 100% H_2SO_4. The non-appearance of signals of PI_3OH^+ from the samples other than $PI_3 + I_2$ tends to support this hypothesis. Alternatively the tetrahalophosphonium ions may be formed, but are unstable in 100% H_2SO_4 and rapidly decompose to $PX_nY_{3-n}OH^+$ species by replacement of a P-I group by a P-OH linkage. The formation of halogen exchanged species from a PI_3OH^+ solution in 100% H_2SO_4 shows that the P-I bond is very susceptible to halogen exchange. The overall results from these reactions are summarized in the following equations.

Heterogeneous oxidation



Homogeneous solution

$$PI_3 \xrightarrow[H_2SO_4]{100\%} PI_3OH^+ \xrightarrow{X_2} PI_2XOH^+ \text{ etc}$$

A further attempt at oxidation of PI_3 by a solution of bromine in 100% H_2SO_4 produced signals at + 75, + 150, + 222, + 305 ppm assignable to the mixed trihalohydroxyphosphonium species already described.

Thus although some interesting species can be formed in 100% H_2SO_4, no evidence for iodine containing tetrahalophosphonium cations was obtained.

3) Summary

i) Phosphorus (III) halides

Solution of phosphorus (III) halides in sulphuric acid, oleums and substituted sulphuric acids is accompanied by oxidation to phosphorus (V).

100% H_2SO_4 $\quad PX_3 + 2H_2SO_4 \longrightarrow PX_3OH^+ + HSO_4^- + H_2O + SO_2$

oleums $\quad PX_3 + H_2S_2O_7 \longrightarrow PX_3OH^+ + HSO_4^- + SO_2$

substituted acids

Y = F, or Cl $\quad PX_3 + YHSO_3 \longrightarrow PX_3OH^+ + YSO_2^-$

$PX_3 + 2YHSO_3 \xrightarrow[\text{minor reaction}]{Y=Cl \text{ only}} PX_3Y^+ + SO_2 + YSO_3^- + H_2O$

As a consequence, the acid is degraded. With sulphuric acid and the oleums, stable counter-ions are formed, but for the halosubstituted acids, the halosulphite ion produced in the initial oxidation is unstable, and may react further.

$$YSO_2^- + YHSO_3 \longrightarrow HY + YSO_3^- + SO_2$$

Reduction of the acid strength in these initial reactions is followed by solvolysis of PX_3OH^+ via $PX_2(OH)_2^+$ and $PX(OH)_3^+$ to yield $P(OH)_4^+$. Some exceptions to the general rule of solvolysis were found.

With PBr_3 in 65% oleum, a hydrogen bromide elimination/condensation reaction seemed to be preferred in the highly acidic medium. In the halosubstituted acids halogen exchange was detected. The rate of this exchange appeared from the limited data available to be more rapid in $FHSO_3$ than in $ClHSO_3$. Some solvolysis was also observed in the halosubstituted acids but this reaction seemed much slower than the halogen exchange. Evidence from the parent POX_3 system, where available, suggests that the source of exchanging halogen is halide ion and not the solvent directly. The rate of solvolysis of phosphorus (V) species formed appears to be very dependent on the acid strength of the medium. Since the initial oxidation and subsequent reactions involve degradation of the solvent it is not possible to compare acid strengths from this data because the final composition of the mixture is not known. The usual oxidation product in all solvents was PX_3OH^+, although $ClHSO_3$ also gave small amounts of PX_3Cl^+ ions.

ii) Phosphorus (V) halides

Phosphorus (V) halides dissolve in sulphuric acid, oleums and halosubstituted acids, in general with the formation of cationic PX_4^+ species. No evidence for halogen exchange was found for systems involving mixed halogeno $[PX_{4-n}Y_n]$ $(0 \leq n \leq 4)$ cations. The only exception appears to be PCl_5, which because of the presence of PCl_6^- as well as PCl_4^+ in the crystal, gave large amounts of the solvolysis product PCl_3OH^+ in 100% H_2SO_4, 25% and 65% oleum. Confirmatory evidence for the instability of PCl_6^- in these solvents was obtained from $Et_4N^+PCl_6^-$, which gave exclusively PCl_3OH^+ on solution.

The subsequent reaction of the PX_4^+ ion was very dependent on the solvent used. Solvolysis was sometimes detected in 100% H_2SO_4 and the oleums, the rate being fastest in 100% H_2SO_4, as expected. This rate was on the whole very slow, however, some species showing no signs of reaction over a period of 10 months.

Solutions of PX_4^+ cations in $FHSO_3$ and $ClHSO_3$ showed evidence for halogen exchange, although it appears that the solvent acts as an indirect source of the exchanging halogen via halide formation. The rate of exchange again seemed to be faster for $FHSO_3$ over $ClHSO_3$ from the limited number of systems investigated. Some solvolysis occured in these solvents and it is interesting to note that no PX_4^+ exchange species were observed in $FHSO_3$ solutions, only POF_3 and related solvolysis products being present. The PF_4^+ ion is known, but only in a 1:3 adduct formed between PF_5 and SbF_5 which has been shown to be $[PF_4^+][Sb_3F_{16}^-]$ by vibrational spectroscopy.[112] In the $ClHSO_3$ solution mixed halogen species of the form $[PX_{4-n}Cl_n]^+$ and $[PX_{3-n}Cl_nOH]^+$ were found.

iii) Phosphoryl halides.

The ^{31}P n.m.r. shift data for $POBr_3$ and $POCl_3$ obtained in these experiments is given in Table 14.

If the observed ^{31}P resonance is regarded as an exchange-averaged signal between protonated and non-protonated species, then some indication of the proton-donor strength of the solvent can be obtained since both $POCl_3$ and $POBr_3$ function as weak bases in these solvents.[15-17] Thus the solvents can be placed in an approximate order of acidity,

100% H_2SO_4 < $ClHSO_3$ < $FHSO_3$

< 25% oleum < 65% oleum

Table 14. ^{31}P n.m.r. chemical shift values (ppm) for phosphoryl chloride and bromide in acidic solvents

Compound \ Solvent	Parent	100% H_2SO_4	$ClHSO_3$	$FHSO_3$	25% oleum	65% oleum
$POCl_3$	- 2.2[74]	-20	-22	-23	-35	-56
$POBr_3$	+103.4[74]	+80	+76	+74	+64	+57

POX_3 compounds in general dissolved in these acids with protonation and no further reaction. Some exceptions were found however. Solutions of $POBr_3$ in 25% oleum and 100% H_2SO_4 appeared to solvolyse slowly to $P(OH)_4^+$, the rate of solvolysis being more rapid in 100% H_2SO_4, while 65% oleum solutions of $POBr_3$ showed some evidence for condensation of PBr_3OH^+ species formed via HBr elimination.

4) Experimental.

Solutions for investigation were generally prepared by placing some of the phosphorus compound in a glass sample bottle, and adding the appropriate acid carefully by a dropping pipette. In many cases instantaneous reaction occurred with solution of the phosphorus compound, and a sample of the resulting solution was transferred to a n.m.r. tube for investigation. All these manipulations were carried out inside a nitrogen-filled glove box and adequate precautions were taken to avoid aerial hydrolysis. Where the process was slow, the bottles were shaken until reaction occured. Then a sample was taken as before and monitored by ^{31}P n.m.r.

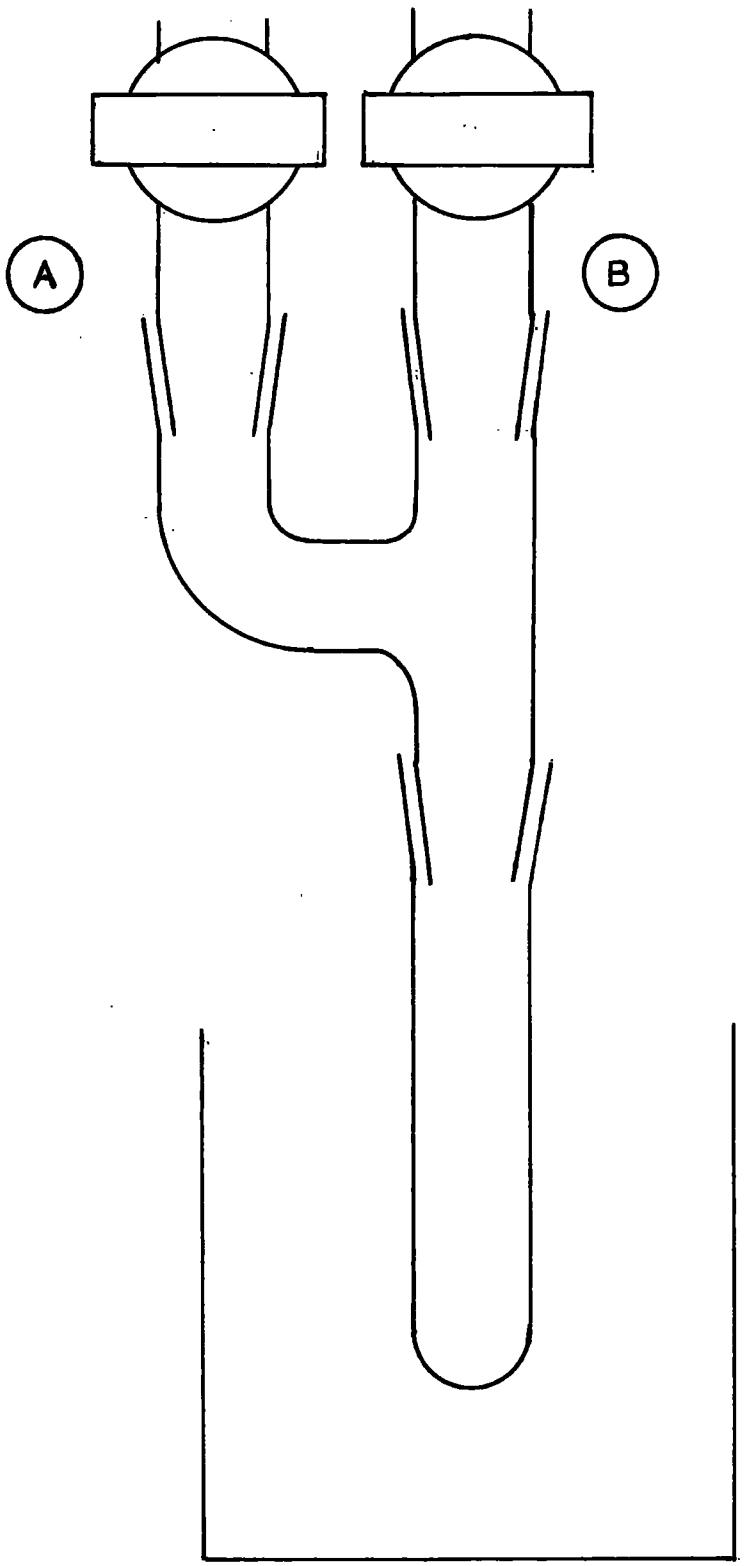


Figure 17

Apparatus used in reactions between phosphorus (III) halides and halogens in acidic media.

Solutions were investigated over varying periods of time until reaction ceased, or until the course of the reaction had been elucidated.

Although the general approach was followed in all instances, the samples in section 2(viiic) which involved initial reaction between a phosphorus (III) halide and a halogen required special attention. The vigorous nature of the reactions, which were carried out in some cases at 233 K, led to the use of the apparatus shown in Figure 17. The reactions were carried out outside the glove-box and special precautions were taken to keep the samples free from water. The apparatus was baked in an oven overnight before use and assembled as shown. The reaction vessel was then evacuated on a vacuum line and opened under an atmosphere of nitrogen. The order of mixing of the reactants was somewhat dependent on their physical properties, and the method of reaction is given in Table 15.

All additions of reactants were carried out via opening (B) under a backflow of dry nitrogen. This method of addition helped to minimize any risks of aerial hydrolysis and also ensured that there was a route for any excess pressure to dissipate during the course of reaction.

Table 15. Experimental data for phosphorus (III) halide-halogen mixtures in acid media.

Reactants	Method	PX_3	X_2	Solvent
$PCl_3 + Br_2$ 1:1	Br_2 added to PCl_3 at 233 K. Acid added after warming to R.T.	1.6 mls (18.3 mmoles)	1 ml (19.3 mmoles)	25% oleum
		1.6 mls (18.3 mmoles)	1 ml (19.3 mmoles)	$FHSO_3$
$PBr_3 + Cl_2$ 1:1	Cl_2 condensed as liquid at 213 K. PBr_3 added at 233 K then acid added after warming to R.T.	2 mls (21.3 mmoles)	1 ml (21.9 mmoles)	25% oleum
		2 mls (21.3 mmoles)	1 ml (21.9 mmoles)	$FHSO_3$
$PI_3 + Br_2$ 1:1	PI_3 immersed under acid at R.T., then Br_2 added	0.22 gms (0.5 mmoles)	0.025 mls (0.48 mmoles)	100% H_2SO_4
	Br_2 added to PI_3 at 233 K. Acid added after warming to R.T.	1.24 gms (3 mmoles)	0.16 mls (3.1 mmoles)	$FHSO_3$
$PI_3 + I_2$ 1:1	PI_3 immersed under acid at R.T., then I_2 added	0.20 gms (0.48 mmoles)	0.12 gms (0.48 mmoles)	100% H_2SO_4
	PI_3 and I_2 mixed at 233 K. Acid added after warming to R.T.	0.59 gms (1.43 mmoles)	0.36 gms (1.42 mmoles)	25% oleum
$PI_3 + IBr$ 1:1	PI_3 immersed under acid and IBr added at R.T.	0.21 gms (0.49 mmoles)	0.10 gms (0.48 mmoles)	100% H_2SO_4
$PI_3 + ICl$ 1:1	PI_3 immersed under acid and ICl added at R.T.	0.21 gms (0.49 mmoles)	0.08 gms (0.49 mmoles)	100% H_2SO_4

CHAPTER 3C

ORGANO-PHOSPHORUS (V) COMPOUNDS IN SULPHURIC ACID, OLEUMS AND CHLOROSULPHURIC ACID.

1) Introduction.

The chemistry of organo-phosphorus compounds in sulphuric acid and related solvents has been little studied. The results of conductivity measurements on triphenyl phosphate in sulphuric acid have been explained in terms of protonation.[96] Gillespie et al[70] deduced that triethyl phosphate and triphenyl phosphine oxide were protonated in sulphuric acid from cryoscopic and conductivity data. Similar evidence for the protonation of Ph_3PO in fluorosulphuric acid was reported by Paul et al.[17] McFarlane and White[89] have observed by ^1H n.m.r. the protonation at phosphorus of several phosphites and phosphines in 100% H_2SO_4. Olah and McFarland have examined the protonation of trialkyl (aryl) phosphates, trialkyl (aryl) phosphites and dialkyl phosphonates in fluorosulphuric acid and in fluorosulphuric acid-antimony pentafluoride solutions using both ^1H and ^{31}P n.m.r.[72] Dillon and Waddington have investigated the behaviour of some phosphoryl compounds in 100% H_2SO_4, 20% and 65% oleum, and chlorosulphuric acid.[18] In compounds such as aryl phosphates containing aromatic substituents, sulphonation of the ring as well as protonation was observed. Slow sulphonation of Ph_3P when dissolved in 100% H_2SO_4 has also been reported[90] in addition to the initial protonation.

The reaction of some alkyl-substituted phosphinic acids and phosphinates in sulphuric acid and oleum has been investigated by cryoscopy and ^{1}H n.m.r.[91] The results were interpreted as protonation of the phosphoryl oxygen, followed by sulphonation in oleums of greater than 10% SO_3 content. Unlike the aryl systems mentioned,[18,90] these workers concluded that the P-OH groups were sulphonated to give $P\text{-}OSO_3H$ units.

The literature results show that phosphoryl compounds are invariably protonated at the phosphoryl oxygen. Where phosphorus (III) species have been studied, the protonation takes place directly at phosphorus. In a limited number of instances some evidence for sulphonation has been found. The data for aryl organo-phosphorus species suggests that sulphonation occurs in the aromatic ring, while sulphonation of OH groups has been suggested for some alkyl derivatives.

Hence a number of phenyl organo-phosphorus species as well as some related alkyl compounds were investigated in sulphuric acid solutions so that a meaningful comparison of the data could be made.

2) Present Work.

i) Phenylphosphonic acid.

The white solid phenylphosphonic acid dissolved in 100% H_2SO_4, 25% and 65% oleums, and $ClHSO_3$ on shaking with no obvious reaction. The 100% H_2SO_4 solution was colourless while the other solutions were pale yellow, the 65% oleum solution being the darkest.

^{31}P n.m.r. spectra of the solutions in 100% H_2SO_4 and 65% oleum showed strong signals at -32 and -13 ppm respectively. A weak signal

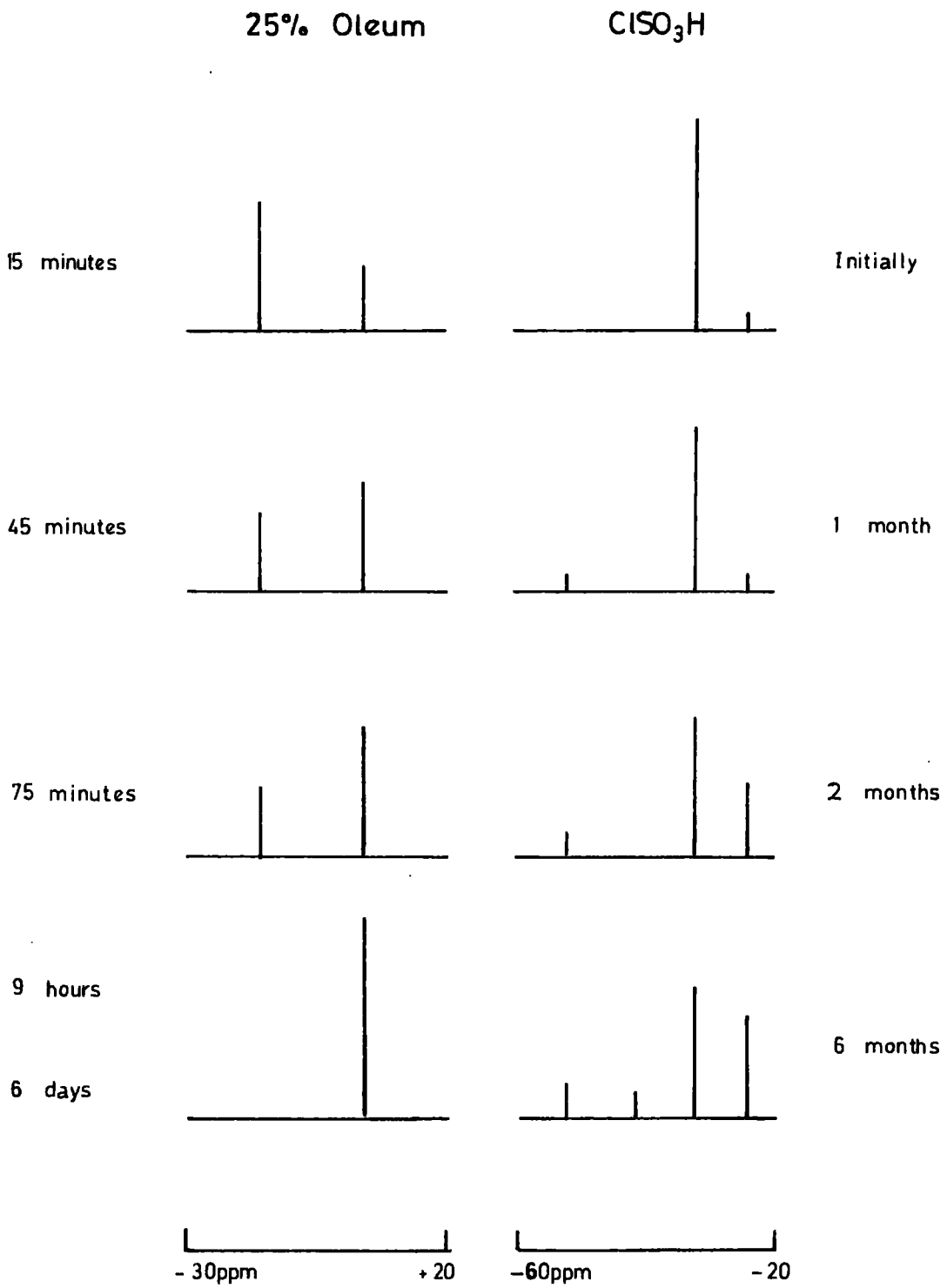


Figure 18

Relative peak heights for the ^{31}P n.m.r. spectra of phenylphosphonic acid in acidic solvents.

at -6 ppm was also present in the 65% oleum solution. No changes were found in these spectra after 8 days. The solutions in $ClHSO_3$ and 25% oleum showed rather more complex patterns, and these results are presented diagramatically in Figure 18.

The ^{31}P n.m.r. shift value of the parent acid, $PhPO(OH)_2$, is -18 ppm[4] and its downfield movement on solution in 100% H_2SO_4 is consistent with protonation of the phosphoryl oxygen.

$$PhPO(OH)_2 \longrightarrow PhP(OH)_3^+$$

The initial strong signal at - 27 ppm found in the 25% oleum solution is also reasonable for the species $PhP(OH)_3^+$. The upfield movement of this resonance relative to its position in 100% H_2SO_4 is at first sight unexpected since solution of $PhPO(OH)_2$ in 25% oleum would be expected to cause either a larger downfield shift from the parent if it is incompletely protonated in 100% H_2SO_4, or a peak in the same position if completely protonated in both solvents. This discrepancy can be explained if the solution behaviour of phosphoric acid and inorganic phosphates in sulphuric acid and oleums is considered.[71] In these systems, an upfield movement of the resonance derived from phosphoric acid in 100% H_2SO_4 with increasing SO_3 concentration was attributed to rapid equilibrium of condensed phosphate species. In view of the similarities between $P(OH)_4^+$ and $PhP(OH)_3^+$, it is reasonable to attribute the upfield shift movement to a similar condensation process of $PhP(OH)_3^+$.

The second signal found in the 25% oleum solution at - 23 ppm which grew with time and finally replaced the original signal can be readily assigned on the basis of the properties of 25% oleum. Sulphonation of aromatic hydrocarbons occurs when they are reacted with a slight excess of concentrated sulphuric acid or fuming sulphuric acid.[56] In some cases heating may be necessary depending on the ring substituents, but in general monosulphonation only takes place. Disulphonation is very slow because of the strong electron-withdrawing influence of the SO_3H group and requires very forcing conditions. Benzene is converted to benzene sulphonic acid by 100% H_2SO_4 at room temperature while substitution of a second SO_3H group requires a temperature of 518 K and fuming sulphuric acid.[56] The second peak found in the 25% oleum solution of $PhPO(OH)_2$ may be assigned to the sulphonated species $(HSO_3C_6H_4)P(OH)_3^+$.

$$PhP(OH)_3^+ \xrightarrow{25\%\ \text{oleum}} (HSO_3C_6H_4)P(OH)_3^+$$

$$-27\ \text{ppm} \qquad\qquad -23\ \text{ppm}$$

In the light of this data, the strong peak at - 13 ppm with a weak signal at - 6 ppm in the 65% oleum solution of $PhPO(OH)_2$ is consistent with production of $(HSO_3C_6H_4)P(OH)_3^+$ from the parent $PhPO(OH)_2$. The difference of 10 ppm between the strong signals found in 25% and 65% oleum is probably due to condensed phosphate-type equilibrium. The weak signal at - 6 ppm which does not change in intensity with time provides

further support for this proposition.[71] It is possible that the weak - 6 ppm signal is due to a disulphonated species, but the similarity between $PhP(OH)_3^+$ and $P(OH)_4^+$ [71] coupled with the known difficulty of disulphonation, makes this less likely.

On the basis of the results in the other solvents, the assignment of the strong peaks in the $ClHSO_3$ solution is relatively straightforward. The initial strong signal at - 32 ppm is due to $PhP(OH)_3^+$ while the second strong peak at - 24 ppm which grows with time over a period of $6\frac{1}{2}$ months is almost certainly due to $(HSO_3C_6H_4)P(OH)_3^+$ produced by sulphonation. The slowness of the sulphonation is in agreement with the hypothesis that the reactive electrophile for this process is either SO_3 or SO_3H^+.[56] These species are readily available in oleums but their production in $ClHSO_3$ depends on the equilibrium[36]

$$2ClSO_2OH \rightleftharpoons HCl + HOSO_2^+ + ClSO_3^-$$

Since the protonation of the phosphoryl group will produce $ClSO_3^-$

$$P=O + ClHSO_3 \rightleftharpoons \overset{+}{P}\text{-}OH + ClSO_3^-$$

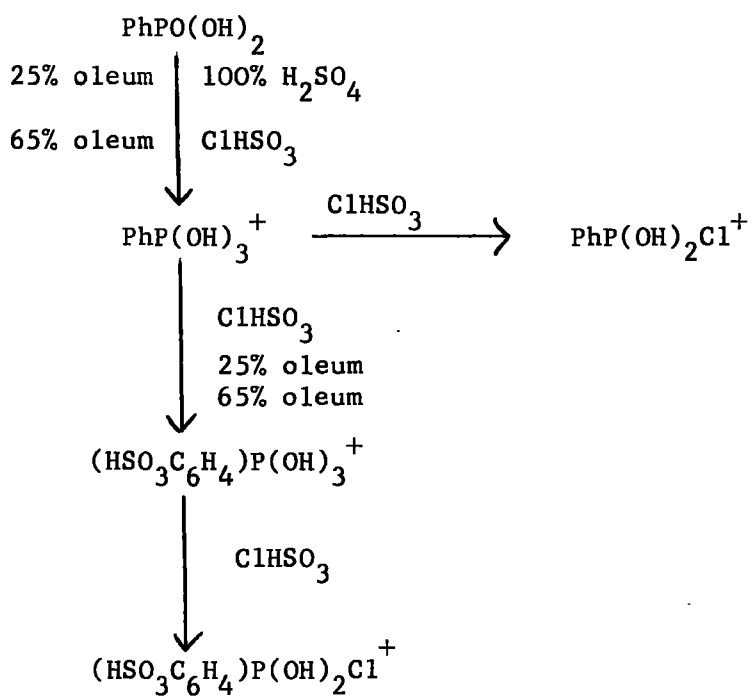
the amount of HSO_3^+ present in $ClHSO_3$ will be reduced because the equilibrium will be disturbed. The two signals at - 52 and - 41 ppm found after some time are in the same region as species observed as intermediates from the sulphonation/solvolysis reactions of $PhPOCl_2$ (Chapter 3C sections 2(ii) and 2(iii)). A reasonable assignment

taking into account later data, and assuming that $ClHSO_3$ is acting as a chlorinating agent, is

$PhP(OH)_2Cl^+$	$(HSO_3C_6H_4)P(OH)_2Cl^+$
- 52 ppm	- 41 ppm

The assignment of the upfield peak to the sulphonated species agrees with the data on the parent acid where sulphonation of the phenyl group appears to cause an upfield shift. Since $PhP(OH)_3^+$ and its sulphonated derivative are present in high concentration in this system, it seems more likely that the two less concentrated species are both mono-chlorinated derivatives rather than a mono-chloro and a di-chloro species derived from just one of the parents.

The reaction sequences can be summarized as follows,



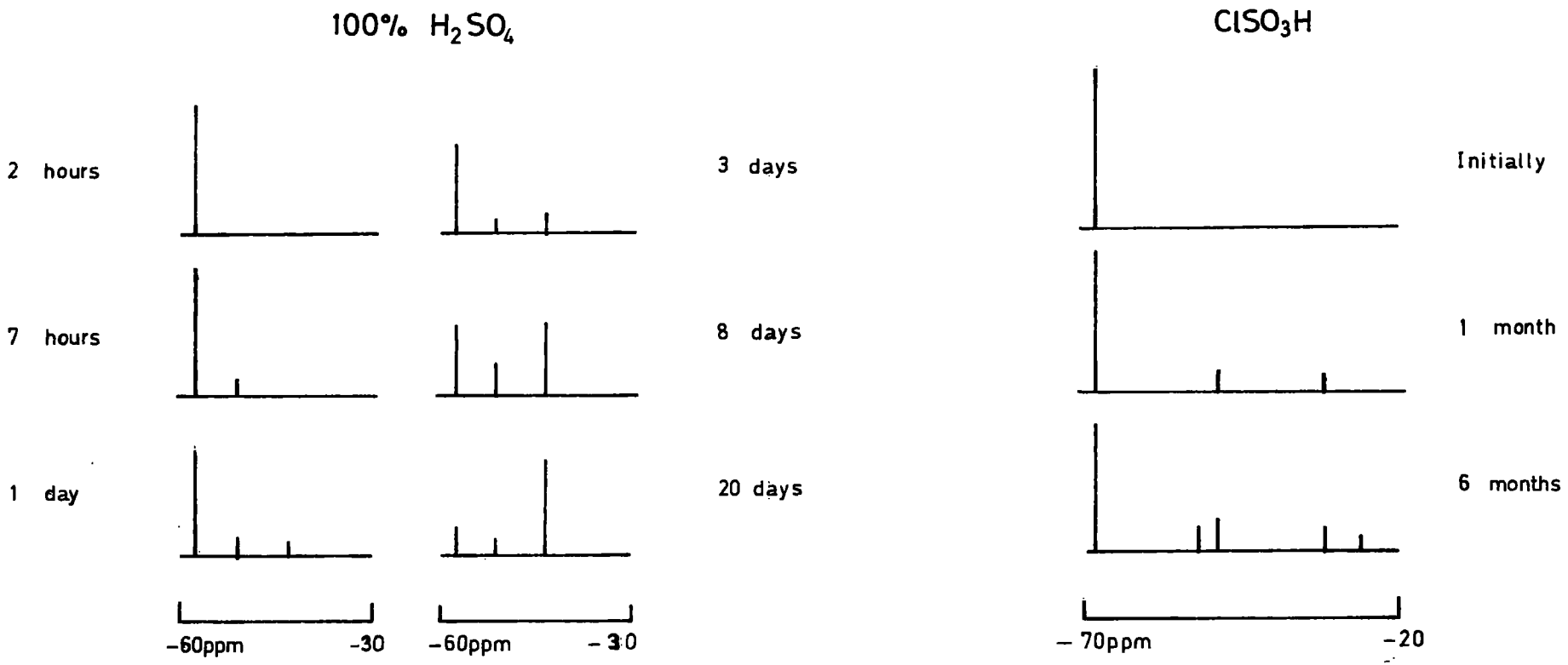


Figure 19

Relative peak heights for the ^{31}P n.m.r. spectra of phenylphosphonic dichloride in acidic solvents.

ii) Phenylphosphonic dichloride

Solutions of $PhPOCl_2$ were prepared in 100% H_2SO_4, 25% and 65% oleums, and $ClHSO_3$. The colourless liquid dissolved immediately in the acids with the evolution of some heat. The 65% oleum solution was very dark brown while the other solutions were pale brown. On standing the solutions in 25% oleum and $ClHSO_3$ darkened considerably, the former much more rapidly than the latter.

The ^{31}P n.m.r. spectrum of the 65% oleum solution showed only one signal at - 70 ppm and no change was found after one month. The other solutions showed more complex signal patterns which are shown diagramatically in Figures 19 and 20. In the 100% H_2SO_4 solution of $PhPOCl_2$, the presence of three signals is consistent with solvolysis of the P-Cl bonds, since the shift of the upfield peak (- 33ppm) is in good agreement with the peak assignment of $PhP(OH)_3^+$ derived from $PhPO(OH)_2$ in 100% H_2SO_4. When the variation of peak intensities with time is taken into account, a reasonable reaction sequence is

$$PhPOCl_2 \xrightarrow[H_2SO_4]{100\%} PhP(OH)Cl_2^+ \quad - 57 \text{ ppm}$$

$$\downarrow$$

$$PhP(OH)_2Cl^+ \quad - 51 \text{ ppm}$$

$$\downarrow$$

$$PhP(OH)_3^+ \quad - 33 \text{ ppm}$$

$PhPOCl_2$ has a ^{31}P n.m.r. shift of - 34 ppm[4] and the assignment of the - 57 ppm peak to $PhP(OH)Cl_2^+$ is consistent with protonation of the phosphoryl oxygen. The assignment of the - 51 ppm peak is compatible with replacement of a Cl group by an OH group.

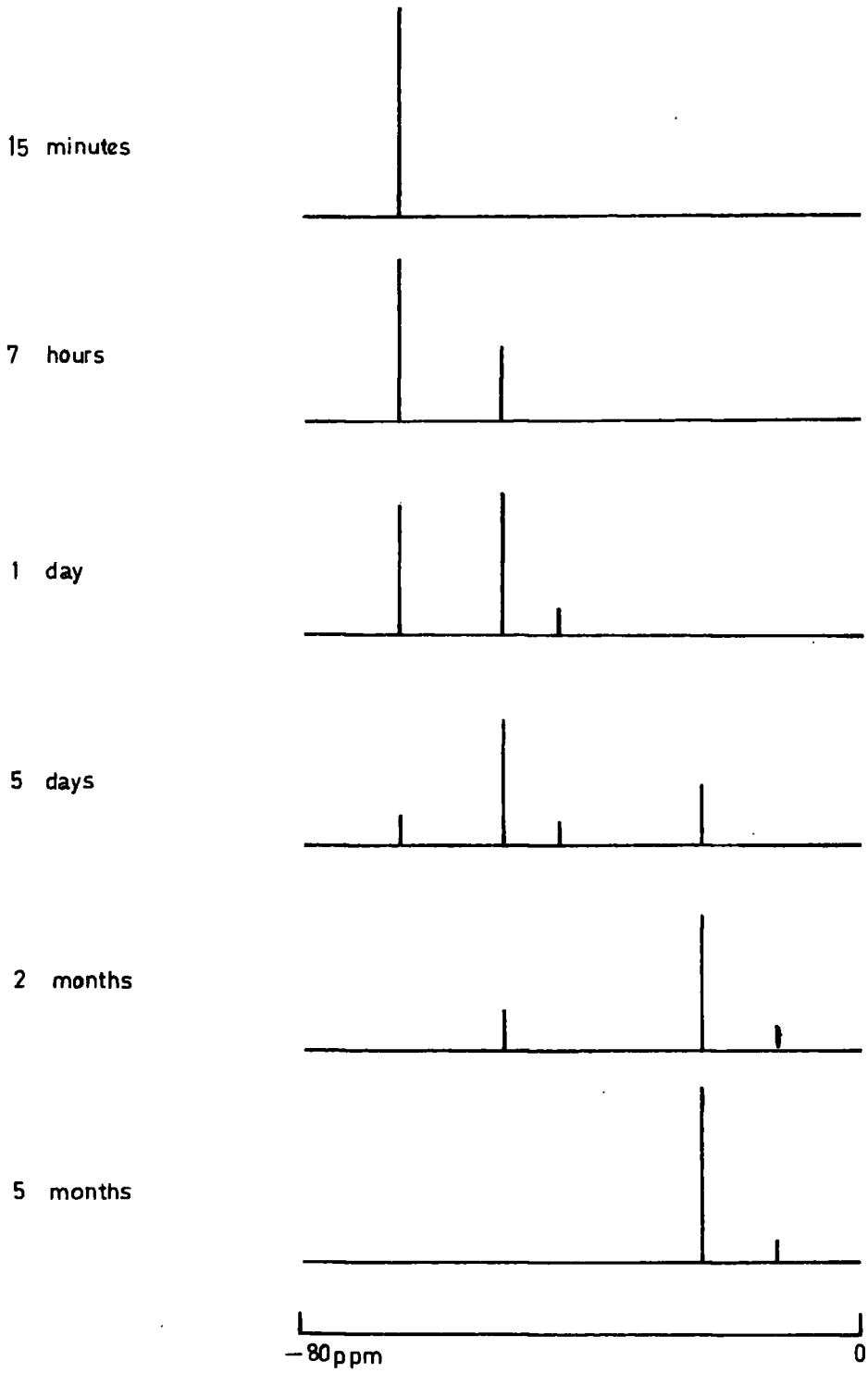
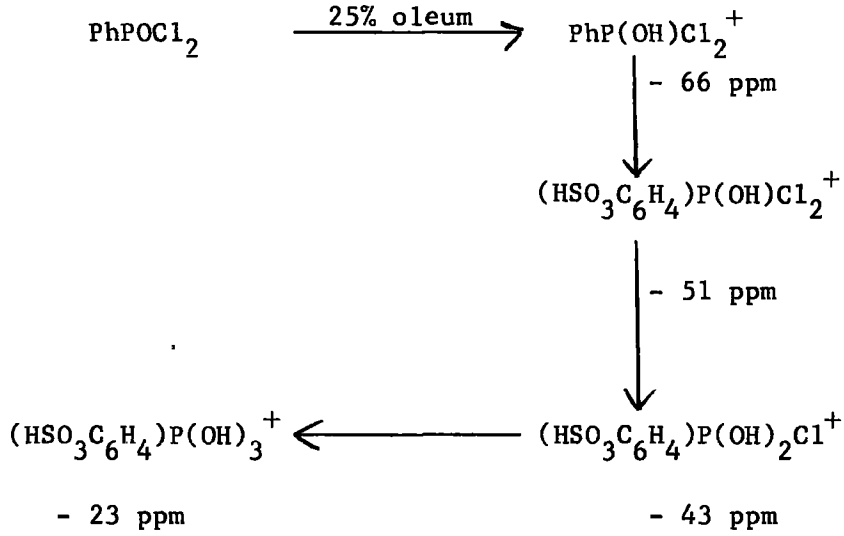


Figure 20

Relative peak heights for the ^{31}P n.m.r. spectrum of phenylphosphonic dichloride in 25% oleum.

In the 25% oleum solution, the appearence of a strong signal at - 23 ppm as the final product suggests that $PhPOCl_2$ dissolves in 25% oleum with protonation of the phosphoryl oxygen. This is followed by sulphonation and solvolysis to yield $(HSO_3C_6H_4)P(OH)_3^+$, since the signal at - 23 ppm agrees well with the final signal found for $PhPO(OH)_2$ in 25% oleum, assigned to the protonated-sulphonated parent. Since no signal assignable to $PhP(OH)_3^+$ is present and the rate of solvolysis is expected to be even slower in 25% oleum than in 100% H_2SO_4, a reasonable peak assignment and reaction sequence consistent with the observed intensity pattern with time is



The weak signal found at - 12 ppm probably arises from condensation equilibria of the $(HSO_3C_6H_4)P(OH)_3^+$ species, in a similar manner to the behaviour of phosphoric acid in oleum solutions.[71]

The downfield shift of the signal assigned to $PhP(OH)Cl_2^+$ from - 57 ppm in 100% H_2SO_4 to - 66 ppm in 25% oleum is probably due to

more extensive protonation of the weak base in the higher acid medium. $POCl_3$ acts as a weak base in highly acidic solvents (Chapter 3B section 2(iv)) whereas Ph_3PO is a much stronger base and appears to be completely protonated in 100% H_2SO_4.[18] Substitution of a phenyl group for a chlorine in $POCl_3$ is thus expected to increase the basicity of the phosphoryl oxygen, although a ^{31}P n.m.r. shift of - 41.1 ppm for $PhPOCl_2$ in liquid HCl[13] shows that it is a fairly weak base. The assignment of the - 66 ppm peak to $PhP(OH)_2Cl^+$ thus appears entirely reasonable. The peaks at - 51 and - 43 ppm have been assigned to $(HSO_3C_6H_4)P(OH)Cl_2^+$ and $(HSO_3C_6H_4)P(OH)_2Cl^+$, the shifts being consistent with sulphonation and solvolysis respectively.

In view of the results for $PhPOCl_2$ in 100% H_2SO_4 and 25% oleum which suggest that sulphonation is much more rapid than solvolysis, a reasonable peak assignment for the single peak found at - 70 ppm in the 65% oleum solution is to $(HSO_3C_6H_4)P(OH)Cl_2^+$. Rapid sulphonation of $PhP(OH)Cl_2^+$ in 65% oleum, which is a strong sulphonating medium, would be expected. Although removal of SO_3 from the solvent will reduce its acid strength, the 65% oleum solution showed no signs of solvolysis. The movement of the peak assigned to $(HSO_3C_6H_4)P(OH)Cl_2^+$ from - 51 ppm in 25% oleum to - 70 ppm in 65% oleum is consistent with increased protonation of a weakly basic phosphoryl oxygen by a stronger acid medium.

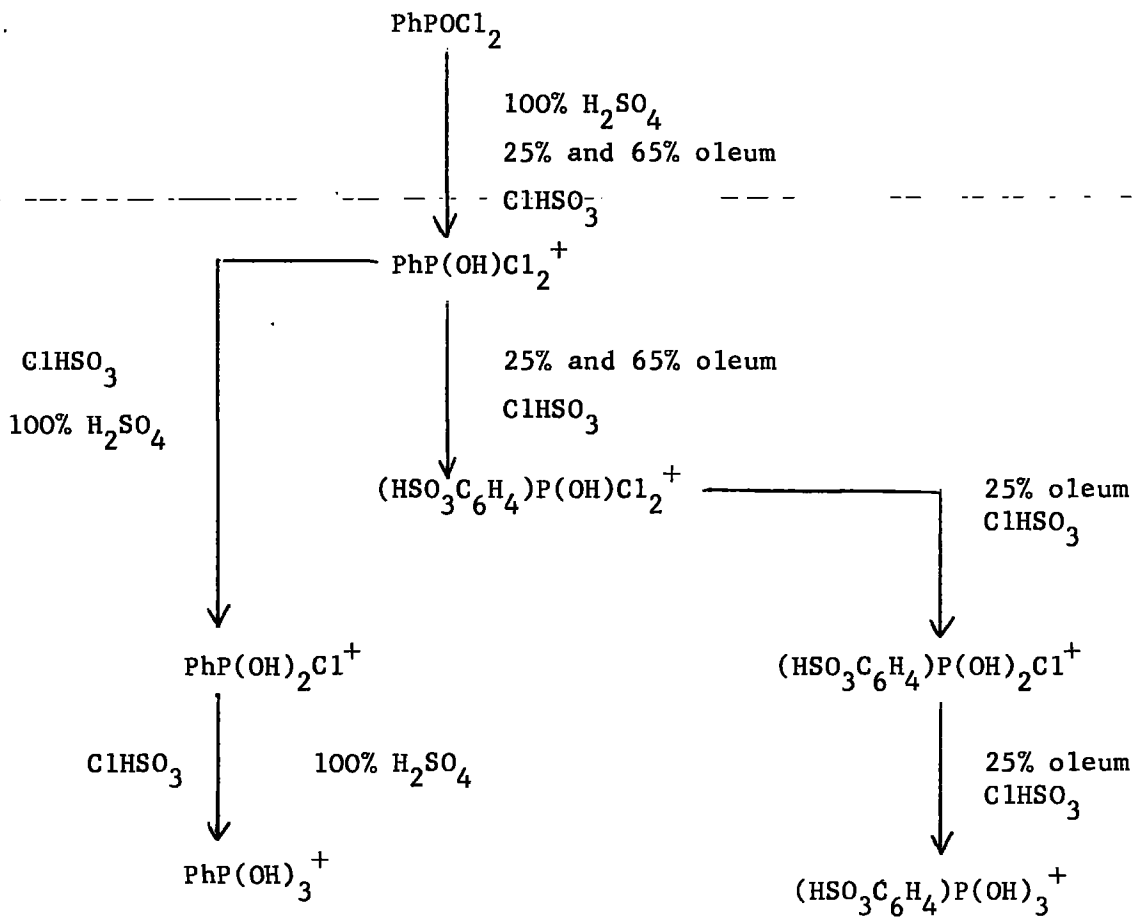
The $ClHSO_3$ solution of $PhPOCl_2$ showed a very slow reaction. The initial peak at - 68 ppm is in good agreement with the peak assigned to $PhP(OH)Cl_2^+$ in 25% oleum and a similar assignment is proposed. The signals at - 32 ppm and - 27 ppm agree well with signals found for $PhPO(OH)_2$ in $ClHSO_3$, assigned to $PhP(OH)_3^+$ and $(HSO_3C_6H_4)P(OH)_3^+$ respectively. The appearence of these species in the solution is consistent with slow competing reactions of sulphonation and solvolysis.

The signal at - 49 ppm occurs with the peak at - 32 ppm after one month of reaction and since the latter is due to $PhP(OH)_3^+$, it is reasonable to attribute the - 49 ppm peak to $PhP(OH)_2Cl^+$. These assignments are supported by the results from $PhPOCl_2$ in 100% H_2SO_4. The appearence of the peaks at -52 and - 27 ppm after $2\frac{1}{2}$ months suggests that the - 52 ppm species is sulphonated and lies in the reaction path between $PhP(OH)Cl_2^+$ and $(HSO_3C_6H_4)P(OH)_3^+$. Since the $PhP(OH)Cl_2^+$ is present in high concentration and sulphonation is slow in $ClHSO_3$, the most probable assignment for this peak is to $(HSO_3C_6H_4)P(OH)Cl_2^+$ rather than to $(HSO_3C_6H_4)P(OH)_2Cl^+$. The non-appearence of a signal from the latter species is probably because it never forms in a high enough concentration to be detected. The assignment of the - 52 ppm peak to $(HSO_3C_6H_4)P(OH)Cl_2^+$ is consistent with the data from the 25% oleum solution.

Results for $PhPOCl_2$ in $ClHSO_3$, 25% oleum and 100% H_2SO_4 thus indicate that solvolysis of the P-Cl bonds in both the sulphonated and non-sulphonated species is possible. It is difficult to compare the rates of solvolysis since in 25% oleum the acid strength must have been much reduced by the initial extensive sulphonation while in $ClHSO_3$ the slow sulphonation only reduces the acid strength gradually. The rate of solvolysis in 100% H_2SO_4 where no complications arise appears to be quite slow. The reaction sequences can be summarized as set out overleaf. The results of sections 2(i) and 2(ii) may be summarized in terms of shift variations.

		Chemical shift ppm
$PhP(OH)_3^+$	Parent	- 27 to - 33
	Monosulphonated	- 13 to - 27
$PhP(OH)_2Cl^+$	Parent	- 49 to - 52
	Monosulphonated	- 41 to - 46
$PhP(OH)Cl_2^+$	Parent	- 57 to - 74
	Monosulphonated	- 52 to - 63

The variations in peak position given on page **126** are due to the effects of acid strength as already discussed.



(iii) Phenyl phosphonic monochloride

In sections 2(i) and 2(ii) of this chapter the species $PhP(OH)_2Cl^+$ and $(HSO_3C_6H_4)P(OH)_2Cl^+$ have been proposed as intermediates in the solvolysis of $PhPOCl_2$, as well as in the reaction of $PhPO(OH)_2$ with $ClHSO_3$. Possible modes of preparation of the compound PhPO(OH)Cl were therefore investigated, to try to obtain some unequivocal data in support of the proposed assignments.

Since PhPO(OH)Cl is derived from $PO(OH)Cl_2$ by replacement of a chlorine by phenyl, the preparation of PhPO(OH)Cl was attempted by a similar route to that used previously for $PO(OH)Cl_2$.[92] Anhydrous $PO(OH)Cl_2$ has been prepared from $POCl_3$ by hydrolysis in an ethereal medium at room temperature, or by reaction of $POCl_3$ and water at temperatures between 263 and 253 K.

$$POCl_3 + H_2O \longrightarrow PO(OH)Cl_2 + HCl$$

Sample A $PhPOCl_2 + H_2O$ 1:1 neat.

Addition of water to liquid $PhPOCl_2$ at 253 K under an atmosphere of nitrogen caused no reaction, and the two liquids appeared immiscible. After stirring for one hour at 253 K a homogeneous solution was obtained and the temperature was allowed to rise to room temperature. After standing at this temperature for approximately one hour a slow evolution of gas was observed from the liquid and the solution was then left to stir overnight. The product of the reaction was a colourless glue-like substance. ^{31}P n.m.r. data on this sample prompted the following experiment.

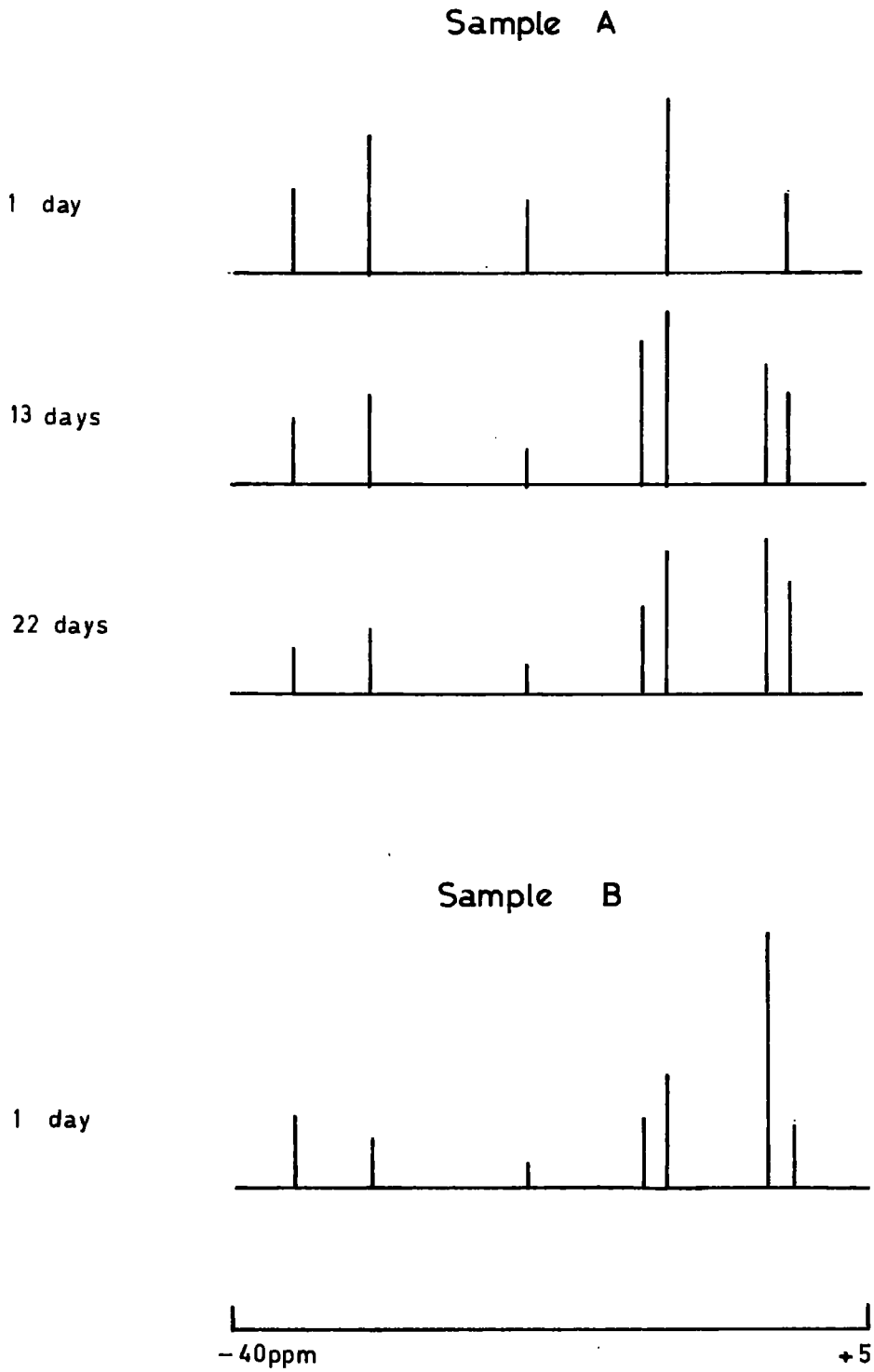


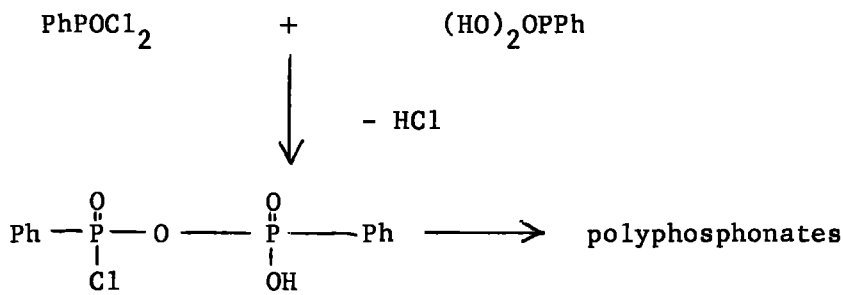
Figure 21

Relative peak heights for the ^{31}P n.m.r. spectra of Samples A and B in CH_2ClCH_2Cl.

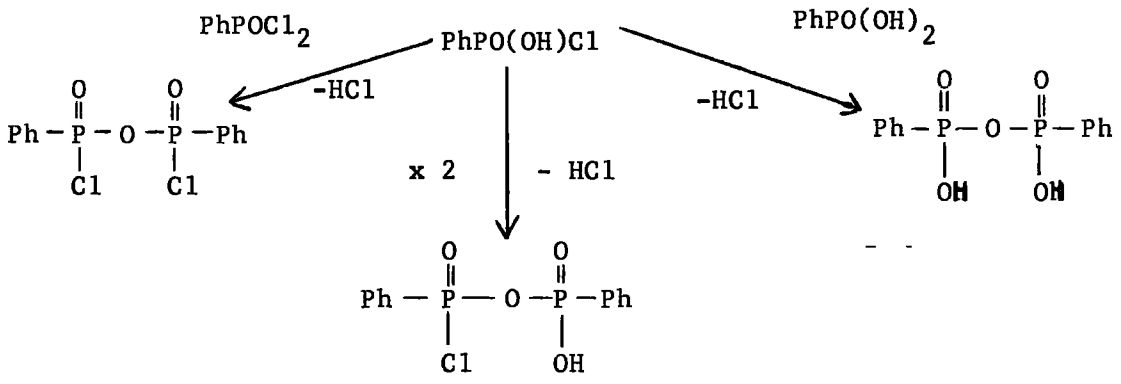
Sample B $PhPOCl_2$ + H_2O 1:1 in Et_2O

Addition of water to a solution of $PhPOCl_2$ in diethyl ether at 233 K under an atmosphere of nitrogen produced no reaction, except that the water turned to ice. The mixture was stirred for 30 minutes and then allowed to warm up to 253 K over which time the water dissolved in the reaction medium. The solution was allowed to warm to room temperature and left to stir overnight. The product of the reaction was a sticky white solid which precipitated from the ethereal solution.

Portions of Samples A and B were dissolved in CH_2ClCH_2Cl and their ^{31}P n.m.r. spectra were investigated. The results are shown diagramatically in Figure 21. The complex pattern in these spectra is not difficult to interpret. In Sample A the initial peaks at - 36 and - 20 ppm are immediately attributable to $PhPOCl_2$ and $PhPO(OH)_2$ respectively.[4] Hence it is reasonable to assign the - 30 ppm signal to PhPO(OH)Cl which is expected to lie at an intermediate position. The peaks found in the region - 12 to 0 ppm are understandable in view of the work of Grant et al,[93] who investigated the products formed by volatilization of HCl from mixtures of $PhPOCl_2$ with $PhPO(OH)_2$ at 338 K. Their results were interpreted as elimination of HCl from the system with consequent formation of polyphosphonates, by reactions of the form



Since these reactions were carried out at 338 K, the condensation was quite rapid. The following reactions seem plausible in the present system

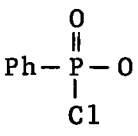


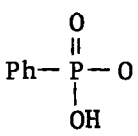
Further condensation is possible but because of the temperature difference it is not expected to be rapid. This is supported by the changes in the spectrum with time. The following initial reaction scheme is proposed.

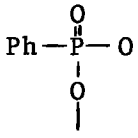
$$PhPOCl_2 \xrightarrow{H_2O} PhPO(OH)Cl \xrightarrow{H_2O} PhPO(OH)_2$$

- 36 ppm - 30 ppm - 20 ppm

followed by reaction between these monophosphorus species producing condensed phases by HCl elimination. The possible units in the polymeric species are given below with tentative shift assignments.


end unit - 12 ppm


end unit - 10 ppm


ring unit 0 ppm

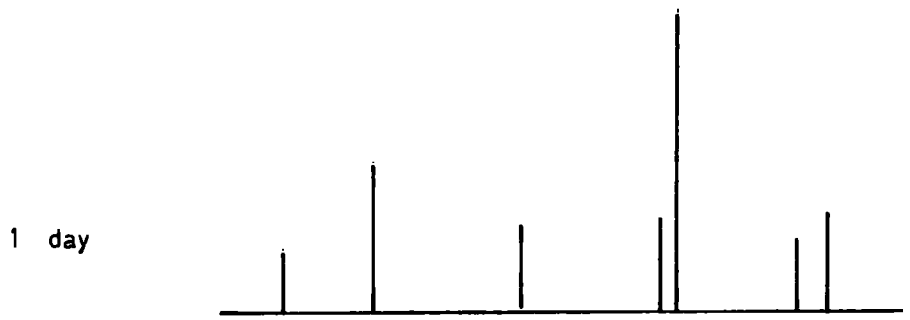
chain unit -2 ppm

Since the condensation has not been forced to completion, the parent monomers are still present in Samples A and B. The various building units are expected to show slightly different shifts depending on the other units to which they are attached. Evidence from other phosphate systems[4] suggests that this effect is quite small, however. It is thus not unreasonable to assign the signals in the - 12 to 0 ppm region as shown, but it must be emphasized that the assignment is tentative. No evidence for P-O-P coupling was found in these samples. If the units making up a condensed phase are such that the phosphorus atoms are non-equivalent, multiplet signals would be expected. The usual size of the P-O-P coupling constant is approximately 20 Hz.[4] If the tentative assignment of the highfield peaks is correct and they are really composite peaks from a number of species, observation of spin-spin coupling would be very difficult. Possible interaction between the phenyl protons and the phosphorus will also tend to complicate the spectrum and these two effects together may well mask the presence of any multiplet splitting.

The data for both Samples A and B is consistent with this explanation. The continuing reaction of Sample A suggests that the process is slow in this medium whereas the sample obtained from the ethereal solution appeared to react more rapidly. The results in these two systems suggests that although PhPO(OH)Cl is formed in quite high amounts, it is unstable to condensation reactions with elimination of HCl.

In an attempt to produce a 'cleaner' product it was decided to attempt the preparation of PhPO(OH)Cl from $PhPO(OH)_2$ and a chlorinating

Sample C



Sample D

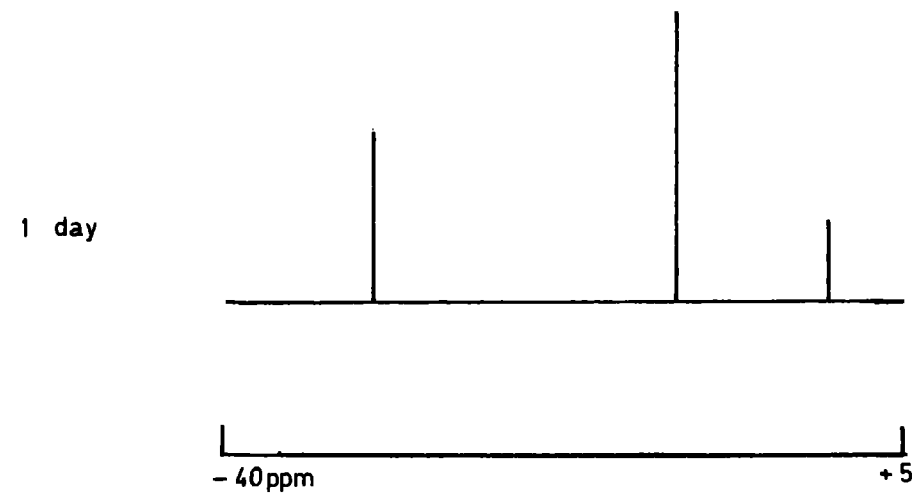


Figure 22

Relative peak heights for the ^{31}P n.m.r. spectra of Samples C and D in CH_2ClCH_2Cl.

agent. Thionyl chloride was chosen as a suitable source of the chlorine since the by-products formed are volatile and will hence be easily removed from the system. It was hoped that reaction would proceed as follows

$$PhPO(OH)_2 + SOCl_2 \longrightarrow PhPO(OH)Cl + SO_2 + HCl$$

Sample C $PhPO(OH)_2 + SOCl_2$ 1:1 neat

Solid $PhPO(OH)_2$ was mixed under an atmosphere of nitrogen with the required amount of liquid $SOCl_2$. No apparent reaction occurred so the mixture was heated at 323 K. After 20 minutes a gas was evolved and $PhPO(OH)_2$ dissolved in the liquid to give a yellow solution. The vessel was maintained at this temperature overnight until gaseous evolution ceased. On cooling to room temperature a brown sticky glue was formed. ^{31}P n.m.r. investigation of this substance prompted the following experiment.

Sample D $PhPO(OH)_2 + SOCl_2$ 1:1 neat

Solid $PhPO(OH)_2$ was mixed under a nitrogen atmosphere with $SOCl_2$. The mixture was warmed to 313 K and after the initial brisk evolution of gas the resulting pale yellow liquid was cooled to room temperature.

Portions of Samples C and D were dissolved in CH_2ClCH_2Cl and their ^{31}P n.m.r. spectra were investigated. The results are shown diagramatically in Figure 22. The results for Sample C are similar to the results obtained from Samples A and B discussed previously and

a probable peak assignment is thus

$PhPOCl_2$	$PhPO(OH)Cl$	$PhPO(OH)_2$	condensed units
- 36 ppm[4]	- 29 ppm	- 19 ppm[4]	- 11 to 0 ppm

The results for Sample D are much more interesting since from the assignments made previously, the species present are

$PhPO(OH)Cl$	PhP(O) - O - OH	PhP(O) - O - O
- 29 ppm	- 10 ppm	0 ppm

This simplicity and absence of $PhPOCl_2$ and $PhPO(OH)_2$ found in the other spectra indicates that the less forcing conditions used to prepare Sample D have given a 'cleaner' product. The intensity of the - 10 ppm peak in Sample D suggests that previously unreacted $PhPO(OH)_2$ reacts with $PhPO(OH)Cl$ formed to produce a polymeric species. The presence of $PhPOCl_2$ in Sample C along with $PhPO(OH)Cl$ and $PhPO(OH)_2$ confirms that the more forcing conditions used in this case caused less selective chlorination. It thus appears that although $PhPO(OH)Cl$ can be prepared quite readily, the presence of P-Cl and P-OH groups in the molecule leads to condensation reactions with other species in the system.

In an attempt to obtain some data to support assignments made in sections 2(i) and 2(ii) of this chapter, portions of Samples A and D were dissolved in 100% H_2SO_4 and $ClHSO_3$, and the results compared with data for $PhPOCl_2$ and $PhPO(OH)_2$ in the same solvents.

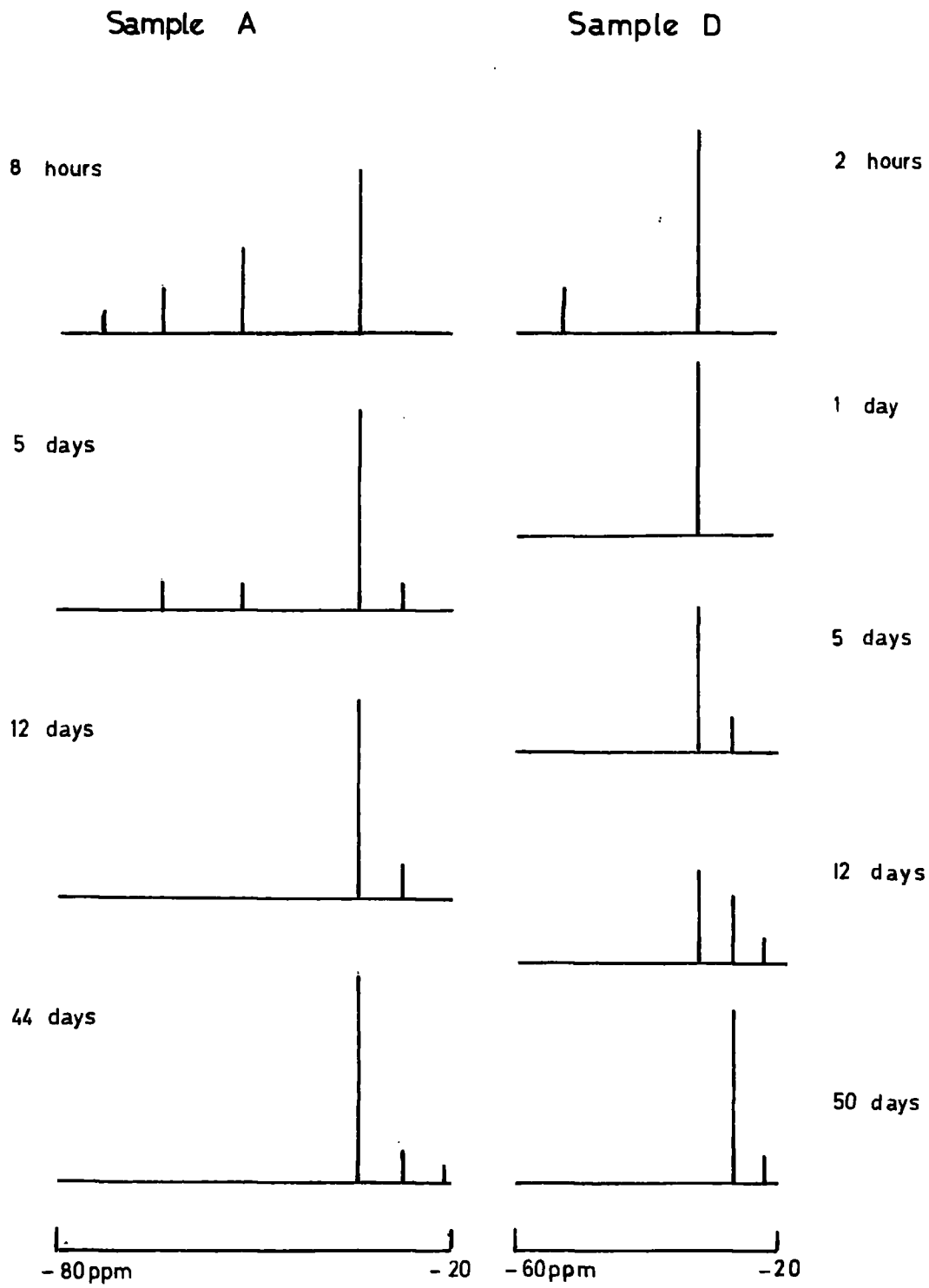


Figure 23

Relative peak heights for the ^{31}P n.m.r. spectra of Samples A and D in 100% sulphuric acid.

Samples A and D dissolved in both 100% H_2SO_4 and $ClHSO_3$ without any obvious reaction to yield clear solutions. The solutions darkened considerably with time, the $ClHSO_3$ solutions more rapidly than the 100% H_2SO_4 solutions. Diagramatic representations of the spectra are given in Figures 23 and 24. The assignments of the signals is quite facile if the shift data (Table 16) is compared with that obtained in sections 2(i) and 2(ii) of this chapter.

These results when compared with the ^{31}P n.m.r. spectra obtained for samples A and D in CH_2ClCH_2Cl indicate that solution of the condensed phases in 100% H_2SO_4 and $ClHSO_3$ is accompanied by rupture of the P-O-P bonds to give monophosphorus species.[71] Protonation of the phosphoryl groups then gives signals comparable with those from $PhPOCl_2$ and $PhPO(OH)_2$ in these acids. The low values of the shifts obtained for most species are reasonable since degradation of the solvent in opening up the P-O-P bonds will increase the acid strength, as shown by the following equations

$$\text{P-O-P} + H_2SO_4 \longrightarrow \text{P-OH} + \text{HO-P} + SO_3$$

$$\text{P-O-P} + ClHSO_3 \longrightarrow \text{P-OH} + \text{Cl-P} + SO_3$$

The results from Samples A and D are in agreement with such reactions and the production of SO_3 during this process is mirrored by the observed sulphonation. The good agreement between the shift values here and those from the solutions of $PhPOCl_2$ and $PhPO(OH)_2$ adds more weight to the assignments made.

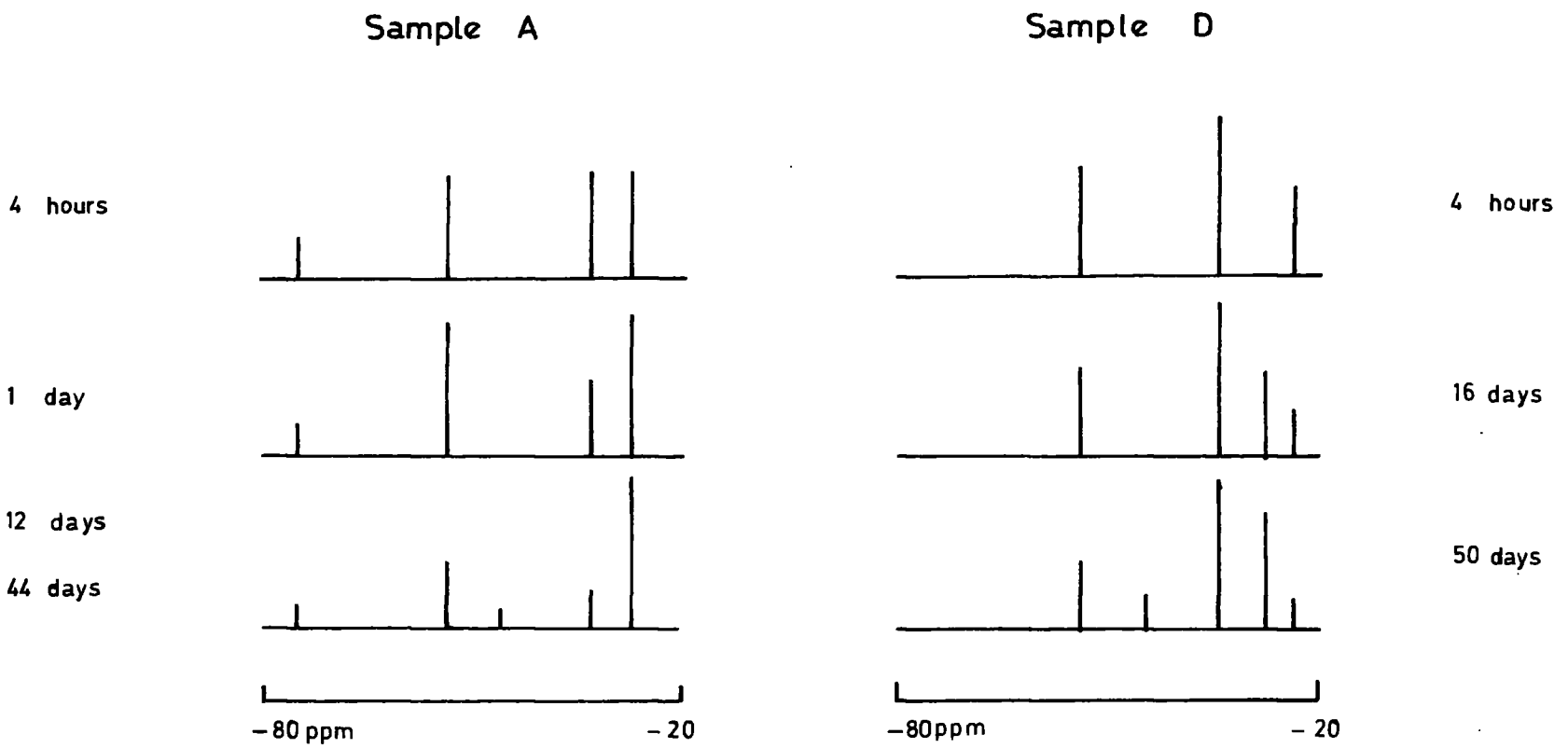


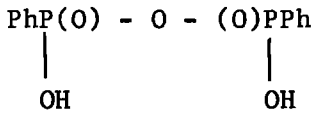
Figure 24

Relative peak heights for the ^{31}P n.m.r. spectra of Samples A and D in chlorosulphuric acid.

Table 16. ^{31}P n.m.r. chemical shift values (ppm) for samples A and D in 100% sulphuric acid and chlorosulphuric acid.

Sample A in 100% H_2SO_4	- 72	- 63	- 51		- 33	- 27	- 21
Sample A in $ClHSO_3$	- 75		- 53	- 46	- 33	- 27	
Sample D in 100% H_2SO_4			- 52		- 32	- 27	- 22
Sample D in $ClHSO_3$			- 52	- 44	- 33	- 27	- 23
Peak assignment with range quoted previously	$PhP(OH)Cl_2^+$ -57 to -74	Sulphonated $PhP(OH)Cl_2^+$ -52 to -63	$PhP(OH)_2Cl^+$ -49 to -52	Sulphonated $PhP(OH)_2Cl^+$ -41 to -46	$PhP(OH)_3^+$ -27 to -33	Sulphonated $PhP(OH)_3^+$ -13 to -27	?

The only signal so far unassigned in the acid solutions of Samples A and D is the one at approximately - 22 ppm. The high initial concentration of this species in the solution of Sample D in $ClHSO_3$ and its subsequent disappearence indicates that it probably arises from a condensed species. The comparatively simple spectrum of Sample D in CH_2ClCH_2Cl with only one strong signal in a position for a condensed product suggests that the - 22 ppm peak may be due to a protonated form of the species



which would cleave in $ClHSO_3$ to $PhP(OH)_2Cl^+$ and $PhP(OH)_3^+$. Such an assignment agrees with the -10 ppm resonance in the original solution being due to  units. The presence of the same peak in later stages of the two other systems can be explained by the increase in acid strength during the cleavage reaction leading to condensation of $PhP(OH)_3^+$.[71]

Despite the failure to prepare pure PhPO(OH)Cl which may well be intrinsically unstable, the results gained do support the postulated appearance of the protonated compound as an intermediate in solvolysis reactions of $PhP(OH)Cl_2^+$.

(iv) Diphenyl phosphinic acid

The white solid $Ph_2PO(OH)$ dissolved in 100% H_2SO_4, 25% and 65% oleum, and $ClHSO_3$ on shaking with little obvious reaction. The

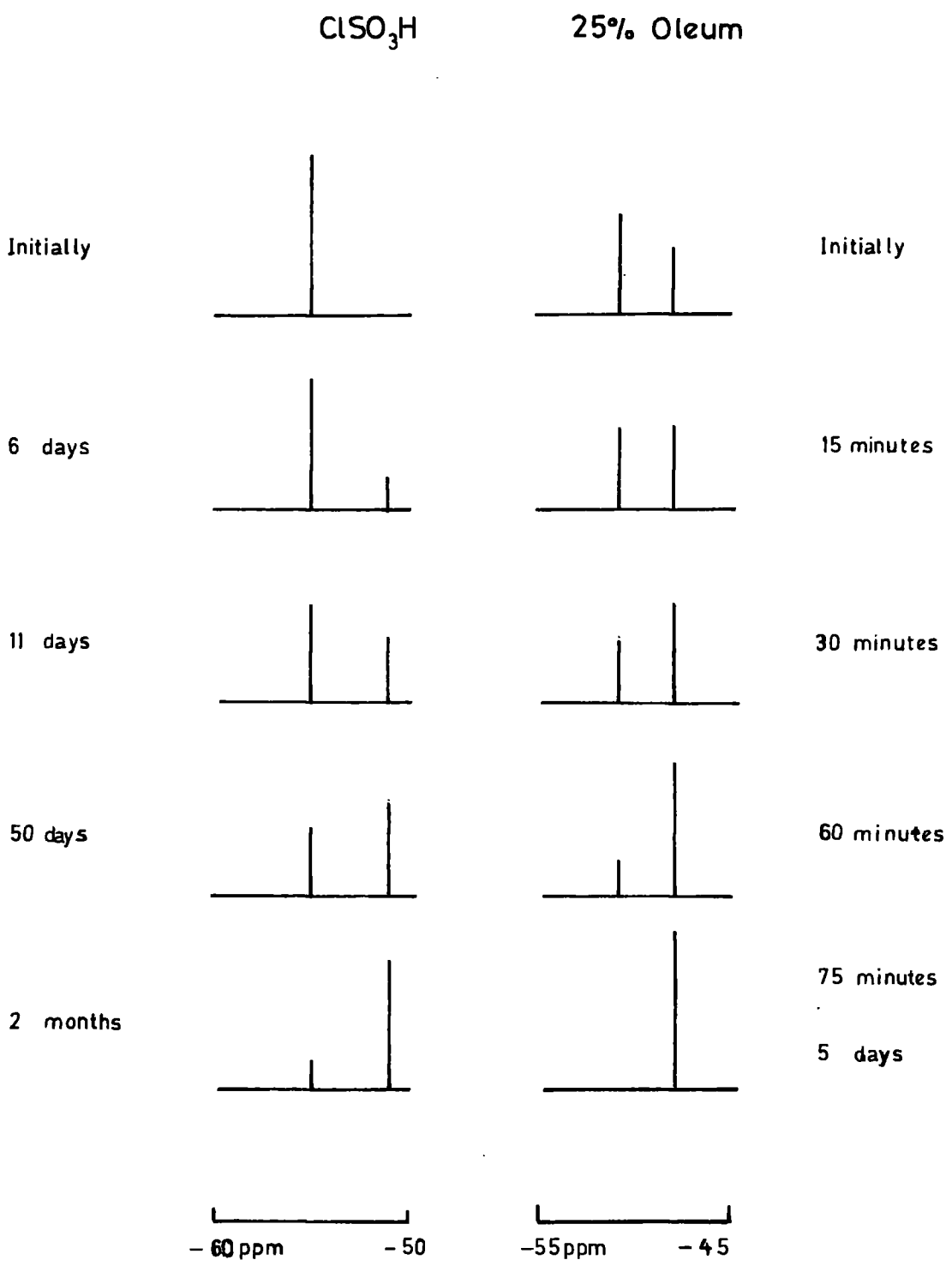


Figure 25

Relative peak heights for the ^{31}P n.m.r. spectra of diphenyl phosphinic acid in acidic solvents.

100% H_2SO_4 solution was a pale brown while the 25% and 65% oleum solutions were a much darker brown. The $ClHSO_3$ solution was initially pale brown but darkened slowly on standing over a period of 2 months.

^{31}P n.m.r. spectra of the solutions in 100% H_2SO_4 and 65% oleum showed single peaks at - 54 and - 48 ppm respectively. No change in these spectra were found after 6 days. The solutions in $ClHSO_3$ and 25% oleum showed rather more complex patterns as shown in Figure 25. The darkening of the $ClHSO_3$ solution and the ^{31}P n.m.r. data are consistent with a slow reaction, while the rapid darkening of the 25% and 65% oleum solutions agrees with the rather more rapid reaction shown by the n.m.r. results. The pale colour of the 100% H_2SO_4 solution agrees with the apparent lack of reaction of $Ph_2P(OH)_2^+$ in this medium.

In section 2(i) of this chapter, $PhPO(OH)_2$ was shown to dissolve in these acids with protonation of the phosphoryl oxygen, and in the higher strength acids, sulphonation of the phenyl ring. If the same reaction path is followed by $Ph_2PO(OH)$, species of the type $Ph_2P(OH)_2^+$, $Ph(HSO_3C_6H_4)P(OH)_2^+$ and $(HSO_3C_6H_4)_2P(OH)_2^+$ are expected. The data for $PhPO(OH)_2$ suggests that it dissolves in 100% H_2SO_4 with protonation of the phosphoryl oxygen only and no sulphonation, while solution in 65% oleum causes protonation and rapid sulphonation. The single peaks found in the $Ph_2PO(OH)$ solutions in 100% H_2SO_4 and 65% oleum at - 54 ppm and - 48 ppm may be reasonably assigned to the species

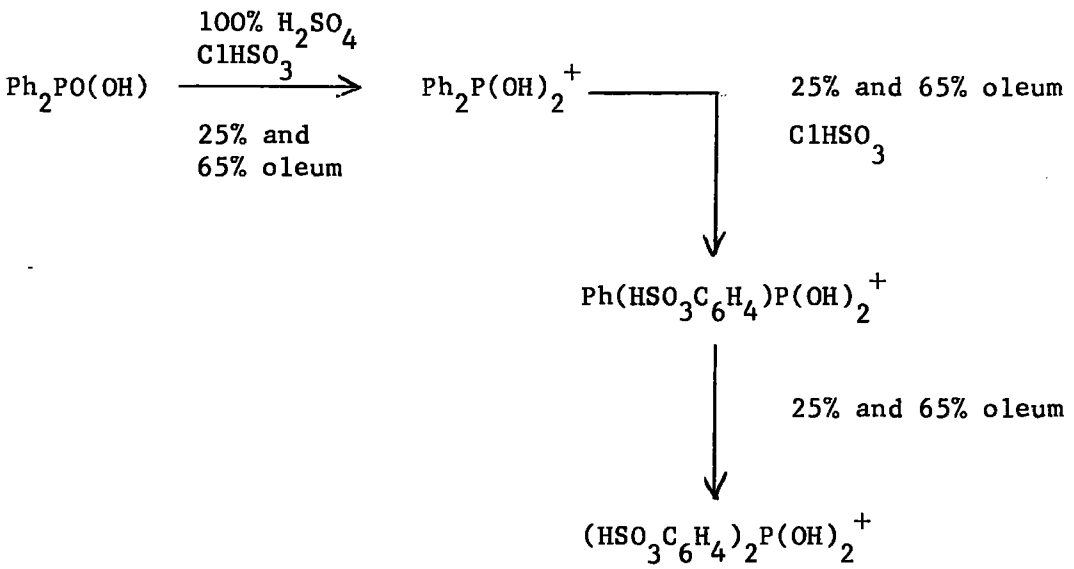
$Ph_2P(OH)_2^+$	$(HSO_3C_6H_4)_2P(OH)_2^+$
- 54 ppm	- 48 ppm

The upfield shift on sulphonation parallels that found for sulphonation of $PhPO(OH)_2$ while the shift from - 25 ppm for the

parent $Ph_2PO(OH)$ is consistent with protonation of the phosphoryl oxygen. Since sulphonation of $PhPO(OH)_2$ in $ClHSO_3$ was found to be slow, the initial peak at - 55 ppm for $Ph_2PO(OH)$ in $ClHSO_3$ may be reasonably assigned to the protonated acid while the slow appearence of an upfield peak at - 51 ppm is consistent with sulphonation. The rapid appearance of a signal at - 48 ppm in the 25% oleum solution of $Ph_2PO(OH)$ and no further reaction suggests that this signal is due to $(HSO_3C_6H_4)_2P(OH)_2^+$ which is expected to form in this strongly sulphonating medium. The lower field signal at - 51 ppm is almost certainly due to the monosulphonated species. The - 51 ppm peak in both $ClHSO_3$ and 25% oleum may be reasonably assigned to the intermediate species $Ph(HSO_3C_6H_4)P(OH)_2^+$. This assignment agrees with the differing rates of sulphonation in $ClHSO_3$ and 25% oleum. In 25% oleum complete sulphonation appeared to have occurred in approximately $1\frac{1}{2}$ hours, so the lack of a signal from $Ph_2P(OH)_2^+$ in this medium is probably because of rapid initial sulphonation. The appearance of the - 51 ppm peak in $ClHSO_3$ over a period of 2 months shows how slow the sulphonation process is in this solvent, and under these circumstances the non-observation of a peak for $(HSO_3C_6H_4)_2P(OH)_2^+$ is understandable.

The results from $Ph_2PO(OH)$ are in general agreement with the data obtained for $PhPO(OH)_2$, with protonation causing a downfield shift and sulphonation an upfield shift. The interesting difference in the $Ph_2PO(OH)$ systems is the apparent constancy of the ^{31}P n.m.r. shifts of the different protonated species, whereas similar ions derived from $PhPO(OH)_2$ showed a marked shift dependence on acid strength consistent with their taking part in condensation equilibria. Since there are only

two OH groups in the $Ph_2P(OH)_2^+$ ion and its sulphonated derivatives, condensation is less likely, and the lack of upfield movement of the resonances in higher acid media suggests that this reaction does not occur. The constancy of shift even in more highly acidic media probably indicates that the compound is fully protonated and that the phosphoryl oxygen is quite strongly basic. Since Ph_3PO and H_3PO_4 are both fully protonated in 100% H_2SO_4,[18] this behaviour of $Ph_2PO(OH)$ is not unexpected. The reaction sequence may be summarized as follows.



(v) Diphenyl phosphinic chloride

Solutions of Ph_2POCl were prepared in 100% H_2SO_4, 25% and 65% oleum, and $ClHSO_3$. The pale brown liquid dissolved immediately in 65% oleum but formed two layers with the other solvents. On shaking, however, complete solution occured with the evolution of heat. The 65% oleum solution was very dark brown while the other solutions were pale brown. On standing the 25% oleum and $ClHSO_3$ solutions darkened considerably, the former much more rapidly than the latter.

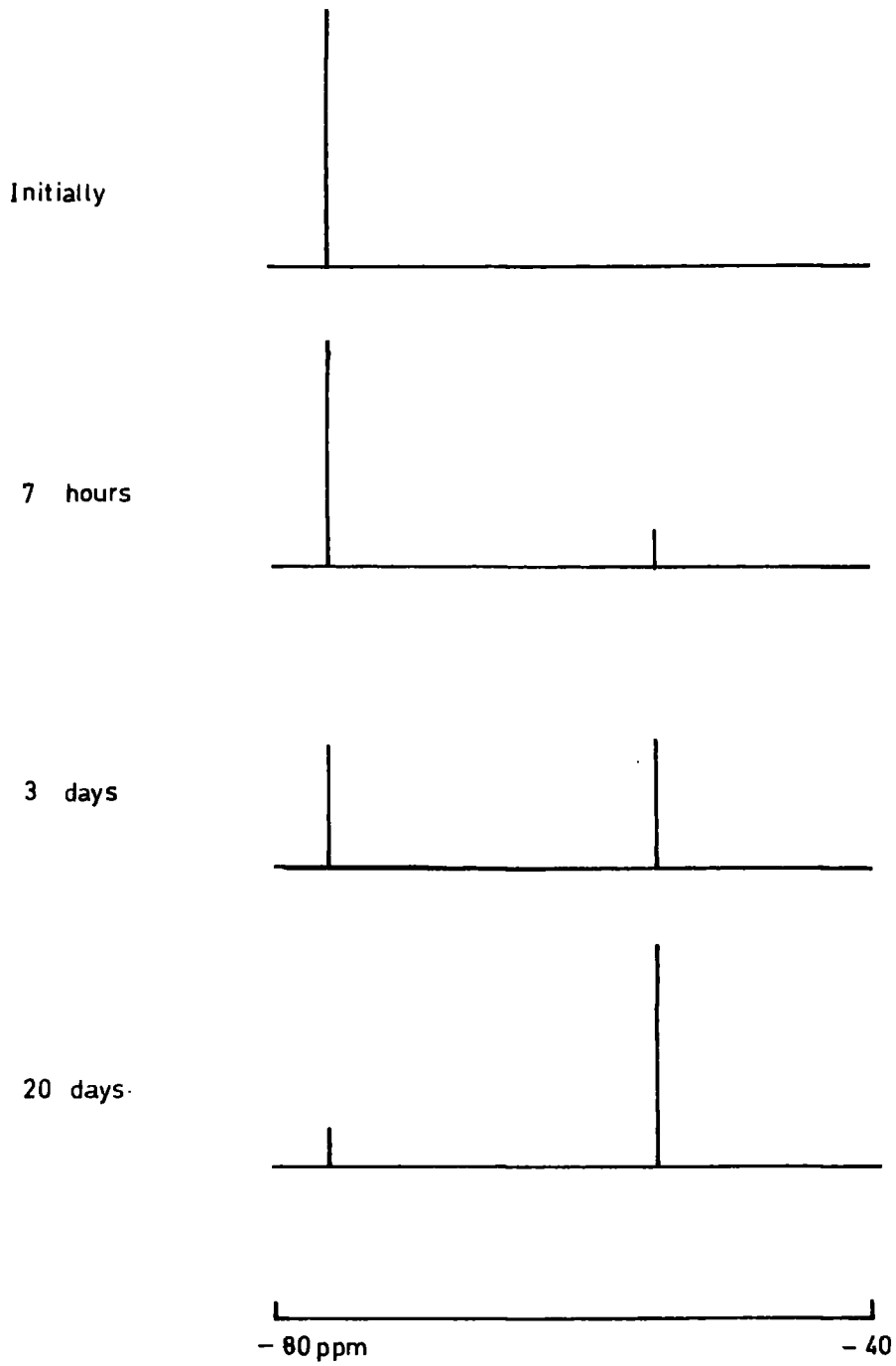


Figure 26

Relative peak heights for the ^{31}P n.m.r. spectrum of diphenyl phosphinic chloride in 100% sulphuric acid.

The ^{31}P n.m.r. spectra of the 65% oleum solution showed only one signal at - 70 ppm while the $ClHSO_3$ solution showed a single peak at - 76 ppm. No further signals were found in these two solutions after $1\frac{1}{2}$ months. The 25% oleum and 100% H_2SO_4 solutions both showed more complex signal patterns as shown diagramatically in Figures 26 and 27. In section 2(ii) of this chapter $PhPOCl_2$ was shown to dissolve in these acids with protonation of the phosphoryl oxygen. The subsequent reactions of $PhPOCl_2$ involved sulphonation of the phenyl ring and solvolysis of the P-Cl bonds, the exact path depending on the acid used. If the same types of reaction occur for Ph_2POCl, species of the form $Ph_2P(OH)Cl^+$, $Ph(HSO_3C_6H_4)P(OH)Cl^+$, and $(HSO_3C_6H_4)_2P(OH)Cl^+$ may be expected, as well as derivatives of $Ph_2P(OH)_2^+$ if solvolysis occurs.

The initial signal at - 76 ppm in the 100% H_2SO_4 solution for Ph_2POCl, which has a reported shift in the liquid phase of - 42. 7 ppm,[4] is consistent with protonation of the phosphoryl oxygen. The slow disappearance of this peak and its replacement by a signal at - 54 ppm suggests that slow solvolysis of the P-Cl bond occurs to yield $Ph_2P(OH)_2^+$ since the shift is in good agreement with that of protonated $Ph_2PO(OH)$ in 100% H_2SO_4.

The initial detection of a signal at - 76 ppm in the 25% oleum solution of Ph_2POCl and the appearance finally of a peak at - 47 ppm suggests that the phosphoryl oxygen is protonated to give $Ph_2P(OH)Cl^+$, which subsequently reacts by sulphonation and solvolysis to yield $(HSO_3C_6H_4)_2P(OH)_2^+$. The slowness of the solvolysis of Ph_2POCl in 100% H_2SO_4 coupled with the absence of signals from either $Ph_2P(OH)_2^+$ or its monosulphonated derivative suggests that sulphonation of

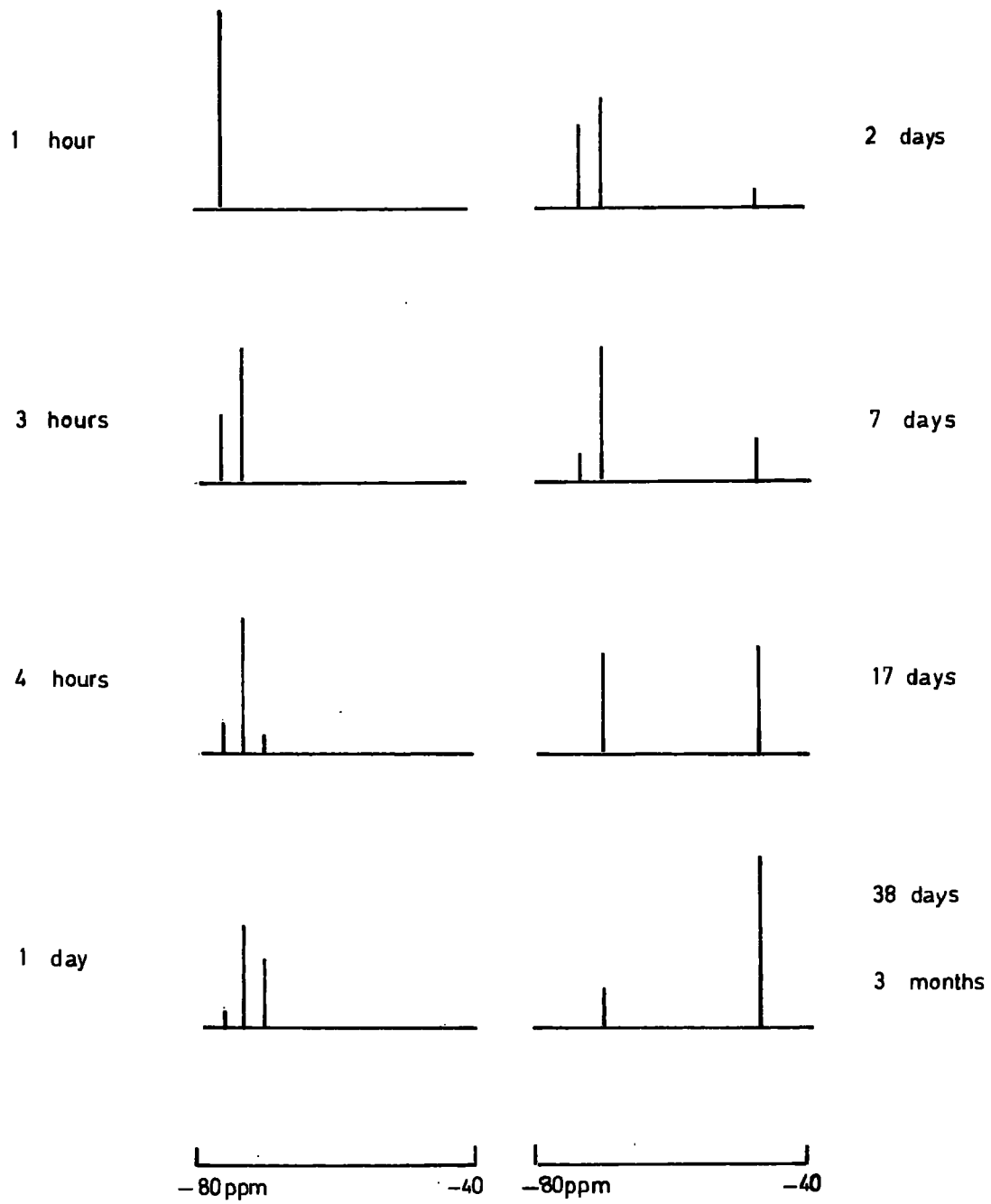
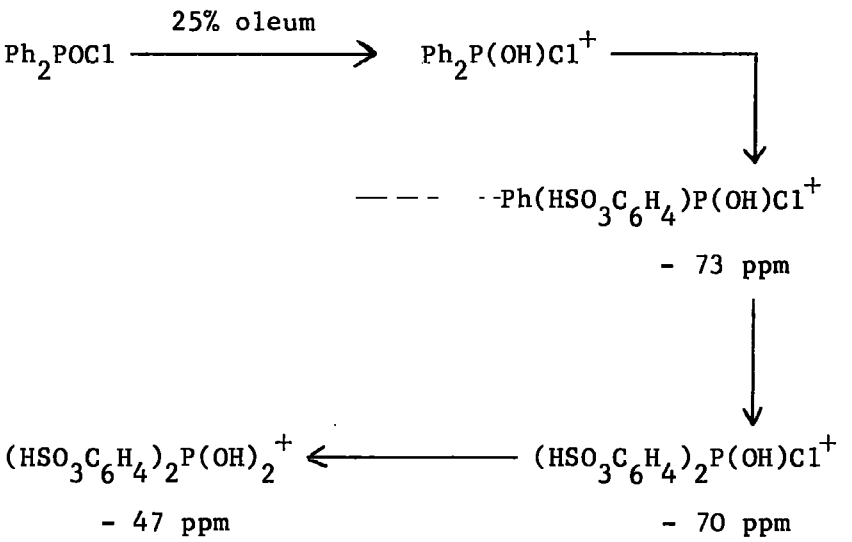


Figure 27

Relative peak heights for the ^{31}P n.m.r. spectrum of diphenyl phosphinic chloride in 25% oleum.

$Ph_2P(OH)Cl^+$ occurs prior to solvolysis. The shift data obtained is in agreement with this hypothesis and a reasonable reaction sequence based on shift position and intensity is as follows, solvolysis occurring when the acid strength has been reduced by sulphonation.

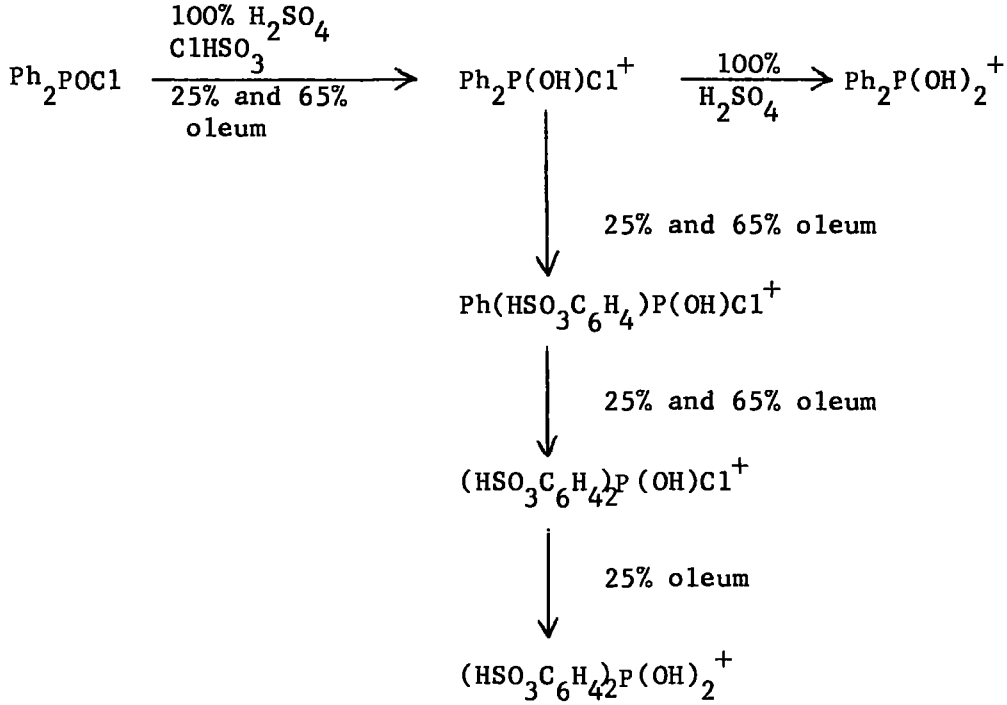


The peaks at - 76 and - 47 ppm are in good agreement with independent data, while the upfield shift on sulphonation of the protonated monochloride is consistent with previous results.

On the basis of these results, the single signals found in the $ClHSO_3$ and 65% oleum solutions are easily assignable. The - 76 ppm peak in $ClHSO_3$ is due to $Ph_2P(OH)Cl^+$, and agrees with the shift of this species in 100% H_2SO_4. The lack of sulphonation and solvolysis of this species with time is in agreement with the results from $PhPOCl_2$ in $ClHSO_3$ which showed little reaction of the protonated parent. The - 70 ppm peak in 65% oleum agrees in shift with the peak assigned to $(HSO_3C_6H_4)_2P(OH)Cl^+$ in 25% oleum. This assignment seems justifiable when the strength of 65% oleum as a sulphonating agent is considered. The lack of solvolysis is understandable since although the sulphonation reactions reduce the acid strength of the medium, the solution will still

be highly acidic. Even in 25% oleum, the solvolysis of the P-Cl bond was still quite slow after reduction of the acid strength by the initial sulphonation.

The apparent constancy of the ^{31}P n.m.r. shift for the various protonated species indicates that Ph_2POCl and its sulphonated derivatives are quite strong bases. This is not unexpected since Ph_3PO is a strong base in sulphuric acid[18] while $POCl_3$ acts as a weak base (Chapter 3B section 2(iv)). This increase in basicity on substitution of phenyl for chlorine in POX_3 compounds appears to be substantiated in the Ph_2POCl and $PhPOCl_2$ systems, $PhPOCl_2$ being a weaker base than Ph_2POCl, on the basis of ^{31}P n.m.r. shift data. The reaction sequences can be summarized as follows



(vi) Triphenyl phosphine oxide

The white solid Ph_3PO dissolved immediately with a vigorous reaction in 65% oleum to yield a dark brown solution. It dissolved more slowly on shaking to yield a pale yellow solution in 100% H_2SO_4 and pale brown

solutions in 25% oleum and $ClHSO_3$. The 25% oleum and $ClHSO_3$ solutions darkened considerably on standing.

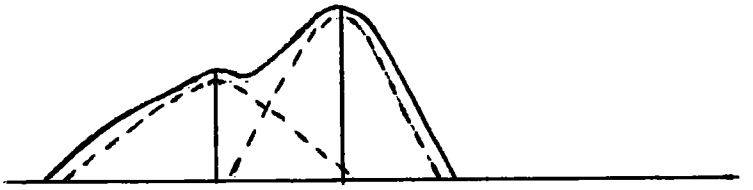
The ^{31}P n.m.r. spectra of the 100% H_2SO_4 and $ClHSO_3$ solutions showed only single peaks at - 58 and - 60 ppm respectively. The 25% oleum solutions showed initially a signal at - 59 ppm but over the period of 2 days this decreased in intensity and was replaced by a single resonance at - 56 ppm. In the 65% oleum solution, 15 minutes after preparation, two signals of equal intensity at - 64 and - 61 ppm could be seen. Over the next two hours the signal at - 64 ppm disappeared to be replaced by the signal at - 61 ppm. All four solutions were monitored over a period of 34 days and no further peaks were detected.

The results from 100% H_2SO_4 and $ClHSO_3$ are not difficult to interpret. Both these solvents appear to be poor sulphonating agents as shown by the data for Ph_2POX and $PhPOX_2$ species (X = Cl or OH). Since there are no solvolysable groups in the molecule these single peaks appear to be due to the Ph_3POH^+ species produced by protonation. This assignment is supported by cryoscopic and conductimetric work on solution of Ph_3PO in 100% H_2SO_4,[70] and conductimetric work in $FHSO_3$.[17] The n.m.r. shift parameters are in agreement with the results of Dillon and Waddington, who observed single peaks at - 60.5 and - 60.8 for 100% H_2SO_4 and $ClHSO_3$ respectively.[18] These results were all interpreted as formation of the completely protonated species Ph_3POH^+.

The spectra for 25% and 65% oleum show that solution of Ph_3PO in these solvents is accompanied by protonation to give Ph_3POH^+ as indicated by the signals at - 59 and - 64 ppm respectively. The quite rapid replacement of these peaks by upfield signals at - 56 and - 61 ppm, in the light of previous data on related species, must be due to sulphonation of the phenyl rings in the protonated parent. The speed of reaction to yield a single peak system stable over a long period of time suggests that complete sulphonation takes place,

$$Ph_3POH^+ \longrightarrow (HSO_3C_6H_4)_3POH^+$$

The lack of signals from the expected intermediates is unfortunate, but is readily explicable. A typical spectrum found in the 25% oleum solution is shown below



The broadness and overlapping of the peaks means that signals from the intermediates, which would be expected to have intermediate shifts, will not easily be detected. The rate of sulphonation is also such that the intermediate species are unlikely to be formed in very high concentrations, and their resonances would not be observed in the spectrum.

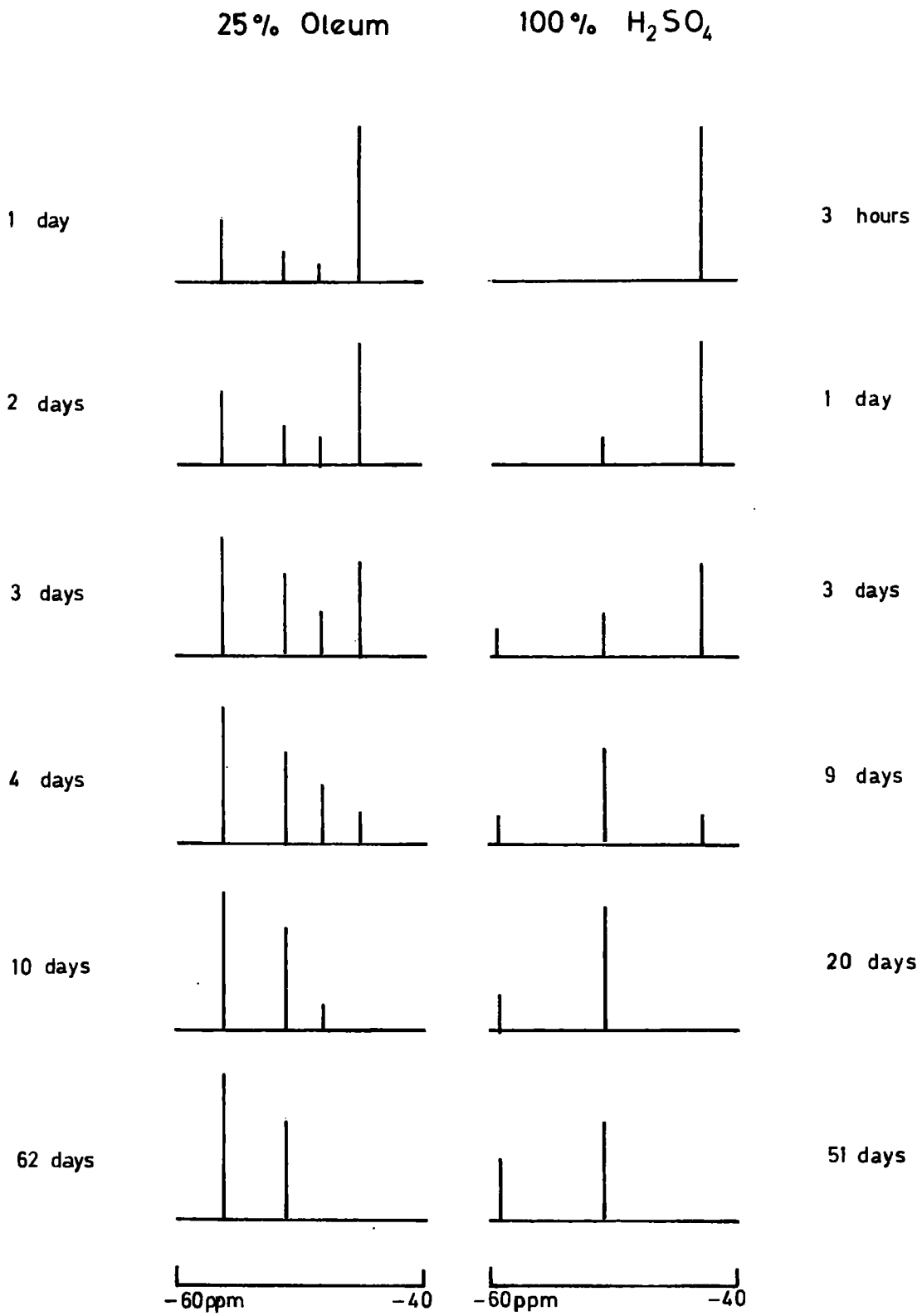
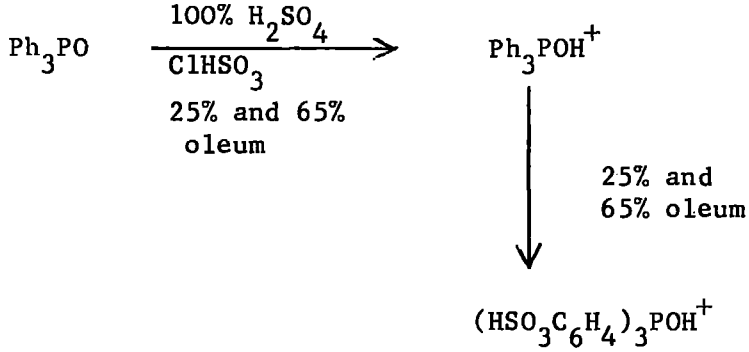


Figure 28

Relative peak heights for the ^{31}P n.m.r. spectra of triphenyl phosphine sulphide in acidic solvents.

The shifts show that the general upfield trend found on sulphonation of phenyl rings is followed, but that the upfield shift is quite small for Ph_3PO. The shift differences for the Ph_3POH^+ species in these solutions are all within 5 ppm of each other at around - 60 ppm compared with a shift of - 25 ppm for the parent.[4] These values show that Ph_3PO is a strong base and that protonation is essentially complete in these acid media. The reaction sequence can be summarized as follows,



(vii) Triphenyl phosphine sulphide

The white solid Ph_3PS dissolved in 65% oleum immediately with a vigorous reaction and the liberation of heat to yield a dark green solution. It dissolved more slowly on shaking to yield a yellow-orange solution in 100% H_2SO_4, and brown solution in 25% oleum and $ClHSO_3$. The 25% oleum and $ClHSO_3$ solutions both darkened on standing.

The ^{31}P n.m.r. spectra of these solutions were complex, and the results are shown diagramatically in Figures 28, 29. The spectra are all very similar and in general a common reaction path appears to be followed. Four main species are apparently present in the system as shown in Table 17.

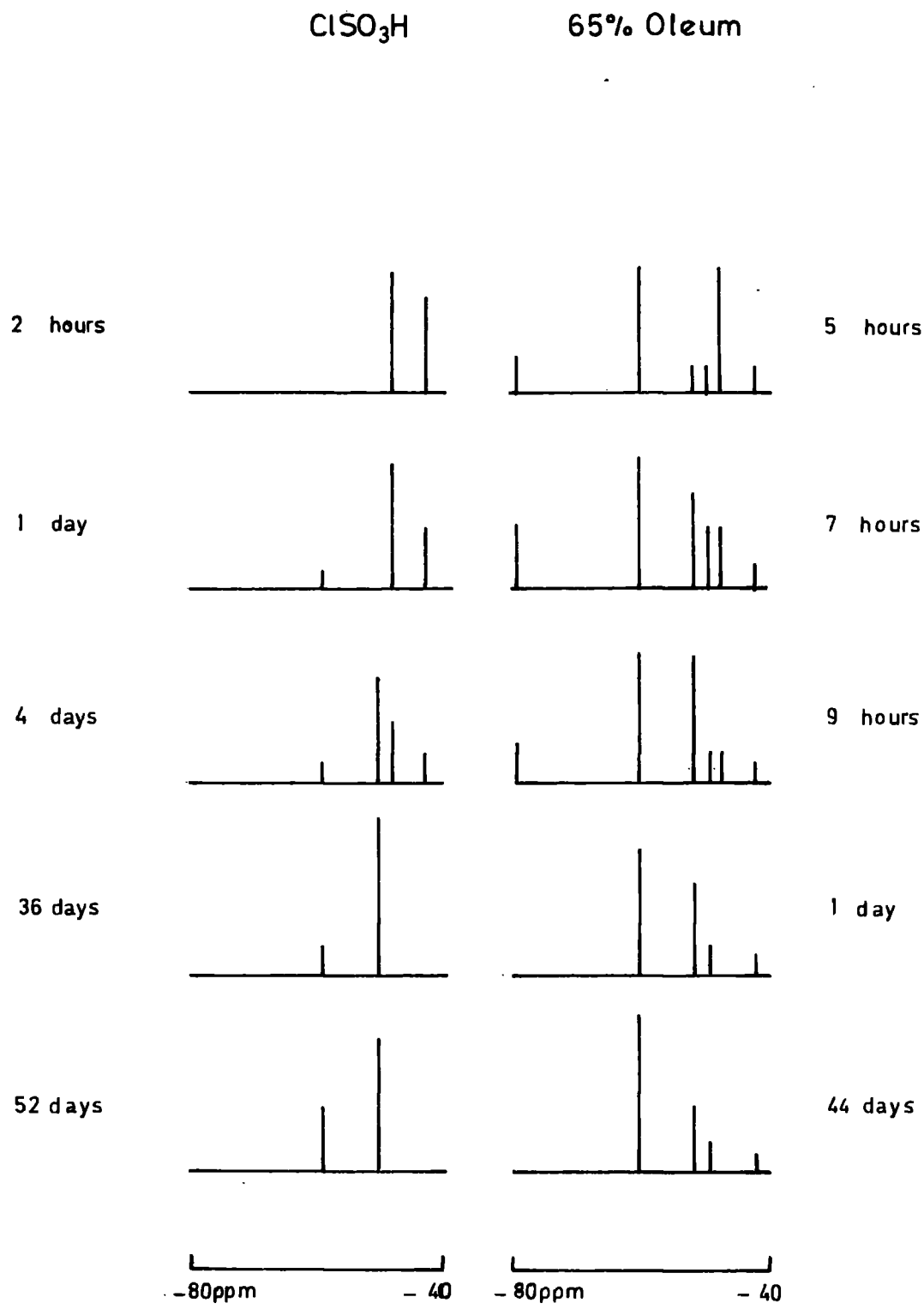


Figure 29

Relative peak heights for the ^{31}P n.m.r. spectra of triphenyl phosphine sulphide in acidic solvents.

Table 17. ^{31}P n.m.r. chemical shift values (ppm) for species derived from triphenyl phosphine sulphide in various acid solvents

Solvent	Species A	Species B	Species C	Species D
100% H_2SO_4	- 43	Not detected Low conc?	- 51	- 59
25% oleum	- 45	- 48	- 51	- 56
$ClHSO_3$	- 43	- 48	- 50	- 59
65% oleum*	- 42	- 49	- 51	- 60

* Two extra signals detected during 1st day of reaction at - 79 and - 47 ppm. Assignment discussed separately.

The species giving high field peaks seem to react over a period of time to produce species at lower field with a general reaction sequence

Species A → Species B → Species C → Species D

Solution of triphenyl phosphine oxide in liquid HCl causes a 30.5 ppm downfield movement of the ^{31}P n.m.r. chemical shift indicating almost complete protonation, whereas the shift of triphenyl phosphine sulphide moves 0.5 ppm upfield in the same solvent suggesting that protonation takes place only to a very limited extent if at all.[13]

The literature value of the chemical shift of Ph_3PS is - 43 ppm,[4] and this coupled with the liquid HCl evidence[13] of the weak basicity of the thiophosphoryl group suggests that Species A in the sulphuric acid solutions is unprotonated Ph_3PS. On the basis of the peak positions and intensity changes with time, a possible peak assignment is as follows

Species A	Ph_3PS
Species B	$Ph_2(HSO_3C_6H_4)PS$
Species C	$Ph(HSO_3C_6H_4)_2PS$
Species D	$(HSO_3C_6H_4)_3PS$

The comparative constancy of the shifts for each species suggests that little or no protonation takes place at the thiophosphoryl group. This peak assignment seems reasonable in view of the known sulphonating properties of the solvent acids. It is interesting to note two differences between the Ph_3PS solutions and those of $PhPOX_2$, Ph_2POX (X = Cl or OH), and Ph_3PO covered previously.

a) In the phosphoryl system, 100% H_2SO_4 showed no sulphonating properties while $ClHSO_3$ showed only slow sulphonation.

b) In the phosphoryl systems, sulphonation of the phenyl ring always caused an upfield shift in the ^{31}P n.m.r. resonance.

In the Ph_3PS solutions, the sulphonating properties of 100% H_2SO_4

and $ClHSO_3$ are probably shown because the thiophosphoryl group is not protonated. Under these circumstances the autoprotolysis equilibrium which produces the sulphonating species[56]

$$2ClHSO_3 \rightleftharpoons HCl + HSO_3^+ + ClSO_3^-$$
$$2H_2SO_4 \rightleftharpoons H_2O + HSO_3^+ + HSO_4^-$$

will not be disturbed by reaction of the form

$$P = X + H_2SO_4 \rightleftharpoons P^+\text{-}XH + HSO_4^-$$
$$P = X + ClHSO_3 \rightleftharpoons P^+\text{-}XH + ClSO_3^-.$$

The protonation reactions produce $ClSO_3^-$ and HSO_4^- ions respectively, which are components of the autoprotolysis equilibria.

The difference in the direction of shift movement on sulphonation in the Ph_3PS system is less easy to explain. The main structural difference between the groups in acid solution is that the phosphoryl species are essentially cationic while the thiophosphoryl species are neutral

$$P^+\text{-}OH \qquad\qquad P = S$$

Since shift positions are dependent on the degree of shielding of the ^{31}P nucleus by its surrounding electrons, this difference in behaviour may well be due to electronic effects. It is not possible to be categoric about the cause but the presence of the positive charge on

phosphorus in the protonated phosphoryl species may overcome the pull on the surrounding electrons by the electron-withdrawing sulphonic acid groups. In the thiophosphoryl compounds there is no charge to help the phosphorus retain its shielding electrons, and the sulphonic acid group may effectively remove electron density from around the ^{31}P nucleus, thus causing a downfield shift. The bulk steric effect of sulphonation in all systems should help to increase shielding and give an upfield shift, so this is clearly not the dominant term in the thiophosphoryl systems.

The only data so far unexplained is the appearance of two extra signals in the 65% oleum solution during the first 9 hours of observation. Since these peaks disappeared afterwards and the system then followed the expected reaction course, they are probably due to species formed as a consequence of the high acid strength of the solvent, which then decomposed to starting material and/or products as the acid strength was reduced by sulphonation.

Various possible species can be postulated to explain the two peaks. 65% oleum is a strong oxidizing medium and oxidation at sulphur may be possible to yield a compound of the type $Ph_3P{=}S{=}O$. Alternatively, the Lewis acid properties of SO_3 may lead to $Ph_3P{=}S \rightarrow SO_3$ adduct formation. The protonic equilibrium of the weak base Ph_3PS with the acid to form Ph_3PSH^+ is possible, but since proton transfers are normally very rapid reactions a time-averaged signal would be expected and not a distinct peak for the Ph_3PSH^+ species. All these tentative suggestions are based on the known properties of 65% oleum rather than on clear evidence. There is also the possibility that the species may be derived from Ph_3PS after sulphonation has occurred.

Overall it is not possible to make a definite assignment for the signals at - 79 and - 47 ppm, although some predictions can be made on the expected shift movements of the postulated species.

The formation of the species $Ph_3P = S \rightarrow SO_3$ would be expected to move the ^{31}P n.m.r. resonance downfield since the process involves removal of electron density from around phosphorus. Lewis adducts of $POCl_3$ with $SbCl_5$, BCl_3 and $SnCl_4$ show a downfield shift of between 33 and 58 ppm in the ^{31}P n.m.r. resonance with respect to liquid $POCl_3$.[80] It is reasonable to expect a downfield movement of a similar size for coordination of Ph_3PS to SO_3 via sulphur and if the exchange process is slow on an n.m.r. time scale, separate peaks would be expected for coordinated and uncoordinated Ph_3PS.

In the case of the species Ph_3PSO, the following structures may contribute to the sulphur-oxygen bond character.

$$Ph_3P = S = O \longrightarrow Ph_3P = S^+ - O^-$$

The formation of the sulphur-oxygen bond involves use of sulphur d orbitals to accommodate the extra electrons. In this species the presence of a positive charge on sulphur will remove electron density from the phosphorus, but back donation from oxygen will reduce the pull on the electron density about the phosphorus by the positive sulphur. Under these circumstances the ^{31}P n.m.r. resonance of Ph_3PSO is expected to show a slight downfield movement relative to Ph_3PS as the electron density about phosphorus is decreased.

From these predictions, the two signals found in the 65% oleum solution may be tentatively assigned to

$Ph_3P = S \rightarrow SO_3$ - 79 ppm

$Ph_3P = S = O$ - 47 ppm

It must be stressed that these assignments are very tentative. The species may not even be derived from Ph_3PS but from sulphonated species. Their appearance in the early stages of the reaction and subsequent disappearence suggest that they arise from Ph_3PS on initial solution in 65% oleum, however.

The reaction sequences can be summarized as follows for Ph_3PS in the solvents used

Ph_3PS —(100% H_2SO_4, $ClHSO_3$, 25% and 65% oleum)→ Ph_3PS unprotonated —(65% oleum)→ unstable side reaction

Ph_3PS unprotonated —(100% H_2SO_4, $ClHSO_3$, 25% and 65% oleum)→ $Ph_2(HSO_3C_6H_4)PS$

$Ph_2(HSO_3C_6H_4)PS$ —(100% H_2SO_4, $ClHSO_3$, 25% and 65% oleum)→ $Ph(HSO_3C_6H_4)_2PS$

$Ph(HSO_3C_6H_4)_2PS$ —(100% H_2SO_4, $ClHSO_3$, 25% and 65% oleum)→ $(HSO_3C_6H_4)_3PS$

(viii) Organophosphonium species

In Chapter 3B the spectra of some phosphorus (V) halo-species were recorded in 25% oleum and good data was obtained, especially for mixed halogen species. The results in the earlier sections of this chapter suggest that useful information may be derived from solutions of similar organophosphorus species in these highly acidic media although some complications such as sulphonation of organo groups and/or solvolysis of phosphorus-halogen bonds may occur. The spectra of a number of phosphorus (V) organo species in 25% oleum were therefore recorded in an attempt to confirm solid state ^{31}P n.m.r. data for the same compounds.[7]

The respective solids dissolved in 25% oleum with a vigorous effervesence. Clear solutions were obtained and the ^{31}P n.m.r. data is collected in Tables 18, 19 and 20. Dissolution was found to produce four-coordinate cations, and the agreement between solid and solution data is very good in all cases. In one or two samples weak signals due to impurities were found, but since no further reaction was observed, these signals are probably due to hydrolysis in the original samples, some of which were quite old.

No evidence for sulphonation of the organic residue was found nor was any hydrolysis of the phosphorus-halogen bond observed during the time that the solutions were studied, usually about two weeks. The results show that 25% oleum may be a useful solvent for the study of such species.

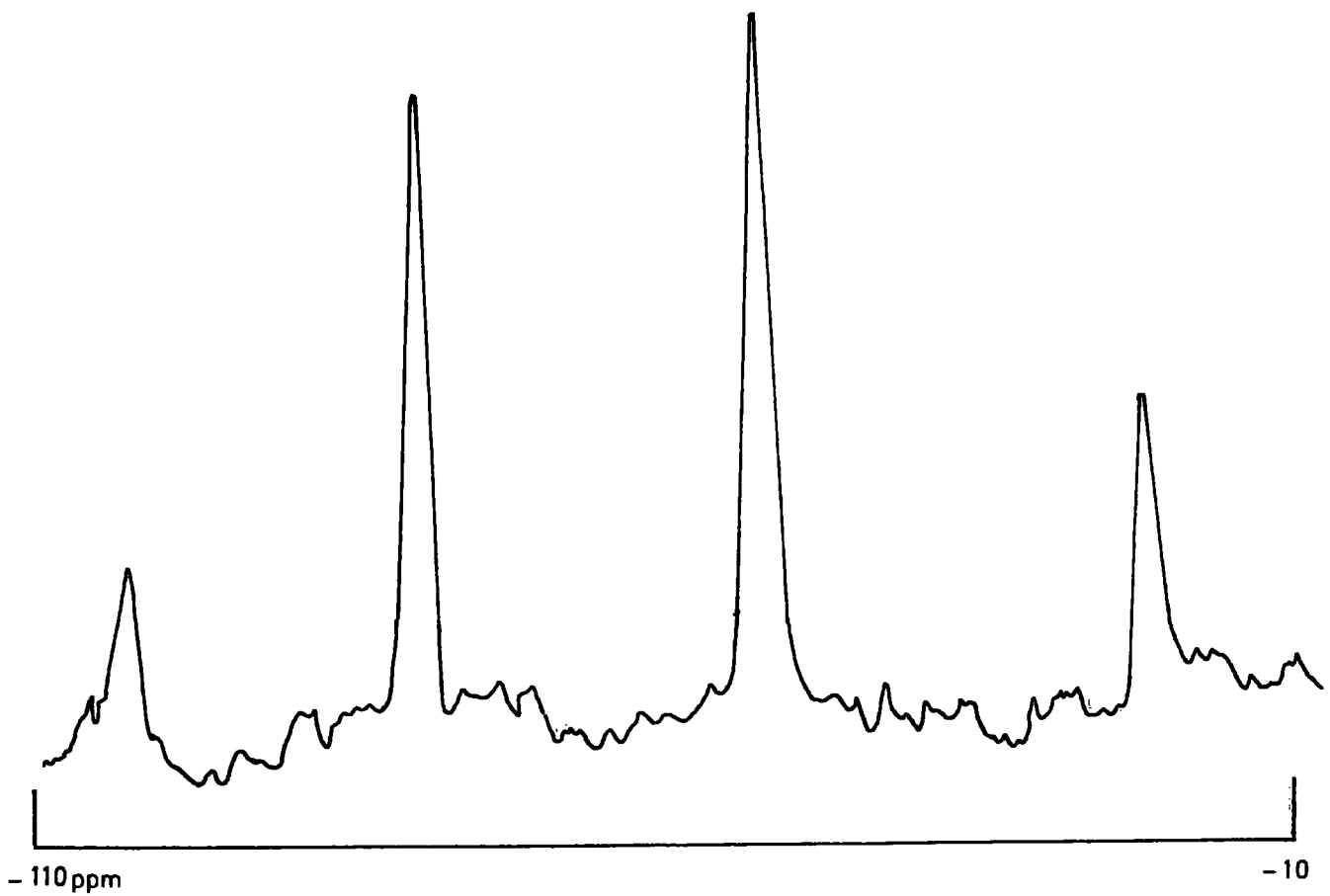


Figure 30

The ^{31}P n.m.r. spectrum of phenyldichlorodibromophosphorane in 25% oleum.

Table 18. ^{31}P n.m.r. chemical shift values (ppm) for monophenyl-chlorobromophosphonium ions in 25% oleum.

Ion	Solid State	Solution	Solution Systems studied
$PhPCl_3^+$	- 101 ± 2 BCl_4^- salt	- 103	$PhPCl_3^+BCl_4^-$ gave a single peak at -103 ppm while both $PhPCl_2Br_2$ and $PhPCl_2Br_4$ gave weak signals at - 103 ppm
$PhPCl_2Br^+$		- 80	$PhPCl_2Br_2$ and $PhPCl_2Br_4$ gave complex spectra in 25% oleum (Figure 30) compatible with the cationic species $[PhPCl_{3-n}Br_n]^+ (0 \leq n \leq 3)$. The signals at -80 and -54 ppm were assigned as shown here.
$PhPClBr_2^+$		- 54	
$PhPBr_3^+$		- 23	$PhPBr_4$ and $PhPBr_3^+BBr_4^-$ gave single signals at -23 ppm while $PhPCl_2Br_2$ and $PhPCl_2Br_4$ gave weak signals at -23 ppm.

Table 19. ^{31}P n.m.r. chemical shift values (ppm) for di-, tri- and tetraphenyl-chlorobromophosphonium ions in 25% oleum

Ion	Solid State[7]	Solution	Solution Systems Studied
$Ph_2PCl_2^+$	-93.6 ± 5 BCl_4^- salt	-95	$Ph_2PCl_2^+BCl_4^-$ gave a single peak at -95 ppm
Ph_2PClBr^+		-74	Ph_2PClBr_2 gave two strong signals at -74 and -58 ppm which suggests that the 'compound' is a mixture containing two halo cations
$Ph_2PBr_2^+$		-58	
Ph_3PCl^+	-64.3 ± 2 PCl_6^- salt	-65	$Ph_3PCl^+BCl_4^-$ gave a single peak at -65 ppm
Ph_3PBr^+	- 48.6[6]	-49	Ph_3PBr_2 and Ph_3PBr_4 both gave single peaks at -49 ppm
Ph_4P^+		-23	$Ph_4P^+Br^-$ gave a single peak at -23 ppm

Table 20. ^{31}P n.m.r. chemical shift values (ppm) for some methyl-, ethyl-, and butyl-chlorophosphonium ions in 25% oleum

Ion	Solid State[7]	Solution	Solution Systems Studied
$MePCl_3^+$	- 118 average	- 120	$MePCl_3^+AlCl_4^-$ and $MePCl_4$ gave strong peaks at -120ppm
$Me_2PCl_2^+$	- 122 average	- 123	$Me_2PCl_2^+SbCl_6^-$, $Me_2PCl_2^+BCl_4^-$ and Me_2PCl_3 gave strong peaks at -123ppm
Me_3PCl^+	- 87 BCl_4^- salt	- 90	$Me_3PCl^+BCl_4^-$ showed strong peak at -90 ppm
$EtPCl_3^+$	- 124.4 $AlCl_4^-$ salt	- 129	$EtPCl_3^+AlCl_4^-$ gave strong peak at - 129 ppm
$Et_2PCl_2^+$	- 138 BCl_4^- salt	- 138	$Et_2PCl_2^+BCl_4^-$ gave strong peak at - 138 ppm
Et_3PCl^+	- 105 BCl_4^- salt	- 108	$Et_3PCl^+BCl_4^-$ showed strong peak at - 108 ppm
Bu_4P^+	- 35 I^- salt	- 31	$Bu_4P^+Cl^-$ showed single peak at - 31 ppm

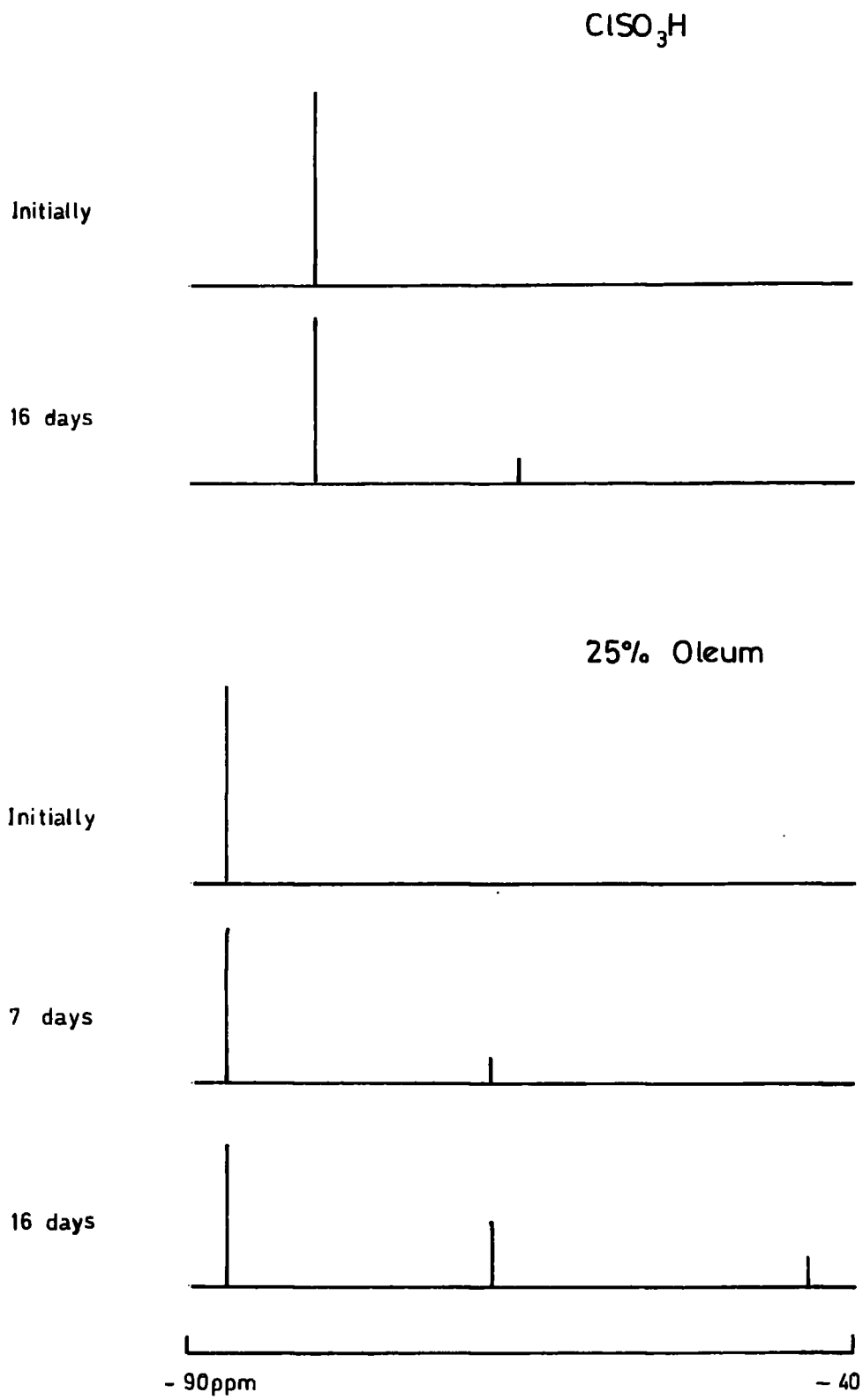


Figure 31

Relative peak heights for the ^{31}P n.m.r. spectra of methyl phosphonic dichloride in acidic solvents.

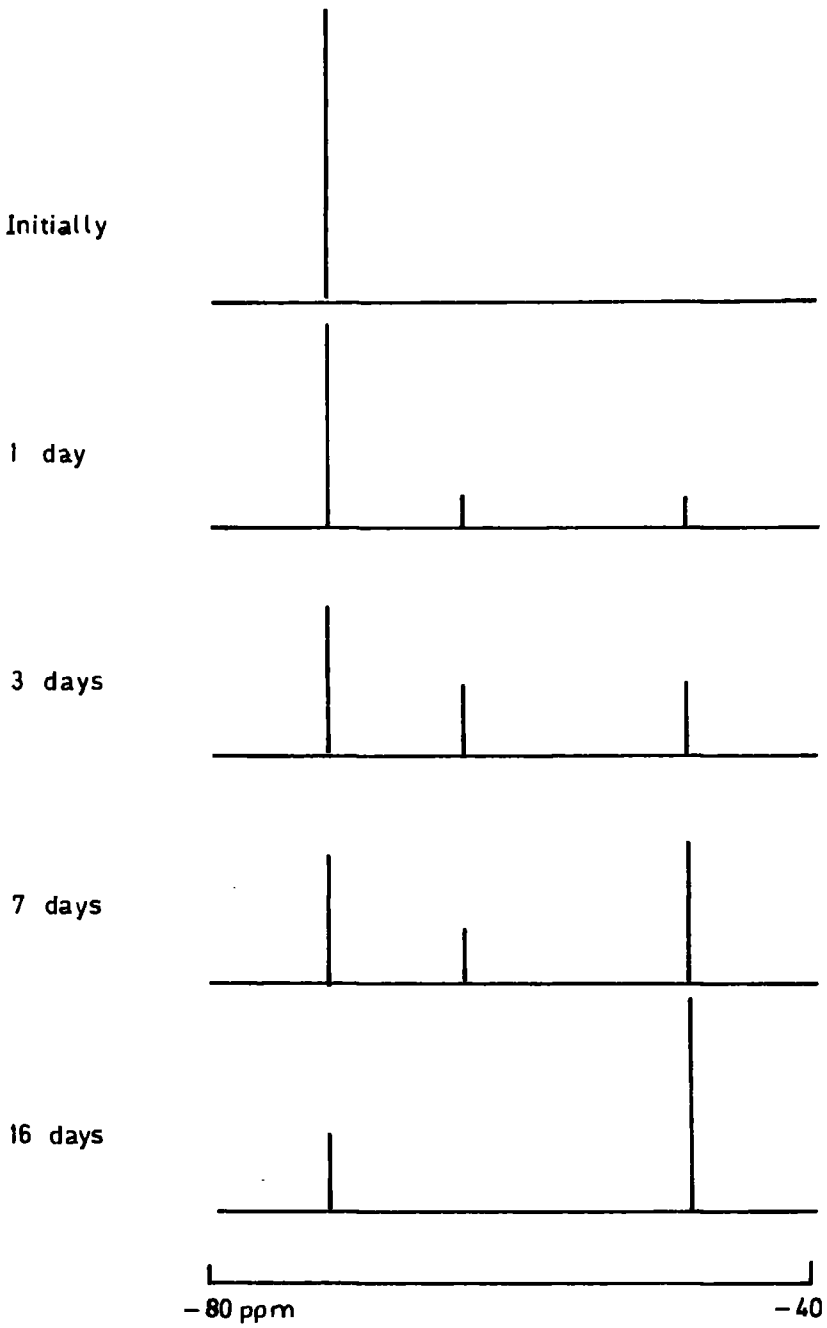


Figure 32

Relative peak heights for the ^{31}P n.m.r. spectrum of methyl phosphonic dichloride in 100% sulphuric acid.

In the solutions where extra signals were found, these signals were assigned to hydrolysis products present in the original sample. The assignments of these peaks were quite facile in most cases, but in the $MePCl_3^+$ salts some difficulty was found because of their relative intensities. Hence a sample of $MePOCl_2$ was dissolved in $ClHSO_3$, 100% H_2SO_4 and 25% oleum to yield a colourless solution in all solvents. The ^{31}P n.m.r. solution spectra were recorded and are represented diagramatically in Figures 31, 32. The initial peak found in each solution is downfield from that of the parent (- 44 ppm in CH_2Cl_2) and is compatible with formation of $MePCl_2OH^+$. The subsequent appearence of highfield signals in all solutions is consistent with slow solvolysis of the phosphorus-chlorine bonds to yield $MePCl(OH)_2^+$ and finally $MeP(OH)_3^+$. No sulphonation of the organo-groups appears to occur as shown by the quartet structure of the ^{31}P n.m.r. peaks which are in agreement with the presence of P-CH_3 groups (see Figure 33). The shift data for this system is summarized in Table 21, and shows the shift dependence of the phosphoryl group in media of differing acid strength.

Table 21. ^{31}P n.m.r. chemical shift values (ppm) for species derived from methyl phosphonic dichloride in various acid solvents

	$MePCl_2OH^+$	$MePCl(OH)_2^+$	$MeP(OH)_3^+$
J_{P-C-H}	15 Hz	17 Hz	18 Hz
100% H_2SO_4	- 72	- 63	- 48
$ClHSO_3$	- 80	- 65	not seen
25% oleum	- 87	- 67	- 43

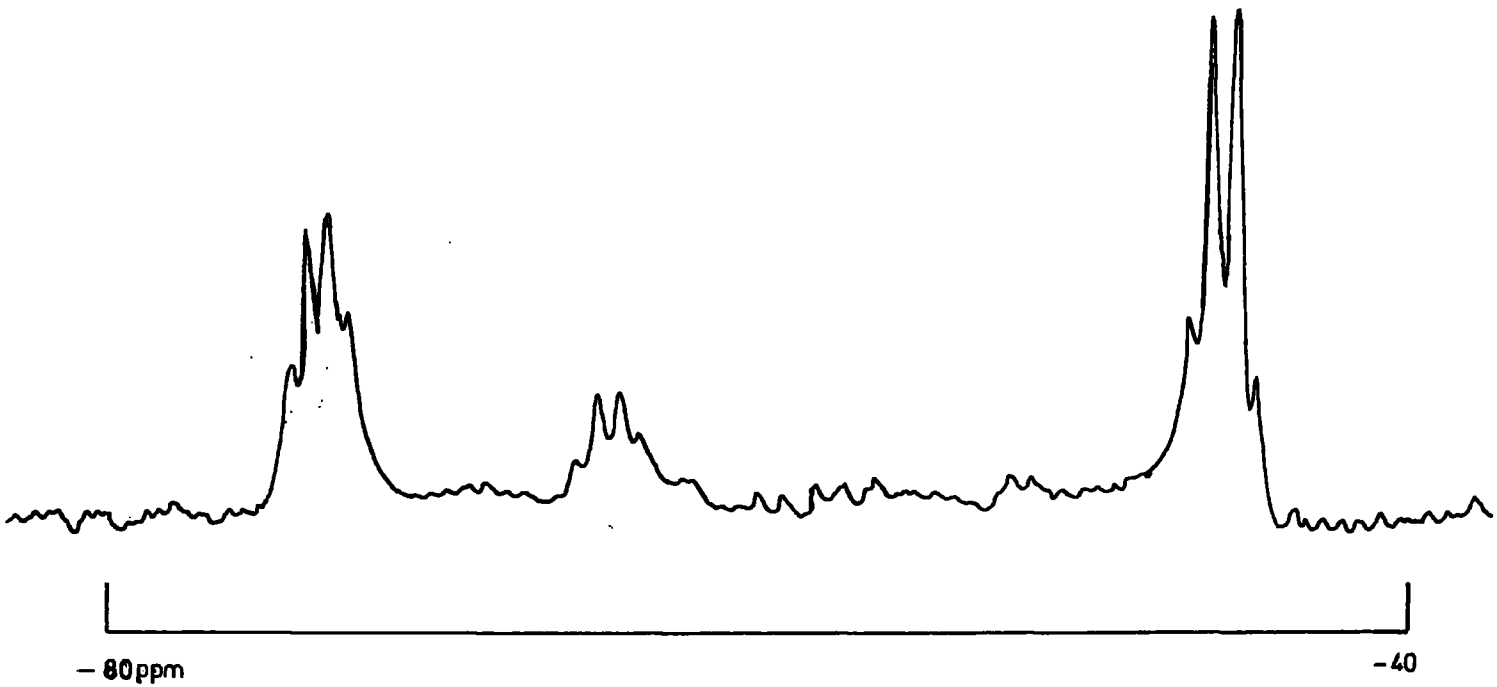


Figure 33

The ^{31}P n.m.r. spectrum of methyl phosphonic dichloride in 100% sulphuric acid, 7 days after preparation of sample.

These results proved useful in confirming the shift position of the $MePCl_3^+$ ion as - 120 ppm in 25% oleum.

3) Summary.

Solution of the compounds $PhPOX_2$, Ph_2POX (X = Cl or OH), and Ph_3PO in various sulphuric acid solvents was accompanied by protonation of the phosphoryl oxygen. Solutions in 25% and 65% oleum showed evidence for rapid sulphonation of each phenyl ring attached to phosphorus, while $ClHSO_3$ acted as a slow sulphonating agent. No sulphonation was observed in 100% H_2SO_4. For species where X = Cl, solvolysis of the P-Cl bond to a P-OH bond was observed in 100% H_2SO_4, with consequent formation of the parent protonated acid. Solutions of the halo species in 25% oleum showed signs of slow solvolysis of the sulphonated species formed initially, probably because the sulphonation reduced the acid strength markedly.

Together with the results for $POCl_3$ (See Chapter 3B section 2(iv)) and data from liquid HCl solutions,[13] the ^{31}P n.m.r. data obtained from the solutions of $PhPOCl_2$, Ph_2POCl and Ph_3PO indicate that substitution of a phenyl group for a chlorine in $POCl_3$ increases the basicity of the phosphoryl group, as shown in Table 22.

Ph_3PO appears to be completely protonated in all four solvents, while Ph_2POCl is probably completely protonated in the three sulphuric acid solvents used. The data also supports previous deductions[19] that liquid HCl is less acidic than the sulphuric acid solvents. The reported shift values for Ph_3PO in aqueous HCl and HBr show downfield displacements of -18.7 and - 28 ppm respectively,[111] showing that the aqueous acids are comparatively weak. (The data for the 65% oleum solutions is not included since it is complicated by the rapid sulphonation of the species).

Table 22. ^{31}P n.m.r. chemical shift values (ppm) for some phenyl substituted phosphorus oxychloride derivatives in acidic solvents.

	$\delta^{31}P$ protonated species - $\delta^{31}P$ parent			
	liquid HCl[13]	100% H_2SO_4	25% oleum	$ClHSO_3$
$POCl_3$	- 6.9	- 18	- 33.5	- 20
$PhPOCl_2$	- 7.1	- 23	- 32	- 34
Ph_2POCl	-18.3	- 33.3	- 33.3	- 33.3
Ph_3PO	-30.5	- 33	- 34	- 35

It is interesting to compare the ^{31}P n.m.r. shift displacements for the acids $PhPO(OH)_2$ and $Ph_2PO(OH)$ in the same solvents (see Table 23).

Table 23. ^{31}P n.m.r. chemical shift values (ppm) for some phenyl substituted phosphoric acid derivatives in acidic solvents

	$\delta^{31}P$ protonated species - $\delta^{31}P$ parent			
	liquid HCl[13]	100% H_2SO_4	25% oleum	$ClHSO_3$
H_3PO_4	+ 0.75	- 2.2*	+ 6.6*	- 1.7*
$PhPO(OH)_2$	- 8.3	- 14	- 9	- 14
$Ph_2PO(OH)$	- 23	- 29	not seen	- 30
Ph_3PO	- 30.5	- 33	- 34	- 35

* Data approximate for $\delta^{31}P[P(OH)_4^+] - \delta^{31}P[H_3PO_4]$ from solutions of KH_2PO_4.[71]

$Ph_2PO(OH)$ and $PhPO(OH)_2$ appear to be fully protonated in the three sulphuric acid solvents studied. The upfield shift for $PhPO(OH)_2$ with increasing acidity in 25% oleum solution suggests that the protonated species takes part in condensation equilibria in a similar way to H_3PO_4.[71] The constancy of the shift for $Ph_2P(OH)_2^+$ in these solvents indicates that it is fully protonated, but the absence of data for the 25% oleum solution gives no information on possible condensation reactions. The apparent constancy of the shift values for the species $Ph(HSO_3C_6H_4)P(OH)_2^+$ at - 51 ppm and $(HSO_3C_6H_4)_2$-$P(OH)_2^+$ at - 48 ppm in these solvents does suggest that the dihydroxyphosphonium species do not take part in condensation equilibria to any appreciable extent.

Sulphonation of the phenyl ring in phosphoryl compounds generally causes an upfield shift of the ^{31}P n.m.r. resonance relative to the parent species.

The results for some of the phosphoryl species were supported by the 'PhPO(OH)Cl' system. Interpretation of the data was complicated in this system by the apparent instability of PhPO(OH)Cl itself. All attempts to make this compound failed to yield pure samples because of the favoured reaction of HCl elimination to yield condensed phosphate phases. Fortunately, data on the solution chemistry of PhPO(OH)Cl in the acid media was obtained because the condensed phases were rehydrated in the acids to yield simple species.

The results for phenyl substituted compounds have been interpreted in terms of sulphonation of the phenyl ring. It must be noted, however,

that Haake and Ossip in their investigations on R_2PO_2H and $R_2P(O)X$ (R = alkyl, X = alkoxy) derivatives in oleums and sulphuric acid by ^1H n.m.r. techniques reach somewhat differing conclusions.[91] Their data was interpreted as protonation of the phosphoryl oxygen, followed by sulphonation of the hydroxyl group so formed in oleums of SO_3 content greater than 10%. For phosphinic acids, oleums greater than 55% SO_3 content caused sulphonation of the second hydroxyl, e.g.

$$(CH_3)_2PO(OH) \xrightarrow[\text{oleums}\ <10\%\ SO_3]{\text{Sulphuric acid}} (CH_3)_2P(OH)_2^+$$

$$(CH_3)_2P(OH)_2^+ \xrightarrow[>10\%\ SO_3]{\text{oleum}} (CH_3)_2P(OH)(OSO_3H)^+$$

$$(CH_3)_2P(OH)(OSO_3H)^+ \xrightarrow[>55\%\ SO_3]{\text{oleum}} (CH_3)_2P(OSO_3H)_2^+$$

Reports by other workers,[18,90] as well as the results of Haake and Ossip[91] who found that attempts to include data on dibenzyl and dimesityl phosphinic acids in their study proved fruitless because of ring sulphonation, suggest that sulphonation of aromatic rings in organo-phosphorus species is a very favourable reaction. The data reported in this chapter appears entirely consistent with sulphonation of the phenyl ring and there is no evidence to support the sulphonation of OH groups. Since it is well known that alkyl groups are difficult to sulphonate,[56] a differing reaction path is not unexpected for such compounds.

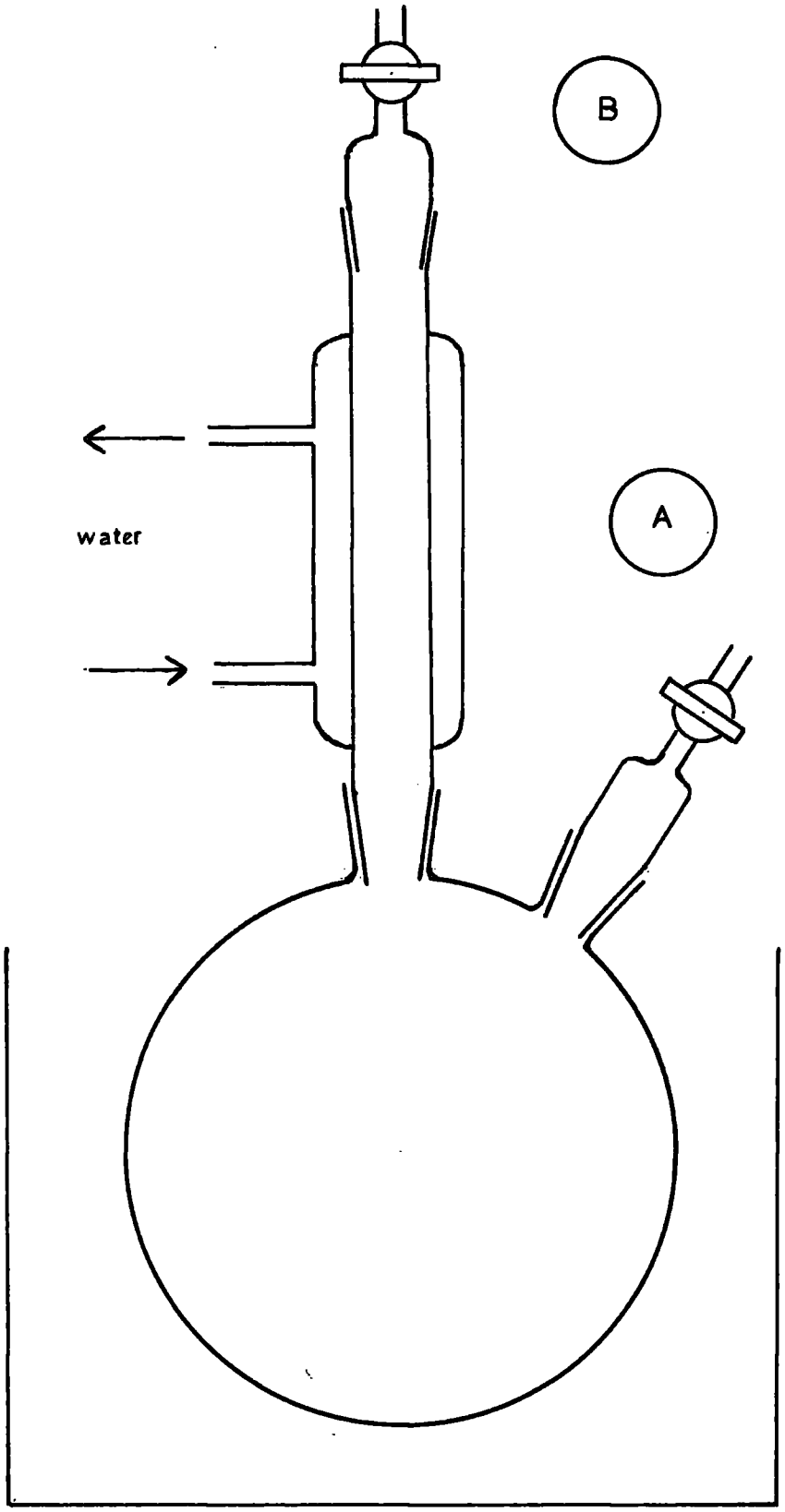


Figure 34

Apparatus used in the attempted preparations of phenyl phosphonic monochloride.

Little or no protonation of the thiophosphoryl bond appears to take place in the solvents used. In consequence sulphonation of the phenyl rings occurs not only in 25% and 65% oleum but in 100% H_2SO_4 and $ClHSO_3$ at appreciable rates. Unlike the phosphoryl compounds, sulphonation of the phenyl rings appears to cause a downfield shift in the ^{31}P n.m.r. signal. The assignment of two extra species in 65% oleum is not easily accomplished because of a lack of comparable data. These species are not particularly stable and appear to decompose to either reactant and/or product.

25% oleum appears to be a useful solvent for phenyl, methyl, ethyl and butyl halophosphonium salts. In all cases the phosphonium ions produced appeared to be quite stable, showing no signs of sulphonation of the organo residues and no solvolysis of phosphorus-halogen bonds.

4) Experimental.

The approach used was to take a sample of the phosphorus - containing species to be investigated and to place it in a sample bottle. The appropriate acid was then added and after complete solution had occurred, sometimes after shaking the sample, a portion of the solution was transferred to an n.m.r. tube. All of these manipulations were carried out in a nitrogen-filled glove box. The sample was then monitored by ^{31}P n.m.r. over a period of time in an attempt to elucidate the reaction path. Stringent precautions were taken to protect the sample from aerial moisture at all stages in this process.

In the attempted preparations of PhPO(OH)Cl, the apparatus shown in Figure 34 was used. A number of samples were prepared using the reactants given in Table 24 and the results for these reactions can be found in section 2(iii) of this chapter.

Table 24. Experimental data for attempted preparations of phenyl phosphonic monochloride.

Sample	Reactants		
Sample A $PhPOCl_2 + H_2O$ 1:1 neat	$PhPOCl_2$ H_2O	10.07 gms (51.6mmoles) 0.93 mls (51.6mmoles)	CO_2/ acetone bath
Sample B $PhPOCl_2 + H_2O$ 1:1 in Et_2O	$PhPOCl_2$ in 100mls ether H_2O	6.30 gms (32.3mmoles) 0.58mls (32.2 mmoles)	CO_2/ acetone bath
Sample C $PhPO(OH)_2+SOCl_2$ 1:1 neat	$PhPO(OH)_2$ $SOCl_2$	10.20gms (63.8mmoles) 4.68 mls (64.5mmoles)	Oil bath
Sample D $PhPO(OH)_2+SOCl_2$ 1:1 neat	$PhPO(OH)_2$ $SOCl_2$	9.11gms (56.9 mmoles) 4.18mls (57.6 mmoles)	Oil bath

The apparatus was baked in an oven overnight then assembled after cooling to room temperature. After being evacuated by means of a vacuum pump, the apparatus was opened under nitrogen. The phosphorus-containing reactant was placed in the flask via opening (A) while the system was flushed out with nitrogen. The second reactant was then added via tap (A) while the nitrogen flushing continued. The mixture was stirred until reaction was complete. Tap (B) was kept open to a nitrogen line so that there was a blow-off point for any gaseous products. The flask was then transferred to a glove box and the product investigated by ^{31}P n.m.r. solution spectroscopy.

CHAPTER 4

SOME ASPECTS OF THE CHEMISTRY OF HALOPHENOXYPHOSPHORANES

1) Introduction.

From the study of the hydrolysis and alcholysis of various aryloxyphosphorus halides, Rydon and Tonge[21] deduced that the phenoxychlorides and bromides are ionic dimers $[(PhO)_xPHal_{4-x}]^+$ $[(PhO)_yPHal_{6-y}]^-$ (or mixtures of such compounds), whereas the iodides are monomeric phosphonium compounds, $[(PhO)_nPI_{4-n}]^+I^-$. The evidence for these structural assignments was far from conclusive.

Ramirez et al[24] have investigated the reaction between phenol and phosphorus pentachloride and interpreted the data in terms of formation of $(PhO)_3PCl_2$ as well as an unidentified 6 co-ordinate phosphorus species, the results being similar to data obtained by Rydon and Tonge for the same system,[21] although the latter workers reported formation of a number of species $(PhO)_nPCl_{5-n}$.

Some related compounds containing catechyl groups instead of phenoxy groups have been studied by Reeve, with particular reference to the acceptor properties of these molecules in the presence of pyridine and related organic bases. Evidence was found which showed clearly that the catechyl-containing phosphoranes act as acceptors.[25]

In the light of this previous work it was decided to investigate various aspects of the chemistry of halophenoxyphosphoranes using ^{31}P n.m.r. spectroscopy as the probe.

2) Present Work.

i) Triphenylphosphite with halogens

The reaction between triphenylphosphite and halogens (Cl, Br) has been clarified by the work of Rydon and Tonge,[21] and Harris and Payne.[22] Reaction appears to proceed in several stages,

$$2(PhO)_3P + X_2 \longrightarrow (PhO)_2PX + (PhO)_4PX$$
$$(PhO)_2PX + (PhO)_4PX + X_2 \longrightarrow 2\,(PhO)_3PX_2$$

X = Cl, Br.

Exchange of cation and anion amongst the dimeric forms of the triphenoxyphosphorus dihalides could lead to all or some of the possible phenoxy-halides $(PhO)_nPX_{5-n}$.

Iodine gives the same reactions at room temperature, but if the reaction is carried out at higher temperatures a different route is followed[23]

$$2(PhO)_3P + I_2 \longrightarrow (PhO)_4PI + (PhO)_2PI$$
$$(PhO)_4PI + (PhO)_2PI + I_2 \longrightarrow [(PhO)_3PI]^+I_3^- + (PhO)_3P$$

Reaction with excess iodine gives the tetraiodide $[(PhO)_3PI]^+I_3^-$ and a compound of formula $(PhO)_3PI_9$, which is believed to contain equal quantities of the two salts $[(PhO)_3PI^+]I_m^-$ where m is 7 or 9.

These systems are thus complex but appear to be quite amenable to investigation by ^{31}P n.m.r. spectroscopy.

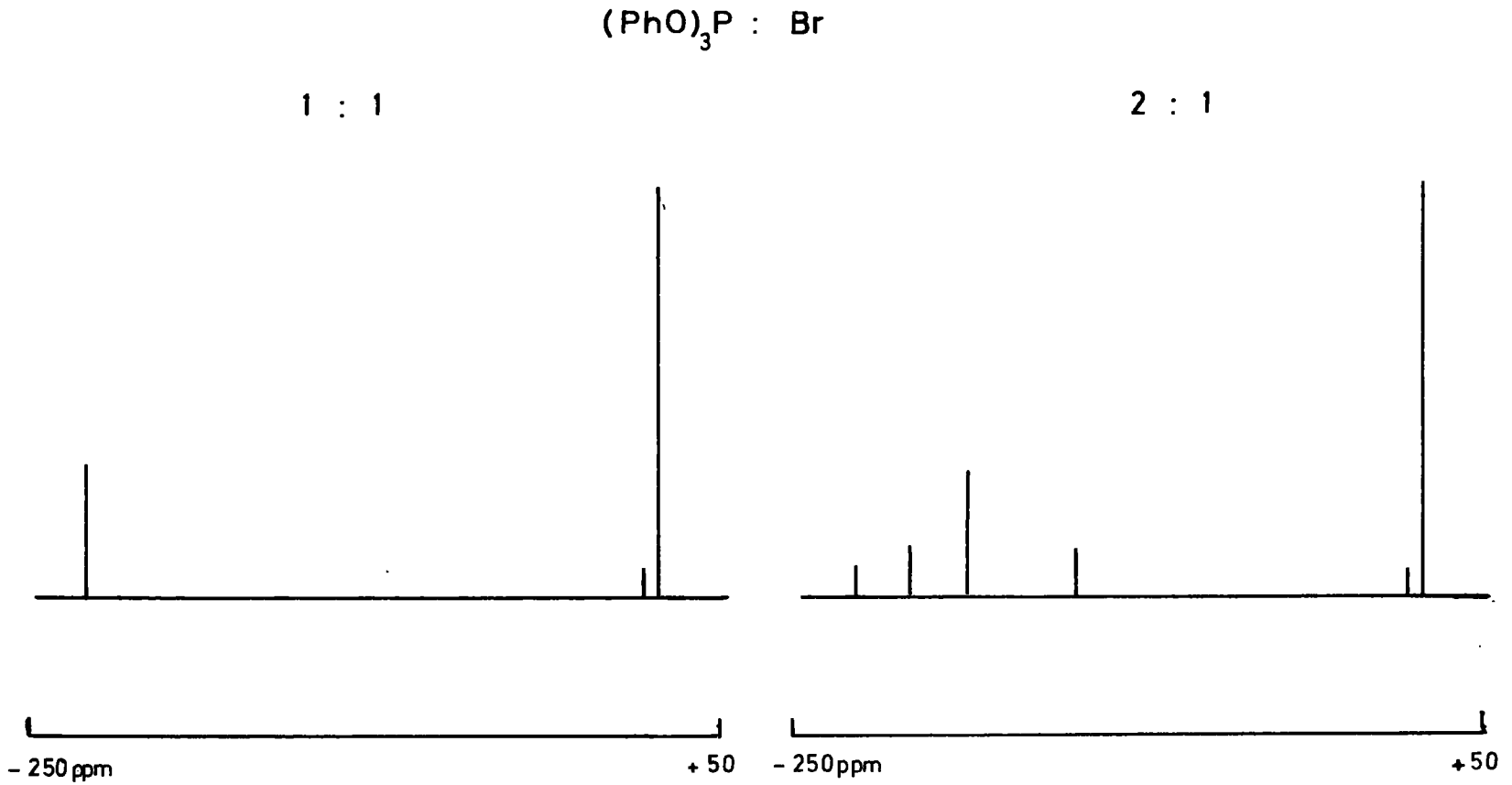


Figure 35

Relative peak heights for the ^{31}P n.m.r. spectrum of triphenyl phosphite and bromine in CH_2BrCH_2Br.

The reaction between $(PhO)_3P$ and bromine in ethylene dibromide was investigated by this technique. $(PhO)_3P$ was dissolved in $BrCH_2CH_2Br$ and bromine was added cautiously in measured proportions to give solutions of mole ratio $(PhO)_3P$ to Br_2 of 1:1 and 2:1. Little sign of reaction was noticed, so the reddish brown (1:1) and pale yellow (2:1) solutions were studied by ^{31}P n.m.r. The results are summarized diagramatically in Figure 35, no changes being observed in the spectra over a period of $4\frac{1}{2}$ months. The downfield peaks are immediately assignable to the mixed phosphorus (III) phenoxy bromides,[4]

PBr_3	$P(OPh)Br_2$	$P(OPh)_2Br$	$P(OPh)_3$	
-226	-200	-176	-128	ppm

The peaks at + 18 and + 23 ppm are due to $(PhO)_3PO$[4] and $(PhO)_4P^+$ [94] respectively. The reddish-brown colour of the 1:1 solution suggests the presence of free bromine and the ^{31}P n.m.r. data is consistent with the reaction

$$4(PhO)_3P + 3Br_2 \longrightarrow 3(PhO)_4P^+Br^- + PBr_3$$

This scheme is in agreement with the data for the 1:1 solution in that the ratio of the peak intensities of PBr_3 to $(PhO)_4P^+$ is approximately 1:3 and the solution is bromine-coloured. The excess bromine probably adds to the bromide formed to give Br_3^-. The data from the 2:1 solution is also in good agreement but since the $(PhO)_3P$ is in excess all the bromine will be used up. Two moles of $(PhO)_3P$

will remain unreacted per mole of PBr_3 formed, thus favouring the phenoxy-containing species in the exchange reaction. This is reflected by the intensity of the $(PhO)_2PBr$ signal at - 176 ppm. No evidence was obtained in these reactions for the formation of $(PhO)_3PBr_2$.

The reaction between $(PhO)_3P$ and Br_2 was repeated on a 1:1 scale in CH_2Cl_2 in an attempt to isolate the $(PhO)_4P^+$ species. A solution of Br_2 [2.15 mls (43.0 mmoles) in 40 mls of CH_2Cl_2] was added dropwise with stirring to $(PhO)_3P$ [10 mls (38.2 mmoles) in 40 mls of CH_2Cl_2]. No obvious reaction occurred, and an orange solution was produced. After stirring for one hour, the bulk of the solvent was removed on a vacuum line to yield an orange viscous oil. This residue was washed with pet ether (30-40) to give an orange solid which was isolated. This solid was investigated by analytical and spectroscopic techniques.

Solutions of this compound in CH_2Cl_2 and $PhNO_2$ showed single ^{31}P n.m.r. peaks at + 23 and + 24 ppm respectively. The ^{31}P n.m.r. solid state spectrum showed a poorly-defined broad peak at approximately + 20 ppm. The analytical data on this compound is set out in Table 25.

Table 25. Analysis figures for the product of the reaction between triphenyl phosphite and bromine 1:1

%	P	C	Br	H	P : C : Br : H ratio
Prep	5.7	51.54	28.75	3.60	1 : 23.4: 1.9: 19.3
Theo. $(PhO)P_4^+Br^-$	6.41	59.62	16.56	4.14	1 : 24 : 1 : 20
Theo.1:1 mixture of $(PhO)_4P^+Br^-$ and $(PhO)_4P^+Br_3^-$	5.50	51.18	28.38	3.58	1 : 24 : 2 : 20

The ^{31}P n.m.r. data and analysis figures are consistent with $(PhO)_4P^+$ as the phosphorus species, and the excess bromine appears to be due to formation of Br_3^-. The presence of this anion could well explain the orange colour of the compound since $(PhO)_4P^+Br^-$ is expected to be colourless.

A sample of this orange compound was reacted with BBr_3 in an attempt to prepare $(PhO)_4P^+BBr_4^-$ and thus confirm the above conclusions. 3.82 gms (7.02 mmoles) were dissolved in 20 mls of CH_2Cl_2 and 0.8 mls (8.46 mmoles) of BBr_3 in 15 mls of CH_2Cl_2 was added dropwise with stirring. There was no obvious reaction, but as more BBr_3 was added the solution darkened from orange to deep red. The solution was concentrated on a vacuum line and 100 mls of pet ether (30-40) added. A pale yellow solid precipitated and was isolated. Further washing of the solid with pet ether (30-40) yielded a pale fawn product. (Excess BBr_3 was used in this process to ensure complete reaction).

Solutions of this solid in CH_2Cl_2 and $PhNO_2$ showed single peaks in the ^{31}P n.m.r. spectra at + 23 and + 24 ppm respectively while the solid state spectrum showed a well-defined peak at + 24 ppm. The presence of the BBr_4^- anion provides an alternative nucleus for n.m.r. investigation.

The ^{11}B solution spectra of this solid in CH_2Cl_2 and $PhNO_2$ showed single peaks at + 42 and + 43 ppm respectively, while the solid state ^{11}B spectrum showed a well-defined peak at + 43 ppm. [The ^{11}B shifts were measured relative to $B(OMe)_3$]. These values are in good

agreement with published shift data for $(PhO)_4P^+$ [94] and BBr_4^- [95] and indicate that these are the only phosphorus and boron species present. The analysis figures further support this structure, see Table 26.

Table 26. Analysis figures for the product of the reaction between '$(PhO)_4PBr_2$' and boron tribromide (excess)

%	P	C	H	Br
Prep	4.06	39.76	2.44	43.67
$(PhO)_4P^+BBr_4^-$ Theoretical	4.22	39.24	2.72	43.60

$(PhO)_3P$ was reacted with excess chlorine in the following manner. Chlorine gas was passed through a colourless solution of $(PhO)_3P$ [30 mls (115 mmoles) in 100 mls of CH_2Cl_2]. As reaction proceeded, the colourless solution turned yellow-green. After no further change in colour could be seen the chlorine flow was stopped and the solvent removed on a vacuum line to give a pale green solid. The solid was washed with pet. ether (30-40) and pumped dry. The analysis figures for this compound are given in Table 27.

Table 27. Analysis figures for the product of the reaction between triphenylphosphite and chlorine (excess)

%	P	C	H	Cl
Prep	7.27	51.38	3.91	26.04
Theoretical '$(PhO)_3PCl_3$'	7.43	51.89	3.63	25.53

If the remaining portion of the material is oxygen, 11.4% (Theo. 11.52%), the C:H:O ratio is 6:5.48:1 which is approximately correct for the presence of the phenoxy group in the material, and the calculated formula is $(PhO)_{3.06}\ PCl_{3.12}$. A sample of the solid dissolved in CH_2Cl_2 showed two strong signals at + 23 and + 295 ppm in its ^{31}P n.m.r. spectrum with approximate intensity ratio of 3:1. The two signals are assignable to $(PhO)_4P^+$ [94] and PCl_6^-.[4] A very weak signal at + 20 ppm may be attributed to small quantities of $(PhO)_3PO$ impurity.[4]

The data from this reaction is consistent with formation of a compound of $(PhO)_4P^+$, Cl_3^- and PCl_6^- in the ratio

$$3(PhO)_4P^+ \ : \ 2Cl_3^- \ : \ PCl_6^-$$

and can be explained by the following reaction sequence analogous to that for $(PhO)_3P$ and bromine.

$$4(PhO)_3P + 3Cl_2 \longrightarrow 3(PhO)_4P^+ + 3Cl^- + PCl_3$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5 \xrightarrow{Cl^-} PCl_6^-$$

$$Cl^- + Cl_2 \longrightarrow Cl_3^-$$

The overall reaction can be represented by the equation

$$4(PhO)_3P + 6Cl_2 \longrightarrow 3(PhO)_4P^+ + 2Cl_3^- + PCl_6^-.$$

Since excess chlorine was passed into the solution, it is not

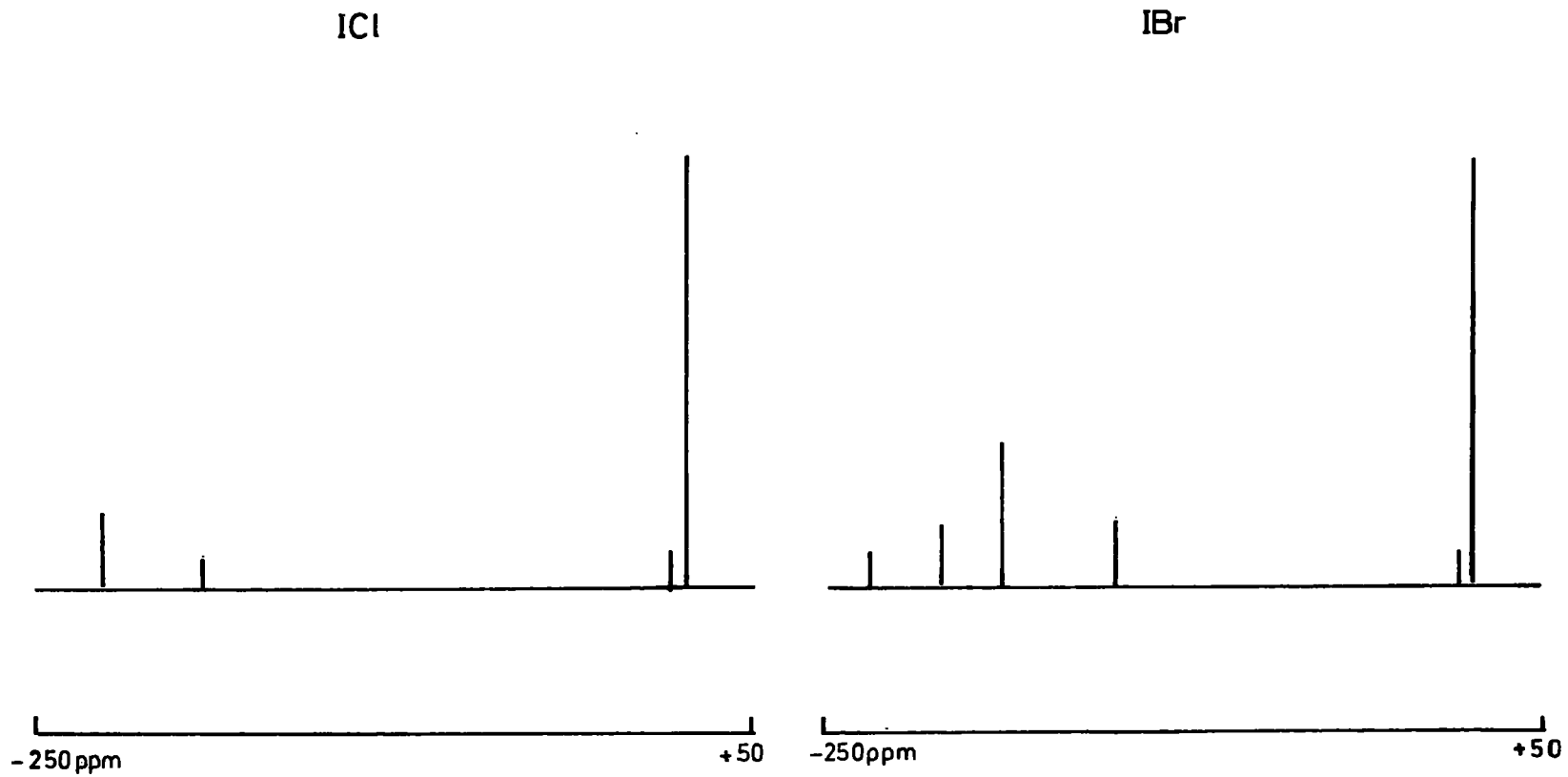


Figure 36

Relative peak heights for the ^{31}P n.m.r. spectra of triphenyl phosphite and interhalogens (1:1) in CH_2Cl_2.

surprising that the most highly chlorinated products possible are formed. The results suggest that a 1:1 reaction of $(PhO)_3P$ and chlorine would proceed as follows:

$$4(PhO)_3P + 4Cl_2 \longrightarrow 3(PhO)_4P^+ + 2Cl^- + PCl_6^-$$

The product would analyse as $(PhO)_3PCl_2$ although it would in reality be a tetraphenoxy phosphonium salt with the mixed anions PCl_6^- and Cl^-. The 1:1 reaction was not attempted since the expected product would not contain the desired mixed phenoxychlorophosphorus species.

The oxidation of $(PhO)_3P$ by ICl, IBr and I_2 was also investigated by similar methods. 1:1 reaction mixtures of $(PhO)_3P$ with ICl and IBr were prepared in CH_2Cl_2. The dark brown solutions formed were allowed to stand for 15 minutes and some precipitation occurred in both cases. A small amount of the liquid in the sample bottle was removed by pipette dropper and diluted with CH_2Cl_2 before investigation by n.m.r., while the bulk of the solution was allowed to continue precipitation. The solids were then isolated by filtration, washed with pet ether (30-40) and investigated by ^{31}P n.m.r. and analytical techniques. In the IBr reaction a purple crystaline solid was obtained while the ICl reaction yielded a brown powder. The ^{31}P n.m.r. data for the reaction solutions is summarized in Figure 36. The peak assignments are quite straightforward

ICl solution	PCl_3	$(PhO)PCl_2$	$(PhO)_3PO$	$(PhO)_4P^+$
	- 219	- 179	+ 17	+ 22 ppm

IBr solution

PBr_3	$(PhO)PBr_2$	$(PhO)_2PBr$	$(PhO)_3P$	$(PhO)_3PO$	$(PhO)_4P^+$
-229	-199	-173	-126	+ 18	+ 24 ppm

and are in agreement with published results.[4,94] The solids obtained from both reactions when dissolved in CH_2Cl_2 yielded single peaks at + 22 ppm assignable to $(PhO)_4P^+$.[94] The analytical figures on the two solids are given in Table 28.

Table 28. Analysis figures for the products of reaction between triphenyl phosphite and iodine bromide, or iodine chloride 1:1

	P	Cl	Br	I	C	H
Product from ICl reaction % composition	4.07	2.8	-	37.7	42.2	3.06
Product from ICl reaction Atomic Ratio	1	0.6	-	2.26	26.8	23.3
Product from IBr reaction % composition	4.5	-	5.7	39.1	39.89	3.69
Product from IBr reaction Atomic Ratio	1	-	0.49	2.12	22.9	25.4

The analysis figures are rather poor, especially for the P:C:H ratio which should be 1:24:20 for $(PhO)_4P^+$, but since the ^{31}P n.m.r. solution data shows that this is the only phosphorus-containing species in the solids, these are probably of the form $(PhO)_4P^+$ [halide,polyhalide]$^-$. The results from the original solutions indicate that there is incomplete reaction of $(PhO)_3P$ as shown by the presence of phosphorus (III)

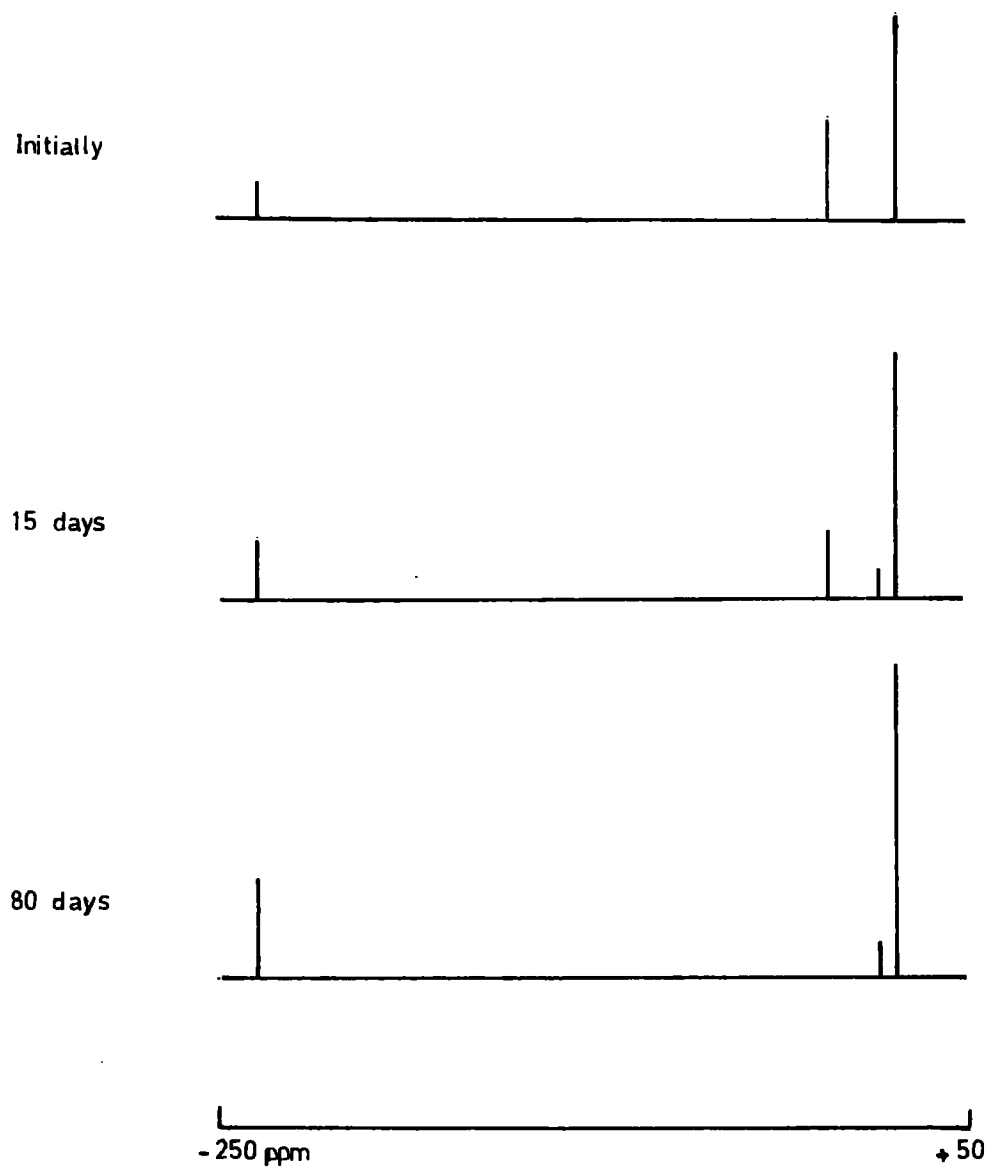


Figure 37

Relative peak heights for the ^{31}P n.m.r. spectrum of triphenyl phosphite and iodine bromide (1:2) in CH_2Cl_2.

phenoxyhalides. The products formed agree with the reaction sequence

$$4(PhO)_3P + 3\ Hal_2 \longrightarrow 3(PhO)_4P^+ + 3\ Hal^- + PHal_3$$

The incomplete reaction of the $(PhO)_3P$ is probably because the counter ion of $(PhO)_4P^+$ as it is formed can remove unreacted halogen by formation of a polyhalide ion. Competing reactions in these media may thus complicate the system and lead to an unstoichiometric product-containing the $(PhO)_4P^+$ cation.

The large amounts of phosphorus (III) phenoxyhalides left in solution in the IBr system prompted a repeat of the reaction using a $(PhO)_3P$ to IBr ratio of 1:2 to try to effect complete oxidation of $(PhO)_3P$. As previously with ICl and IBr, the solution was prepared in a sample bottle. No precipitation occurred and the dark brown solution was investigated by ^{31}P n.m.r. The spectrum showed a somewhat unexpected complexity and is represented diagramatically in Figure 37. The 80 day spectrum shows two strong signals at - 229 and + 22 ppm in the ratio of 1:3 respectively, together with a weak signal at + 18 ppm. These 3 peaks are easily assignable to PBr_3(- 229),[4] $(PhO)_3PO$ (+ 18)[4] and $(PhO)_4P^+$ (+ 22 ppm)[94] respectively. The intensity ratio of 1:3 between the PBr_3 and $(PhO)_4P^+$ signals suggests that the overall reaction is

$$4(PhO)_3P + 6IBr \longrightarrow 3(PhO)_4P^+ + 3I_2Br^- + PBr_3$$

Since the solution was prepared in the mole ratio $(PhO)_3P$:IBr of 1:2, this leaves sufficient IBr to complex with all the iodide produced and give polyhalide anions such as I_2Br^-.

The signal at - 6 ppm which disappears with time is puzzling but since the final products are PBr_3 and $(PhO)_4P^+$, this species must decompose to one or both of these compounds. The peak must be due to some intermediate in the reaction sequence. A possible explanation is that it arises from the initial reaction of $(PhO)_3P$ and IBr in a fast equilibrium,

$$(PhO)_3P + IBr \rightleftharpoons (PhO)_3PIBr$$

although no n.m.r. evidence for such a species was obtained in the other solutions. If the decomposition of this species is retarded by ionization via polyhalide formation

$$(PhO)_3PIBr + IBr \xrightarrow{A} (PhO)_3PI^+IBr_2^-$$

$$\downarrow B$$

$$(PhO)_3PBr^+I_2Br^-$$

the decomposition process may be slowed down by partial stabilization of the ionized species. Since no evidence for $(PhO)_3PBr^+$ was found in the $(PhO)_3P/Br_2$ system, step A seems the more likely route. These species were not detected, however, presumably because of low concentration and must decompose to yield $(PhO)_4P^+$ and PBr_3 according to the equation:

$$4(PhO)_3PI_2Br_2 \longrightarrow 3(PhO)_4P^+I_2Br^- + PBr_3 + 2IBr$$

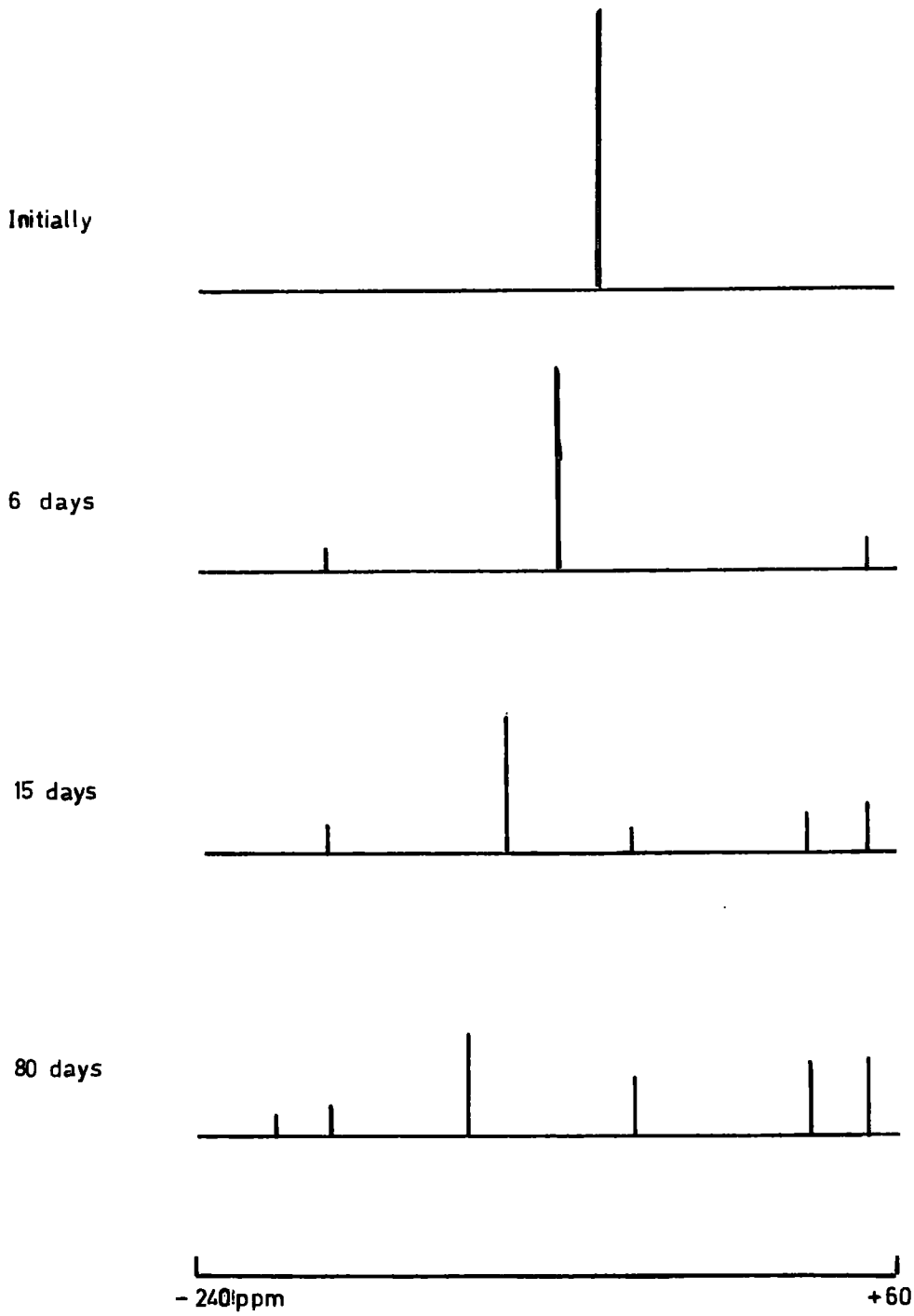


Figure 38

Relative peak heights for the ^{31}P n.m.r. spectrum of triphenyl phosphite and iodine (1:1) in CH_2Cl_2.

$(PhO)_3P$ and iodine (1:1) were dissolved in CH_2Cl_2 in a sample bottle to give a deep brown solution. A specimen of this solution was studied by ^{31}P n.m.r., and the results are represented diagramatically in Figure 38. In the spectrum taken after 80 days a number of the signals are easily explicable.

- 203 ppm	$(PhO)PI_2$ *
- 179 ppm	$(PhO)_2PI$ *
- 123 ppm	$(PhO)_3P$ 4
+ 23 ppm	$(PhO)_4P^+$ 94

* Independent result from a solution of PI_3 in $(PhO)_3P$ see later discussion.

No change occurred in the spectrum on continued monitoring for a further 40 days.

The initial signal in this system at - 68 ppm appears to move downfield with time first to - 80 ppm and then to - 100 ppm after 15 days. After 6 days some reaction seems to have accompanied the movement of the strong signal with production of $(PhO)_2PI$ and $(PhO)_4P^+$. A possible explanation of the system is shown below

$$(PhO)_3P + I_2 \rightleftharpoons [(PhO)_3PI_2] \xrightarrow{x\ 2} (PhO)_2PI + I_2 + (PhO)_4P^+I^-$$

The first stage is an equilibrium and if this is rapid a single time-averaged peak is expected. The formation of $(PhO)_4P^+I^-$ will

disturb this equilibrium if I^- removes I_2 as polyiodide anions. Such a reaction will put the $(PhO)_3P$ in excess and the time-averaged peak will move closer to the $(PhO)_3P$ resonance. The downfield movement of the initial signal from - 68 to - 100 ppm is in agreement with this hypothesis, while the 80 day old spectrum shows that a large amount of free $(PhO)_3P$ is present. This would not be expected from the original composition of the solution and indicates that removal of iodine must have occurred. The signals at - 52 and + 48 ppm are very interesting. If the initial resonance is due to the postulated equilibrium, various other reactions are possible

$$[(PhO)_3PI_2] \xrightarrow{I_2} (PhO)_3PI^+ I_3^-$$

$$2(PhO)_3PI^+ \longrightarrow (PhO)_2PI_2^+ + (PhO)_4P^+$$

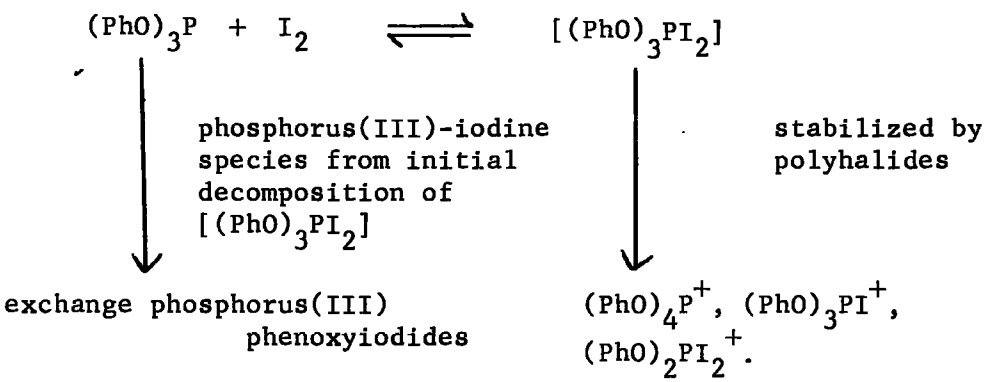
Such cations could be stabilized by the presence of large polyiodide ions in solution. Only a limited amount of exchange would be expected, since species with several P-I bonds should be less stable, and if formed would probably disproportionate as follows

$$(PhO)PI_3^+I_3^- \longrightarrow (PhO)PI_2 + 2I_2$$

Possible assignments of the - 52 and + 48 ppm signals are to the species $(PhO)_3PI^+$ and $(PhO)_2PI_2^+$ respectively. The detection of $(PhO)_4P^+$ prior to the appearance of the - 52 and + 48 ppm signals is not unreasonable if polyiodide anions are required to stabilize the

iodo-containing cations, since in the early stages of the reaction the concentration of polyiodides will be low and $(PhO)_4P^+$ will be the most stable species. The relative order of the ^{31}P n.m.r. shifts $(PhO)_3PI^+$ (- 52), $(PhO)_4P^+$ (+ 23), and $(PhO)_2PI_2^+$ (+ 48 ppm) appears quite odd at first sight. The shift difference of 100 ppm between $(PhO)_3PI^+$ and $(PhO)_2PI_2^+$, together with known shifts of - 40 and - 20 ppm for $(PhO)_3PMe^+$ [100] and $(PhO)_3PPh^+$ [110] respectively, shows that the assignments are possible, however.

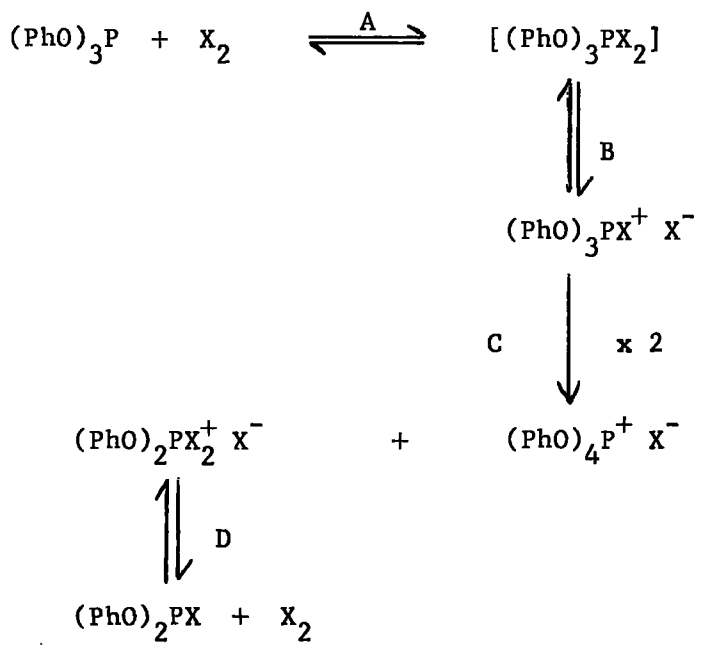
The presence of only 3 signals in the phosphorus (III) region is probably due to the high final concentration of $(PhO)_3P$ which will favour the phenoxy-containing mixed phenoxyiodides in the equilibrium process. A similar result was obtained when PI_3 was dissolved in $(PhO)_3P$. Only 3 signals at - 200, - 174 and - 126 ppm of intensity ratio 1:2:10 were found. The non-observation of the fourth signal due to PI_3 is probably due to the excess $(PhO)_3P$ used. It must be noted that the signal assigned to $(PhO)_2PI$ is in a similar region to the expected position for the PI_3 resonance, but the intensity ratio suggests that the - 174 ppm signal is due to $(PhO)_2PI$. The sequence for the reaction between $(PhO)_3P$ and I_2 (1:1) seems to be



The results thus suggest that in most of these systems the stable phosphorus (V) species is the $(PhO)_4P^+$ cation. In the reactions of $(PhO)_3P$ with IBr and I_2, stabilization of the intermediates may be possible when large polyhalide anions are present. No evidence for the formation of mixed halophenoxy phosphorus cations and anions[21] was found except for the iodine systems where iodophenoxy phosphorus cations[23] may be present.

The unexpected stability of the phosphorus (V) - iodine ions, which are expected to be the least thermodynamically stable of the phenoxy-halo species is probably due to kinetic factors.

Oxidation of $(PhO)_3P$ by halogen thus gives a complex system in which the production of the stable $(PhO)_4P^+$ species is favoured, but complications arise due to side reactions. A possible overall reaction is



a) $X_2 = Cl_2$, Br_2, ICl, IBr all 1:1 mole ratios with respect to $(PhO)_3P$

Steps A to D are fast and the only products seen are $(PhO)_4P^+$ and phosphorus (III) halide species. Step D yields a source of phosphorus-halogen bonds which can take part in exchange equilibria with $(PhO)_3P$ if any remains unreacted. If enough halogen is present the reaction will proceed until PX_3 is formed unless the PX_3 species is oxidizable in the solvent.

b) X_2 = IBr, 1:2 mole ratio $(PhO)_3P : X_2$

For $(PhO)_3P$: IBr of 1:2, step A appears to be fast but step B is slow, followed by fast steps C and D. The mixed phosphorus (V) phenoxy-halo species were not detected since they disproportionate in solution. The presence of polyhalide anions in high concentration probably stabilize the $(PhO)_3P^+X$ species sufficiently to retard step B but not enough to slow down steps C and D.

c) $X_2 = I_2$ 1:1 mole ratio with respect to $(PhO)_3P$

In the case of iodine, step A appears to be fast while steps B, C and D are comparatively slow. The presence of the large polyiodide ions probably stabilizes the mixed phenoxy-iodo phosphorus cations sufficiently for them to increase in concentration. The slow kinetics of phosphorus-iodine systems[97] may well be another important factor.

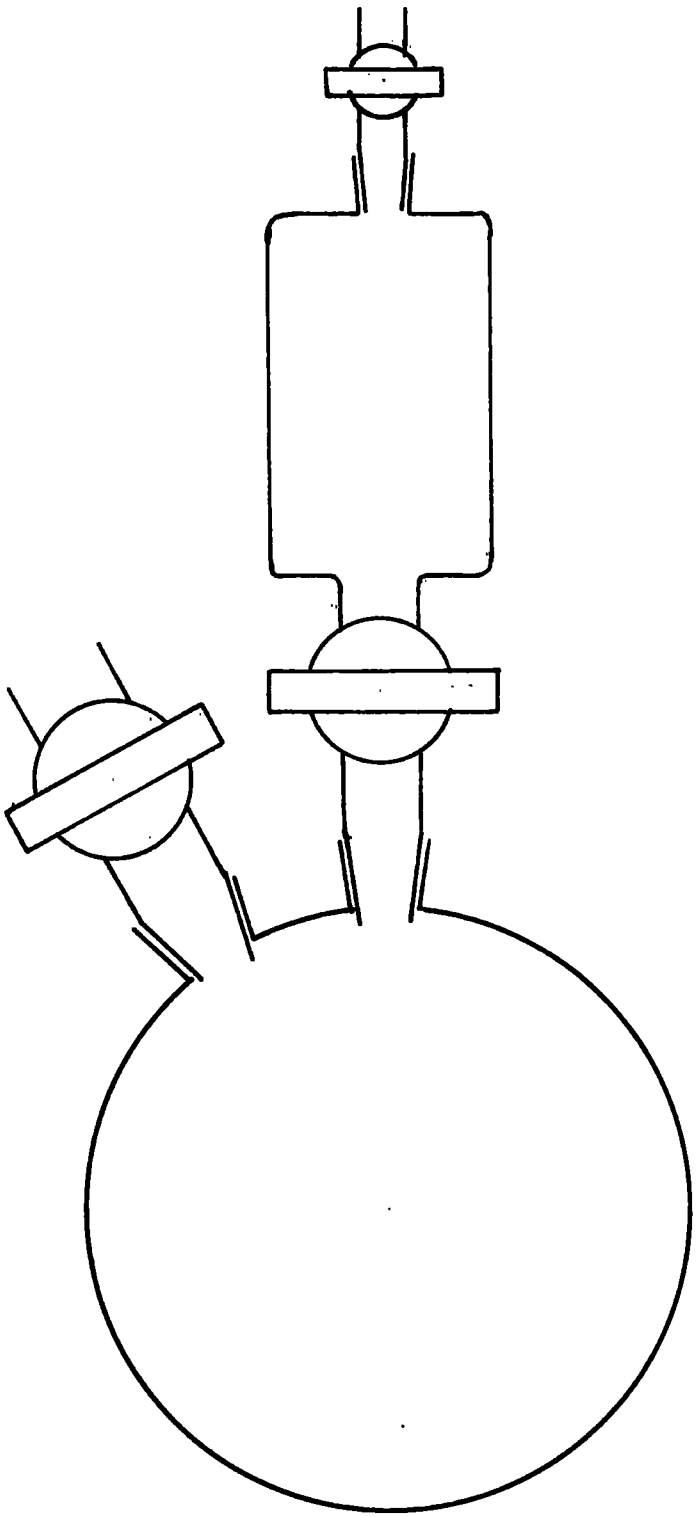


Figure 39

Apparatus used in the investigation of the reaction between triphenyl phosphite and bromine (1:1).

The mixed phenoxy-halo phosphorus (V) species thus appear to be not very stable, but the presence of polyhalide counter-ions may slow down the process of decomposition sufficiently in some iodine systems to allow appreciable quantities of these species to form.

Experimental

The general technique was as follows. The required amount of $(PhO)_3P$ was pipetted into a sample bottle and the requisite solvent added to give a homogeneous solution. The required quantity of the halogen was weighed in another sample bottle, dissolved in the appropriate solvent and then added slowly to the $(PhO)_3P$ solution. The resulting homogeneous mixtures were allowed to stand for 15 minutes before an n.m.r. sample was taken. In the bromine systems, no further reactions occurred but with ICl and IBr in 1:1 mole ratios to $(PhO)_3P$, some solid precipitated and samples of these solids were isolated, as mentioned previously. Table 29 summarizes the experiments performed using this technique.

The other reactions were attempted on a rather larger scale using the apparatus shown in Figures 39, 40.

The apparatus shown in Figure 39 was used for the reactions

$$(PhO)_3P + Br_2 \quad 1:1 \text{ in } CH_2Cl_2$$

$$'(PhO)_4PBr_2' + BBr_3 \text{ (excess) in } CH_2Cl_2$$

In both of these the phosphorus-containing reactant was dissolved in CH_2Cl_2 in the flask, while the other reactant was added dropwise with stirring as a CH_2Cl_2 solution. These manipulations were carried out in a glove box.

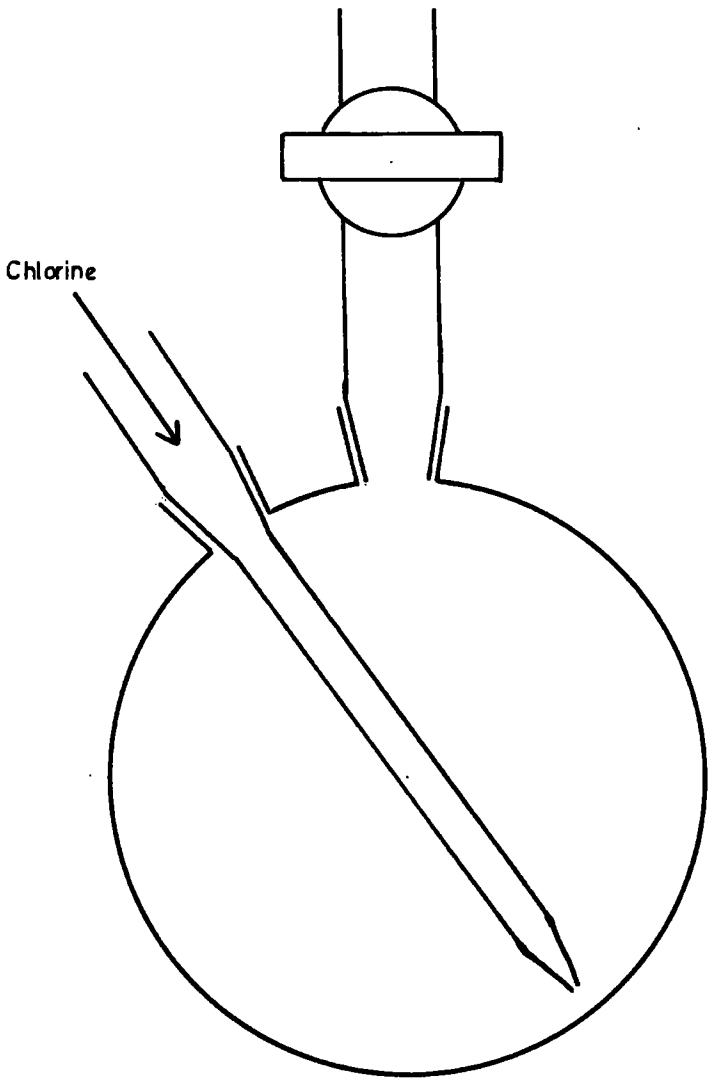


Figure 40

Apparatus used in the reaction between triphenyl phosphite and chlorine (excess).

Table 29. Experimental details for reactions of triphenyl phosphite with halogens

Reaction		$(PhO)_3P$	Halogen	Solvent
$(PhO)_3P + Br_2$	1:1	1 ml (3.82 mmoles)	0.2 mls (4.0 mmoles)	$BrCH_2CH_2Br$
$(PhO)_3P + Br_2$	2:1	2 mls (7.64 mmoles)	0.2 mls (4.0 mmoles)	$BrCH_2CH_2Br$
$(PhO)_3P + ICl$	1:1	2.6 mls (9.93 mmoles)	0.5 mls (9.98 mmoles)	CH_2Cl_2
$(PhO)_3P + IBr$	1:1	2.35 mls (8.97 mmoles)	1.8330 gms (8.86 mmoles)	CH_2Cl_2
$(PhO)_3P + IBr$	1:2	1.15 mls (4.39 mmoles)	1.7676 gms (8.55 mmoles)	CH_2Cl_2
$(PhO)_3P + I_2$	1:1	1.36 mls (5.19 mmoles)	1.3195 gms (5.19 mmoles)	CH_2Cl_2

The apparatus shown in Figure 40 was used in the reaction between $(PhO)_3P$ and excess chlorine. Chlorine was passed into the solution of $(PhO)_3P$ in CH_2Cl_2 via a P_2O_5 drying tube while the outlet from the flask was open to the atmosphere via a bubbler to allow release of any pressure build-ups. This reaction was performed outside the glove box, but under nitrogen to protect the reactants and products from atmospheric moisture.

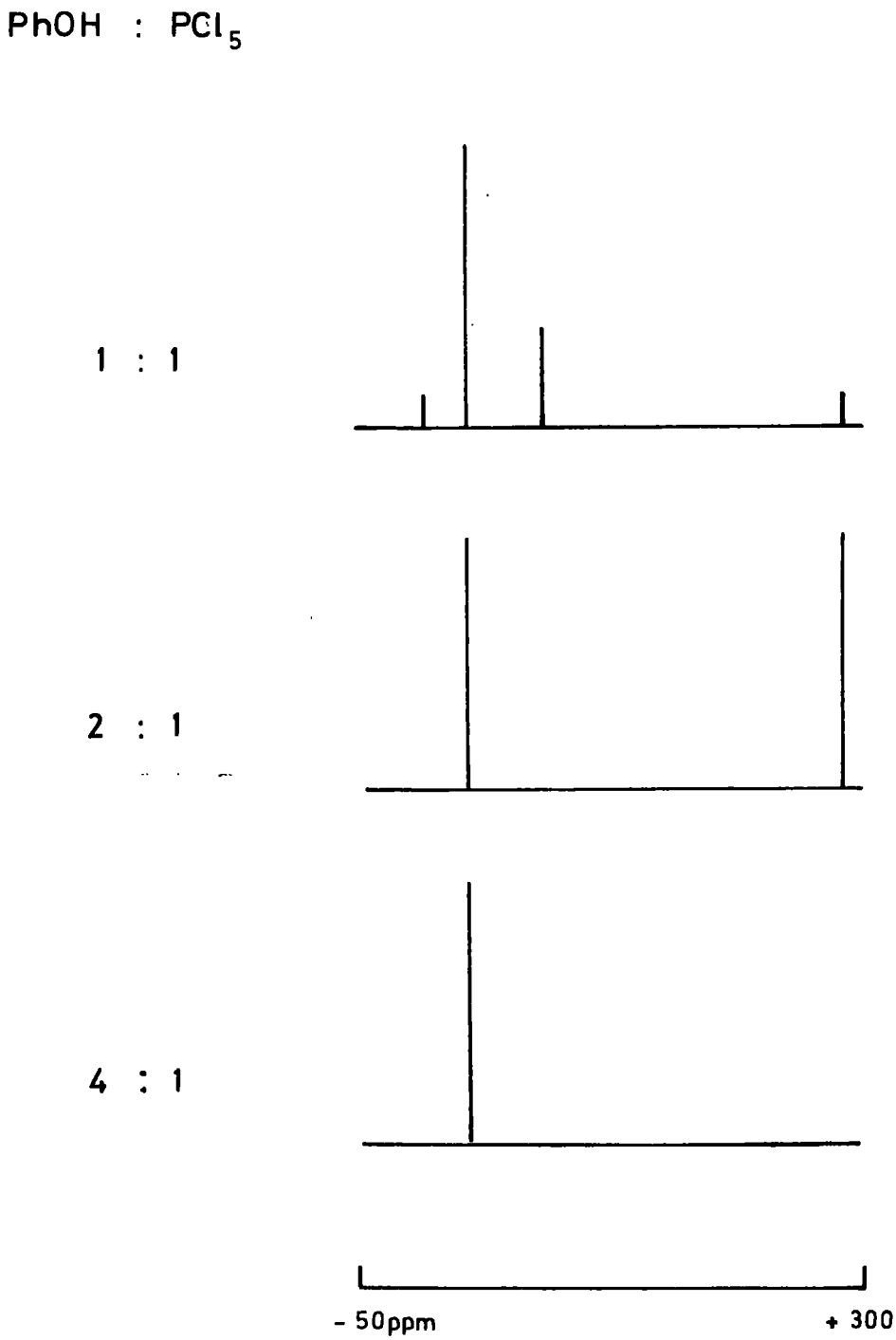


Figure 41

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (V) chloride and phenol in CH_2Cl_2.

All the glassware used in these prep scale reactions was initially dried in an oven overnight, cooled to room temperature, evacuated on a vacuum line and then opened under nitrogen. All manipulations were carried out either in a glove box or under an external nitrogen pressure to ensure as little hydrolysis of the materials as possible.

ii) Phosphorus pentachloride with phenol

The products of the reaction between phenol and PCl_5 were investigated by Rydon and Tonge.[21] They reported the preparation of the phenoxychlorophosphoranes $(PhO)_nPCl_{5-n}$ $[1 \leq n \leq 4]$ by taking PhOH and PCl_5 in the required proportions and heating as a melt and identified the products by hydrolysis and alcholysis methods. Ramirez et al[24] investigated the reaction between PhOH and PCl_5 using ^{31}P n.m.r. techniques and interpreted the data in terms of formation of $(PhO)_3PCl_2$ as well as an undefined 6 co-ordinate phosphorus species.

In view of the results from the oxidation of $(PhO)_3P$ by halogens, it was decided to reinvestigate the reaction between PhOH and PCl_5 by means of ^{31}P n.m.r. techniques.

Solutions of PhOH and PCl_5 in CH_2Cl_2 were prepared in the following molar ratios, 1:1, 2:1 and 4:1. The PhOH was dissolved in the minimum quantity of CH_2Cl_2 and added to the solid PCl_5 in a sample bottle. A vigorous reaction occurred with gaseous evolution in all three cases to yield green solutions for the 1:1 and 2:1 mixtures and a colourless solution for the 4:1 mixture. The solutions were investigated by ^{31}P n.m.r., and the results are shown diagramatically in Figure 41.

The assignment of these peaks is facile except for the one at - 8 ppm.

+ 292 ppm	PCl_6^-	4
+ 80 ppm	PCl_5	98
+ 22 ppm	$(PhO)_4P^+$	94

This indicates a general reaction

$$x\ PCl_5 + y\ PhOH \rightarrow (PhO)_4P^+Cl^-$$

irrespective of the ratios of PhOH to PCl_5 taken. In the 4:1 solution complete conversion of PCl_5 to $(PhO)_4P^+Cl^-$ occurs while in the 2:1 solution the compound produced is $(PhO)_4P^+PCl_6^-$ as indicated by the 1:1 ratio of the two ^{31}P n.m.r. signals. In the 1:1 solution a large quantity of PCl_5 remained unreacted but a small amount of PCl_6^- was formed. In this solution the weak signal at - 8 ppm is of some interest. It could be due to small quantities of $(PhO)_3PCl_2$ since the amount of phenol is very limited. An alternative assignment is to $(PhO)_3PCl^+$ but since $(PhO)_3PI^+$ has been assigned a resonance of - 52 ppm this is unlikely. The appearance of unreacted PCl_5 in this solution suggests that $(PhO)_4P^+$ is formed as the predominant phosphorus (V) cation. Addition of phenol to PCl_5 appears to yield $(PhO)_4P^+$ rapidly, so in the 1:1 solution the - 8 ppm peak may well be due to $(PhO)_3PCl_2$ which is formed because the limited quantity of PhOH available is exhausted before complete conversion to $(PhO)_4P^+$ can occur.

The reaction between phenol and PCl_5, 4:1 molar ratio, was repeated on a preparative scale in an attempt to isolate $(PhO)_4P^+Cl^-$.

6.5106 gms (31.26 mmoles) of PCl_5 were dissolved in 50 mls of CH_2Cl_2 and 11.6847 gms (124.31 mmoles) of PhOH as a solution in 30 mls of CH_2Cl_2 were added dropwise with stirring over a period of one hour. After stirring for a further hour the bulk of the CH_2Cl_2 was pumped off and a white solid was obtained. The solid was purified by recrystallisation as shown by the analysis figures in Table 30.

Table 30. Analysis figures for the product of the reaction between phosphorus (V) chloride and phenol 1:4

Sample		% P	% C	% H	% Cl
$(PhO)_4P^+Cl^-$	Theoretical	7.06	65.67	4.56	8.09
$(PhO)_4P^+Cl^-$ recrystallised from CH_2Cl_2	prep	6.6	61.13	4.89	16.16
$(PhO)_4P^+Cl^-$ recrystallised from CH_2ClCH_2Cl	prep PhCl and 1:1	6.93	61.95	3.87	10.96
$(PhO)_4P^+Cl^-$ 2nd recrystallisation from PhCl and CH_2ClCH_2Cl 1:1	prep	6.88	63.24	5.05	10.85

The rather poor analysis figures in Table 30 are a little surprising. The ^{31}P n.m.r. solution spectrum of the final solid dissolved in CH_2Cl_2 showed only one strong peak at + 22 ppm assignable to $(PhO)_4P^+$. [94]

A weak signal at + 18 ppm was probably due to some contaminant $(PhO)_3PO$ formed by hydrolysis of the parent $(PhO)_4P^+$. From this n.m.r. data the phosphorus and chlorine analysis should be low while the carbon and hydrogen figures should be a little high. The table shows that this is not so. A possible explanation is that small amounts of either CH_2Cl_2 or CH_2ClCH_2Cl are present in the molecular lattice and raise the chlorine percentage. The extremely high chlorine percentage in the sample after recrystallisation from CH_2Cl_2 supports this hypothesis since no PCl_6^- was found in its solution spectrum. The reduction of the chlorine percentage on further recrystallisation from a PhCl and CH_2ClCH_2Cl mixture without much effect on the relative phosphorus, carbon and hydrogen analysis figures also appears to agree with this explanation.

In the light of this data it was decided not to attempt further purification of this sample since the impurities were such that they would not interfer with reactions involving the $(PhO)_4P^+$ species.

Whatever the ratio of phenol to PCl_5, the predominant cationic product of the reaction appears to be $(PhO)_4P^+$. When the PhOH to PCl_5 ratio is low, in addition to the unreacted PCl_5, some $(PhO)_3PCl_2$ may be formed. The deductions of Ramirez et al[24] that $(PhO)_3PCl_2$ is formed at higher molar ratios of phenol to PCl_5 are not substantiated and it must be pointed out that the shift values obtained by these workers are more consistent with $(PhO)_4P^+$. No evidence for formation of the polyphenoxychlorophosphate anions proposed by previous workers was found.[21,24]

Experimental

All the solution n.m.r. reactions were carried out using the same general approach. The required amount of phenol was weighed in a sample bottle and dissolved in the minimum volume of CH_2Cl_2. This solution was then added to solid PCl_5 and when the reaction had subsided to yield a clear solution, a sample was taken and studied by ^{31}P n.m.r. techniques. The materials used in these reactions are given in Table 31.

Table 31. Experimental details for the reaction between phosphorus (V) chloride and phenol.

PhOH : PCl_5	PCl_5 used	PhOH used
1 : 1	0.9144 gms (4.39 mmoles)	0.4155 gms (4.42 mmoles)
2 : 1	0.7100 gms (3.41 mmoles)	0.6464 gms (6.88 mmoles)
4 : 1	0.9000 gms (4.32 mmoles)	1.6220 gms (17.26 mmoles)

The preparative scale reaction between PhOH and PCl_5, 4:1, was carried out in apparatus similar to that shown in Figure 39, the PCl_5 being kept in the flask while the PhOH was added via a measuring funnel. All additions were carried out in a glove box under nitrogen with apparatus previously dried overnight in an oven, pumped down to vacuum and opened under nitrogen.

iii) Chlorophenoxy-phosphoranes with organic bases

Ramirez et al reported that when the 1:5 reaction between PCl_5 and phenol was carried out in the presence of 5 mole equivalents of γ-collidine, a solid was obtained which analysed as $(PhO)_5P$.[24] This product was not formed in the absence of the base. A number of related compounds containing catechyl groups, cat PCl_3, cat_2PCl and related species, have been studied by Reeve with particular reference to the acceptor properties of these molecules with pyridine and similar organic bases. Evidence was found that these catechyl containing phosphoranes act as acceptors.[25]

It was decided to investigate the interaction of $(PhO)_4P^+$ with pyridine and 2,2'dipyridyl, initially in the absence of added phenol, and later with phenol present.

The sample of $(PhO)_4P^+Cl^-$ in these reactions was the final product from the preparation outlined in section 2(ii) of this chapter. This sample appeared to contain small traces of solvent but no phosphorus species other than $(PhO)_4P^+$. Because of this, all the figures given for mole ratios of reactants are approximate, and will contain slightly less $(PhO)_4P^+$ than stated, since the quantity of base was calculated on the assumption that the $(PhO)_4P^+Cl^-$ was pure. Table 34 in the experimental details of this section gives the weights of reactants used and corrected mole ratios for the reactions involving the impure $(PhO)_4P^+Cl^-$.

$(PhO)_4P^+Cl^-$ was dissolved in CH_2Cl_2 and the required amount of pyridine or 2,2' dipyridyl added to give solutions of 1:1 and 1:5 mole ratio of $(PhO)_4P^+$ to organic base. The ^{31}P n.m.r. spectra of these solutions all showed a single strong peak at + 22 ppm and a weak

signal at + 17 ppm. Over the period of 16 days the + 17 ppm signal increased slightly in intensity and a new weak signal appeared at + 85 ppm, but the main signal was still at + 22 ppm.

The constancy of the + 22 ppm signal in all solutions irrespective of the concentration of the organic base suggests that no adduct is formed between $(PhO)_4P^+$ and the base. When the related catechyl cation $(cat)_2P^+$ was dissolved in solutions containing pyridine, an upfield shift of the order of + 140 ppm from that of the parent, - 42 ppm, was observed.[25] This upfield movement has been attributed to the formation of the species $(cat)_2P^+py_2$ in solution. The $(cat)_2P^+$ cation is very unstable and is stabilized by co-ordination of the two pyridine molecules, whereas the $(PhO)_4P^+$ cation is quite stable. It is also interesting to note that $(cat)_2PCl$ is molecular,[25] while $(PhO)_4PCl$ is ionic. It has been suggested that increased coordination in the catechyl compounds tends to relieve the ring strain in the five-membered catechyl-phosphorus (V) units, which is greatest in the tetrahedral cations.[25] If this is the case, the coordination of pyridine to $(cat)_2P^+$ and the molecular form of $(cat)_2PCl$ are understandable. The poor acceptor properties of $(PhO)_4P^+$ may thus be rationalized since no such driving force is present, and indeed increased coordination must lead to steric crowding.

The signal at + 17 ppm is assignable to $(PhO)_3PO$ [4] while the peak at + 85 ppm is due to $(PhO)_5P$.[24] The appearence of the $(PhO)_5P$ signal at first sight seems a little strange, but it is readily explicable when the growth of the signal for $(PhO)_3PO$ with time is considered.

Slow hydrolysis of $(PhO)_4P^+$ probably occurs to yield $(PhO)_3PO$ and PhOH. The phenol so formed then interacts with $(PhO)_4P^+$ to form $(PhO)_5P$ due to the presence of the organic base. The reaction sequence would be

$$(PhO)_4P^+ + H_2O \longrightarrow (PhO)_3PO + PhOH + H^+$$

$$(PhO)_4P^+Cl^- + PhOH + py \longrightarrow (PhO)_5P + pyH^+Cl^-$$

This reaction scheme is similar to that used by Ramirez et al[24] to prepare $(PhO)_5P$ from PCl_5 and PhOH in the presence of γ-collidine to remove HCl liberated in the reaction.

In an attempt to verify this suggestion, a tube was prepared containing PhOH : $(PhO)_4P^+Cl^-$: py in the ratio 1:1:5 approximately. The phenol and $(PhO)_4P^+Cl^-$ were dissolved in the minimum volume of CH_2Cl_2 and the required amount of pyridine was added. No obvious reaction occurred and the pale yellow solution was studied by ^{31}P n.m.r. The spectrum showed a strong signal at + 85 ppm assignable to $(PhO)_5P$[24] and a weak signal at + 16 ppm due to $(PhO)_3PO$.[4] No signal was found at + 22 ppm, indicating complete conversion of $(PhO)_4P^+$ to $(PhO)_5P$. The reaction was repeated on a preparative scale with slight modifications in an attempt to isolate $(PhO)_5P$ and confirm its shift assignment.

2.65 gms (5.88 mmoles) of $(PhO)_4P^+Cl^-$ were stirred with 35 mls of benzene to form a suspension and 0.5 mls (6.20 mmoles) of pyridine were added to the suspension. Over a period of one hour 0.56 gms (5.96 mmoles) of phenol in 35 mls of benzene were added with stirring. The resulting mixture was stirred for 5 hours and was then filtered. The filtrate

was freed from solvent to yield a white solid. This crude material was analysed and the results suggested that some impurity was present. The crude material was recrystallised from hexane to yield a white crystalline solid (Table 32).

Table 32. Analysis figures for pentaphenoxyphosphorane

$(PhO)_5P$	% P	% C	% H	Others
Theoretical	6.2	72.6	5.1	-
Crude	5.57	66.10	4.56	No chlorine or nitrogen found
Recrystallised	6.02	71.91	4.98	No chlorine or nitrogen found

A solution of this white crystalline solid was prepared in CH_2Cl_2 and separated into 3 portions. To one portion was added enough pyridine to give a solution of mole ratio $(PhO)_5P$ to pyridine of 1:5 while to another was added $(C_5H_{11})_4N^+Cl^-$ to give a solution of mole ratio $(PhO)_5P$ to Cl^- of 1:4. These two solutions and the parent solution were studied by ^{31}P n.m.r. In all cases the same spectrum was obtained of a strong signal at + 85 ppm and a weak signal at + 18 ppm assignable to $(PhO)_5P$[24] and $(PhO)_3PO$[4] respectively.

These results are consistent with the presence of $(PhO)_5P$ in each solution, and indicate that $(PhO)_5P$ shows no acceptor properties towards pyridine or chloride anion, since an interaction should cause a change in the resonance position. If adduct formation take place,

two possible courses of action depending on peak positions and exchange rates are open. If the exchange process between coordinated and uncoordinated $(PhO)_5P$ with the base is rapid, a time averaged upfield peak would be expected, but if the exchange is slow, two signals would be seen, one at higher field due to the coordinated $(PhO)_5P$ and one due to uncoordinated $(PhO)_5P$. The results obtained from these three solutions eliminate both of these possibilities since no change in the ^{31}P n.m.r. spectrum was observed. The related compound $(cat)_2PCl$ interacts with pyridine and chloride to give upfield shift movements of the order of 50 ppm on coordination.[25] The parent $(cat)_2PCl$ has a solution shift of approximately + 10 ppm while the $(cat)_2PClpy$ species has a shift value of + 85 ppm. For coordination of chloride, the shift value depends upon the concentration of the chloride ion, but appears to reach a limiting value of + 66 ppm when the $(cat)_2PCl$ to Cl^- ratio is 1:3.2. The difference in acceptor properties between $(PhO)_5P$ and $(cat)_2PCl$ is marked and may be due to the absence in $(PhO)_5P$ of the driving force for coordination in the catechyl system, relief of ring strain.

The results from this section indicate that both $(PhO)_5P$ and $(PhO)_4P^+$ show no acceptor properties towards pyridine and dipyridyl while $(PhO)_5P$ shows no interaction with chloride. $(PhO)_4P^+$ will interact in the presence of an organic base, however, with a further mole of phenol to give $(PhO)_5P$. This confirms the preparation of $(PhO)_5P$ by Ramirez et al,[24] but suggests that the presence of the organic base is only necessary for the addition of the final phenoxy group.

Experimental

All the solution n.m.r. investigations were carried out using the same general approach. The required amount of $(PhO)_4P^+Cl^-$ or $(PhO)_5P$ was weighed in a sample bottle and dissolved in CH_2Cl_2. The other reactants were added to this solution, either as neat liquids, or as solutions in CH_2Cl_2 for solids. A sample of the solution was then taken and studied by ^{31}P n.m.r. (see Table 33) for experimental details. Where $(PhO)_4P^+Cl^-$ was used, weights show amount of solid taken, while the number of moles used is based on the phosphorus percentage of 6.88% in the sample compared with the theoretical percentage of 7.06.

The preparative scale reaction between $(PhO)_4P^+Cl^-$ and PhOH in the presence of pyridine was carried out in apparatus similar to that shown in Figure 39, with the $(PhO)_4P^+Cl^-$ and pyridine together in the flask, and the phenol solution added via a measuring funnel.

Table 33. Experimental details for the reactions of tetraphenoxyphosphonium chloride and pentaphenoxyphosphorane with bases.

Reaction	Amount of phosphorus species used	Amount of organic base used	Other reactants	Exact mole ratio
$(PhO)_4P^+Cl^-$ and py 1:1	0.3296 gms (0.73 mmoles)	0.06 mls (0.74 mmoles)	-	1:1.02
$(PhO)_4P^+Cl^-$ and py 1:5	0.3851 gms (0.85 mmoles)	0.38 mls (4.72 mmoles)	-	1:5.52
$(PhO)_4P^+Cl^-$ and dipy 1:1	0.3140 gms (0.70 mmoles)	0.1150gms (0.74 mmoles)	-	1:1.06
$(PhO)_4P^+Cl^-$ and dipy 1:5	0.3533 gms (0.78 mmoles)	0.6589 gms (4.22 mmoles)	-	1:5.41
$(PhO)_4P^+Cl^-$ with py and PhOH 1:5:1	0.3510 gms (0.78 mmoles)	0.325 mls (4.03 mmoles)	0.0781 gms (0.83 mmoles)	1:5.17:1.07
$(PhO)_5P$ and py 1:5	0.4231 gms (0.94 mmoles)	0.39 mls (4.84 mmoles)	-	1:5.15
$(PhO)_5P$ and $(C_5H_{11})_4N^+Cl^-$ 1:4	0.2101 gms (0.47 mmoles)	-	0.5433 gms (1.63 mmoles)	1:3.49

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The application of ^{31}P n.m.r. spectroscopy to the study of solution reactions of some simple phosphorus compounds close to room temperature has provided clear evidence in most cases for the course of reaction, and helped considerably in the identification of products.

Mixed bromochlorophosphonium ions were produced by the oxidation of PBr_3 or PCl_3 and stabilized in sulphuric acid media, while some mixed halohydroxyphosphonium species have been detected in similar solutions. Attempts to generate mixed halophosphonium cations containing iodine were partially successful in that $PI_2Cl_2^+$ and PCl_3I^+ appear to have been formed by solution of PI_3 in $ClHSO_3$, although oxidation by halogen proved less successful.

The production of iodine-containing species of the type $[PI_{4-y}X_y^+]$ (X = halogen, $0 \leq y \leq 4$) from mixtures of PI_3 and halogen in sulphuric acid solvents seems possible. The use of a variable temperature ^{31}P n.m.r. probe would obviously be of value in these studies but probably the most important requirement is an inert solvent, capable of dissolving PI_3, which is miscible with the acidic solvents used. By such means it may be possible to overcome the problems caused by the heterogeneous nature of the PI_3-halogen reaction found in this work.

Further investigation of the reactions between PI_3 with $SbCl_5$ and PCl_5 at low temperature (Appendix 2), either in solution or in

the solid state would be desirable, as would repetition of a number of other reactions such as PI_3 in 25% oleum although in the latter case some problems will arise with the limited liquid range of the acid solvents.

The discovery of a solvent in which phosphorus (V) six-coordinate anions are stable would facilitate the investigation of mixed species such as $PCl_4F_2^-$,[113,114] $PCl_2F_4^-$[115] and PCl_5Br^-.[7] An extension of the work to cover the fluorine-containing solutes PF_3, POF_3 and PF_5, together with other strong acids such as 'magic acid' would also be interesting. Very recently some oxidations of phosphorus (III) halides in acetic anhydride have been reported and mixed halogeno-phosphorus (V) compounds claimed.[73] A ^{31}P n.m.r. investigation of these reactions would establish the validity of the results.

The solution chemistry of the organophosphorus species studied in the sulphuric acid solvents is on the whole quite understandable. One interesting point is that in the phosphoryl compounds sulphonation caused an upfield shift of the ^{31}P n.m.r. signal while in Ph_3PS, the shift was downfield. The relationship between this phenomenon and the basicity of the species could be further investigated by means of analogous sulphur, selenium and tellurium compounds. Further work on aryl- (and alkyl-) substituted organophosphorus compounds using complementary techniques such as ^1H n.m.r. to establish with certainty the site of sulphonation, including deuteration studies with selectively deuterated reagents or D_2SO_4 as solvent, could also prove useful.

The chemistry of the phenoxyhalophosphoranes studied suggests that mixed halophenoxy species are unstable. Certainly no evidence was obtained consistent with 5- or 6-coordinate phenoxyhalophosphorus derivatives. The possibility of the formation of 4-coordinate phenoxyiodophosphonium cations cannot be discounted, however, although the results were not conclusive. In view of the slow kinetics observed in some P-I compounds, isolation of such species might be possible in the presence of suitable large anions which could effect rapid precipitation.

The present work has shown that ^{31}P n.m.r. is an invaluable probe in investigating the chemistry of phosphorus-containing species. There clearly remains considerable scope for future work in these fields especially in conjunction with Fourier Transform techniques for the investigation of unstable and reacting systems where results would be difficult to obtain by any other means. This is well exemplified by the work on PI_3 solutions in 100% sulphuric acid and chlorosulphuric acid.

APPENDIX 1

SOME LEWIS ACID AND LEWIS BASE REACTIONS OF PHOSPHORUS (III) IODIDE

1) Introduction

The donor-acceptor properties of PI_3 have been little studied. The very nature of the interactions, which involve an alteration in the coordination number of the phosphorus atom and substantial changes in the electron density around it, makes these systems particularly suitable for study by ^{31}P n.m.r. techniques. A limited investigation of some Lewis acid and Lewis base reactions of PI_3 was therefore carried out.

2) Present Work

i) Phosphorus (III) iodide as a Lewis base with boron (III) halides

The preparation of $PI_3.BI_3$ was first reported in 1964[101] and by 1966 much more data was available on the PX_3BX_3 systems, where X = halogen. Investigations of the reactions between PCl_3, PBr_3 or PI_3 and BCl_3, BBr_3 or BI_3 showed that the three phosphorus (III) halides complex with both BBr_3 and BI_3, but not with BCl_3 even at 233 K.[102] No n.m.r. data for these adducts was reported, however.

The reaction between PI_3 and BBr_3 or BI_3 was re-investigated by ^{31}P n.m.r. techniques. The details of the samples prepared are given in Table 34.

Table 34. Experimental details for the reactions of phosphorus (III) iodide with boron (III) bromide and boron (III) iodide

System	Remarks
PI_3 + BBr_3 excess BBr_3 used as solvent	Addition of BBr_3 to solid PI_3 in an n.m.r. tube yielded a pale orange solution. After 30 mins a yellow solid precipitated and the remaining liquid turned slightly purple. The ^{31}P n.m.r. spectrum showed a broad solid state peak at approximately + 30 ppm, while the ^{11}B spectrum contained solution peaks at -10 and -21 ppm.
PI_3 + BBr_3 1:1	0.35 mls (3.70 mmoles) of BBr_3 was added to 1.4415 gms (3.50 mmoles) of PI_3 in an n.m.r. tube. After 4 days, the solid/liquid mixture solidified to a yellow solid. Both the ^{31}P and ^{11}B n.m.r. solid state spectrum showed well-defined peaks centred at + 20 ppm and + 45 ppm respectively.
PI_3 + BI_3 excess BI_3	An n.m.r. tube containing PI_3 and excess BI_3 was heated to 348 K when both solids melted, and on shaking a dark red solution formed. The sample was heated for one hour and an orange solid precipitated. On cooling the mixture solidified and gave a solid state ^{31}P n.m.r. peak at + 12 ppm. No solid state ^{11}B n.m.r. spectrum was obtained.

The ^{31}P n.m.r. peaks obtained from the products of the PI_3 + BBr_3 and PI_3 + BI_3 reactions at approximately + 25 and + 12 ppm respectively are nearly 200 ppm upfield from the PI_3 resonance.[4] This shift is large enough to reflect a coordination change about phosphorus and is thus consistent with adduct formation. In the PI_3 + BI_3 system the product is presumably the 1:1 adduct PI_3BI_3 but the results for the PI_3 + BBr_3 system are more complex. The strong signal at - 21 ppm and weak signal at - 10 ppm in the ^{11}B n.m.r. spectrum from the tube containing excess BBr_3 are assignable to BBr_3 and BBr_2I respectively,[103] and as the BBr_3 was in large excess, appreciable amounts of BBr_2I may be present. The ^{11}B n.m.r. signal at + 45 in the PI_3 + BBr_3 1:1 reaction tube is immediately assignable to a 4-coordinate boron atom,[105] but the precise halogen distribution in the system cannot be ascertained, since halogen exchange may have taken place at both boron and phosphorus. This ^{11}B shift compares favourably with the shift values of other 4-coordinate BBr_3 adducts.

BBr_3,	- 22.4 ppm[103]
BBr_3.py,	+ 25.4 ppm[104]
BBr_4^-,	+ 42.4 ppm [95]

Thus the ^{11}B and ^{31}P n.m.r. data are consistent with increased coordination at both boron and phosphorus in these systems.

The adduct PI_3BI_3 was prepared on a larger scale in a glove box. 4.56 gms (11.07 mmoles) of PI_3 were dissolved in 140 mls of CS_2 and 5.20 gms (13.27 mmoles) of BI_3 were added as a solution in 130 mls of CS_2, dropwise with stirring over a period of one hour. The

orange precipitate was filtered off, washed with CS_2 to remove any unreacted material, and washed finally with pet ether (40-60). The analysis figures for this compound confirm that it is $PI_3.BI_3$

		% P	% I
$PI_3.BI_3$	theoretical	3.85	94.80
	found	3.92	92.26

An attempt at solid state n.m.r. was unsuccessful, no peaks being observed. Difficulty in detecting ^{31}P solid state peaks for phosphorus (III) compounds has been found for PI_3 where no resonance was observable. A broad signal was detected for the more symmetrical compound P_2I_4, however, centred at approximately - 90 ppm. This compares with a solution shift of about - 108 ppm[31] and an experimental value of - 102 ppm in CS_2.

ii) Phosphorus (III) iodide as a Lewis acid with pyridine and 2,2'dipyridyl

Up to the present time, little work has been done on the Lewis acid chemistry of PI_3. Addition of pyridine to a hexane solution of PI_3 produced a creamish-white precipitate analysing as PI_3. 3 to 4 py according to a 1969 report.[106] From more recent work it was deduced that reaction of PI_3 with pyridine in dry benzene yields P_2I_4, iodine, and an adduct $PI_3.2py$.[107] The change in coordination number at phosphorus on coordination of pyridine should be readily amenable to ^{31}P n.m.r. techniques, so this system was re-investigated.

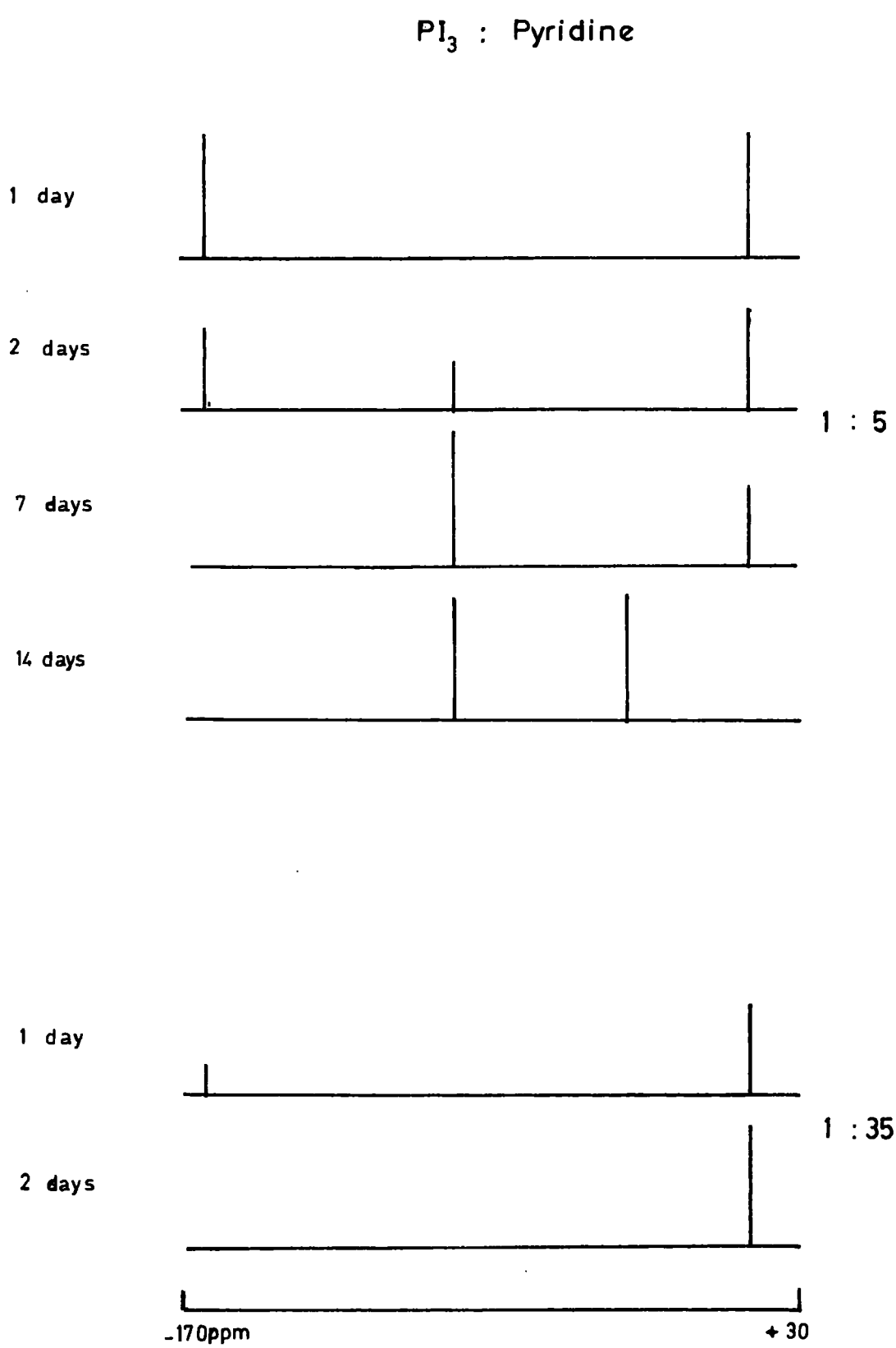


Figure 42

Relative peak heights for the ^{31}P n.m.r. spectrum of phosphorus (III) iodide in pyridine.

Two solutions of PI_3 were prepared in pyridine with PI_3:py ratios of 1:5 and 1:35 respectively. The mixtures in both cases yielded a dark brown solution and an orange-brown solid. The 1:5 mixture remained during the period of investigation as a suspension of the solid in the solution, but in the 1:35 solution, the solid settled out very quickly and continued investigation of the sample required decantation of the liquid. Indeed the solid became so well-packed at the bottom of the n.m.r. tube that a solid state spectrum was obtained from it. The ^{31}P n.m.r. results are summarized in Figure 42. The solid obtained from the 1:35 mixture gave a not very well-defined signal centred at approximately 0 ppm. The spread of the signals over a range of about 180 ppm suggests that there are various coordination numbers present for the phosphorus species but assignment is difficult. It is interesting to note that the reaction appears to be the same in both systems initially but that further reaction occurs in the 1:5 solution.

The initial signal at - 160 ppm is probably due to the parent PI_3. This shift is a little higher than the normal value of - 178 ppm[4] but its appearance in the initial solution coupled with the slowness of reaction makes this assignment quite reasonable. The signal at + 16 ppm can be assigned to a species of the form PI_3.py, the upfield shift from the parent of nearly 180 ppm being consistent with an increase of the coordination number of phosphorus from 3 to 4. The appearance of two separate signals in the spectrum from these two related species with wide frequency separation indicates that the equilibrium is quite slow. The strength of the + 16 ppm peak in the 1:35 solution compared with the - 160 ppm signal is in agreement

with this explanation. The coordination compound between PI_3 and pyridine appears to be stable in the 1:35 solution but notin the 1:5 solution. The signal found at - 80 ppm in the 1:5 solution could be due to the slow formation of P_2I_4 in this system. The position of this resonance is higher than the reported shift of approximately - 108 ppm,[31] but as the PI_3 resonance appears at higher field than usual in the solution, this assignment seems quite justified. These upfield shifts may reflect weak complex formation in this system. Further evidence to support this assignment is that P_2I_4 was found as a major product of the reaction between PI_3 and pyridine in benzene.[107]

The 1:5 and 1:35 solutions may follow different reaction paths because two competing reactions are likely

$$\tfrac{1}{2}\,P_2I_4 + \tfrac{1}{2}\,I_2 \underset{A}{\rightleftharpoons} PI_3 \overset{py}{\underset{B}{\rightleftharpoons}} PI_3.py$$

Equilibrium A is known to occur in PI_3 solutions,[31] while equilibrium B is not unreasonable in these systems. In the 1:35 solution the vast excess of pyridine is expected to push equilibrium B so far over to the right that little free PI_3 will remain. The equilibrium appears to be slow but the production of a stable peak at + 16 ppm after two days in this solution supports this hypothesis. In the 1:5 solution, the initial appearance of appreciable quantities of free PI_3 will mean that equilibrium A will be quite important. It is well known that pyridine forms a stable charge-transfer complex with iodine.[108] Interaction between the iodine so produced in equilibrium A and pyridine

will disturb the equilibrium, leading to formation of P_2I_4 and finally to decomposition of the free PI_3.py complex. The disappearance of the - 160 and + 16 ppm signals with the appearance of a - 80 ppm peak in the 1:5 solution is in agreement with this idea. The - 24 ppm resonance in the 1:5 solution could be due to formation of a pyridine complex of P_2I_4. Since the signal is a singlet, it cannot arise from $pyPI_2$-PI_2 but can only be due to $pyPI_2$-PI_2py. The incomplete conversion of P_2I_4 to its complexed derivative is understandable if the process involved is a slow equilibrium since the concentration of pyridine in the solution is not high. The spectrum of this solution after 16 days showed two equal intensity signals at - 80 and - 24 ppm, and no change was seen over a further 30 days.

The solid state signal found at approximately 0 ppm for the precipitate in the 1:35 reaction is probably due to the adduct PI_3py (see analysis figures in Table 36). Although the adduct appears to be susceptible to decomposition in solution, its isolation may be possible by precipitation. Preparation of the PI_3-py adduct by precipitation was therefore attempted as summarized in Table 35. The strong base 3,5 lutidine was also tried as shown.

Samples of the filtrates from these reactions after the precipitates were filtered off were studied by ^{31}P n.m.r., but no resonances were found. This is probably because precipitation removes all the phosphorus from solution. The analysis figures for the solids formed in the pyridine reactions are given in Table 36.

Table 35. Experimental details of the reactions of phosphorus (III) iodide with bases

System	Comments
Reaction 1 PI_3 + py in CH_2Cl_2 1:10	3.1828 gms (7.73 mmoles) of PI_3 in 50 mls of CH_2Cl_2 were added dropwise to 6.2 mls (77mmoles) of pyridine in 30mls of CH_2Cl_2. The brown precipitate formed was isolated after washing with pet ether (30-40)
Reaction 2 PI_3 + py in benzene 1:9	5.8318 gms (14.15 mmoles) of PI_3 in 100 mls benzene placed in a flask and 10 mls (124mmoles) of pyridine added dropwise with stirring. The brown solid formed was washed with pet ether (30-40) and isolated.
Reaction 3 PI_3 + py in benzene 2:1	0.58 mls (7.20mmoles) pyridine were added to 6.0361 gms (14.65 mmoles) PI_3 in 100mls of benzene. After stirring for two hours the solid formed was filtered off, washed with pet ether (30-40) and isolated.
Reaction 4 PI_3 + 3,5 lutidine in CH_2Cl_2 1:5.8	4.9883 gms (12.11 mmoles) PI_3 were dissolved in 100 mls of CH_2Cl_2 and 8 mls (70.9 mmoles) of 3,5 lutidine added dropwise with stirring. The orange-brown precipitate was washed with pet ether (30-40) and isolated.

Table 36. Analysis figures for the products of the reaction between phosphorus (III) iodide and pyridine

Source	% P	% I	%C	% H	% N
Reaction 1	9.29	84.93	4.16	0.43	0.76
Reaction 2	6.33	81.33	10.23	1.05	2.53
Reaction 3	6.58	84.92	6.30	0.70	1.86
PI_3 + py neat 1:35	6.41	80.01	10.11	0.98	2.41
PI_3 theoretical	7.52	92.43	-	-	-
PI_3.py theoretical	6.31	77.59	12.21	1.01	2.85
P_2I_4 theoretical	10.87	89.12	-	-	-
P_2I_4py theoretical	9.55	78.27	9.24	0.77	2.15
P_2I_4.2py theoretical	8.51	69.78	16.48	1.37	3.84

Comparison of the experimental and theoretical analyses does not shed much light on the composition of the solids, except for that from reaction 2 and the neat liquid reaction, where the brown product is quite close to PI_3.py. The analysis of the orange-brown solid obtained from the reaction with 3,5 Lutidine is given below

P	19.14%
I	80.02%
C	1.33%
H	0.35%
N	absent

The P:I mole ratio in this solid is approximately 1:1 and there is very little organic material. The products of all these reactions appear to contain large amounts of phosphorus and iodine with smaller amounts of the organic base, but the analysis figures are not consistent with any particular composition. No solid state ^{31}P n.m.r. spectra were obtained from the solids, so little can be said about their composition. The solids are probably mixtures of species such as PI_3py, P_2I_4, I_2py, and similar compounds which could be formed under the experimental conditions.

The data from these reactions suggests that there is some interaction between PI_3 and pyridine with the formation of a 1:1 adduct. The reaction is slow, however, and is complicated by the ease of formation of P_2I_4 via iodine elimination, which is facilitated by organic base. In two reactions, PI_3 + pyridine neat 1:35 and PI_3 + pyridine in benzene 1:9, the analysis figures are in the correct region for $PI_3.py$ formation but agreement is far from perfect. The solid state peak at approximately 0 ppm for the solid from the PI_3 + py neat 1:35 reaction is compatible with a 4-coordinate phosphorus atom but the data is on the whole inconclusive.

APPENDIX 2

THE REACTION BETWEEN PHOSPHORUS (III) IODIDE AND SOME OXIDIZING AGENTS

1) Introduction

There is no evidence for the existence of PI_5, but the tetraiodophosphonium cation may be capable of preparation, since other tetraiodo derivatives of non-metals are known such as CI_4 and SiI_4. The small number of known phosphorus (V)-iodine systems suggests that its stability may be low, but rapid isolation in the presence of a suitable anion might be possible. Some similar mixed iodine-containing phosphonium cations such as PI_3X^+, $PI_2X_2^+$ and PIX_3^+ (X = OH or Hal) have been characterized in strongly acidic solution in Chapter 3B.

Iodine is probably too weak an oxidizing agent to react directly with PI_3, while liquid bromine is strong enough but causes iodine replacement also,[13]

$$PI_3 + Br_2(\text{liquid}) \longrightarrow PBr_4^+.$$

Large anions such as BBr_4^- or BI_4^- may be required to stabilize cationic species such as PI_4^+ or PI_3X^+, prepared using bromine, iodine chloride, iodine bromide or even chlorine as oxidizing agents in an inert solvent. Similar work carried out by Ruff[83] on other

phosphorus (III) compounds used $SbCl_5$ as both the oxidizing agent and the source of a stabilizing anion in reactions such as

$$R_3P + 2SbCl_5 \longrightarrow R_3PCl^+SbCl_6^- + SbCl_3$$

$$Br_3P + 2SbCl_5 \longrightarrow PSbBr_3Cl_7 + SbCl_3$$

$$Cl_2 + PFCl_2 + SbCl_5 \longrightarrow PFCl_3^+SbCl_6^-$$

2) Present Work

The first reaction attempted was between PI_3, IBr, and BBr_3 to try to prepare $PI_4^+BBr_4^-$. Addition of a molar equivalent solution of PI_3 in CH_2Cl_2 to a 1:1 mixture of BBr_3 and IBr in $CClF_3$ at 276 K over a period of one hour gave a purple solution and an orange precipitate. A sample of the solution was taken and studied by ^{31}P n.m.r. Initially four signals at - 230, - 221, - 198 and - 182 ppm were discernible, assigned to PBr_3, PBr_2I, $PBrI_2$ and PI_3 respectively.[4] After 14 days only one signal at - 230 ppm due to PBr_3 could be seen. The orange solid was washed with pet ether (30-40) and since the washings were purple, it seemed likely that free iodine was being removed. When the washings were colourless, the solid had turned yellow. Analysis of this solid gave the following results:

P 4.69% I 49.68% Br 43.66%

which corresponds to a ratio of P:Br:I of 2:7:5. The remainder of the compound, 1.97% by weight, is presumably boron, and if this is so the empirical formula of the compound is $B_2P_2Br_7I_5$ which probably

corresponds to a mixture of PX_3BY_3-type adducts. Attempts at obtaining solid state spectra from this solid failed (cf Appendix 1). In this reaction there was no apparent oxidation of the PI_3. The products suggest that both halogen exchange and adduct formation between the phosphorus (III) halides and boron (III) halides occurs. Halogen exchange continues with time as shown by the final production of PBr_3 exclusively in the solution.

Addition of a one molar equivalent solution of PI_3 in CH_2Cl_2 to a 1:1 mixture of BCl_3 and ICl in CCl_2FCCl_2F at 273 K gave a purple solution when addition was completed after one hour. A sample of this solution was taken and studied by ^{31}P n.m.r. Initially four signals at - 230, - 220, - 207 and - 180 ppm were observable, easily assigned to PCl_2I, PCl_3, $PClI_2$ and PI_3 respectively[4]. After 11 days only one signal was present in the solution at - 220 ppm, due to PCl_3. As in the previous reaction, the PI_3 did not appear to have been oxidized. The products suggest that slow exchange of halogen occurs at phosphorus to yield PCl_3. Unlike the BBr_3/IBr case no adduct was formed. This is in agreement with the work of Armington et al who reported that PI_3 and BCl_3 do not give an adduct.[102]

Addition of a molar equivalent solution of bromine in CH_2Cl_2 to a 1:1 mixture of PI_3 and AlI_3 in CH_2Cl_2 at 253 K gave a purple solution. No solid precipitated so a sample was taken, after allowing the mixture to warm up to room temperature, and studied by ^{31}P n.m.r. Only one peak at - 170 ppm was present in this solution. This signal is probably due to PI_3 but is about 8 ppm upfield from the expected position.[4]

This upfield shift could be due to interaction with the aluminium halide, but since the shift of PI_3 is quite variable, this evidence is inconclusive, although free PI_3 was found to have a shift of - 175 ppm in CH_2Cl_2. The PI_3 did not seem to have been oxidized, and the purple colour of the solution coupled with the appearance of a PI_3 signal only suggests that bromine exchange has occurred with AlI_3.

In the light of the results from the previous reaction, it was decided to repeat the experiment using $AlBr_3$ in place of AlI_3 at room temperature in CS_2. A purple solution was again formed which showed two signals in the ^{31}P n.m.r. spectrum at - 226 and - 219 ppm assignable to PBr_3 and PBr_2I respectively. As in the previous mixtures the only reaction appears to be halogen exchange and not oxidation.

The failure of these attempted oxidations of PI_3 directly by halogen in the presence of an acceptor molecule capable of forming a stabilizing anion prompted the abandonment of this course of action. Variations of the procedure adopted by Ruff[83] who used oxidizing agents capable of forming the required stabilizing anion directly such as $SbCl_5$, were attempted instead.

A solution of PI_3 in CH_2Cl_2 was added dropwise with stirring to a solution of $SbCl_5$ in CH_2Cl_2 at 223 K, the PI_3 to $SbCl_5$ molar ratio being 1:2. A yellow-orange precipitate formed immediately. Attempts to isolate this solid at room temperature by filtration failed as the solid decomposed rapidly to yield an iodine-coloured liquid. A sample of the reaction mixture was kept at 243 K for some days and under these conditions the decomposition of the solid was rather slower.

The yellow solid turned brown, while the solution turned purple, suggesting iodine liberation. Because of the lack of low temperature facilities for ^{31}P n.m.r., all samples had to be run at the operating temperature of the spectrometer, 307 K. The ^{31}P n.m.r. spectra of the decomposed solid and reaction solution showed a single peak at - 220 ppm assignable to PCl_3.[4] Although no conclusive evidence for oxidation of the PI_3 was obtained, the appearance of an unstable intermediate in the reaction sequence is very interesting. When Ruff oxidized PBr_3 under similar conditions he obtained a white compound analysing as PBr_3SbCl_7, which soon turned yellow and then red on standing.[83] The compound was not further characterized but from the formula proposed it seems likely to contain a phosphorus (V) species. A possible explanation of the course of the $PI_3 + 2SbCl_5$ reaction is that at low temperature a comparatively stable oxidation product is formed which decomposes slowly at 243 K but rapidly at room temperature liberating iodine. The reaction sequence would then be

$$PI_3 + 2SbCl_5 \xrightarrow{223\ K} PI_3SbCl_7 + SbCl_3$$

$$PI_3SbCl_7 \xrightarrow{243\ K} PCl_3 + \text{mixed chloroiodides of antimony} + I_2.$$

This is of course purely speculative.

A similar reaction was attempted using PI_3 and PCl_5 in the molar ratio of 1:2. A solution of PI_3 in CH_2Cl_2 was added dropwise to a solution of PCl_5 in CH_2Cl_2 at 243 K. Immediately a blood red

precipitate formed but soon darkened and redissolved in the solvent to yield a purple solution. On complete addition of the PI_3 no precipitate could be seen. After warming up to room temperature, a sample of the solution was studied by ^{31}P n.m.r. Only one ^{31}P n.m.r. resonance could be found, at - 220 ppm, assignable to PCl_3.[4] The formation of the blood red precipitate shows that there is a reaction but the product is clearly unstable, decomposing rapidly to PCl_3 and iodine. This may well be analogous to the $SbCl_5$ reaction. PCl_3 should be produced in this reaction as a reduction product of PCl_5 if the reaction is of the form

$$PI_3 + 2PCl_5 \longrightarrow PI_3Cl^+PCl_6^- + PCl_3.$$

Hence the signal due to PCl_3 found in the ^{31}P n.m.r. solution spectrum does not necessarily arise from decomposition of the precipitate, although the appearance of only one peak makes it likely that the complex decomposes to give PCl_3. A possible decomposition route is

$$PI_3Cl^+PCl_6^- \longrightarrow 2PCl_3 + I_2 + ICl$$

The failure to observe signals from PCl_4^+ or PCl_5 suggests that the original PCl_5 has been reduced.

Solutions of PI_3 were prepared in $SbCl_5$, $SnCl_4$, $TiCl_4$ and SO_2Cl_2 in an attempt to gain further data on the oxidation of PI_3. The addition of both $SbCl_5$ and SO_2Cl_2 to PI_3 gave rise to a violent reaction

with the liberation of heat and iodine, producing deep purple solutions. PI_3 dissolved in $SnCl_4$ and $TiCl_4$ to give orange-red solutions on shaking, both of which darkened slowly on standing.

The $SbCl_5$ solution showed a strong signal at - 84 ppm and a very weak signal at - 24 ppm. The signal at - 84 ppm is assignable to PCl_4^+ [4] but the - 24 ppm peak is a little unusual. Over a period of 12 days the - 24 ppm signal increased slightly in intensity. The solution work on PI_3 in $ClHSO_3$ indicates that this signal is not due to an iodo-substituted chlorophosphonium species (Chapter 3B section 2(vii)). It probably arises from $POCl_3$ produced by hydrolysis of PCl_4^+, interaction of which with $SbCl_5$ causes the downfield shift from its usual position at - 2 ppm.[4,80] The solid adduct $POCl_3.SbCl_5$ shows a ^{31}P n.m.r. shift of - 55 ppm.[80]

The solution formed by reaction of PI_3 with excess SO_2Cl_2 showed one signal at - 3 ppm which is immediately assignable to $POCl_3$.[4]

The $TiCl_4$ solution of PI_3 showed initially a strong signal at - 176 ppm and a weak signal at - 213 ppm. After 3 days the - 213 ppm signal had increased a little in intensity and two further weak intensity signals had appeared at - 220 and - 228 ppm. The solution in $SnCl_4$ showed initially four signals at - 178 (medium), - 213 (weak), - 220 (medium) and - 228 ppm (strong). After two days only one signal at - 221 ppm remained. The four signals found in these solutions are assignable to PI_3, PI_2Cl, PCl_3 and $PICl_2$ respectively.[4]

The results from these solutions show that $SbCl_5$ and SO_2Cl_2 are capable of acting as oxidizing agents but the data does not show

whether PI_3 is oxidized before or after halogen exchange. Both PCl_4^+ and $POCl_3$ could be formed from PCl_3. In the $SnCl_4$ and $TiCl_4$ solutions no oxidation appears to take place, but the halogens exchange rapidly with $SnCl_4$ and more slowly with $TiCl_4$.

In all these reactions no evidence for direct oxidation of PI_3 was found. The only phosphorus (V) species identified were PCl_4^+ and $POCl_3$ which may have been formed by oxidation of chlorine-exchanged phosphorus (III) species. The reactions considered have analogues in other phosphorus halide systems where phosphorus (III) is oxidized to phosphorus (V). The formation of solids in the $PI_3 + 2SbCl_5$ and $PI_3 + 2PCl_5$ reactions without immediate release of iodine may be due to oxidation but the unstable nature of the products leaves the question open. It seems that reactions may prove fruitful where oxidation is immediately followed by stabilization of the cationic phosphorus (V) species using suitable anions, but that the inherant instability of the systems will make characterization difficult. Low temperature physical techniques such as solid state ^{31}P n.m.r. may well prove useful since the known chlorobromophosphonium species give comparatively sharp lines.[85,86] Iodine has a smaller quadrupole moment than either chlorine or bromine and is thus expected to give even sharper lines for ^{31}P n.m.r. spectra of iodine-containing phosphonium cations.

3) Experimental

For solutions of PI_3 in $SbCl_5$, SO_2Cl_2, $SnCl_4$ and $TiCl_4$, the following procedure was used. A little PI_3 was placed in a sample

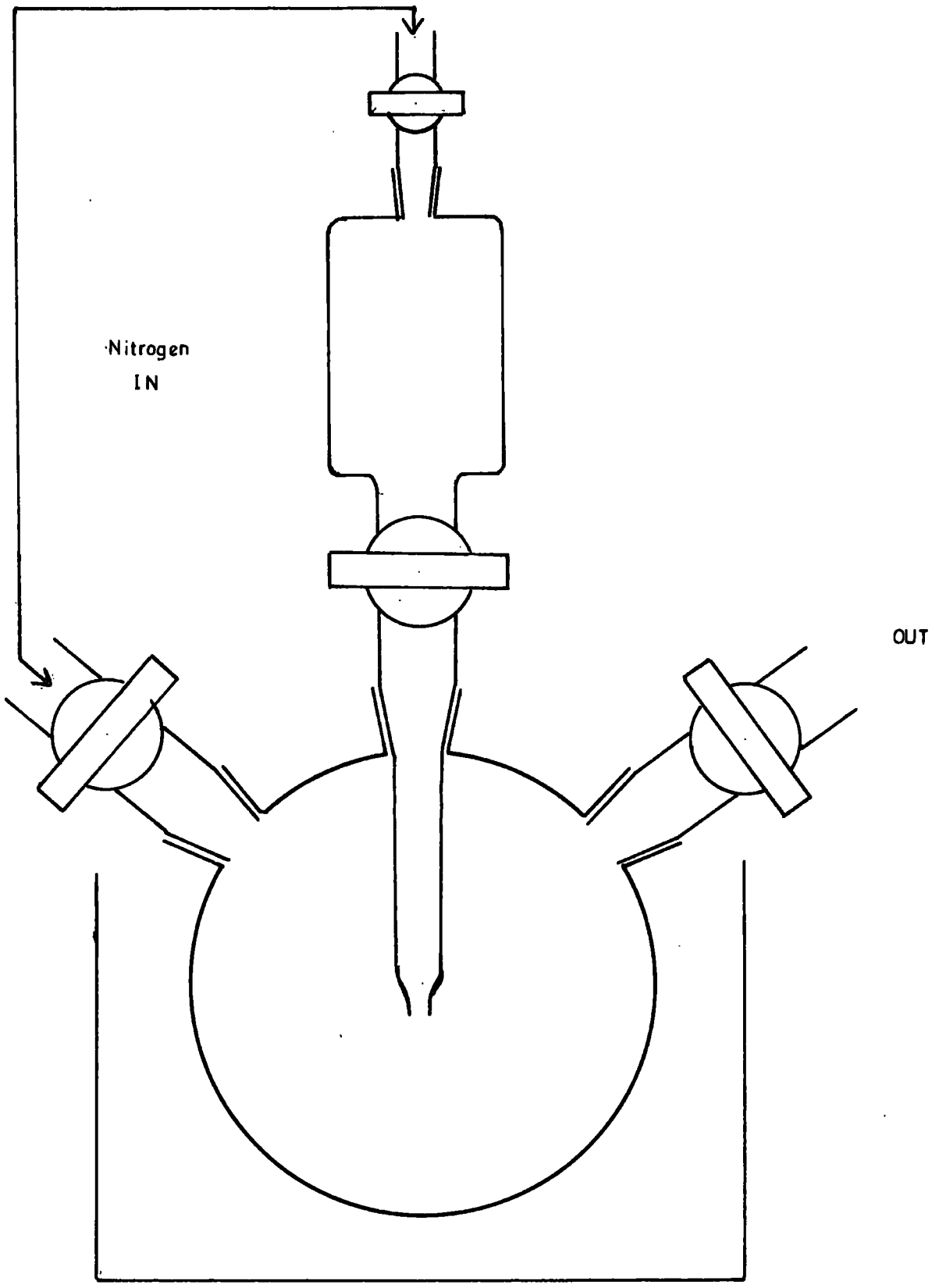


Figure 43

Apparatus used in the attempted oxidation reactions of phosphorus (III) iodide.

bottle and the solvent was added via a pipette dropper. If there was no reaction the mixture was shaken until solution occurred. A sample was then taken and studied by ^{31}P n.m.r. All manipulations were carried out in a glove box under nitrogen and the usual precautions against atmospheric moisture were taken.

Some of the reactions were carried out on a preparative scale using the apparatus shown in Figure 43.

The apparatus was baked in an oven overnight, cooled to room temperature and assembled as shown. After pumping down on a vacuum line, the system was opened to nitrogen. All additions were made under a nitrogen flow to prevent atmospheric hydrolysis. The experimental details are given in Table 37.

Table 37. Experimental details for the reactions between phosphorus (III) iodide and some oxidizing agents

Reaction	Flask contents	Measuring funnel contents
$PI_3 + BBr_3 + IBr$ 1:1:1	BBr_3 5.6gms(22.3mmoles) IBr 4.5gms(21.8mmoles) in 100mls CCl_3F	PI_3 9.0 gms (21.8 mmoles) in 90 mls CH_2Cl_2
$PI_3 + BCl_3 + ICl$ 1:1:1	BCl_3 2.7gms(23.1mmoles) ICl 3.2gms(19.7mmoles) in 100mls CCl_2FCCl_2F	PI_3 8.3 gms (20.1 mmoles) in 50mls CH_2Cl_2/ 50mls CCl_2FCCl_2F
$PI_3 + Br_2 + AlI_3$ 1:1:1	AlI_3 3.95gms(9.7mmoles) PI_3 4.09gms(9.9mmoles) in 200mls CH_2Cl_2	Br_2 1.56 gms (9.8 mmoles) in 40 mls CH_2Cl_2
$PI_3 + Br_2 + AlBr_3$ 1:1:1	$AlBr_3$ 1.92gms(7.2mmoles) PI_3 2.68gms(6.5mmoles) in 80 mls CS_2	Br_2 1.06 gms (6.6 mmoles) in 40 mls CS_2
$PI_3 + SbCl_5$ 1:2	$SbCl_5$ 5.67 gms (19.0 mmoles) in 50 mls CH_2Cl_2	PI_3 4.10 gms (10.0mmoles) in 80 mls CH_2Cl_2
$PI_3 + PCl_5$ 1:2	PCl_5 3.93 gms (18.9 mmoles) in 200 mls CH_2Cl_2	PI_3 3.87 gms (9.4 mmoles) in 80 mls CH_2Cl_2

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