REACTIONS OF PHOSPHORUS PENTAFLUORIDE AND RELATED COMPOUNDS

by

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TEXT

The addition compounds of phosphorus pentafluoride with nitrogen and oxygen bases should offer a rich but as yet virtually unknown field of chemical study.

A. B. Burg[a].

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ABSTRACT

The reaction of phosphorus pentafluoride with a variety of ligands has been studied using standard high vacuum-line techniques. Thermal decomposition of the complexes formed produced several new compounds containing phosphorus-fluorine bonds; the structures of which were investigated using Infrared and Nuclear Magnetic Resonance Spectroscopy.

Phosphorus pentafluoride was found to form new compounds with dialkylamines. Thermal decomposition of these complexes produced the new compounds dialkylamino tetrafluoro phosphoranes, PF_4NR_2, and bis dialkylamino trifluoro phosphorane $PF_3(NR_2)_2$. Infrared and Nuclear Magnetic Resonance spectroscopy show these compounds are monomeric in the gaseous and liquid states and that the amino groups occupy the equatorial positions of the trigonal bipyramid. Reaction of phosphorus pentafluoride and primary alkyl amines was complex yielding non-stoichiometric mixtures. Thermal decomposition produced a solid liquid mixture which was not identified.

The reaction of phosphorus pentafluoride with phosphorus ligands was investigated to obtain information on the strength of the novel phosphorus-phosphorus bond produced. Complexes were prepared with trialkyl phosphines, bisdialkylamino

phosphines and trialkyl phosphites. The stability of the complexes were found to fall in the following order:-

$$PR_3 > P(NR_2)_3 > P(OR)_3$$

Possible explanations for this stability order are discussed on the basis that the fluorine lone pairs are overlapping with the trivalent phosphorus unfilled 'd' orbitals.

Thermal decomposition of the tris dimethylamino phosphine complex yielded the compounds dimethylamino tetrafluoro phosphorane, PF_4NMe_2, bis dimethylamino trifluoro phosphorane $PF_3(NMe_2)_2$ as well as dimethylamino difluoro phosphine, PF_2NMe_2, and bismethylamino fluoro phosphine, $PF(NMe_2)_2$, while the trimethyl phosphite complex decomposed to give the new compounds methyl difluoro phosphate, CH_3OPOF_2, and methyl trimethoxy phosphonium hexafluoro phosphate, $(CH_3O)_3\overset{+}{P}CH_3\overset{-}{P}F_6$. The kinetics of the decomposition of this salt, (which is an Arbuzov Rearrangement intermediate), in acetone and acetonitri solution, were observed from Nuclear Magnetic Resonance spectroscopy and electrical conductivity measurements. As the behaviour in these two solvents is so different the solvent must play a major part in the kinetic interpretations.

The reaction of a variety of lithium salts with phosphorus pentafluoride and other non-metal fluorides in ether and pentane solution were investigated. Several new lithium salts including the novel propyl pentafluorophosphate salt were prepared while simpler methods of producing pure lithium hexafluoro phosphate than these described in the literature were developed.

The use of some of the new amino phosphorus fluorine compounds, as ligands to transition metal salts and metal carbonyls, confirmed the belief that the nitrogen lone pairs are π bonded into the vacant 'd' orbitals of the phosphorus and complexes can only be obtained under specific conditions.

Attempts to prepare metal carbonyl fluorosulphates from the metal carbonyl halides and silver fluorosulphate produced impure gluey compounds which could not be obtained crystalline. The ready solubility in water of the carbonyl compounds formed suggested the existence of the carbonyl fluorosulphate although only in the impure state.

CONTENTS

INTRODUCTION

Introduction

Fluorine occupies the ninth place in the periodic table and is the smallest of the halogen series of molecules. It exists as a greenish yellow diatomic gas and, in common with the other halogens, is very reactive. The bond dissociation energy is only 37 kcals/mole compared with 58 kcals/mole for chlorine.

This is believed to be caused by repulsion between non-bonding electrons on the fluorine atoms and the lack of any multiple bonds between them, as no low lying unfilled molecular orbitals are available.

This factor, combined with its high electronegativity and small size causes it to react with many elements to form fluorides in high oxidation states. The electron withdrawing power of the fluorine atoms cause an electron deficiency on the central atom in the fluoride. This deficiency is partly removed by back donation of the fluorine lone pairs into the unfilled p or d orbitals of the central atom so that multiple bonds are formed. These bonds are thermally very stable but are vigorously hydrolyzed by traces of moisture to form the corresponding oxide and hydrogen fluoride. If glass apparatus is used, the hydrogen fluoride reacts with it to form silicon tetrafluoride and water. The water reacts with more of the fluoride to produce more hydrogen fluoride so that moisture acts as a catalyst in the destruction of the glass. If the apparatus is heated to 200°C under vacuum the film of moisture is removed from the surface and the volatile fluorides can then be handled in glass apparatus with very little decomposition.

Phosphorus pentafluoride and its derivatives which were prepared in this work were all moisture sensitive and were handled in a high vacuum apparatus. Evacuation to 10^{-3} mm. pressure was achieved using an A.E.I. pump of type BC 2408 together with a mercury diffusion pump made in the Imperial College Chemical Laboratories, London. Standard Quick-fit cones, sockets and stopcocks were used in assembling the vacuum line; the connections being sealed with Edwards 'Apiezon L' grease.

The infrared spectra of the compounds prepared were measured on Grubb-Parson(type DBI) and Perkin Elmer Infracord (type 137) spectrometers. Spectra were measured on samples in the vapour phase as liquid films or in nujol mulls.

The ^{1}H and ^{19}F nuclear magnetic resonance spectra were measured on a Perkin Elmer 40 m/c spectrometer. Wherever possible the spectra were obtained on neat liquids. Concentrat solutions in inert solvents were also used. The chemical shift of the ^{1}H resonances were measured with respect to tetramethyl silane as reference while the ^{19}F spectra were measured using trifluoromethyl benzene as reference standard. Samples were analyzed by Alfred Bernhardt in Germany. They were prepared on the vacuum line or in the dry box and sent for analysis in sealed tubes.

CHAPTER I

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH NITROGEN LIGANDS

Introduction

The two known binary fluorides of phosphorus, the trifluoride and the pentafluoride, were among the first non-metal fluorine compounds to be prepared and studied. Since the initial preparation over eighty years ago, improved preparative and handling techniques have produced a vast new number of other non-metal fluorine compounds such as the sulphur fluorides and the fluorides of chlorine, bromine, iodine, xenon and krypton.

Phosphorus pentafluoride was prepared by Thorpe in 1876[1] by the action of arsenic trifluoride on phosphorus pentachloride Other fluorides e.g. lead fluoride[2], zinc fluoride and antimony trifluoride were also found to complete this conversion. Phosphorus pentafluoride is now most conveniently prepared in the laboratory by thermal decomposition of an aryl diazonium salt at 150°C which allows large quantities of phosphorus pentafluoride to be used easily and safely.

Phosphorus pentafluoride is a white solid which melts at -93.8°C and boils at -84.6°C[3]. It can be handled in glass apparatus without reaction, provided traces of moisture have bee removed by heating the glass to 250°C under vacuum[4]. Physical measurements, e.g. electron diffraction[5] and infrared spectroscopy[6] suggest that phosphorus pentafluoride adopts the trigonal bi pyramidal structures rather than the square pyramidal configuration. This structure seems to be easily attacked by Lewis bases especially when a stable octahedral configuratio is formed by the adduct. For instance phosphorus pentafluoride is more rapidly hydrolyzed by moisture than the tetrahedral phosphorus trifluoride[8]. Phosphorus pentafluoride is similar to boron trifluoride in being a very strong Lewis acid[9]. It is rapidly attacked by fluoride ion when the highly stable hexafluoro phosphate ion is formed.

It reacts with ammonia to form a complex ammoniate $2PF_5 5NH_3$ and also reacts with nitrogen dioxide at -10°C to form an addition compound which dissociates on warming[10].

Phosphorus pentafluoride readily combines with organic donor molecules such as amines, ketones, esters, ethers and nitriles.

Woolf suggested these complexes were 1:1 adducts on the basis of weighing the residue obtained when a weighed amount of ligand reacted with excess phosphorus pentafluoride[11].

Muetterties prepared a variety of complexes and confirmed they were 1:1 adducts[9]. He prepared trimethylamine and pyridin complexes but found that the triethylamine and collidine (2,4,6, trimethyl pyridine) complexes were partially dissociate at 25°C. He suggested that this was due to steric reasons sinc the P^{5+} atom is only slightly larger than the B^{3+} atom yet must accommodate two more fluorine atoms in its complexes. This was further supported by the observation that while the diethyl ether complex is partially dissociated at 25°C the tetrahydrofuran complex can be distilled at 116°C/0.15mm. without decomposition.

All the complexes of phosphorus pentafluoride were found t be hydrolyzed by moisture and decomposed by alcohols much more readily than the boron trifluoride complexes. This suggested rapid dissociation of the complex in solution which resulted in molecular weight determination producing low results.

Further understanding of these steric considerations should be enhanced by studying the complexing properties of substituted fluoro phosphoranes[12]. It has been recently reported that phenyl tetrafluoro phosphorane $C_6H_5PF_4$ forms solid complexes with strong bases such as pyridine and dimethylformamide but it does not react with weak bases such as acetonitrile or highly hindered amines such as triethylamine. Unfortunately very little further data are available on this subject, even though the alkyl and aryl fluoro phosphoranes are well known and have been extensively studied[13]. They are easil prepared by direct fluorination of the corresponding chloro phosphine with arsenic or antimony trifluoride and are isolated by distillation, as stable colourless liquids. Mono, di and tri substituted fluoro phosphoranes containing a variety of alkyl and aryl groups have been synthesized by this method. Interest in the phosphoranes has centred on their structure which can be determined using nuclear magnetic resonance spectroscopy. The results indicate that substitution by both alkyl and aryl groups occur in the equatorial positions of the trigonal bipyramidal structure[14].

Similarly the series of chloro fluoro phosphoranes (PF_xCl_{5-x}) are known[15], now that chloro tetrafluoro phosphorane has been synthesized[16] by the low temperature fluorination of dichloro trifluoro phosphorane with antimony trifluoride. These compounds can be isolated as stable colourless liquids at -78°C but slowly deposit white solids on standing at room temperature. The latter are ionic species and their structures depend upon the number of each halogen atoms present. This ionization tendency seems to be a property of the phosphorus-chlorine bond as no evidence of self ionization has been observed in the organo fluoro phosphoranes or in phosphorus pentafluoride.

The tendency to ionization makes the study of the complexing properties of the chloro fluoro phosphoranes more difficult to determine than those of phosphorus pentafluoride and little definite evidence is available[16].

The synthesis of chloro tetrafluoro phosphorane is of great importance in fluoro phosphorane chemistry as it may be used as an intermediate in the preparation of other tetrafluoro phosphoranes. The compound octafluoro diphosphorane P_2F_8 would be of special interest since the stability of the phosphorus-phosphorus bond in its complexes would be highly dependent on the strength of the Lewis base used.

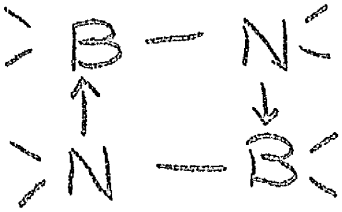
Discussion

Reaction of phosphorus pentafluoride with secondary amines.

The complexing properties of boron trifluoride are now well known and have been reviewed[17]. Brown examined the reaction of boron trifluoride with dimethylamine to for a 1:1 complex which decomposed at 240-295°C to yield dimethylamino difluoro borane in its dimeric form[18]. The other major product was dimethyl ammonium tetrafluoro borate. He suggested that the reaction could be represente by the equation.

$$2(CH_3)_2NH.BF_3 \longrightarrow (CH_3)_2NH_2^+BF_4^- + (CH_3)_2NBF_2.$$

Dimeric dimethylamino difluoroborane has since been extensively investigated;[1,2] the four membered ring system is formed by donation of the lone pair of electrons on the nitrogen atom into the vacant orbitals of the boron atoms. The monomeric species can be prepared by heating the dimer under vacuum when a monomer-dimer equilibrium is obtained.



The corresponding reaction between phosphorus pentafluori and dimethylamine had not been investigated nor had the likely decomposition product dimethylamino tetrafluoro phosphorane been prepared. The investigation was therefore undertaken to obtain information on the structures and properties of the compounds formed.

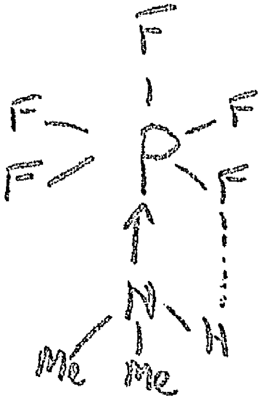
A white solid was prepared by reacting phosphorus pentafluoride with a toluene solution of dimethylamine. The solid was purified by sublimation under vacuum and identified as a 1:1 complex by analysis and its ^{19}F nuclear magnetic resonance spectrum in dimethylamine solution. The details of the ^{19}F nuclear magnetic resonance spectrum are given in Table 3 and the infrared spectrum is discussed with those of other phosphorus pentafluoride complexes in Chapter II.

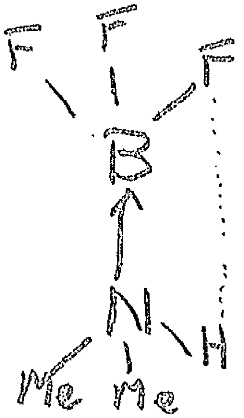
The complex was heated on an oil bath to 150°C under vacuum to effect decomposition. It melted at 100°C and eventually resolidified at 150°C which suggested that the decomposition was complete. The volatile product, which was condensed out, melted to a colourless liquid which was identified as dimethylamino tetrafluoro phosphorane by analysis. The vapour phase infrared spectrum is recorded in Tables1 and 2 and is shown in Fig. 1. The ^{1}H and ^{19}F nuclear magnetic resonance spectra are also recorded in Table 3 and are shown in Fig. 2. Vapour phase molecular weight measurements showed that the vapour is monomeric while the ^{1}H and ^{19}F nuclear magnetic resonance spectra suggested the liquid is also monomeric.

Phosphorus pentafluoride reacted with diethylamine to form a while solid which decomposed on heating to 150°C to give diethyl tetrafluoro phosphorane as a colourless volatile liquid. This liquid showed similar physical properties to the corresponding dimethylamino tetrafluoro phosphorane. The spectroscopic details of this compound are given in Tables 1 and 3.

The slightly volatile liquid di-n-propylamino tetrafluoro phosphorane was prepared from phosphorus pentafluoride di-n-propylamine complex by heating it to 225°C. The details of its ^{19}F nuclear magnetic resonance spectrum are given in Table 3.

The observations confirm the expected similarity in the decomposition of the dialkylamino complexes of boron trifluoride and phosphorus pentafluoride. An unexpected feature was the much lower temperature required for the decomposition of the phosphorus pentafluoride complexes (100-150°C) than the boron trifluoride compounds (240-295°C). The B-F bond energy (154 kcals./mole) is much greater than the P-F bond energy (117 kcals./mole for PF_5)[20] so that more energy is required to break the B-F bond. Steric factors may also be important since in the octahedral phosphorus pentafluoride complex, the H-F interatomic distance is much less than in the tetrahedral boron trifluoride complex.





These two factors would explain the greater thermal stability of the boron trifluoride complexes than the phosphorus pentafluoride complexes. The above method of preparation of the dialkylamino tetrafluoro phosphoranes produced low yields since two moles of the 1:1 complex are required to produce a maximum of 1 mole of dialkylamino tetrafluoro phosphorane. The formation of the dialkylamino tetrafluoro phosphoranes can be represented by the equation.

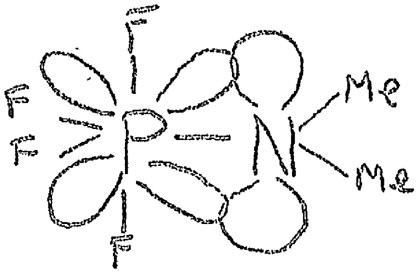
$$2R_2NHPF_5 \longrightarrow R_2NPF_4 + R_2NH_2^+ + PF_6^-$$

The hexafluoro phosphate ion was identified from its ^{19}F nuclear magnetic resonance spectrum.

Other methods of preparation of these derivatives have recently been reported by MacDiarmid[21] and Schmutzler[22]. Phosphorus pentafluoride reacts with dimethylamino trimethyl silane (Me_2NSiMe_3) by cleaving the Si-N bond to form trimethyl fluoro silane and dimethylamino tetrafluoro phosphorane.

No evidence for dimerization of the dialkylamino tetrafluoro phosphoranes could be found. The low melting and boiling points, the molecular weights and ^1H and ^{19}F nuclear magnetic resonance spectra all suggested the compounds were monomeric. This is probably due to steric reasons since a four-membered ring would require octahedral coordination around the phosphorus atom which would include two bulky dialkylamino groups.

The monomeric nature of the dialkylamino tetrafluoro phosphoranes suggest that the phosphorus-nitrogen bond should have partial double bond character through $p_{\pi} - d_{\pi}$ overlap of the orbitals.



The acceptor properties of the dialkylamino tetrafluoro phosphoranes should be less than those of phosphorus pentafluoride. However, dimethylamino tetrafluoro phosphorane reacted vigorously with dimethylamine to form a white solid. When equimolar quantities of dimethylamino tetrafluoro phosphorane and dimethylaminewere reacted, the solid melted and decomposed at 0°C to form bis-dimethylamino trifluoro phosphorane and the 1:1 dimethylamine phosphorus pentafluoride complex. No further reaction occurred when the mixture was kept at 35°C for 24 hours; the ^{19}F nuclear magnetic resonance spectrum remained unaltered. This observation suggests that dimethylamino tetrafluoro phosphorane is also a Lewis Acid and complexes with dimethylamine to form a 1:1 complex. This is much less thermally stable than the phosphorus pentafluoride dimethylamine complex probably because the increased electron density around the phosphorus atom weakens the phosphorus-fluorine bonds. The removal of hydrogen fluoride from the 1:1 dimethylamino tetrafluoro phosphorane complex can thus occur at lower temperatures than from the corresponding phosphorus pentafluoride dimethylamine complex. Bis-diethylamino trifluoro phosphorane can be prepared from diethylamino tetrafluoro phosphorane and triethylamine by a similar method.

The bis-dialkylamino trifluoro phosphoranes could also be prepared from phosphorus pentafluoride and excess dialkylamine by heating the mixture to 80-100°C. The dialkylamino tetrafluoro phosphorane first formed immediately reacts with the excess dialkylamine in the manner described above to produce the bis-dialkylamino trifluoro phosphorane and the phosphorus pentafluoride dialkylamine complex which further decomposes to the dialkyl ammonium hexafluoro phosphate. This decomposition can be represented by the equation

$$3\ PF_5 + 4NR_2H \longrightarrow PF_3(NR_2)_2 + 2NR_2NH_2^+\ PF_6^-$$

The bis-dialkylamino trifluoro phosphoranes are slightly volatile, colourless liquids which solidify to highly crystalline solids. They are chemically unreactive; they do not fume in air and are immiscible with water. The ^{19}F nuclear magnetic resonance spectrum shows that the two dialkylamino groups occupy two of the equatorial positions in a trigonal bipyramidal structure. The non-reactivity of the bis-dialkylamino trifluoro phosphoranes is due to steric hindrance caused by the bulky dialkylamino groups and the lack of Lewis acidity because of the increased electron density around the phosphorus atom from the dialkylamino groups.

The lack of reactivity was evident when bis-dimethylamin trifluoro phosphorane was reacted with dimethylamine in an attempt to prepare tris-dinethylamino difluoro phosphorane. No reaction was observed between these two compounds under a variety of conditions while reaction of bis-dimethylamino trifluoro phosphorane with tris-dimethylamino phosphine was very slow even at 120°C. The use of bis-dimethylamino trifluoro phosphoranes as a solvent should be investigated as the only non-reactive liquid fluorine compounds known are the fluoro carbons. Other methods of preparation of bis-dialkylamino trifluoro phosphoranes have been reported recently which would allow them to be prepared in large quantities[38]. When phosphorus pentafluoride is reacted with excess dimethylamino trimethyl silane at 150-170°C bis-dimethylamino trifluoro phosphorane and trimethyl fluoro silane are produced. The volatile trimethyl fluoro silane is easily removed at -78°C leaving the bis-dimethylamino trifluoro phosphorane which can be purified by distillation.

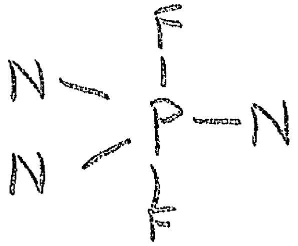
The considerable interest shown[38] in the synthesis of tris-dialkylamino difluoro phosphoranes is due to their expected highly symmetrical structure, with the three dialkylamino groups occupying the equatorial positions and the fluorine atoms occupying the axial position of the trigonal bipyramid. This structure would make the molecules chemically inert since the dialkylamino groups would help form a very compact molecule and also completely remove the Lewis acidity of the phosphorus atom, so that chemical reaction would be possible only under extreme conditions. In many ways these compounds would behave as 'liquid sulphur hexafluoride'.

However, so far it has not been possible to prepare any of these derivatives although many methods have been tried for their preparation.

Infrared spectra of the dialkylamino fluoro phosphoranes

The highly symmetrical nature of tris-dimethylamino difluoro phosphorane would allow valuable information to be obtained from its vapour phase infrared spectrum.

The molecule would possess D_{3h} symmetry and therefore have five absorbtion bands due to the



skeleton. Two of these absorbtions would be the asymmetric F-P-F stretching vibration and $N-P<^{N}_{N}$ asymmetric stretching vibration and assignment of these vibrations would be of great help in analyzing the spectra of the more complex dialkylamino and bis-dialkylamino fluoro phosphoranes.

The vapour phase infrared spectra of the dialkylamino tetrafluoro phosphoranes and bis-dialkylamino trifluoro phosphoranes are given in Table I.

Partial assignments of dimethylamino tetrafluoro phosphorane can be made if the absorbtions are compared with the vapour phase infrared spectra of dimethylamino fluoro borane[19] dimethylamino difluoro phosphine and chloro tetrafluoro phosphorane[16]. The relationships between these spectra

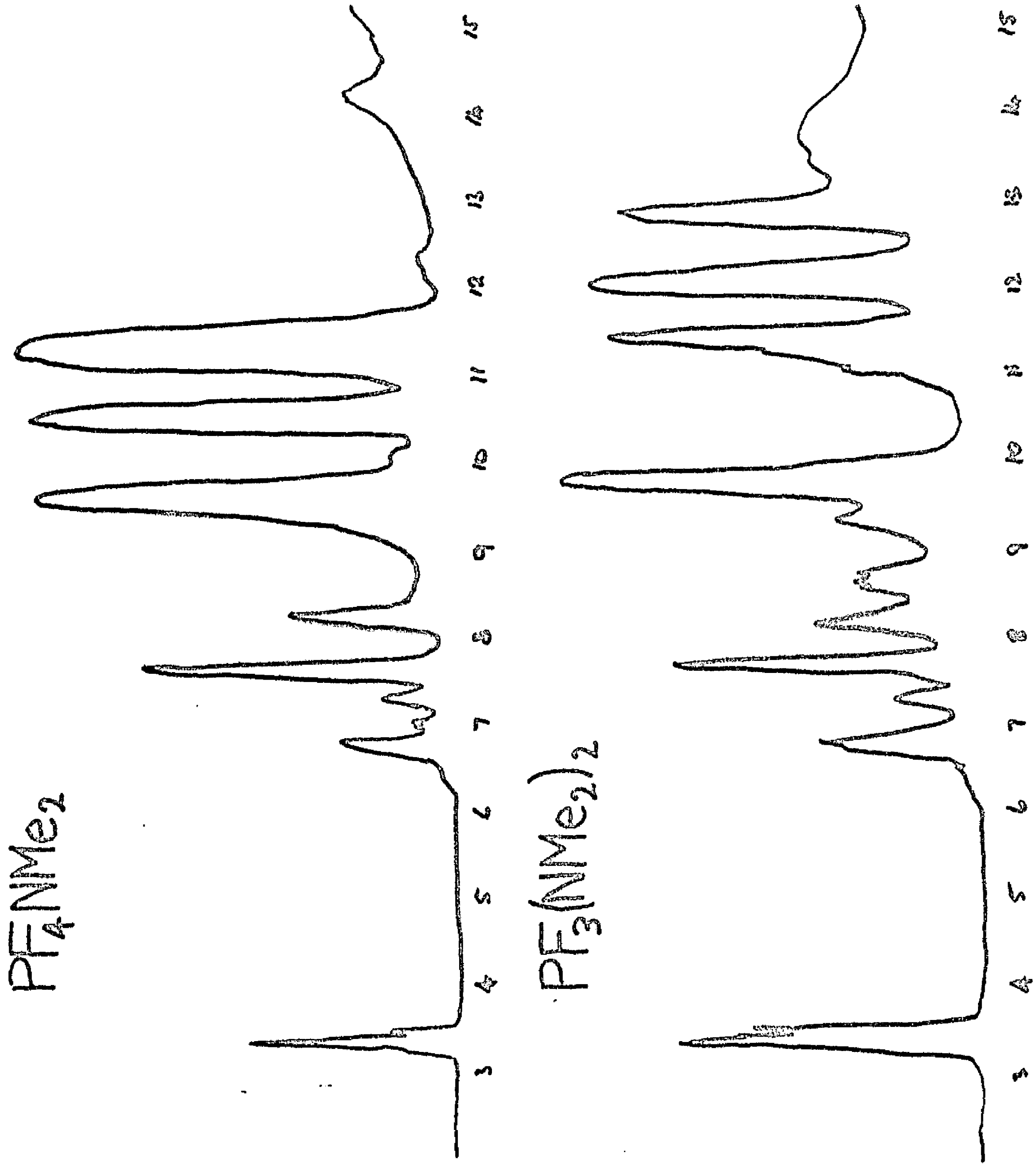


Fig. 1 Infrared spectra of the dimethylamino fluoro phosphoranes

TABLE I

Vapour phase infrared spectra of the dialkylamino fluoro phosphoranes.

PF_4NMe_2	PF_4NEt_2	$PF_3(NMe_2)_2$	$PF_3(NEt_2)_2$
2960(s)	2960(s)	2970(s)	3000(s)
2900(sh)	2930(sh)	2900(sh)	2930(sh)
2860(w)		2840(w)	
1464(m)	1470(m)	1466(m)	1493(m)
	1430(m)		
	1415(m)		
1368(w)	1393(s)	1370(w)	1389(s)
	1355(s)		1342(s)
1302(s)	1300(w)	1295(s)	
1211(m)	1217(s)	1224(m)	1212(m)
	1185(s)		1190(m)
		1070(w)	
1042(vs)	1060(vs)	1020(vs)	1047(vs)
	985(vs)		965(m)
950(vs)	945(vs)		900(s)
882(vs)	870(vs)	870(vs)	875(s)
		830(vs)	820(m)
806(w)	799(m)		798(sh)
		775(vs)	730(m)
701(m)	685(m)		

are shown in Table 2. The assignments given in Table 2 suggest that all the absorbtion bands above 1000 cm^{-1} in dimethylamino tetrafluoro phosphorane are due to the vibrations of the dimethylamino group. These are similar to the assignmen made for dimethylamino difluoro borane and dimethylamino difluoro phosphine since the vibrations of this group will only be slightly affected by the main part of the molecule. The only curious point relating to these assignments is the absence of a band in the 1300 cm^{-1} region in dimethylamino difluoro borane compared with the very intense absorbtion at 1300 cm^{-1} of dimethylamino tetrafluoro phosphorane.

The infrared spectrum of dimethylamino tetrafluoro phosphorane in the region 1000 cm^{-1} - 600 cm^{-1} is almost identical to that of chloro tetrafluoro phosphorane. This suggests that the absorbtions in this region are associated with the PF_4 group rather than the chloro or dimethylamino group. The very intense bands at 950 cm^{-1} and 822 cm^{-1} are therefore assigned to phosphorus-fluorine stretching vibrations. Previous workers have suggested that asymmetric stretching vibrations occur at higher frequencies than the symmetric vibrations and that equatorial phosphorus-fluorine vibrations occur at higher frequencies than the axial phosphorus-fluorine vibrations. The band at 950 cm^{-1} is

TABLE 2

Assignment of vapour phase infrared spectrum of dimethylamino tetrafluoro phosphorane

BF_2NMe_2	PF_2NMe_2	PF_4NMe_2	PF_4Cl	Assignment.
3000				
2947	2925	2960		
2911	2865	2900		CH_3 stretch
2827	2820	2860		
1473	1507	1464		CH_3 asym. deform.
1433	1432	1368		CH_3 sym. deform.
	1307	1300		CH_3 sym. deform.
1209	1195	1211		asym.$N-C_2$ stretch
1035	989	1042		sym.$N-C_2$ stretch
	(814)	950	945	asym.P-F(e)stretch
			927	
	(770)		921	
		882	903	sym.PF_2(e) stretch
			895	asym. PF_2(a) stretch
		806	(817w)	P-N stretch
		701	692	sym. PF_2(a)stretch

therefore assigned to the asymmetrical equatorial P-F stretching frequency while the rather complex band at 822 cm^{-1} is assigned both to the symmetrical equatorial P-F vibration and to the asymmetrical axial P-F vibration. The only two other bands observed in this region are the weak absorbtion at 806 cm^{-1} and the rather stronger absorbtion at 701 cm^{-1}. One of these must be due to the P-N stretching vibration and the other to the symmetrical axial P-F stretching vibration. Previous workers have suggested the phosphorus-nitrogen single bond stretching vibration occurs in the region 820-680 cm^{-1} [26]. In a recent paper this vibration has been assigned to a band at 704 cm^{-1} in the spectrum of $PF_2(NMe_2)$ while the spectrum of dimethylamine phosphorus pentafluoride complex has a sharp absorbtion at 702 cm^{-1}. If there is any double bonding through $p_\pi - d_\pi$ overlap in the P-N bond the absorbtion will move to higher frequencies. The absorbtion at 806 cm^{-1} is therefore assigned to a phosphorus-nitrogen stretching frequency since partial $p_\pi - d_\pi$ overlap will probably occur. This band moves to 722 cm^{-1} in the bis-dimethylamino trifluoro phosphorane as the $p_\pi - d_\pi$ overlap is reduced by the presence of a second dimethylamino group. The absorbtion at 701 cm^{-1} is assigned to the symmetric axial P-F stretching frequency and is similar to the absorbtion at 692 cm^{-1} in chlorotetrafluoro phosphorane.

In diethylamino and di-n-propylamino tetrafluorophosphoranes the P-N stretching frequencies occur at 799 cm^{-1} and 790 cm^{-1} respectively.

The increase in the number of absorbtion bands in the spectra of bis-dialkylamino trifluoro phosphoranes is due to the increased number of atoms in the molecules. The phosphorus-fluorine vibrations move to lower frequencies because the increased electron density on the phosphorus atom weakens the phosphorus-fluorine bonds. The spectra are too complex to attempt assignments without further investigations.

Nuclear Magnetic Resonance Spectra of the dialkylamino fluoro phosphoranes.

The nuclear magnetic resonance spectra of the dialkylamino fluoro phosphoranes are much easier to decipher. The phosphorus hydrogen and fluorine atoms all have spins of $\frac{1}{2}$ so that coupling can occur between them. This coupling allows the structures to be identified unambiguously.

The coupling constants between the phosphorus hydrogen and fluorine atoms and the chemical shifts of the hydrogen and fluorine resonances are given in Table 3.

The ^{19}F spectrum of the dimethylamine phosphorus

TABLE 3

^{1}H and ^{19}F Nuclear Magnetic Resonance data for the dialkylamino fluoro phosphoranes.

Compound	J_{P-F}	J_{P-H}	J_{H-F}	J_{H-F}	δ H	δ F
PF_3NMe_2H	752(a)			50		+16.7
	808(e)					+7.3
PF_4NMe_2	836	11	2		2.57	+5.3
$PF_3(NMe_2)_2$	752(a)		2.8(a)	42	-2.65	-8.5(a)
	871(e)		1.5(e)			+10.2(e)
PF_3NEt_2H	756(a)			50		16.7(a)
	813(e)					+4.2(e)
PF_4NEt_2	868					+4.2
$PF_3(NEt_2)_2$	753(a)			44		-3.0(a)
	876(e)					+5.2(e)
PF_4NPr_2	856					3.7
PF_3MeNH_2	688(a)	14		41	-2.57	0(a)
decomposition product	865(e)					+15.7(e)
PF_3EtNH_2	705(a)			43		-1.3(a)
decomposition product	872(e)					+12.5(b)

pentafluoride adduct was complex and consisted of two doublets and two resonances containing nine lines. The observation of the nine line structures instead of the expected quintets identify the resonance as a AB_4 system instead of the usual AX_4 system. The difference between these systems is essentially mathematical and is described by Pople[35]. A similar spectrum has also been observed in sulphur pentafluoride derivatives with fluoroalkyl groups[36].

The spectrum of the diethylamine phosphorus pentafluoride complex was similar to that of the dimethylamine complex.

The high resolution ^1H and ^{19}F nuclear magnetic resonance spectra of dimethylamino tetrafluoro phosphorane are shown in Figure 2. The initial doublet in the ^1H spectrum is due to the six equivalent hydrogen atoms coupling with the phosphorus atom. The doublet is shown under high resolution to consist of two quintets caused by further coupling to four equivalent fluorine atoms. The ^{19}F spectrum also shows a doublet which under high resolution resolves into two heptuplets. These are caused by the four equivalent fluorine atoms coupling to the phosphorus atom to produce a doublet and further coupling to the six equivalent hydrogen atoms to produce two heptuplets.

Two structures are possible in which all the hydrogen and

PF_4NMe_2

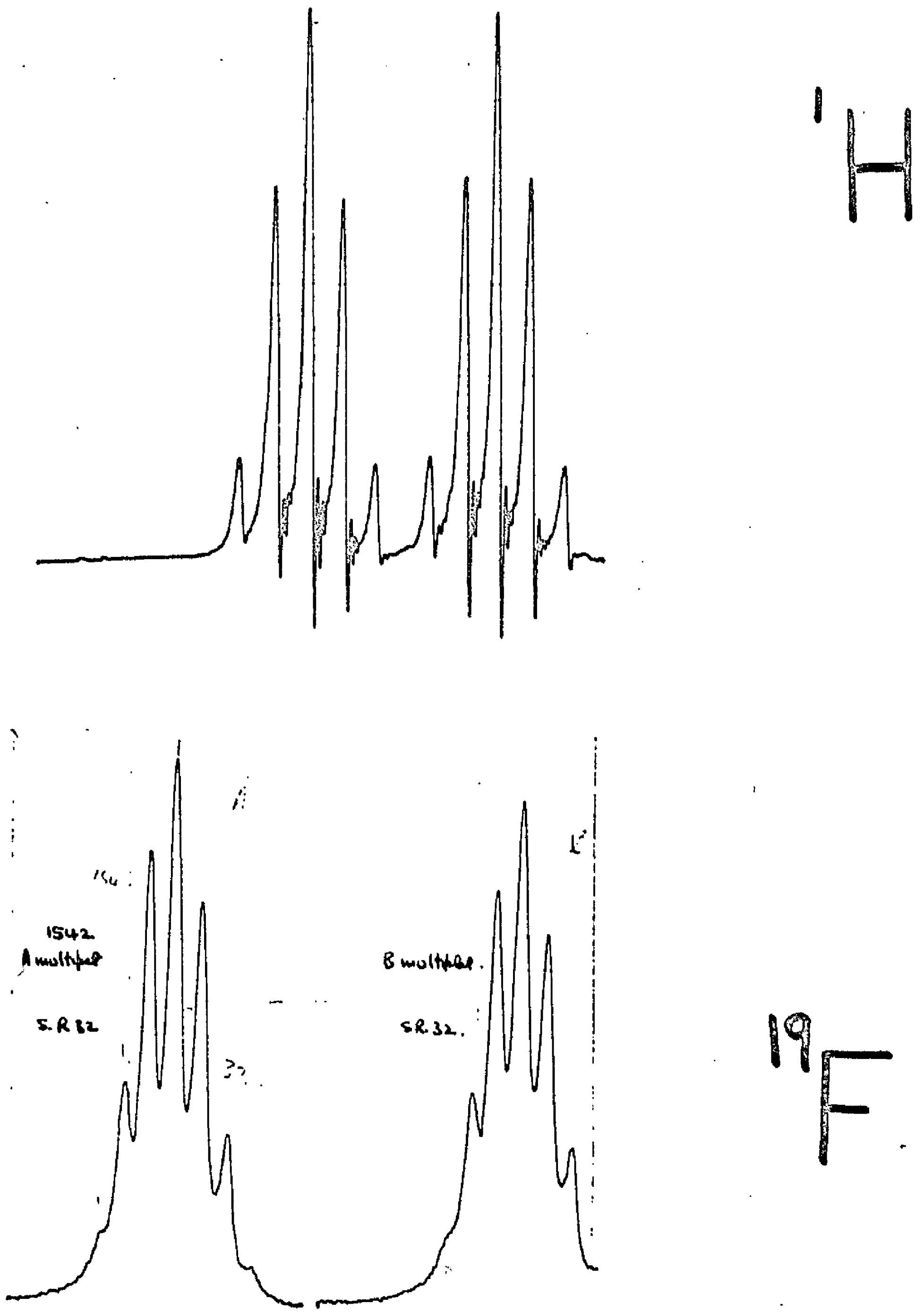
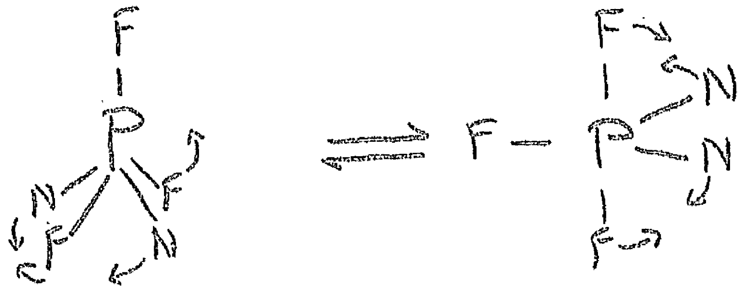


Fig. 2 Nuclear magnetic resonance spectra of dimethylaminc
tetrafluoro phosphorane

fluorine atoms are in equivalent environments. If dimethylamino tetrafluoro phosphorane adopted the square pyramidal configuration the four fluorine atoms would form the base and be equivalent. This structure would be unaffected by temperature so that the ^{19}F spectrum would not alter significantly. If the trigonal bipyramidal structure is adopted, the fluorine atoms would have to exchange rapidity to make them appear equivalent since there is no ~~t~~ static configuration of this structure in which all the fluorine atoms are equivalent. Since the phosphorus-fluorine coupling is observed, no phosphorus-fluorine bonds are broken and the exchange must be intramolecular. The exchange process would be highly dependent on temperature so that a low temperature ^{19}F nuclear magnetic resonance spectrum would show two types of fluorine environments. Muettertíes [39] has recently reported the low temperature ^{19}F nuclear magnetic resonance spectrum of diethylamino tetrafluoro phosphorane. As the temperature is lowered the sharp doublet gradually broadens until at -85°C four well resolved triplets are observed. This is consistent with two sets of equivalent fluorine atoms and they must occupy two axial and two equatorial positions of the trigonal bypyramidal structure. This is the first tetrafluoro phosphorane which has been conclusively shown to exist in the trigonal bipyramidal configuration. A low energy exchange process is possible between the square pyramidal and trigonal bipyramidal structures which would satisfy these observations is shown below



Dimethylamino and dipropylamino tetrafluoro phosphoranes probably also undergo this rapid exchange since their ^{19}F nuclear magnetic resonance spectra at 35°C are similar to the diethylamino tetrafluoro phosphorane.

The structure of bis-dimethylamino trifluoro phosphorane was determined from its ^1H and ^{19}F nuclear magnetic resonance spectra; figures of which are shown in Figure 3. The ^{19}F nuclear magnetic resonance spectrum consists of two doublets and two triplets of relative intensities 2:1. Two fluorine atoms are therefore in similar environments while the other fluorine atom is not. These will couple with each other and with the phosphorus atom to produce two doublets and two triplets respectively. If the trigonal bipyramidal structure is adopted two fluorine atoms will occupy either the axial or two of the

$PF_3(NMe_2)_2$

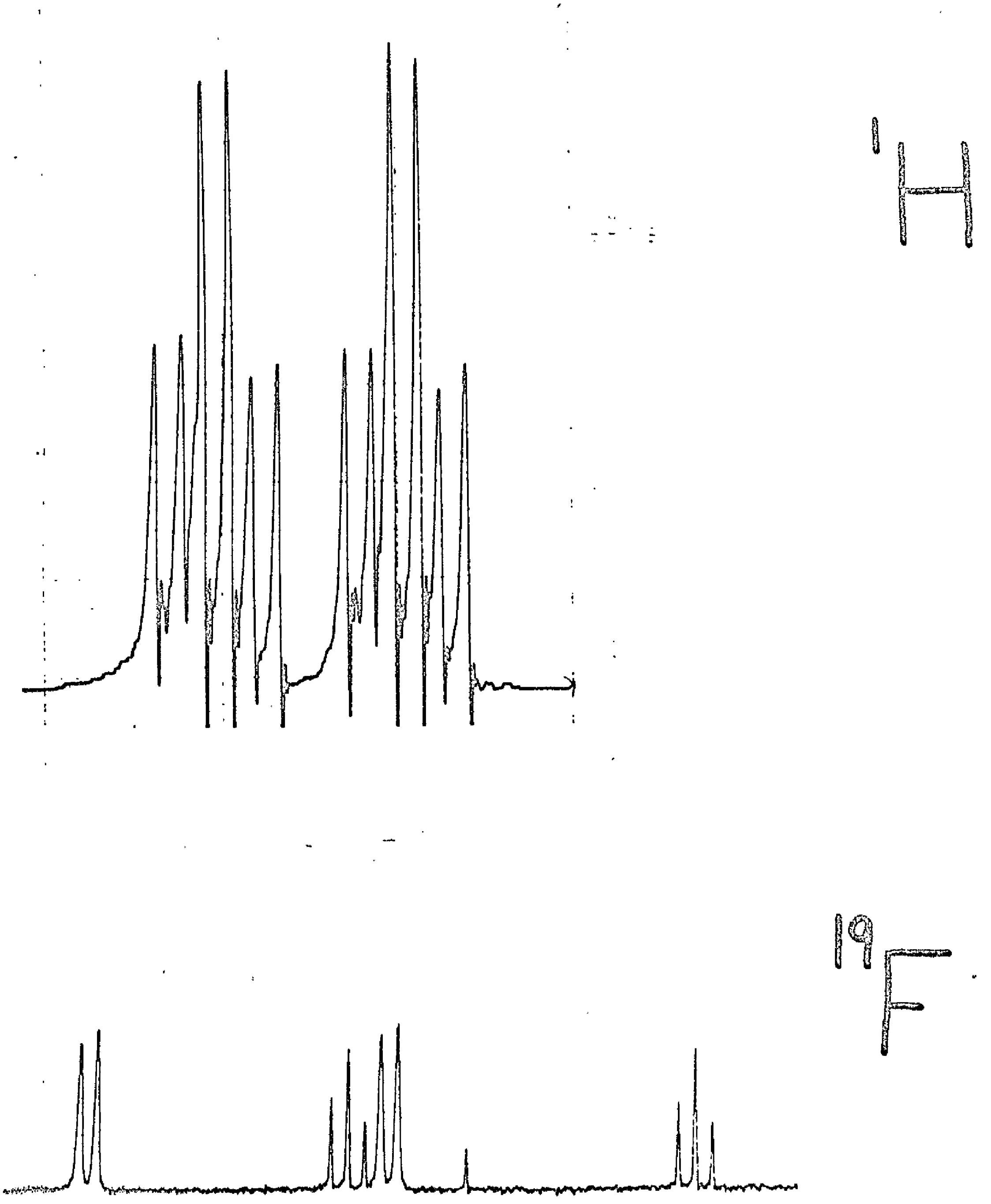


Fig. 3 Nuclear magnetic resonance spectra of bis-dimethylamino trifluoro phosphorane

equatorial positions while the other fluorine will occupy either an equatorial or an axial position. In the first case both dimethylamino groups will be in equatorial positions and be equivalent while in the second case one will be in the axial and one will be in the equatorial positions so that they will be non-equivalent. The ^{1}H spectrum consists of four triplets which suggest all the equivalent hydrogen atoms are coupled to two fluorine atoms and then are further coupled to the phosphorus atom and the non equivalent fluorine atom. The dimethylamino groups must therefore occupy two of the equatorial positions of the trigonal bipyramid. A square pyramidal configuration is also feasible in which two fluorine atoms and two dimethylamino groups are diagonally opposite on the base while the other fluorine atom is at the apex. Since diethylamino tetrafluoro phosphorane and trimethyl difluoro phosphorane[14] have been shown to adopt the trigonal bipyramidal structure it is unlikely that the trifluoro phosphorane will adopt the square pyramidal configuration.

The coupling constants and chemical shifts are all within the expected range of values for substituted phosphorus pentafluoride compounds[23].

Reactions of phosphorus pentafluoride with primary amines.

Preparation of compounds from non-metal fluorides and methylamine are much more difficult than those from secondary amines due to the polymerization of the intermediate X-M-NHMe to form chain polymers of the type $X-M-(NMe-M)_n-NHMe$ or ring polymers of the type $(M-NMe)_n$ rather than the monomeric species M=NMe. The result is that very few intramolecular reactions of methylamine complexes give simple products. Sulphur tetrafluoride was found to react with methylamine to give methylimino sulphur difluoride $MeN = SF_2$ which reacted with more methylamine to form bis-methylimino sulphur MeN =S = NMe. Both of these derivatives polymerise on standing at room temperature. The decomposition of the boron trifluoride methylamine complex has not been reported although the likely decomposition product $NN^{1}N^{11}$ trimethyl $BB^{1}B^{11}$ trifluoro borazole has been prepared from the reaction of methylamine and dimethyl fluoro borane at 400°C [31] and from the decomposition of methyl disilylamine boron trifluoride complex[3]

The reaction of phosphorus pentafluoride and methylamine was of interest as the likely decomposition product methylimino trifluoro phosphorane had not been reported. The corresponding chloro compound was prepared by Paddock[33] and was found to be dimeric. If the fluoro compound was monomeric valuable information would be obtained from its infrared spectrum regarding the P=N stretching vibration. If it was associated, the degree of association would be of interest in view of the extensive chemistry of the phosphonitrilic compounds[34].

The reaction between phosphorus pentafluoride and methylamine was found to be complex. When the two compounds reacted at -78°C a white solid was obtained which evolved methylamine continuously on warming. When the methylamine compound was heated to 270°C only a little volatile material was obtained. In order to reduce polymerization to a minimum, the decomposition was carried out in the high-boiling inert solvent 1,methyl naphthalene. The yields of the volatile produce were greatly increased and a colourless liquid (VP(20°C) = 10 mm.) was obtained. The analysis of the liquid were not reproducible and it gradually deposited a white solid over a period of a few days. This solid was not identified.

The reaction between phosphorus pentafluoride and ethylami in pentane solution produced a white solid analogous to that from the methylamine reaction. Analysis of the white solid showed it was not a simple 1:1 complex but contained excess ethylamine. The decomposition of this solid in 1, methyl naphthalene produced a slightly volatile liquid with similar infrared and nuclear magnetic resonance spectra to the methylamine phosphorus pentafluoride decomposition product.

Infrared Spectra

The vapour phase infrared spectra of these two liquids are given in Table 4.

The infrared spectrum of the methylamine reaction product was very simple. If it is compared with spectrum of phosphorus oxyfluoride^{35} it could be readily assigned to the monomeric methylamino trifluoro phosphoranes $PF_3{=}NCH_3$. The absorbtions at 909 and 806 cm^{-1} are the asymmetric and symmetric P-F stretching vibrations, the absorbtion at 1163 cm^{-1} is in the region expected for the P=N stretching vibration while the peaks at higher frequencies are associated with the N-Me group. The ethylamine reaction product could be similarly assigned, the 'extra' absorbtions being assigned to the ethyl group. The ^{19}F nuclear magnetic resonance spectrum of the methylamine reaction product was recorded, the details of which are given in Table 3. It consisted of two very broad peaks and two sharp triplets, the number of fluorine atoms associated with these resonances are in the ratio 2:1. It is difficult to relate these resonances as the broad peaks alter with temperature while the triplets do not^{36}. However the spectrum implies that two fluorine atoms are in equivalent

TABLE 4

Vapour phase infrared spectra of the phosphorus pentafluoride-primary amine decomposition products

POF_3	$MeNH_2+PF_5$	$EtNH_2+PF_5$
	3480(m)	3480(m)
	2950(m)	2960(m)
	2825(w)	2900(w)
	1445(s)	1443(s)
		1385(w)
		1300(w)
1415	1163(vs)	1160(vs)
		1087(m)
		990(m)
		952(m)
990	909(vs)	893(s)
		870(s.sh)
873	806(vs)	799(v.s.)

environments and one fluorine atom is non-equivalent. The single fluorine atoms couple with the two equivalent fluorine atoms and the phosphorus atom to form two triplets while the two equivalent fluorine atoms couple with the non-equivalent fluorine atom and the phosphorus atom to form two doublets. The broad peaks may in fact be doublets their broadness maybe due to the effect of the nitrogen quadropole moment in which case the triplets should be similarly broadened. The non-equivalence of the third fluorine atom suggests either a bent monomeric configuration $PF_3=N^{CH_3}$ or an polymeric species such as a cyclic structure is present. The analytical data however indicates a more complex species is present. The hoped for decomposition product methylamino trifluoro phosphoranes has recently been prepared in its dimeric form by the reaction of phosphorus pentafluoride with heptamethyl disilazane $(Me_3Si)_2NCH_3$ as a stable colourless liquid[37]. The physical and spectroscopic properties were completely different to those of the compound described above. The monomeric form could not be obtained from the dimer under any conditions. The ethylamine phosphorus pentafluoride decomposition product showed similar spectroscopic properties to the methylamine reaction product; the ^{19}F nuclear magnetic resonance spectrum was almost identical. This suggests there is a relationship between the stoichiometry of the original solids and the decomposition products.

The reactions were not investigated further but are worthy of further studies if larger quantities of the decomposition products can be obtained.

Some reactions of the dialkylamino fluoro phosphoranes

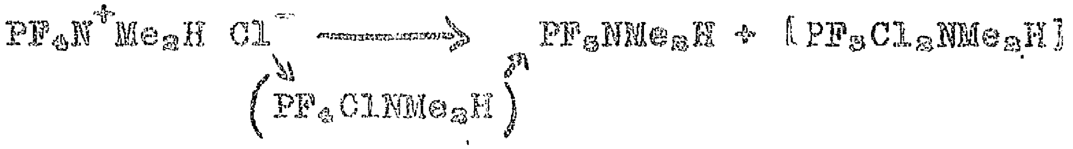
In the dialkylamino fluoro phosphoranes, the lone pairs of electrons on the nitrogen atoms are used to form partial double bonding in the phosphorus-nitrogen bond. The reaction of dimethylamino tetrafluoro phosphorane with hydrogen chloride and methyl iodide were investigated to see if the lone pair of electrons were available for bond formation.

Hydrogen chloride reacted with dimethylamino tetrafluoro phosphorane at low temperature to form a white solid which melted to a colourless liquid. The ^{19}F nuclear magnetic resonance spectrum of the liquid was complex and showed the main products to be phosphorus pentafluoride dimethylamine complex and an unidentified compound. When the mixture was heated these two products together with a little dimethylamino tetrafluoro phosphorane were obtained.

The ^{19}F nuclear magnetic resonance spectrum of the unidentified compound consisted of two heptuplets

(J_{P-K} = 995c/s, J_{H-F} = 2c/s and δ_P = +19.1 p.p.m.) while
the (J_{P-K} = 995c/s, J_{H-F} = 2c/s and δ_P = +19.1 p.p.m.) while
The the ^1H spectrum consisted of two triplets (J_{F-H} = 2 c/s). coupling constant and chemical shift suggested that it was either dimethylamino difluoro phosphine oxide[49] (POF_2NMe_2) or a phosphonium ion[50] e.g. $(PF_2ClNMe_2)^+$.

The inital reaction between hydrogen chloride and dimethylamino tetrafluoro phosphorane is believed to be caused by the dimethylamino group abstracting a proton from the hydrogen chloride to form the tetrafluoro phosphorane dimethylammonium ion $PF_4{}^+NMe_2H$. Subsequent reactions are believed to be complex and are not fully understood although the formation of the phosphorus pentafluoride dimethylamine adduct can be explained by simple rearrangement of the tetrafluoro phosphorus dimethylammonium ion as shown by the following equation.



$$\begin{tikzcd}
PF_4N^+Me_2H\ Cl^- \arrow[rr] \arrow[dr] & & PF_5NMe_2H + [PF_3Cl_2NMe_2H] \\
& (PF_4ClNMe_2H) \arrow[ur] &
\end{tikzcd}$$

Dimethylamino tetrafluoro phosphorane did not react with methyl iodide at 110°C. This is believed to be due to the larger energy required in forming the sterically-hindered tetrafluoro phosphorane trimethyl ammonium ion $[PF_4{}^+NMe_3]$.

Since bis-dimethylamino tetrafluoro phosphorane has two nitrogen atoms attached to the phosphorus atom, the $p_{\pi} - d_{\pi}$ overlap is less than in dimethylamino tetrafluoro phosphorane and the nitrogen lone pairs should be more readily available for coordination to the other compounds. The reaction of dimethylamino tetrafluoro phosphorane and bis-dimethylamino trifluoro phosphorane with molybdenum hexacarbonyl was therefore investigated under similar conditions.

The reaction between dimethylamino tetrafluoro phosphorane and molybdenum hexacarbonyl produced a black residue which was not identified but appeared to be a decomposition product. However, bis-dimethylamino trifluoro phosphorane reacted with molybdenum hexacarbonyl to form a pale yellow solid. The infrared spectrum of the solid showed three absorbtions in the carbonyl region at 2100, 2041 and 1942 cm^{-1}. These absorbtions were similar to those of molybdenum pentacarbonyl methyl cyanide complex[63], $Mo(CO)_5MeCN$ which occur at 2083, 1948, 1931cm and suggests that the yellow solid is the molybdenum pentacarbonyl bis-dimethylamino trifluoro phosphine complex $Mo(CO)_5PF_3(NMe_2)_2$.

The formation of this complex confirms that bis-dimethylamino trifluoro phosphorane is more likely to be a stronger coordinating agent that dimethylamino tetrafluoro phosphorane.

The use of these compounds as coordinating agents is worthy of further investigation. Bis-dimethylamino trifluoro phosphorane may also be found to behave as a bidentate ligand since the nitrogen-nitrogen interatomic distance (~ 2.5A) is suitable for chelation to transition-metal ions.

Experimental

Phosphorus pentafluoride was prepared from phosfluorogen (Ozark Mahoning Company). The aryl diazonium hexafluorophosphate was heated to 150°C when it decomposes according to the equation.

$$ArN_2^+PF_6^- \longrightarrow ArF+N_2+PF_5$$

The volatile products were passed through two cold traps at -78°C (solid carbon dioxide-acetone slush) which condensed out the organic components and then through a trap at -196°C (liquid nitrogen) which condensed out the phosphorus pentafluoride.

Phosphorus pentafluoride obtained in this way contained a little silicon tetrafluoride as impurity (identified from its infrared gas spectrum) and was purified by distillation at -120°C, (ether-liquid nitrogen slush), when the more volatile silicon tetrafluoride was removed first. The phosphorus pentafluoride remained in the coldtrap as a pure white solid.

Toluene was distilled from metallic sodium the fraction boiling at 110°C being stored over sodium wire.

Dimethylamine and ethylamine were obtained in sealed ampules and were dried by distillation at -78°C before use.

Methylamine was obtained from its alcohol solution by reaction with potassium hydroxide pellets and collecting the volatile material. It was purified by distillation at -78°C, the purity being confirmed from its infrared spectrum.

Diethylamine and di-propylamine were distilled at their boiling points (54°C and 110°C respectively) and stored over molecular sieves (Type 5A).

Preparation of phosphorus pentafluoride dimethylamine adduct (PF_5NMe_2H).

Dimethylamine (2 mls.) and toluene (10 mls.) were condensed at -196°C into the base of a sublimer tube and warmed to -78°C to cause mixing. Phosphorus pentafluoride gas was condensed into the mixture when a white solid was produced. When no further absorbtion of phosphorus pentafluoride occurred, even om vigorous shaking, the volatile products were removed by pumping under vacuum at room temperature for several hours. The adduct was then sublimed at 60°C and 10^{-3} mm. pressure onto a -78°C cold finger as a white crystalline solid. Yield 4 gs.

Analysis	%C=14.1	%H=4.3	%N=8.2	%P=18.1	%F=55.5
$C_2H_7NPF_5$ requires	%C=14.3	%H=4.1	%N=8.1	%P=18.1	%F=55.6

Preparation of dimethylamino tetrafluoro phosphorane (PF_4NMe_2)

(a) From phosphorus pentafluoride dimethylamine adduct.

The phosphorus pentafluoride dimethylamine adduct prepared above was placed in the vacuum line and heated in a closed system under a few mm. pressure. A −196°C trap removed any volatile materials produced in the decomposition. At 100°C the complex melted and began to decompose. Further heating to 150°C (using an oil bath) caused the melt to resolidify and no more volatile material was obtained.

The solid in the −196°C trap melted quickly to a colourless liquid which contained a trace of silicon tetrafluoride (from infrared gas spectrum). This was removed and the ${}^{1}H$ and ${}^{19}F$ nuclear magnetic resonance spectra showed the liquid to be pure. Melting point −78°C boiling point = 60°C(ext) V.P.(0°C)=41mm. V.P.(22°C)=116mm.

<u>Analysis</u> %C=15.7 %H=4.1 %N=9.5 %P=20.9 %F=54.6 M.Wt.=1

$C_2H_6NPF_4$ requires %C=15.9 %H=3.9 %N=9.3 %P=20.5 %F=50.3 M.Wt.=1

(b) <u>From sulpholane solution</u>

A B24 round bottomed flask was connected to the vacuum line with an adapter fitted with a B19 socket at an angle of 60°. This allowed a bent B19 sidearm tube to be rotated through 180° and this was a convenient method of adding a non-volatile liquid or powdered solid to the reaction mixed under reduced pressure.

Dimethylamine was condensed into the round bottomed flask at − 96°C and warmed to −78°C. Phosphorus pentafluoride was added until no further absorbtion occurred. The mixture was warmed to room temperature and sulpholane (tetramethylene-sulphone dried over lithium hydride and distilled under vacuum) was dropped onto it from the sidearm. The excess dimethylamine was removed by warming under high vacuum. The mixture was now heated on an oil bath, the volatile product between 100 and 160°C being condensed into a cold trap. This was shown by its infrared gas spectrum to consist of dimethylamino tetrafluoro phosphorane PF_4NMe_2 and bis-dimethylamino trifluoro, phosphorane, $PF_3(NMe_2)_2$. The more volatile PF_4NMe_2 was separated from the $PF_3(NMe_2)_2$ by distillation at 50°C under high vacuum.

<u>Preparation of diethylamino tetrafluoro phosphorane</u> PF_4NEt_2

Diethylamine and toluene were condensed into a reaction tu and were warmed to -78°C. Phosphorus pentafluoride was absorbe until reaction was complete depositing a white solid. The toluene was removed by distillation under vacuum leaving a sticky white solid. This was heated on an oil bath to 85-90°C when a vigorous evolution of diethylamine,(identified by its infrared gas spectrum) occurred leaving a white crystalline solid. Further heating of this solid to 100-120°C produced decomposition and a volatile liquid was condensed out. This wa pure diethylamino tetrafluoro phosphorane, PF_4NEt_2 melting poin -73°C V.P. (19°C) = 25 mm.

Analysis $\%C=27.0$ $\%H=5.7$ $\%N=7.9$ $\%P=17.2$ $\%F=42.5$

$C_4H_{10}NPF_4$ requires $\%C=26.8$ $\%H=5.6$ $\%N=7.8$ $\%P=17.3$ $\%F=42.4$

Preparation of di-n-propylamino tetrafluoro phosphorane PF_4NPr_2

Di-n-propylamine and toluene were condensed into a reactio flask at -196°C and warmed to -78°C. Phosphorus pentafluoride was absorbed and deposited a white solid. The toluene was removed at room temperature under vacuum leaving a sticky white solid. This was heated slowly, causing it to lose di-n-propylamine (identified by its infrared gas spectrum); this loss becoming rapid at 80-85°C. The solid was now heated to 225°C on an oil bath and the volatile portion was collected as a white solid, which melted to a viscous liquid. V.P.(19°C)=4mm. The H and ^{19}F nuclear magnetic resonance spectra were very similar to Et_2NPF_4 and this together with the vapour pressure, identified the liquid as Pr_2NPF_4. The product was not further identified.

Preparation of bis-dimethylamino trifluoro phosphorane $PF_3(NMe_2$

(a) From Phosphorus pentafluoride

Dimethylamine was condensed into a reaction flask at -196° and warmed to -78°C. Phosphorus pentafluoride was absorbed causing the dimethylamine to become more viscous until it became a glue. When no more gas was absorbed the mixture was heated gradually to 100°C; the gas evolved being dimethylamin (identified from its infrared spectrum). As the dimethylamine was removed the mixture became still more viscous so that, on cooling, it gradually solidified. It was now heated to 250°C on an oil bath, the products volatile between 120°C and 250°C being condensed at -196°C. The volatile products were found to consist of dimethylamine (which was readily removed by pumping under vacuum at -78°C) and a slightly volatile liquid which was found to be bis-dimethylamino trifluoro phosphorane [$PF_3(NMe_2)_2$]. This liquid was purified by fractionating it under vacuum at 0°C through a -40°C trap (acetone-carbon dioxide) which separated it from traces of dimethylamine, as a white highly crystalline solid which melted to a colourless liquid.

Melting point = -22°C. V.P. (20°C) = 4mm.

<u>Analysis</u> %C=27.1 %H=6.6 %N=16.0 %P=17.5 %F=33.0

$C_4H_{12}N_2PF_3$ requires %C=27.3 %H=6.8 %N=15.9 %P=17.6 %F=32.4

(b) From dimethylamino tetrafluoro phosphorane

Equal volumes of gaseous dimethylamino tetrafluoro phosphorane (~ 1g.) and dimethylamine were condensed at -196°C and warmed until they melted. A vigorous reaction took place and a white solid was deposited. On warming to room temperature the solid melted to give a clear liquid. This liquid had a vapour pressure of approx. 3cms. at room temperature and was found to be a mixture of bis-dimethylamino trifluoro phosphorane and dimethylamine from its infrared spectrum. No dimethylamino tetrafluoro phosphorane was observed. After the volatile products were removed, the residue was sublimed at 80°C under high vacuum and was identified as the dimethylamine phosphorus pentafluoride adduct from its ^{19}F nuclear magnetic resonance spectrum. Only a trace of residue was left after sublimation. This suggests that the reaction can be represented by the following equation.

$$2PF_4NMe_2 + NMe_2H \longrightarrow PF_3(NMe_2)_2 + PF_5NMe_2H.$$

(c) From sulpholane solution

The apparatus designed to prepare dimethylamino tetrafluoro phosphorane, using sulpholane as solvent, was used.

Phosphorus pentafluoride reacted with excess of dimethylamine at -78°C and the reaction mixture was warmed to room temperature. Sulpholane was then poured onto the mixture from the rotating sidearm and the mixture was heated under vacuum. The initial volatile product was dimethylamine and at 100°C some dimethylamino tetrafluoro phosphorane was produced. This reacted with the dimethylamine in the cold trap to form a white solid. Further heating produced bis-dimethylamino trifluoro phosphorane which was separated by fractionation through a $-40^\circ C$ trap as described above.

Bis-diethylamino trifluoro phosphorane

(a) From Phosphorus Pentafluoride

Phosphorus pentafluoride reacted with diethylamine at its melting point ($-50^\circ C$) (acetone-carbon dioxide) to form a sticky solid. This solid was heated to $80^\circ C$ for one hour under vacuum. This is the maximum temperature obtainable without vigorous loss of the excess of diethylamine which occurs at $85-90^\circ C$. The volatile materials collected in a cold trap consisted of diethylamine (identified by its infrared spectrum) and a high melting, slightly volatile liquid. The diethylamine was removed by pumping under vacuum at $-10^\circ C$ (ice-salt mixture) until a white crystalline solid was left in the cold trap. This was bis-diethylamino trifluoro phosphorane $PF_3(NEt_2)_2$. Melting point = $+5^\circ C$.

Analysis %C=41.4 %H=8.7 %N=12.2 %P=13.5 %F=24.4

$C_8H_{20}N_2PF_3$ requires %C=41.4 %H=8.6 %N=12.1 %P=13.4 %F=24.6

(b) From diethylamino tetrafluoro phosphorane

Diethylamino tetrafluoro phosphorane and excess diethylamine were condensed at $-196^\circ C$ in a nuclear magnetic resonance tube. The initial white solid which formed dissolved on warming in the excess diethylamine to give a clear solution A ^{19}F nuclear magnetic resonance spectrum showed diethylamine phosphorus pentafluoride adduct and bis-diethylamino trifluoro phosphorane were present, suggesting a reaction had occurred similar to the corresponding methyl compounds. This reaction was not investigated further.

Attempted preparation of tris-diethylamino difluoro phosphora

(a) Bis-dimethylamino trifluoro phosphorane and dimethylamin

Bis-dimethylamino trifluoro phosphorane (0.5gs.) and dimethylamine (0.1g.) were condensed into a large tube fitted with a break-seal sidearm. The tube was then heated at 120°C for 12 hours after which a clear liquid was left. A ^{19}F nuclear magnetic resonance spectrum showed only bis-dimethylamino trifluoro phosphorane.

(b) Bis-dimethylamino trifluoro phosphorane and tris-dimethyl amino phosphine $P(NMe_2)_3$

The preparation of the tris-dimethylamino phosphine is described in Chapter 3. Bis-dimethylamino trifluoro phosphorane (0.5 gs.) and tris-dimethylamino phosphine (0.4gs. were heated in a sealed tube at 120°C for 40 hours. The volatile products were condensed into a nuclear magnetic resonance tube and the ^{1}H and ^{19}F nuclear magnetic resonance spectra showed a mixture of bis-dimethylamino fluoro phosphine $PF(NMe_2)_2$ and tris-dimethylamino phosphine. A little white solid residue was not identified.

(c) Tris-dimethylamino phosphine, chlorine and sodium fluoride

Tris-dimethylamino phosphine reacted with chlorine at -78°C and after removal of the excess chlorine a pale yellow solid remained. This was dissolved in sulpholane and heated to 120-140°C with a large excess of sodium fluoride. The yellow solid became orange-brown and a little volatile produc was obtained. This was identified as bis-dimethylamino trifluoro phosphorane from its ^{19}F nuclear magnetic resonance spectrum.

(d) Trichloro difluoro phosphorane and excess dimethylamine

Trichloro difluoro phosphorane (a gift from the University of Glasgow) was reacted with excess of dimethylamine at -78°C. A vigorous reaction took place and a white solid was deposited. Distillation of the volatile material under vacuum on a warm water-bath gave only dimethylamine.

Reaction of phosphorus pentafluoride with methylamine

Methylamine was condensed into a cold reaction tube at -196°C and warmed to -78°C. Phosphorus pentafluoride was now absorbed and a white solid was obtained. When absorbtion ceased, the solid was heated to 270°C, the volatile materials being condensed into a −196°C trap. Only a trace of volatile liquid was obtained even on using 5 gs. of phosphorus pentafluoride.

If the thermal decomposition of the phosphorus pentafluori methylamine compound was completed in 1,methyl naphthalene as solvent, at a temperature of 160-180°C, a small quantity of liquid was obtained which had identical infrared and ^{19}F nuclear magnetic resonance spectra to the trace amount describe above.

Analysis of this liquid varied from sample to sample and did not relate to any simple species. This liquid tended to deposit a white solid over a period of several days. V.P.(20°C) 10mm.

Analysis %C=21.8 %H=5.6 %N=21.8 %P=16.2 %F=34.3

Approximate empirical formula $C_3H_8N_3PF_3$.

Reaction of phosphorus pentafluoride with ethylamine

Ethylamine and pentane were condensed at −196°C and warmed to −78°C to produce mixing. Phosphorus pentafluoride wa absorbed by the mixture and a sticky white solid was deposited. When absorbtion ceased the volatile products were removed under vacuum and the solid pumped under high vacuum for 24 hours.

Analyses %C=17.0 %H=5.4 %N=9.8 %P=16.8 %F=51.3

$4PF_5 5EtNH_2$ requires %C=16.4 %H=4.8 %N=9.6 %P=17.0 %F=52.0

When the solid was heated in 1, methyl naphthalene an almost non-volatile liquid was obtained with similar infrared and ^{19}F nuclear magnetic resonance spectra to the product obtained from the methylamine reaction.

Reactions of dimethylamino tetrafluoro phosphorane

(a) Hydrogen chloride

The hydrogen chloride was prepared by the action of aqueous hydrochloric acid on phosphorus pentoxide and was purified by distillation at -78°C. Dimethylamino tetrafluoro phosphorane was condensed into a reaction tube at -196°C and warmed to -78°C. Hydrogen chloride was now absorbed by the dimethylamino tetrafluoro phosphorane and a white solid was deposited. After 1 hour only a white solid was present in the reaction tube. This solid was stable at -78°C but decomposed on warming to give a volatile material identified as dimethylamino tetrafluoro phosphorane. The reaction was repeated in a sealed nuclear magnetic resonance tube and a complex mixture was obtained. When the tube was heated to 80°C the products were dimethylamine phosphorus pentafluoride adduct, a little dimethylamino tetrafluoro phosphorane and an unidentified mater containing P-F bonds.

(b) Methyl iodide

The methyl iodide was purified by distillation at -78°C. When the dimethylamino tetrafluoro phosphorane and methyl iodide were condensed at -196°C and warmed to room temperature, no visible reaction took place. The mixture was heated at 110° for 24 hours but only starting materials were observed in the infrared spectrum.

Reactions of bis-dimethylamino trifluoro phosphorane

(a) Molybdenum hexacarbonyl

The molybdenum hexacarbonyl was purified by sublimation under vacuum and added to bis-dimethylamino trifluoro phosphorane in a Carius tube in approximately equimolar proportions. The tube was heated at 65°C for 13 hours, during which time the mixture gradually turned yellow, until a yellow solid and yellow liquid were left. The tube was then opened and the yellow solid gradually darkened as the volatile liquid was removed under vacuum. Sublimation of this solid at 50°C under vacuum yielded pale yellow crystals.

The infrared spectrum showed this was molybdenum hexacarbonyl with a small quantity of compound which was believed t be a molybdenum pentacarbonyl derivative from its absorptions in the carbonyl region (2200-1800 cm^{-1}). It was not possible to effect separation from the molybdenum hexacarbonyl and a pure specimen could not be obtained.

CHAPTER IX

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH PHOSPHORUS LIGANDS

Introduction

Although complexes of phosphorus pentafluoride with nitrogen ligands have been widely investigated[8], the preparation and properties of complexes with phosphorus ligands have not previously been reported.

The reaction of boron trifluoride with trimethyl phosphine yields the 1:1 complex[38]. The complex decomposed in water, ethanol and acetone and was insoluble in carbon tetrachloride and carbon disulphide but was slight soluble in chloroform. The infrared spectrum of the solid[39] confirmed that it was a donor-acceptor complex; the boron-fluorine stretching frequencies moved from 1450 cm^{-1} to 1100 cm^{-1} indicating the formation of the tetrahedral complex from the planar boron trifluoride molecule.

The preparation of the corresponding phosphorus pentafluoride, trimethyl phosphine complex was of interest since a novel pentavalent-trivalent phosphorus-phosphorus bond would be produced.

In recent years many types of compounds containing phosphorus-phosphorus bonds have been prepared[40]. In most cases the bond occurs in trivalent phosphorus compounds e.g. P_2Cl_4 and $P_2(CH_3)_4$ while in hypophosphoric acid $H_4P_2O_6$ the phosphorus-phosphorus bond is formed between pentavalent phosphorus atoms. Compounds which contain elements bonded together in two different valency states are very rare. The only other example is sulphur in which the compounds disulphur monoxide S_2O and disulphur-difluoride[41] S_2F_2 contain divalent and tetravalent sulphur bonded to each other.

The complexes formed between phosphorus pentafluoride and tris-dimethylamino phosphine and trimethyl phosphite should also contain the pentavalent-trivalent phosphorus-phosphorus bond. The corresponding complexes of boron trifluoride with tris-dimethylamino phosphine[42] and trimethyl phosphite[43] are unstable and decompose to the dimeric compounds dimethylamino difluoro borane $(Me_2NBF_2)_2$ and methoxy difluoro borane $(CH_3OBF_2)_2$.

Discussion

Compounds containing phosphorus phosphorus bonds are of interest spectroscopically as well as chemically . The nuclear magnetic resonance spectra should show resonances attributable to both phosphorus atoms; the difference in valency states should cause these resonances to be widely separated, since the chemical shifts depend upon the electronic surroundings of the phosphorus atoms. In addition coupling may occur between these atoms and the fluorine and hydrogenatoms in the molecule and this coupling may produce information regarding the structure of the complexes.

The infrared spectra of phosphorus pentafluoride phosphine complexes are also of interest as it should be possible to assign the phosphorus-phosphorus stretching vibration. In most of the molecules containing phosphorus-phosphorus bonds a high degree of symmetry exists which causes the stretching vibration to be infrared inactive.

Reaction with trimethyl and tripropyl phosphine

Holmes[44] found that trimethyl phosphine and phosphorus pentachloride did not react at 0°C. If the mixture was heated to 100°C the vapour pressure of the trimethyl phosphine decreased but the reaction was still incomplete after 24 days at this temperature. If trimethylphosphine and phosphorus pentachloride were mixed in bromobenzene a white solid was obtained. This was identified as $(PMe_3)_2PCl_5$ from the ratio of the mass of trimethylphosphins to phosphorus pentachloride used. The product was not investigated further.

By comparison the reaction between phosphorus pentafluori and trimethyl phosphine was very simple. Phosphorus pentafluoride gas was rapidly absorbed by trimethyl phosphine at -78°C and a white solid was formed. The volatile products were removed under vacuum and a white powder was obtained. It was thermally stable and sublimed at 70°C under high vacuum. The compound was identified by analysis and the ^{19}F nuclear magnetic resonance spectrum as the 1:1 complex. The ^{19}F nuclear magnetic resonance spectrum in sulphur dioxide solution was measured by Muetterties[38]. It consisted of two doublets and two quintets which identified the compound as a PF_5 complex. The resonances arise from the axial fluorine atom coupling with the four equatorial fluorine atoms and also to the phosphorus atom to give the two quintets while the four equatorial fluorine atoms couple to the axial fluorine and phosphorus atoms to give two doublets. The spectrum was similar to that of PF_5 complexes with amines. No coupling between the phosphine phosphorus atom and the fluorine atoms J_{P-F} was observed. The other coupling constants are J_{P-F_e} = 716 c/s J_{P-F_a} = 775 c/s $J_{F_A-F_e}$ = 52 c/s.

The infrared spectrum of the complex was recorded in Nujol. The details are given in Table 5 in which the spectrum is compared with that of trimethyl phosphine and the boron trifluoride trimethyl phosphine complex.

TABLE 5

Infrared spectra of trimethyl phosphine complexes in the range 1500-625cm^{-1}.

PMe_3^{39} (gas)	BF_3PMe_3^{33} (nujol)		PF_5PMe_3 (nujol)	
1430	1425		1440	
1417				
1310			1320	
1298	1300		1305	
1067				
	1125			
	1085	B–F	870	P–F
	1060		800	
	1037			
960	970		975	
947				
	785			
717	705		690	
707	675		660	
652			x	

x Expected below the range of the instrument.

The similarity between the spectra of the boron trifluoride and phosphorus pentafluoride complexes is shown in the Table. All of the absorbtions above 900 cm^{-1} in the phosphorus pentafluoride complex are attributed to vibrations of the methyl phosphine group. The absorbtions at 870 and 800 cm^{-1} are assigned to the phosphorus-fluorine stretching vibrations of the PF_5 group while the strong absorbtion at 660 cm^{-1} is assigned to the asymmetric phosphorus-carbon stretching vibration, which occurs at 717 and 707 cm^{-1} in the infrared spectrum of trimethyl phosphine.

The tri-n-propyl phosphine complex was prepared by the reaction of phosphorus pentafluoride with tri-n-propyl phosphine at 20°C. It was purified by sublimation at 120°C under high vacuum.

The stability of these complexes is considered along with the stability of the other phosphine complexes at the end of the discussion.

Reaction with tris-dimethylamino phosphine

The interest in the coordinating properties of tris-dimethylamino phosphine arises from the possibility of coordination through both the phosphorus and the nitrogen atoms.

The reaction of tris-dimethylamino phosphine with a wide range of transition metal compounds has been studied. King[62] prepared complexes with metal carbonyls and substituted metal carbonyls, and Noth prepared complexes of tris-dimethylamino phosphines with metal halides.[63] The complexes were isolated as stable crystalline solids.

The complexes formed between tris-dimethylamino phosphine and non-metal acceptor molecules are unstable and decompose to yield a mixture of products. Nolmes[64] reacted boron trimethyl, boron trichloride and boron trifluoride with tris-dimethylamino phosphine and obtained the dimeric dialkylamino boron dimethyl, dichloride and difluoride $(Me_2NBR_2)_2$ $(R=CH_3, Cl, F)$.

A possible explanation of the variation in the stability of tris-dimethylamino complexes with metals and non-metals is that in the former the phosphine is coordinated through its phosphorus atom while in the latter the coordination occurs through one of the nitrogen atoms.

The reaction of tris-dimethylamino phosphine with phosphorus pentafluoride was investigated in order to determine whether coordination occurred through the nitrogen or phosphorus lone pair of electrons.

The solution of tris-dimethylamino phosphine in pentane at −78°C absorbed phosphorus pentafluoride and deposited a white solid. When absorbtion ceased, the volatile products were removed at room temperature and a white powder was obtained. The analysis of this powder confirmed that it was the 1:1 tris-dimethylamino phosphine phosphorus pentafluoride complex. $PF_5.P(NMe_2)_3$.

The complex was stable at room temperature and sublimed at 70°C under high vacuum. However, the pale yellow sublimate was very unstable and fumed in air. The instability of the sublimate compared with the complex suggested that decompositio had taken place during sublimation. Because of its reactivity, the analysis of the sublimate was not obtained.

If the complex was heated to 70°C in a closed system the vacuum line, an initial increase in vapour pressure was observed but this quickly subsided. The white solid did not seem to change further until 130°C when decomposition took place and the vapour pressure steadily increased. The ^{19}F nuclear magnetic resonance spectra of the volatile products identified them as dimethylamino tetrafluoro phosphorane and bis-dimethylamino fluoro phosphine, $PF(NMe_2)_2$ together with a little bis-dimethylamino trifluoro phosphorane and dimethylamino difluoro phosphine PF_2NMe_2.

The decomposition of tris-dimethylamino phosphine phosphorus pentafluoride can be represented by the following equations.

$$PF_5\ P(NMe_2)_3 \longrightarrow PF_4NMe_2 + PF(NMe_2)_2$$
$$\longrightarrow PF_3(NMe_2)_2 + PF_2NMe_2$$

The infrared spectrum of the complex was recorded in the region 4000-400 cm^{-1} on a Perkin Elmer 125 spectrophotometer. The details of the spectrum are recorded in Table 6 in which they are compared with the absorbtions of tris-dimethylamino phosphine and the molybdenum pentacarbonyl tris-dimethylamino phosphine complex. The spectrum of the tris-dimethylamino phosphine phosphorus pentafluoride complex contained very broad absorbtion bands due to the difficulty in obtaining a good mull. No assignments of the spectra were possible and very few conclusions regarding the structure of the tris-dimethylamino phosphine phosphorus pentafluoride complex can be drawn.

The structure of the complex cannot be deduced from the infrared spectrum since the phosphorus-fluorine stretching vibration which occurs at 840 cm^{-1} is similar to those of other phosphorus pentafluoride complexes with either nitrogen or phosphorus ligands.

The ^1H, ^{19}F and ^{31}P nuclear magnetic resonance spectra of the complex were observed in sulphur dioxide and

TABLE 6

Infrared Spectra of tris-dimethylamino phosphine complexes in the range 1500-400cm^{-1}.

$PF_5P(NMe_2)_3$ (nujol)	$P(NMe_2)_3$ (liquid)	$Mo(CO)_5P(NMe_2)_3$ (nujol)
1455	1458	1455
1311	1264	1251
1187	1193	1178
		1150
1069	1058	1058
993	970	968
	950	952
	932	
840		
788		
739		
692	668	688
674		
641	642	645
		609
557		
525		
495	497	505
471	418	435

deutero acetonitrile solution. The ^{31}P spectra of both solutions consisted of a heptuplet and indicated the presence of hexafluoro phosphate ions. The ^{1}H spectra were complex; the main resonance was a single line which suggested that the compound producing the resonance did not contain phosphorus as no phosphorus-hydrogen coupling was observed. The ^{19}F spectra confirmed that the main product was a hexafluoro phosphate salt, but in addition, the spectrum of the sulphur dioxide solution showed the presence of other compounds.

One of these compounds produced a resonance of four doublets which could be assigned to the four equatorial fluorine atoms in the complex as follows. The coupling constants (J_{P-F} = 740c/s J_{F-F} = 55c/s) and the chemical shift (δ_F= -1.0 ppm.) are similar to those of other phosphorus pentafluoride complexes. (Table 3).

The remaining coupling constant is small (~ 7c/s) and is believed to be due to the coupling of the four equatorial atoms with the phosphorus atom of the phosphine. This coupling constant had not been previously observed in phosphine complexes e.g. PF_5PMe_3 and $WF_6P\phi_3$ [38] probably because the coupling constants in these cases were too small to be measured. The resonances attributed to the coupling of the axial fluorine atom were not observed since the concentration of the complex was so small that the expected resonance of two quintets could not be distinguished from the background noise of the instrument.

This assignment of the ^{19}F spectrum is supported by the observation of a similar set of resonances (4 doublets) in the ^{19}F spectrum of the decomposition of trimethoxy methyl phosphonium hexafluoro phosphate in deutero acetonitrile In addition to the doublets the quintets were also observed. The coupling constants (J_{P-F} = 760c/s J_{F-F} = 56.5c/s J_{P-F} = 6.5c/s) and chemical shift (δ_F = -5.0ppm) were very similar to those described above.

The coupling constant of 6.5c/s is similar in value to that obtained when a methyl group is directly attached to a phosphorus atom in an organo-phosphorus-fluorine compound. However it is not possible to devise structures of phosphorus pentafluoride compounds in which coupling occurs with a single hydrogen atom in both these reactions. Because of the similarity in the coupling constants J_{P-F} (6.5c/s and 7.0c/s), the complexes are postulated to be coordinated through the phosphorus atom rather than the nitrogen or oxygen atoms.

The observation of the small concentration of the tris-dimethylamino phosphine complex suggest that rearrangement must be taking place in solution. It was not possible to identify the cation although the single resonance in the ^{1}H spectrum suggested the formation of a methyl ammonium ion rather than the dimethylamino phosphonium ion.

Reaction with trimethyl phosphite.

Reaction with trimethyl phosphite.

The reaction of trimethyl phosphite with phosphorus pentafluoride was investigated, in order to obtain information on whether the coordination in the complex occurred through the phosphorus or the oxygen atoms. Goubeau[48] reacted boron trifluoride with trimethyl phosphite and obtained dimeric methoxy difluoro borane $(MeOBF_2)_2$.

Trimethyl phosphite in ether of pentane solution absorbed phosphorus pentafluoride to form a white solid. The volatile products were removed at -20°C under vacuum and the solid was obtained as a white powder. The powder seemed to be stable at -20°C but became moist at 0°C suggesting that decomposition was taking place. The instability of the compoun at this temperature prevented identification by analytical or spectroscopic means. The similarity of this compound to that of the other phosphine complexes implied that it was a 1:1 trimethyl phosphite phosphorus pentafluoride complex.

The solid decomposed rapidly at 20°C, and evolved volatile materials which were removed by condensing them in a trap at -196°C. During the decomposition the solid remained dry and powdery which suggested that a simple decomposition was probably occurring in which all the products were volatile at room temperature. After approximately an hour the solid had completely decomposed and only a trace of very viscous liquid was left in the reaction flask. The product in the cold trap consisted of a white solid, part of which melted at very low temperature (< -100°C) and part of which melted at approx. -78°C. The liquids were fractionated through three traps at -78°C -95°C and -196°C respectively. No product was obtained in the -78°C trap but a colourless liquid was present in the -95°C trap and a white solid was obtained in the -196°C trap. The volatility of the products at -78°C suggested that a simple decomposition has taken place in which the products were molecules with low molecular weights.

A quantitative study of the volatile products by weighing the fractions in sealed ampules was not conclusive. The mass of solid in the -196°C trap was 0.224 gs. while the mass of liquid in the -95°C trap was 0.165 gs. The most likely decomposition reaction (in view of the decomposition of the tris-dimethyl amino phosphine phosphorus pentafluoride complex) is one of the following

$$(MeO)_3PPF_5 \longrightarrow (MeO)_2PF + MeOPF_4 \qquad (1)$$

$$(MeO)_3PPF_5 \longrightarrow MeOPF_2 + (MeO)_2PF_3 \qquad (2)$$

If the decomposition followed equation (1) the solid in the -196°C trap would be methoxy tetrafluoro phosphorane while for equation (2) the most volatile product would be methoxy difluoro phosphine. The ratio of the weights of the products $\frac{0.224}{0.165}$ is more closely related to the ratio of the molecular weights of the products in equation (1) $\frac{138}{112}$ than those in equation (2) $\frac{100}{150}$. This would suggest that the intermediates are methoxy tetrafluoro phosphorane and dimethoxy fluoro phosphine rather than dimethoxy trifluoro phosphorane and methoxy difluoro phosphine but the formation of other product e.g. methoxy difluoro phosphine oxide CH_3OPOF_2 and methoxy methyl trifluoro phosphorane $CH_3OP(CH_3)F_3$ is also possible.

The liquids in the two traps began to deposit colourless solids at 0°C. This indicated that fractionation was not complete since dimethoxy fluoro phosphine and methoxy difluoro phosphine are thermally stable.

The solids were formed in an exothermic reaction in which the temperature of the mixtures increased from 20 to ~40°C. As solidification occurred, a volatile material was produced and the vapour pressure increased sharply. When the formation of the solid ceased and the mixture cooled to room temperature, the volatile materials were removed and a white crystalline solid was formed. It was identified by analysis as trimethoxy methyl phosphonium hexafluoro phosphate $(CH_3O)_3P^+CH_3\ PF_6^-$. The compound was obtained in fairly large quantities and seemed to be the major product in the reaction. The compound is the first simple crystalline intermediate in the Michaelis Arbuzov rearrangement to be isolated. The properties and decomposition of this compound are discussed in Chapter III.

The volatile liquids which formed the other products of the reaction contained several components, most of which could be identified from the ^{19}F nuclear magnetic resonance spectrum the details of which are given in Table 7. The quantities of each liquid obtained varied with each experiment and also depended upon the solvent used. If ether was used as solvent, the products were methoxy difluoro phosphine oxide (CH_3OPOF_2) methoxy difluoro phosphine (CH_3OPF_2) and a little methyl difluoro phosphine oxide

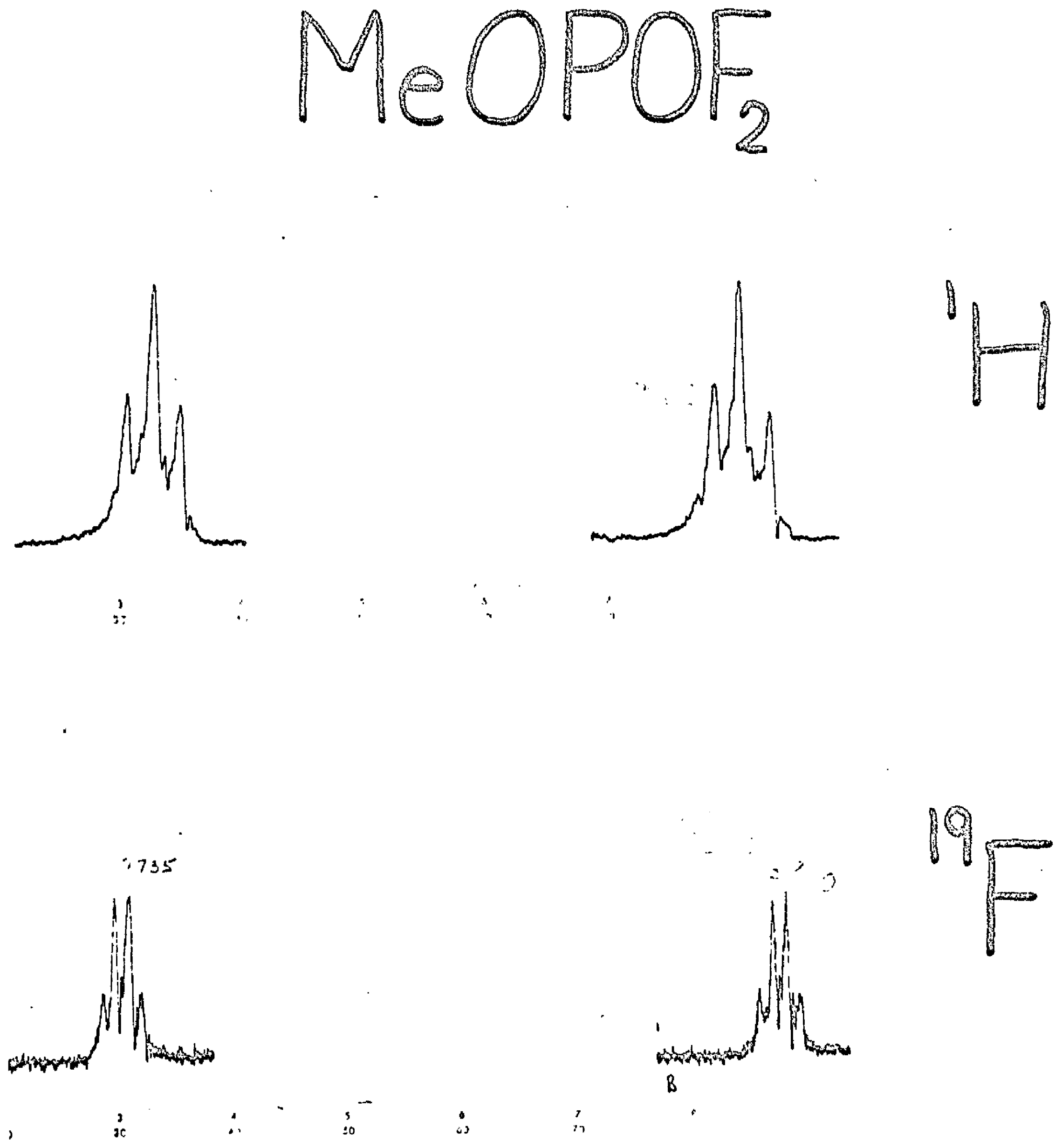


Fig. 4 Nuclear magnetic resonance spectra of methoxy difluoro phosphine oxide

(CH_3POF_2). When pentane was used as solvent none of the latter compound was present but another liquid believed to be dimethoxy fluoro phosphine $(CH_3O)_2PF$ was obtained. Methoxy difluoro phosphine oxide has not been reported in the literature although the ethyl and phenyl derivatives are well known[45]. It is a colourless liquid boiling point = 76°C which only fumes slightly in air.

The decomposition of the trimethyl phosphite phosphorus pentafluoride complex can be represented by the following equation.

$$2(CH_3O)_3PPF_5 \longrightarrow (CH_3O)_3\overset{+}{P}CH_3\overset{-}{PF_6} + CH_3OPOF_2 + CH_3OPF_2 + CH_3POF$$

Although the equation described the final products the reaction must be more complicated than this but, until further details of the volatile intermediates are known, no positive explanation of the decomposition is possible. A study of these volatile intermediates by observing the ^{1}H ^{19}F and ^{31}P nuclear magnetic resonance spectra at low temperatures would help in understanding this reaction.

<u>Reaction with triethyl phosphite</u>

Triethyl phosphite and ether were condensed into a reaction tube and warmed to -78°C. Phosphorus pentafluoride was absorbed by the mixture until excess phosphorus pentafluoride was present. The mixture was warmed to 0°C and all the volatile materials were removed under vacuum to leave a white solid. Above 0°C the solid began to decompose in a similar manner to be analogous trimethyl phosphite compound. However the decomposition was much slower and the mixture had to be warmed to 40°C for it to proceed at a reasonable rate. The solid was completely decomposed after approximately 12-24 hours. The volatile products which were removed during the decomposition consisted of a white solid which melted at ~ -78°C into a colourless liquid. The liquid was fractionated through -78°C and -196°C traps, the former of which contained a colourless liquid and the latter contained a white solid. Both of these fractions deposited white solids at room temperature which suggested that complete fractionation had not been obtained or that further reaction had occurred. The formation of the solids sometimes took several days compared with their immediate formation in the trimethyl phosphite reaction.

The slowness in solid formation was due to either a different decomposition path being followed or to rearrangements being slower because of a steric effect.

After four days the volatile products were removed and were identified by their ^{19}F nuclear magnetic resonance spectr the details of which are given later. Several products were always obtained and these compounds produced a very complex spectrum. The liquids were therefore distilled at atmospheric pressure and three fractions boiling points 40°C, 85°C and 115°-120°C were obtained. The ^{19}F nuclear magnetic resonance spectrum of the 85°C fraction identified the product as ethoxy difluoro phosphine oxide $EtOPOF_2$ which contained a trace of ethoxy difluoro phosphine $EtOPF_2$. The 40°C fraction consisted of ethoxy difluoro phosphine and ethoxy difluoro phosphine oxide together with another product which was believed to be diethoxy fluoro phosphine $(EtO)_2PF$. The 120°C fraction consisted of ethoxy difluoro phosphine oxide, ethyl difluoro phosphine oxide $(EtPOF_2)$, a little hexafluoro phosphate ion (MPF_6) and diethoxy fluoro phosphine oxide $(EtO)_2POF$.

The solid obtained from the reaction analysed to triethyl oxonium hexafluoro phosphate $(Et_3O^+PF_6^-)$. The ^1H nuclear magnetic resonance spectrum of this crude solid in deuteroacetone CD_3COCD_3 solution showed one very strong ethyl resonance and a small concentration of a second ethyl resonance which disappeared in approximately ten minutes. A solid obtained from another reaction between triethyl phosphite and phosphorus pentafluoride analysed to diethoxy diethyl phosphonium hexafluoro phosphate $(EtO)_2PEt_2^+PF_6^-$. Unfortunately the ^{1}H nuclear magnetic resonance spectrum of this product was not obtained due to the lack of a suitable deuterated solvent.

One possible explanation of this variation would be the presence of some diethyl ether phosphorus pentafluoride complex is the first reaction which was not present in the second reaction. The complex formed triethyl oxonium hexafluoro phosphate as the stable solid while in the second case when the diethyl ether complex was not present, the reaction proceeded in a similar manner to the corresponding trimethyl phosphite complex.

Because of the toxicity of certain products from the reaction of triethyl phosphite and phosphorus pentafluoride, no further identification of the reaction products was attempted.

TABLE 7

Nuclear magnetic resonance data from the reaction of trimethyl and triethyl phosphite with phosphorus pentafluoride.

Compound	J_{P-F}	J_{P-H}	J_{H-F}	δ_F	δ_H	Literature Reference
CH_3POF_2	1124		7	+2.5		45
CH_3OPF_4	1288			-10.2		45
CH_3OPOF_2	1004	10	0.5	+26.3	-3.9	New
$(CH_3O)_2PF$	1205			+2.0		New
$C_2H_5POF_2$	1121		5(CH_3)	+6.0		45
$C_2H_5OPF_4$	1271			-13.5		New
$C_2H_5OPOF_2$	1009			+22.7		23
$(C_2H_5O)_2PF$	1189			-3.6		New
$(C_2H_5O)_2POF$	975			+19.5		23

The assignment of these compounds is discussed in the Appendix.

The mechanism of coordination and decomposition of phosphorus pentafluoride complexes with substituted phosphines

The mechanism of coordination and decomposition of phosphorus

The thermal stability of phosphorus pentafluoride complexes with trimethyl phosphine, tris-dimethylamino phosphine and trimethyl phosphite decrease in the following order.

$$Me_3P > (Me_2N)_3P > (MeO)_3P$$

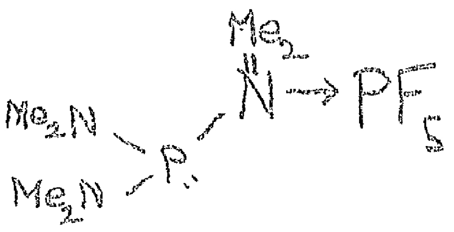
This difference in thermal stability can be explained fairly simply if coordination occurs through the nitrogen and oxygen atoms of the amino phosphine and the phosphite rather than the phosphorus atom. However the stability can also be explained if the compounds contain phosphorus-phosphorus bonds by a more complex but equally feasible mechanism.

In view of the lack of evidence regarding the coordinate bond in the phosphorus pentafluoride complexes both mechanisms are discussed below.

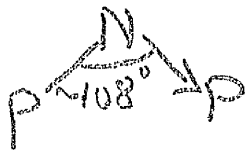
The discussion is based on the reaction of phosphorus pentafluoride with tris-dimethylamino phosphine. The mechanism for the decomposition of the trimethyl phosphite complex is similar to that of the tris-dimethylamino phosphine complex and is not discussed.

(a) Coordination through the nitrogen and the oxygen atoms

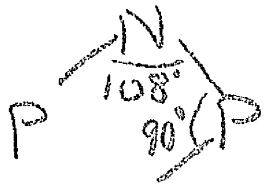
The postulated structure of tris-dimethylamino phosphine phosphorus pentafluoride complex is shown below.



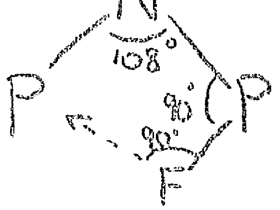
The nitrogen atom which is coordinated to the phosphorus pentafluoride has a tetrahedral configuration so that the phosphorus-nitrogen-phosphorus bond angle is approximately 108°



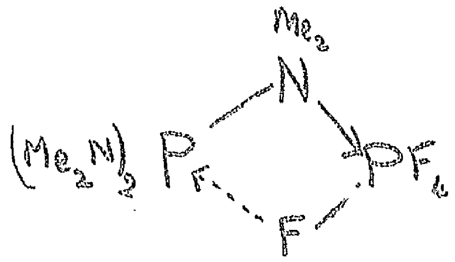
The phosphorus pentafluoride complex which is formed has an octahedral configuration which results in the nitrogen-phosphorus-fluorine bond angle being ~ 90°.



The filled p_x and p_y orbitals on the fluorine atoms are at

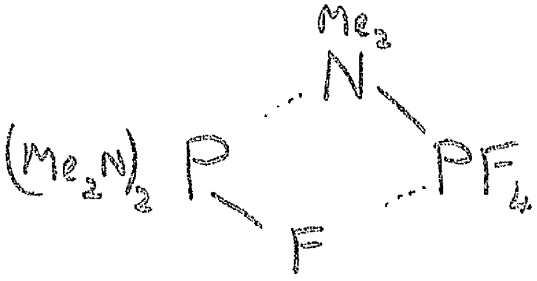


90° to the phosphorus-fluorine bonds and are therefore directed towards the phosphorus atom of the aminophosphine so that a fluorine bridge can be formed by donation of the lone pairs of electrons on the fluorine atom into the unfilled d orbitals on the phosphorus atom.



(i)

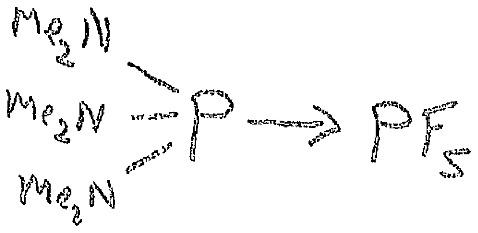
The rearrangement of the tris-dimethylamino phosphine into dimethylamino tetrafluoro phosphorane and bis-dimethylamino fluoro phosphine can easily take place by a 'switch' occurring between the dimethylamino group and the fluorine atom.



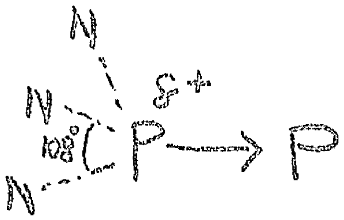
The formation of small quantities of bis-dimethylamino trifluoro phosphorane and dimethylamino difluoro phosphine can be explained by a second 'switch' occurring after recombination.

(b) Coordination through the phosphorus atoms

The structure of tris-dimethylamino phosphine complex in this case is shown below.

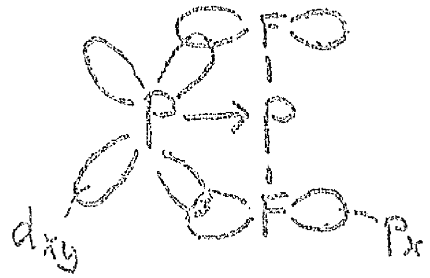


Since the phosphorus atom in the tris-dimethylamino phosphine part of the molecule is tetrahedral the nitrogen-phosphorus-nitrogen bond angle is approximately 108°. The donation of the lone pair of electrons on the phosphorus atom makes it slightly positively charged.



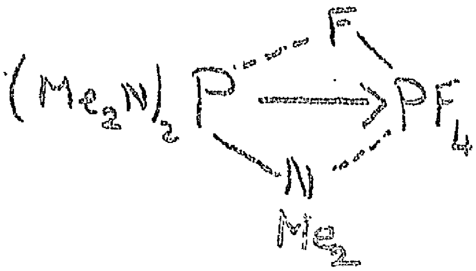
Since the lobes of the unfilled $d_{x^2-y^2}$, d_{xy}, d_{yz} and d_{xz} orbitals on the phosphorus atom of the phosphine are at 90° to each other, very little overlap can occur between these orbitals and the lone pair of electrons on each of the nitrogen atom.

However, since the phosphorus-phosphorus-fluorine bond angle is 90° the lone pairs of electrons in the p_x and p_y orbitals are directed towards the unfilled d_{xy} orbital on the phosphorus atom so that overlap can occur as shown below.



The overlap permits electron flow from the p_x orbital of the fluorine into the d_{xy} orbital of the phosphorus atom. Consequently the phosphorus atom in the phosphine part of the complex shown some sp^3d hybridization and adopts a distorted trigonal bipyramidal structure. The formation of the trigonal bipyramidal structure would cause one of the dimethylamino groups to move close to the phosphorus atom in the phosphorus pentaflucride part of the complex.

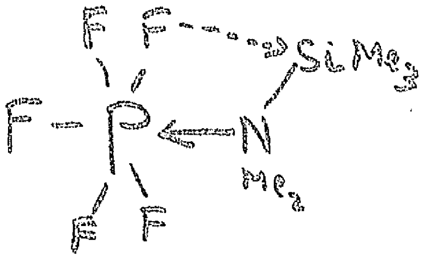
The orbital containing the lone pair of electrons on th nitrogen atom of this dimethylamino group can then overlap with the unfilled d_{xz} orbital on the phosphorus atom of the pentafluoride. It is believed an intermediate would thereby form in which one fluorine and one dimethylamino group is coordinated to both phosphorus atoms as shown below.



The intermediate can then rearrange to form dimethylamino tetrafluoro phosphorane and bis-dimethylamino fluoro phosphine. The evidence available suggests that the coordination is more likely to occur through the nitrogen atom for the following reasons.

The reaction of phosphorus pentafluoride and dimethylamino trimethyl silane $SiMe_3NMe_2$ also yieldsdimethylamino tetrafluoro phosphorane.

The reaction is believed to occur via an intermediate in which the lone pair of electrons on the nitrogen atom coordinate with the phosphorus atom as shown below[28].



One of the fluorine atoms then coordinates to the trimethylsilyl group to form trimethyl fluoro silane Me_3SiF.

The reaction between boron trifluoride and tris-dimethylamino phosphine yields dimethylamino difluoro borane[42,64]. Sincethe boron atom has no low energy d orbitals available the second mechanism is less feasible as the intermediate which is shown in Fig.(i)is unlikely to be formed.

However the nuclear magnetic resonance spectra of the tris-dimethyl amino phosphine complex is believed to identify a compound which contains a phosphorus-phosphorus bond and indicates that the coordination occurs through the phosphorus atom.

The nuclear magnetic resonance spectra of phosphorus pentafluoride complexes with other amino phosphines e.g. dimethyl amino dimethyl phosphine PMe_2NMe_2 may help in understanding the work which has been discussed.

Experimental

Reaction with trimethyl phosphine

The trimethyl phosphine was prepared according to the method of Mann[46] and isolated as its silver iodide complex . The complex was warmed under vacuum and the trimethyl phosphine was condensed out at -196°C. It was distilled at -78°C under vacuum to remove traces of impurities (especially moisture).

The trimethyl phosphine was condensed into the base of a sublimer tube at 196°C and warmed to -78°C. Phosphorus pentafluoride was absorbed by the trimethyl phosphine at -78°C and a white solid was deposited. When absorbtion of the phosphorus pentafluoride ceased the volatile products were removed and a white solid was obtained. The solid was sublimed at 70°C under high vacuum and the phosphorus pentafluoride trimethyl phosphine complex was obtained as a white crystalline solid.

Analysis %C = 18.0 %H = 4.6 %P = 30.6 %F = 46.9

$C_3H_9PPF_5$ requires %C = 17.8 %H = 4.5 %P = 30.7 %F = 47.0

Reaction with tripropyl phosphine

Tripropyl phosphine was prepared by the method of Davis[47].

The Grignard complex was destroyed by adding ammonium chloride solution to it. After the reaction ceased the aqueous layer was extracted with ether. The ether was distilled off and the phosphine distilled at 80-90°C at 4 mm. pressure. It was dried over molecular sieves.

The tri-n-propyl phosphine was poured into a reaction tube and attached to the vacuum line. Phosphorus pentafluoride was condensed by the tri-n-propyl phosphine at room temperature and a white solid was deposited.

When absorbtion ceased the volatile products were removed and the complex purified by sublimation at 120°C under high vacuum.

Analysis %C = 37.5 %H = 7.5 %P = 22.3 %F = 32.3
$C_9H_{21}PPF_5$ requires %C = 37.7 %H = 7.5 %P = 21.5 %F = 33.2

Reaction with tris-dimethylamino phosphine

Tris-dimethylamino phosphine was prepared from dimethylamine and phosphorus trichloride by the method of Burg[48]. The fraction distilling at 160-165°C at atmospheric pressure was collected and dried over molecular sieves.

Analysis %C = 44.0 %H = 11.2 %N = 25.7 %P = 18.9
$C_6H_{18}N_3P$ requires %C = 44.2 %H = 11.0 %N = 25.8 %P = 19.0

The tris-dimethyl phosphine was condensed with a large excess of pentane into a reaction tube at -196°C and warmed to -78°C. Phosphorus pentafluoride gas was absorbed by the mixture and a white solid was deposited. When absorbtion ceased the volatile products were removed to leave a white powder.

Analysis $\%C=25.1$ $\%H=6.7$ $\%N=14.5$ $\%P=21.2$ $\%F=32.7$

$C_6H_{18}N_3PPF_5$ requires $\%C=25.0$ $\%H=6.2$ $\%N=14.5$ $\%P=21.4$ $\%F=32.9$

Thermal decomposition of tris-dimethylamino phosphine phosphorus pentafluoride complex.

The complex was heated on an oil bath in a closed system to observe its thermal decomposition. A small increase in vapour pressure was observed at 60-70°C but after a few minutes it decreased again. During this period the solid began to melt but resolidified which suggested that some form of decomposition had taken place. At 130°C the vapour pressure began to increase quickly. The volatile material was now condensed out until only a trace of dark yellow solid was left in the tube and a white solid was obtained in the -196°C trap. Part of this solid melted at a low temperature and the vapour pressure began to increase quickly on raising the temperature. The volatile fraction was condensed off and examined and found to be dimethylamino difluoro phosphine PF_2NMe_2 from its molecular weight (found 115, 116 calc. 113) and its infrared and ^{19}F nuclear magnetic resonance spectra. The other product was not identified.

In another experiment phosphorus pentafluoride was condensed together with tris-dimethylamino phosphine into a sealed tube at -196°. The tube was heated at 120°C for 12 hours after which a liquid and a little solid was obtained. The tube was connected to a fractionating system and the volatile products fractionated through at -50°C -78°C and -196°C traps. The -196°C trap contained a little phosphorus trifluoride which was identified by its gas infrared spectrum. A complete fractionation of the other materials was not obtained but the ^{19}F nuclear magnetic resonance spectra of the fractions showed that dimethylamino tetrafluoro phosphorane PF_4NMe_2 and a little dimethylamino difluoro phosphine PF_2NMe_2 were present in the -78°C trap and bis-dimethylamino fluoro phosphine $PF(NMe_2)_2$ was obtained in the -50°C trap. The ^1H spectrum showed that this fraction also contained a little unreacted tris-dimethylamino phosphine $P(NMe_2)_3$.

Reaction with trimethyl phosphite

Trimethyl phosphite (Kodak Ltd.) was dried over molecular sieves and was condensed into a reaction tube at -196° together with a large excess of diethyl ether. Phosphorus pentafluoride was absorbed by the mixture and a white solid was deposited. When excess phosphorus pentafluoride was present (calculated from volume of trimethyl phosphite used) the mixture was warmed to -20°C and the volatile products removed. As the diethylether phosphorus pentafluoride complex is also stable at this temperature the mixture was pumped under vacuum at 0°C for 30 mins. when a dry white solid was obtained.

The solid was also obtained when phosphorus pentafluoride was absorbed by a pentane solution of trimethyl phosphite. The volatile products were removed at -20°C to leave a white solid.

Both of these solids began to decompose at 0°C so that no analytical or spectroscopic data was obtained on them. In view of the reaction of trimethyl phosphine and trisdimethylamino phosphite, the solids are believed to be 1:1 trimethyl phosphite phosphorus pentafluoride complexes.

Thermal decomposition of the trimethyl phosphite-phosphorus pentafluoride complex.

The complex began to decompose at 0°C, the volatile products being collected at -196°C. The complete decomposition of approximately 3 gs. of the complex took between 1 and 2 hours. After this time only a very viscous, colourless non-volatile liquied remained. The trap at -196°C contained a white solid which melted at a low temperature to a colourless liquid.

The liquid was kept at -78°C for one hour with no obvious change. The liquid was warmed slowly from -78°C and the pressure slowly increased until at -20 to -10°C it was 3-4 cms. As the liquid approached 0°C a violently exothermic reaction began, a white solid was slowly deposited and the vapour pressure increased sharply. After approximately 1 hr. the vapour pressure was almost one atmosphere. If approximately 3 gs. of complex was used as starting material the evolution of volatile material and formation of the white solid ceased when the vapour pressure was slightly less than 1 atmosphere. If bigger quantities were used the pressure continued to increase. When the reaction ceased the volatile products were condensed into a nuclear magnetic resonance tube at -196°C. The ^{19}F nuclear magnetic resonance spectrum was always complex and indicated the presence of several species. Different samples tended to give different nuclear magnetic resonance spectra which suggested that the concentration of the products formed were very sensitive to the reaction conditions. The samples which were prepared from ether solution decomposed to give volatile products which included a little methyl difluoro phosphine oxide $MePOF_2$ and some of the isomeric methoxy difluoro phosphine.

The third product which was always in the largest concentration was a new compound which was identified by analysis as methoxy difluoro phosphine oxide CH_3OPOF_2. The mixture obtained from pentane solution contained no methyl difluoro phosphine oxide but contained another product which the coupling constant and chemical shift indicated to be dimethoxy phosphine.

The new liquid product was purified by taking the last fraction remaining in a -78°C trap which was being pumped under vacuum or by distillation at atmospheric pressure when the liquid distilled at 76°C. The ^1H and ^{19}F nuclear magnetic resonance spectra showed that the liquid was methoxy difluoro phosphine oxide CH_3OPOF_2. VP(0°C)=23mm. VP(20°C)=62mm. MWt =125(Calc.116).

Analysis %C=10.4 %H=2.8 %P=26.6 %F=33.0 [%O=17.2]

CH_3OPOF_2 requires %C=10.3 %H=2.6 %P=26.7 %F=32.8 %O=17.5

<u>Reaction with triethyl phosphite</u>

CAUTION

Because of the toxic nature of the products of this reaction extreme care must be taken in handling them.

Triethyl phosphite (Kodak) was condensed into a reaction tube together with an excess of ether. Phosphorus pentafluoride was absorbed by the mixture until a slight excess of phosphorus pentafluoride to triethyl phosphite was obtained. The volatile products were removed at -20°C to leave a white solid when the temperature reached 0° C the solid began to decompose slowly and the volatile products were condensed out. The decomposition was much slower than in the trimethyl phosphite case and the reaction tube was warmed to 40°C at regular intervals to increase the rate of decomposition. When the decomposition was complete only a little viscous liquid was left in the reaction tube.

The decomposition product were warmed to room temperature but the precipitation of a solid was very slow. After 24 hours the volatile products were condensed into an nuclear magnetic resonance tube. The nuclear magnetic resonance spectrum showed the presence of ethoxy difluoro phosphine oxide ($C_2H_5OPOF_2$) ethoxy difluoro phosphine ($C_2H_5OPF_2$) and ethyl difluoro phosphine oxide ($EtPOF_2$). The ethoxy difluoro phosphine oxide was purified by distillation(bpt.85°C lit. 86°C). The ^1H nuclear magnetic resonance spectrum of the solid product showed only one ethyl resonance and analysed to triethyl oxonium hexafluoro phosphate.

Analysis	%C=28.8	%H=6.0	%P=12.6	%F=46.0	[%O=6.5]
$C_6H_{15}OPF_6$ requires	%C=28.6	%H=6.1	%P=12.5	%F=46.0	%O=6.6

A second analysis on a different sample indicated the solid was diethoxy diethyl phosphonium hexafluoro phosphate

Analysis %C=29.5 %H=6.4 %P=19.2 %F=35.1 [%O=9.8]

$C_8H_{20}O_2P1F_6$ requires %C=29.6 %H=6.2 %P=19.1 %F=35.2 %O=9.9

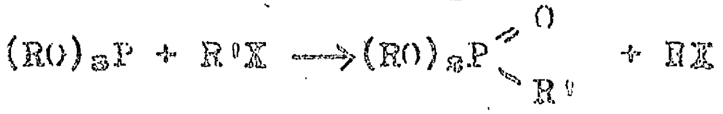
The work was abandoned because of the toxicity of one of the compounds formed. The compound diethoxy fluoro phosphine oxide $(EtO)_2POF$ which was identified by its nuclear magnetic resonance spectrum is very poisonous and probably caused the toxic effects which were noticed. These consisted of contraction of the pupils to 'pin point' size and difficulty in breathing. The effects of this compound are explained in greater detail by Saunders[23,36] who also suggests antidotes.

CHAPTER III

TRIMETHOXY METHYL PHOSPHONIUM HEXAFLUOROPHOSPHATE AND ITS DECOMPOSITION PRODUCTS

Introduction

The Michaelis-Arbuzov reaction which was discovered by Michaelis[67] in 1898 consists of reacting a trivalent phosphorus ester with an alkyl halide to form a pentavalent phosphorus ester according to the following equation.



$$(RO)_3P + R'X \longrightarrow (RO)_2P\overset{O}{\underset{R'}{\diagup\!\!\diagdown}} + RX$$

When $R = R'$ the isomerization reaction is catalyzed by the alkyl halide. Although the reaction is of very great importance in the synthesis of phosphorus compounds its mechanism is not very well understood. The reaction is believed to pass through a phosphonium ion intermediate which subsequently decomposes into the final products. Very few phosphonium ion intermediates containing alkoxy groups have been isolated as they tend to be unstable and non-crystalline and exist for only a short period of time. Dimroth[68] prepared trialkoxy ethyl phosphonium tetrafluoro borates by the reaction of triethyl oxonium tetrafluoro borate ($Et_3O^+BF_4^-$) with trialkyl phosphites at room temperature. The trimethyl phosphite derivative was isolated as a colourless oil while the triethyl phosphite and other derivatives were isolated as white crystalline solids. The alkoxy trialkyl phosphonium iodides[69] are more stable than the trialkoxy alkyl derivatives and were isolated as crystalline solids which decompose on warming to yield the trialkyl phosphine oxide according to the equation.

$$(R'O)P^{+}R_3I^{-} \longrightarrow R_3PO + R'I$$

The formation of the intermediate phosphonium salt is believed to be a fast reaction. When triethyl phosphite and methyl iodide were heated together diethoxy methyl phosphine oxide $(EtO)_2P(O)Me$ was obtained and ethyl iodide was evolved[60]. No reaction was observed between the ethyl iodide and triethyl phosphite which suggested that the intermediate triethoxy methyl phosphonium ion was formed very quickly and its decomposition then proceeded more slowly.

The decomposition of the phosphonium ion is therefore believed to be the rate determining step. Several attempts have been made to interpret the kinetic data obtained when trialkyl phosphites were reacted with alkyl halides. Zawidski[61] observed the change in volume during the reaction and suggested that complex autocatalysis was taking place when triethyl phosphite reacted with ethyl iodide but Staronka [62] later suggested that the rate of reaction was dependent upon the reaction medium and was not autocatalytic. Isbell[63] used continuous density measurements and concluded that the reaction was zero order with respect to triethyl phosphite and was first order with respect to ethyl iodide. Yoke[64] obtained conductivity measurements on the reaction between tributyl phosphite and methyl iodide and showed that the formation of the phosphonium salt was the faster reaction and was second order while its decomposition was considered to be first order.

Discussion

Trimethoxy methyl phosphonium hexafluoro phosphate is the first compound of the type $(RO)_3P^+RX^-$ where (R = Me) which has been obtained as a crystalline solid.

It was prepared from the reaction of trimethyl phosphite with phosphorus pentafluoride, the details of which are given in the previous chapter. It was soluble in acetone, acetonitril and nitromethane and was recrystallized from acetonitrile-ether mixtures.

The infrared spectrum of the solid was recorded as a mujol mull in the region 4000-400 cm^{-1} on the Perkin Elmer 125 spectrophotometer. The details of the spectrum are given in Table 8 in which they are compared with the liquid film spectru of trimethyl phosphite.

TABLE 8

Infrared spectrum of trimethoxy methyl phosphonium hexafluoro phosphate

$P(OMe)_3$	$(MeO)_3PMe^+PF_6^-$
2940(m)	3010(m)
2835(m)	2845(m)
1455(m)	1450(m)
	1314(m)
1262(m)	
1178(m)	1188(m)
1008(vs)	1060(vs)
	918(m)
	840(vs)
728(s)	
	551(vs)
	480(m)

Bellamy[26] has suggested that methyl phosphorus compounds show a characteristic absorbtion in the range 1320-1280cm^{-1} which is assigned to the asymmetric deformation of the methyl group. The absorbtion at 1314 cm^{-1} in the phosphonium salt which is not present in the spectrum of trimethyl phosphite confirms the suggestion. The absorbtions at 1188 cm^{-1} and 1060 cm^{-1} are in good agreement with the values which he suggests are assigned to the methoxyl group attached to the phosphorus atom (1190 cm^{-1} and 1030cm^{-1} respectively). The very strong absorbtions at 840 and 551cm^{-1} are assigned to the hexafluoro phosphate ion and are in good agreement with the values published by Sharp[65] (845 and 559 cm^{-1}) for other hexafluoro phosphate salts.

The ^{1}H, ^{19}F and ^{31}P nuclear magnetic resonance spectra of the phosphonium salt in deutero acetone or deutero acetonitrile solution confirmed its molecular structure. The ^{1}H spectrum consisted of two sets of doublets in the ratio 3:1 which are assigned to the protons in the three methoxyl and the methyl groups respectively and coupling with the phosphorus atom. The ^{19}F spectrum consisted of a doublet identical to that obtained from solutions of other hexafluoro phosphate salts. The ^{31}P spectrum was kindly observed by Schmutzler and consisted of a symmetrical heptuplet which was assigned to the hexafluoro phosphate ion and a broad line which was assigned to the trimethoxy methyl phosphonium ion. The numerical data which were obtained from these spectra are given in Table 9.

During the recording of the ^1H nuclear magnetic resonance of trimethoxy methyl phosphonium hexafluoro phosphate in deutero acetone solution, the spectrum was observed to change with time. The resonances due to the phosphonium salt decreased in intensity until after 90 minutes they had disappeared. Several new resonances appeared during this time, one of which consisted to two doublets in the ratio 2:1 which identified the product as dimethoxy methyl phosphine oxide. $(CH_3O)_2P(O)CH_3$. The other resonances consisted of single lines and were believed to be due to attack on the solvent by methyl groups (Fig. 5).

Since the height of the resonance signal is proportional to the concentration of the compound producing it, the decomposition of the phosphonium salt and the formation of the dimethoxy methyl phosphine oxide could be measured with time. A simple method for studying the kinetics and mechanism of the Michaelis Arbuzov reaction was therefore investigated.

A solution of trimethoxy methyl phosphonium hexafluoro

Fig. 5 Nuclear magnetic resonance spectra of trimethoxy methyl phosphonium hexafluoro phosphate in acetone

phosphate in deuteroacetone was prepared in a nuclear magnetic resonance tube which was sealed under vacuum. Its spectrum was recorded at regular intervals (~ 7 mins.) and the peak height of either the methoxyl or methyl resonances was plotted on a graph against time. The peak heights of dimethoxy methyl phosphine oxide resonances were also plotted against time. The results are shown in Figs. 6 and 7.

The decomposition of the phosphonium salt in deutero acetonitrile solution was also investigated but was found to be too slow for the continuous recording of the nuclear magnetic resonance spectrum to be undertaken. The slowness of the reaction however, allowed several other intermediate in this solvent to be identified after 24 hours. These proved to be of great value in the understanding of the decomposition of the phosphonium salt as the corresponding intermediates were much more difficult to identify in deutero acetone solution because of their instability in this solvent.

The ^{19}F and ^{31}P nuclear magnetic resonance spectra of the deutero acetonitrile solutions were recorded so that complete identification of the intermediates was obtained.

The decomposition of the phosphonium salt in acetone and acetonitrile solution was also investigated by electrical conductivity measurements. These were recorded at regular intervals ($\sim$ 10 mins.) using a Wayne Kerr conductivity bridge. The solutions of the phosphonium salt in acetone were initially colourless but gradually darkened as the decomposition proceeded until dark brown solutions were obtained. The formation of these polymeric products is probably catalyzed by the phosphorus pentafluoride or its derivatives which are formed during the reaction. The corresponding decomposition of the acetonitrile solutions did not produce the dark coloured products and the colourless solution only turned very pale yellow after several days.

Figs. 6-9 show the results obtained when the decompositio of the phosphonium salt was investigated by both nuclear magnetic resonance and electrical conductivity measurements. The plot of the decrease in concentration of the trimethoxy methyl phosphonium hexafluoro phosphate salt with time in aceto solution was similar when studied by both nuclear magnetic resonance and electrical conductivity measurements. Both measurements showed that the concentration of the phosphonium salt in acetone solution was almost zero after a few hours. The decomposition of the phosphonium salt in acetonitrile solution also proceeds in a similar manner as shown by the shape of the curve, but in this case the decrease in the conductivity is slower while the decomposition product which is formed has ~ 50% of the conductivity of the phosphonium salt.

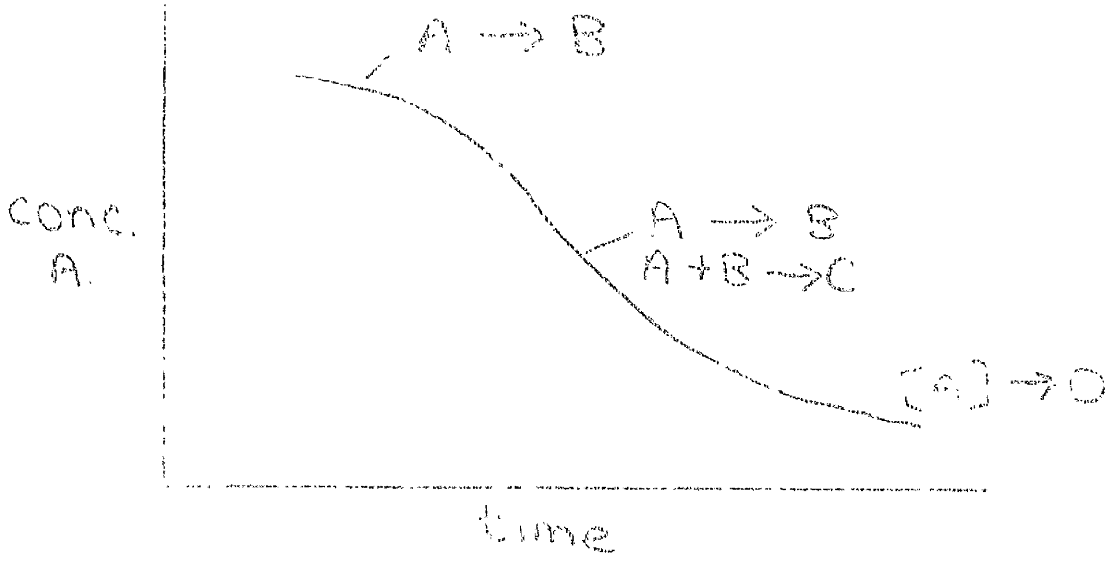
The shapes of the curves of the decomposition of the phosphonium salt and the formation of the dimethoxy methyl phosphine oxide suggested that a second order autocatalytic reaction was occurring[68]

A second order autocatalytical reaction consists of a compound A forming B which then reacts with A to form C. The reaction can be represented by the following equations.

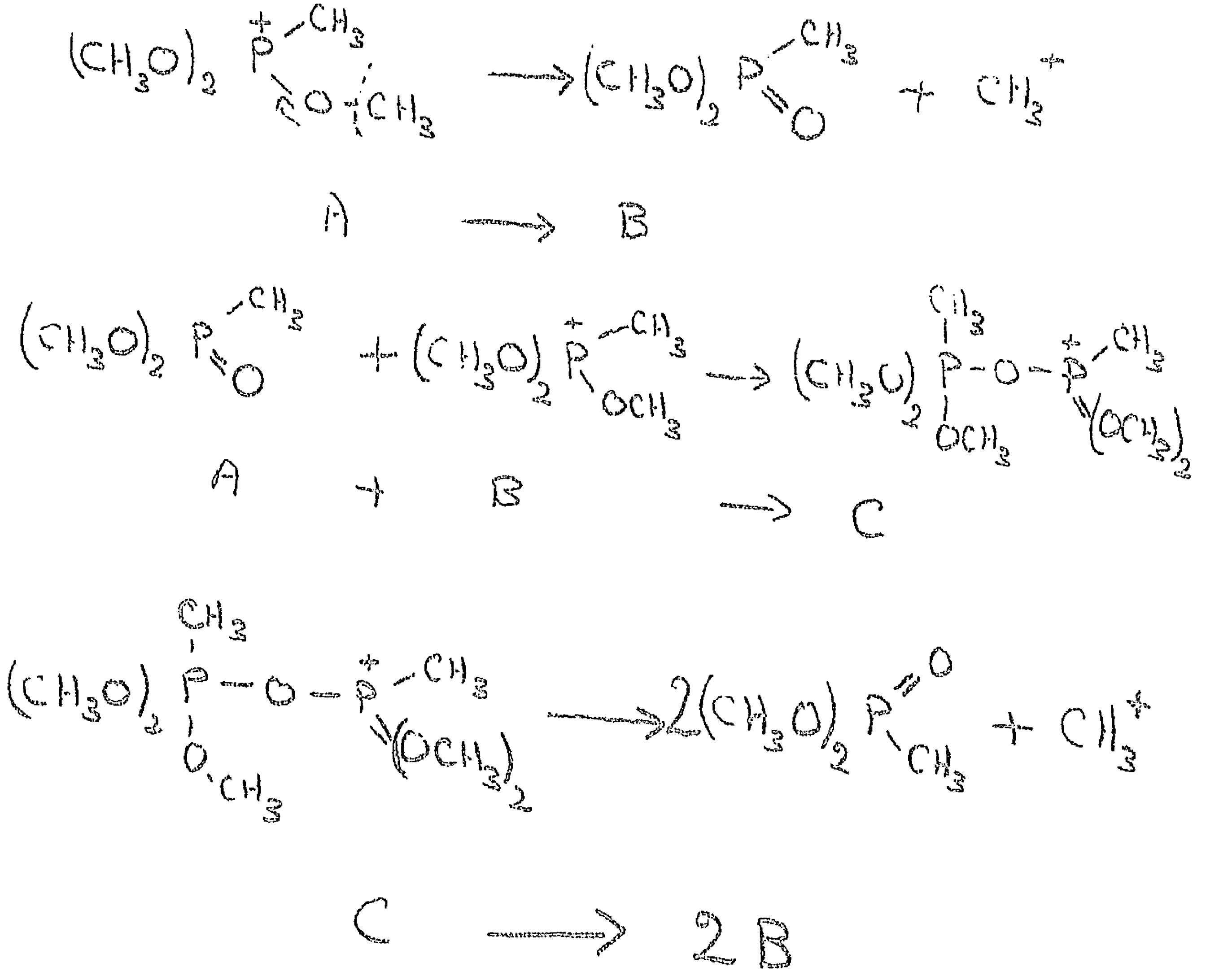
$$A \longrightarrow B \qquad (1)$$

$$A + B \longrightarrow C \qquad (2)$$

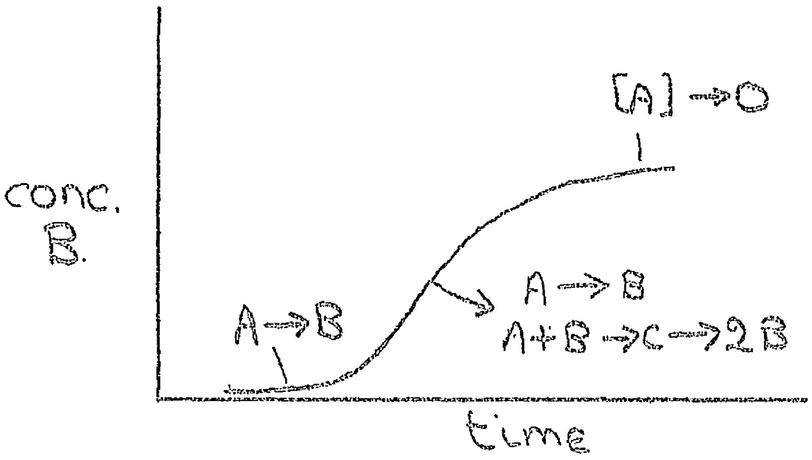
As the concentration of B increases from reaction (1) the rate of removal of A increases as both reactions (1) and (2) proceed. When the concentration of A is small, the rate of removal of A decreases more slowly. The rate of removal of A is shown below



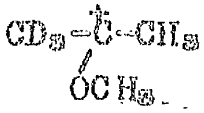
The decomposition of trimethoxy methyl phosphonium ion is postulated to occur as follows.

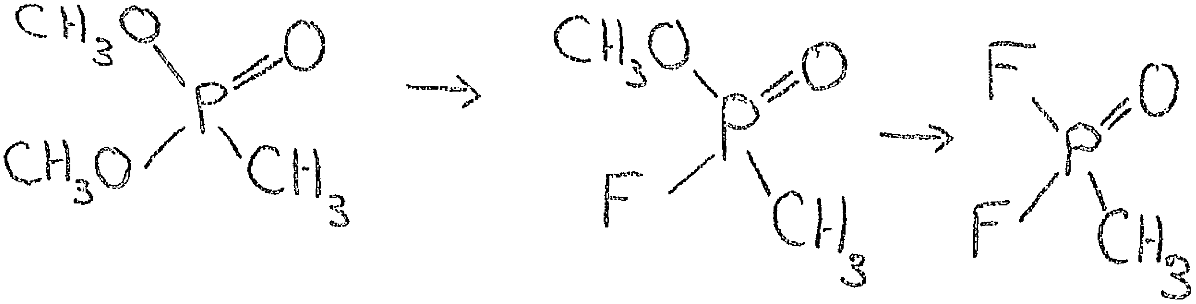


As no phosphorus containing intermediate other than dimethoxy methyl phosphine oxide was identified in the ^1H nuclear magnetic resonance spectrum, product C is considered to have only a transient existence and rapidly decomposes to give two molecules of dimethoxy methyl phosphine oxide. The formation of the dimethoxy methyl phosphine oxide(B) is summarized below.



The shape of the curve is in good agreement with the experimental results obtained in deuteroacetone solution.

The methyl cations are believed to react rapidly with the solvent to form products such as  $CD_3-\overset{+}{C}(OCH_3)-CH_3$ which show single peaks in the ^1H nuclear magnetic resonance spectrum. The subsequent reactions were not identified. The decomposition of the phosphonium salt in deuteroacetonitrile solution also produced dimethoxy methyl phosphine oxide but after 1 hour only ~ 10% of the phosphonium salt had decomposed. However after 24 hours complete decomposition of the salt had occurred and the ^{1}H nuclear magnetic resonance spectrum was complex. The only resonance, other than the single peaks which were due to attack by methyl cations on the solvent, consisted of four doublets. The compound which produced this resonance was identified by its ^{1}H nuclear magnetic resonance spectrum as fluoro methoxy methyl phosphine oxide $CH_3OP(O)(CH_3)F$. The ^{19}F spectrum of the same sample confirmed the presence of this compound and also showed a small amount of difluoro methyl phosphine oxide. The formation of these two products suggested that successive replacements of methoxyl group by fluorine atoms had occurred in the dimethoxy methyl phosphine oxide. The fluorine atoms were obtained by partial decomposition of the hexafluoro phosphate ion into phosphorus pentafluoride and fluoride ion.



A little fluoro methoxy methyl phosphine oxide was also observed in the ^1H spectrum of the deuteroacetone solution after ~ 2 hours.

The fluorine spectrum after 24 hours also showed the presence of a phosphorus pentafluoride complex (which was discussed in Chapter 2) and a large concentration of the hexafluoro phosphate ion. As none of the original trimethoxy methyl phosphonium ion was present a fairly stable carbonium ion must have been formed. The presence of the hexafluoro phosphate ion explained the conductivity of the acetonitrile solution after several days being 50% of the initial conductivity. The cation formed in acetone solution was believed to be unstable and the conductivity of the solution decreased to only a small residual value.

The disadvantage of studying the decomposition of trimethoxy methyl phosphonium hexafluoro phosphate by the ^1H nuclear magnetic resonance technique was not being able to measure the initial stage of the decomposition, due to the time required to dissolve the salt in the solvent and to reach temperature equilibrium in the spectrometer. The first measurement could only be obtained after ~ 10 mins. The ^1H nuclear magnetic resonance method has the advantage that the concentration of each product could be measured at any

TABLE 9

Nuclear magnetic resonance data obtained from the decomposition of trimethoxy methyl phosphonium hexafluoro phosphate

Compound	J_{P-H}	J_{P-F}	J_{H-F}	δ_H	δ_F
$(MeO)_3PMe^+PF_6^-$	11(OMe)	707		-4.3(OMe)	+9.5
	18(Me)			-2.4(Me)	
$(MeO)_2P(O)Me$	11(OMe)			-3.9(OMe)	
	18(Me)			-1.8(Me)	
$MeOP(O)(Me)F$	12(OMe)	1036	1(OMe)	-4.0(OMe)	-0.2
	19(Me)		6(Me)	-1.9(Me)	
$MeP(O)F_2$		1105	6		-2.8

The assignments of these spectra are discussed in the Appendix.

particular time. Complete identification of the products was possible using this method whereas no previous workers had been able to do this.

The decomposition will be further studied by recording the ^{31}P nuclear magnetic resonance spectra in acetone and acetonitrile solutions over a period of time. The method can also be extended to study the reaction of trimethyl phosphite with methyl iodide. As both of these compounds are liquids, they can be mixed at the temperature of the machine and the spectra recorded immediately. The results of this experiment should be of great value in understanding the kinetics and the mechanism of the Michaelis-Arbuzov reacti

Experimental

Deuteroacetone CD_3COCD_3 (C.I.B.A. Ltd.) was dried by distillation under vacuum at -78°C and condensed at -196°C onto the trimethoxy methyl phosphonium hexafluoro phosphate in a nuclear magnetic resonance tubes. The tube was sealed and the mixture warmed until the solid dissolved.

The nuclear magnetic resonance spectra were recorded at regular intervals until no further change in the spectrum was observed. The measurements in deutero acetonitrile solution were completed by Schmutzler at Du Pont, Wilmington, U.S.A.

Electrical Conductivity

The conductivity cell was designed by Baillie[87] and the conductivities were measured on a Wayne Kerr Universal Bridge 13221.

The solutions were prepared by placing a weighed amount of the phosphonium salt in the cell and adding a weighed amount of the phosphonium salt in the cell and adding a weighed amount of solvent to it. They were stirred continuousl to ensure mixing. The conductivity of the solution was recorded every few minutes until a constant value was obtained.

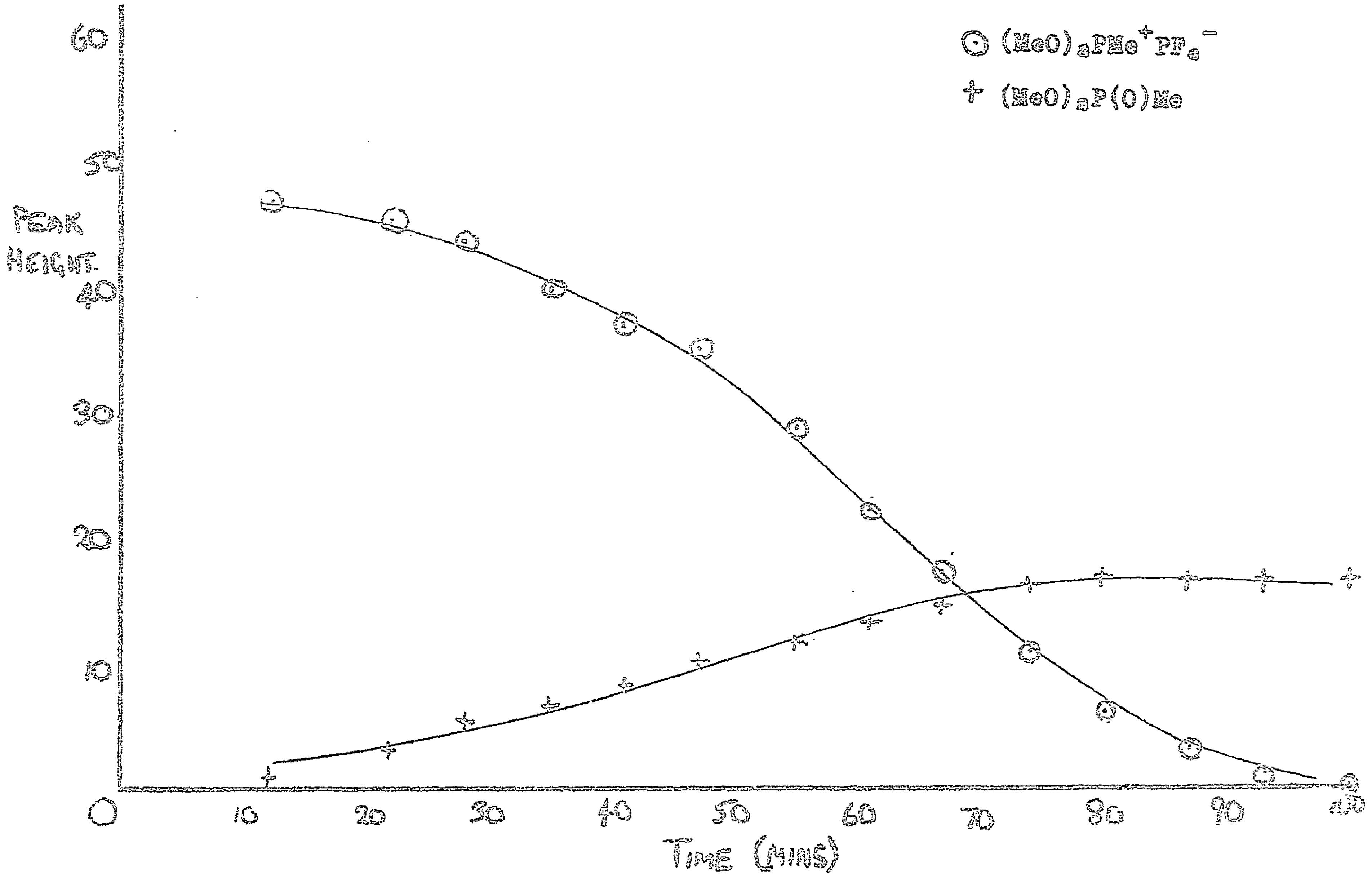


Fig. 6 Decomposition of trimethoxy methyl phosphonium hexafluoro phosphate in acetone by ^1H nuclear magnetic resonance.

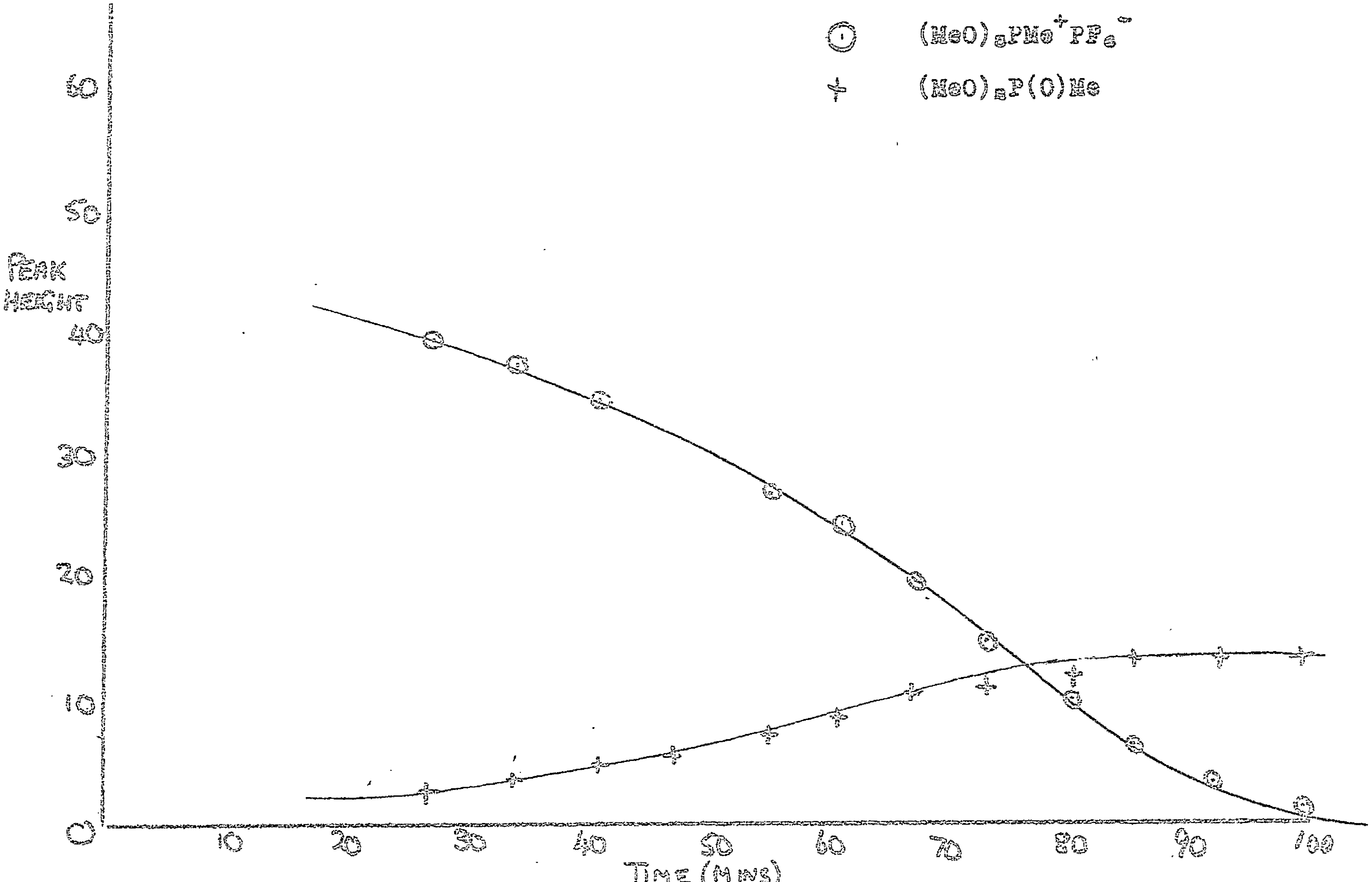


Fig. 7 Decomposition of trimethoxy methyl phosphonium hexafluoro phosphate in acetone by ^1H nuclear magnetic resonance.

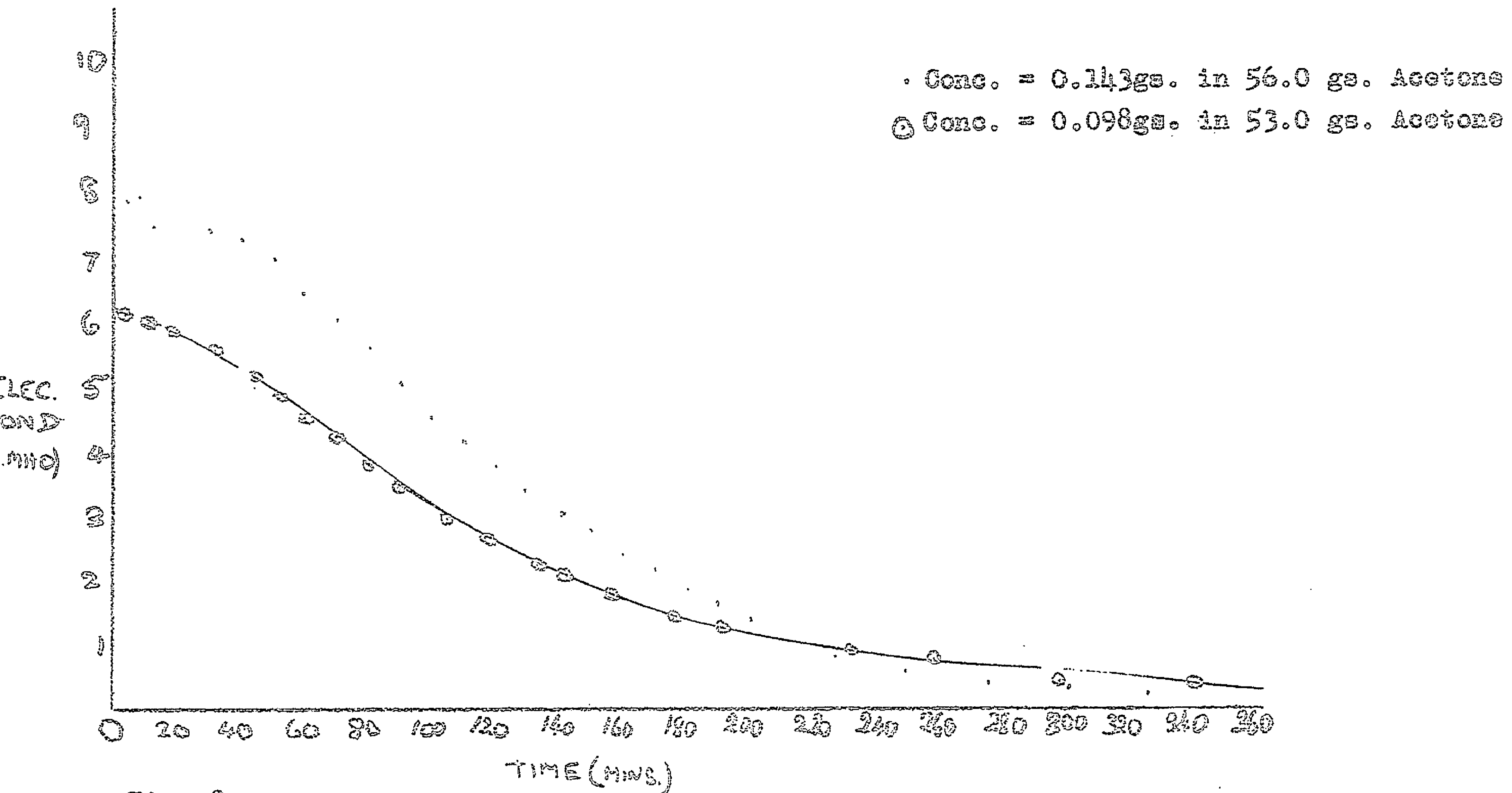


Fig. 8 Decomposition of trimethoxy methyl phosphonium hexafluoro phosphate in acetone using electrical conductivity

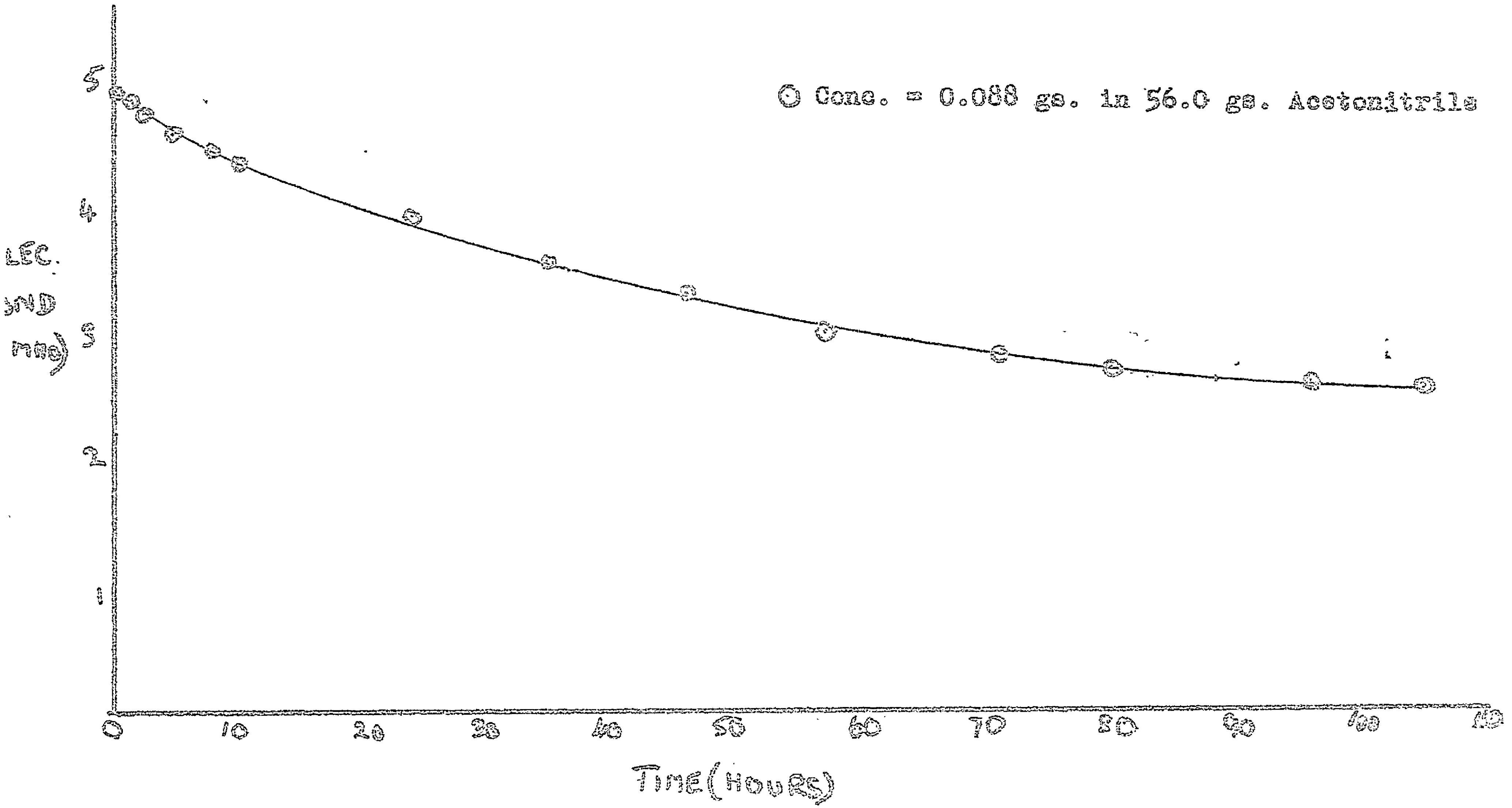


Fig. 9 Decomposition of trimethoxy methyl phosphonium hexafluoro phosphate in acetonitrile using electrical conductivity

CHAPTER IV

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH SULPHUR LIGANDS

Introduction

Whereas trimethylamine, pyridine and other nitrogen ligands form stable complexes with Lewis acids, the corresponding complexes with phosphorus, oxygen and sulphur ligands are much less stable and usually exist only in the solid state. This instability has resulted in very few reports of sulphur complexes of non metal fluorides[88].

Stone[89] prepared the dimethyl sulphide boron trifluoride complex at low temperature and compared its stability with other boron trifluoride complexes. He found that boron trifluoride-dimethyl sulphide complex was 96% dissociated at room temperature while the dimethyl ether complex was ~20% and the dimethyl selenide complex was 100% dissociated. As steric strain was unlikely to be the reason for this dissociation, he believed the relative instabilities were due to the electron donor power decreasing with increasing size of the ligand.

Gregor[90] has recently reported the preparation of phosphorus pentafluoride complexes with dimethyl ether, dimethyl sulphide and dimethyl selenide. He found that their percentage dissociation at 0°C was 94%, 96% and 100% respectively. No phosphorus pentafluoride complexes with mercaptans, RSH, disulphides, RSSR, or amino sulphides, $(R_2N)_2S$, have been reported.

Discussion

The reactions of phosphorus pentafluoride with methane thiol, ethane thiol, dimethyl disulphide and bis-dimethyl amino sulphide were investigated.

Phosphorus pentafluoride reacts with a solution of methane thiol in toluene at -78°C to deposit a white solid. The volatile components were removed under vacuum at 0°C leaving a pale yellow solid. The analysis of this solid $(CH_3)_8P_3F_6S_4)$ suggested either a complex compound or a mixture had been obtained. The infrared spectrum in nujol was very simple and absorbtion occurred at 1429cm^{-1}, 1325cm^{-1} 993 cm^{-1}, 840 cm^{-1}, 745cm^{-1} and 670 cm^{-1}. The very strong absorbtion at 840 cm^{-1} indicates a hexafluoro phosphate ion or a phosphorus pentafluoride complex. The bands at 1429 and 1325 cm^{-1} are due to the C-H deformation of the methyl group while the band at 670 cm^{-1} is in the region of the spectrum suggested by Bellamy as identifying a C-S stretching frequency. The solid sublimed at 100°C under high vacuum to give a yellow solid which darkened to orange or pale red on standing under vacuum for 12 hours. The sublimed compound analysed to tetra methylthio phosphonium hexafluoro phosphate $(P(SMe)_4^{+}PF_6^{-})$. Its infrared spectrum in nujol showed absorbtion as follows.

$1422cm^{-1}$, $1319cm^{-1}$, $985cm^{-1}$, $970cm^{-1}$, $840cm^{-1}$, $712cm^{-1}$ and $678cm^{-1}$

The spectrum is identical to the unsublimed product except for the absorbtion at 712 cm^{-1}. The spectrum of another sample which was sublimed at 100°C and 10^{-3} mm. did not have this absorbtion band and was identical to that of the starting material.

The reaction of phosphorus pentafluoride with ethane thiol was expected to yield to corresponding ethyl derivative, tetra ethylthio phosphonium hexafluoro phosphate $(EtS)_4P^+PF_6^-$.
Phosphorus pentafluoride reacted with a toluene solution of ethanethiol to form a yellow solid. As the toluene was removed by pumping under vacuum at room temperature the solid liquified and eventually only a trace of a yellow oil was left. The ethanethiol complex must have dissociated during the removal of the solvent indicating its much lower stability than the corresponding methanethiol complex.

The formation of a product of empirical formula $PF_3(SCH_3)_2$ form phosphorus pentafluoride and methanethiol probably occurs by a similar mechanism to the formation of bis-dimethylamino trifluoro phosphorane from phosphorus pentafluoride and dimethylamine.

The methanethiol phosphorus pentafluoride complex loses hydrogen fluoride below the temperature at which it dissociates. The methylthio tetrafluoro phosphorane PF_4SMe reacts with excess methanethiol and bis-methylthio trifluoro phosphorane $PF_3(SMe)_2$ is formed which probably ionizes to form tetramethylthio phosphonium hexafluoro phosphate. The hydrogen fluoride liberated in the reaction reacts at low temperature with methanethiol to form a methyl sulphonium salt which dissociates on warming into methanethiol and hydrogen fluoride as is removed.

The ethanethiol complex however dissociates with the solvent on pumping under vacuum below the temperature at which hydrogen fluoride is removed and is removed with toluene. The salt may be formed if ethanethiol and phosphorus pentafluoride are reacted in a sealed tube when the dissociation pressure would be reduced by the pressure of the excess ethanethiol.

The two reactions can be formulated as follows.

$$CH_3SHPF_5 \xrightarrow{T^\circ C} CH_3SPF_4 \longrightarrow (CH_3S)_2PF_3 \longrightarrow (CH_3S)_4P^+PF_6^-$$

$$C_2H_5SHPF_5 \xrightarrow{<T^\circ C} C_2H_5SH + PF_5$$

$$[CH_3SHPF_5 \xrightarrow{T^\circ C} CH_3SH + PF_5]$$

No reaction was observed between dimethyl disulphide and phosphorus pentafluoride when the two compounds were mixed at room temperature. When they were condensed together in a large breakseal tube and reacted at room temperature for 10 months, a little yellow solid was formed. The tube was opened under vacuum and the volatile products were identified from their gas infrared spectrum as the starting materials. The solid compound has not yet been identified.

The reaction between bis-dimethylamino sulphide and phosphorus pentafluoride was investigated in conjunction with Mr. K.D. Crosbie of these laboratories, to determine if a complex was formed by donation from the nitrogen or the sulphur atoms.

A white solid was obtained when the two compounds were reacted together in trichloro fluoro methane at ~ -40°C. The solid did not analyse to a 1:1 complex but was closer to the empirical formula $3PF_5 2S(NMe_2)_2$.

The infrared spectrum of this solid showed absorbtions assigned to the phosphorus pentafluoride part of the molecule at $830cm^{-1}$ and $555cm^{-1}$. The remaining part of the spectrum was complex especially in the region $1000-1500cm^{-1}$. The sharp increase in the number of absorbtion bands in this region compared with the spectrum of bis-dimethylamino sulphide suggested that donation through the nitrogen atom had occurred as this would increase the number of absorbtion bands due to the different environment of the two dimethylamino groups.

The formation of the complex white solid from bis-dimethylamino sulphide and phosphorus pentafluoride is in direct constrast to the 1:1 phosphorus pentafluoride complex with tris-dimethylamino phosphine. The reason for this difference in coordination is not understood.

Experimental

Methanethiol and ethanethiol (Eastman Organic Chemicals were dried by distillation at -78°C under vacuum, the middle portions being used.

Dimethyl sulphide was distilled at atmospheric pressure(116°C) and dried over molecular sieves. Bis-dimethylamino sulphide was prepared by the reaction of sulphur dichloride with excess dimethylamine and was purified by distillation at atmospheric pressure(121°C)[82].

Analysis %C=40.3 %H=10.2 %N=23.1 %S=26.5

$S(NMe_2)_2$ requires %C=40.0 %H=10.0 %N=23.3 %S=26.7

Reaction with methanethiol

Methanethiol was condensed into a reaction tube at -196°C together with toluene and the mixture warmed to -78°C. Phosphorus pentafluoride was absorbed by the liquids and a white solid was deposited. The white solid slowly turned pale yellow as the volatile products were removed and finally a yellow solid was obtained.

Analysis %C=10.5 %H=3.0 %P=18.0 %F=33.0 %S=36.4

$C_3H_9P_2F_6S_4$ requires %C=10.3 %H=2.6 %P=17.7 %F=32.6 %S=36.5

The yellow solid was placed in a sublimer tube and sublimed at 100°C under high vacuum. The product in the base of the sublimer tube became very dark red and was not investigated. The sublimate was a pale yellow solid which darkened overnight to orange or pale red.

Analysis %C=13.1 %H=3.4 %P=17.0 %F=31.6 %S=34.8

$(CH_3S)_2PF_3$ requires %C=13.2 %H=3.3 %P=17.0 %F=31.3 %S=35.1

Reaction with ethanethiol

Ethanethiol and toluene were condensed into a reaction tube at −196°C and then warmed to −78°C. Phosphorus pentafluoride was absorbed and a white solid was deposited; the absorbtion, rapid at first, gradually decreased. When no further absorbtion occurred, the mixture was warmed to room temperature and the volatile products were removed under vacuum. As the temperature increased the solid disappeared and after 1 hour only a trace of yellow oil was left in the reaction flask.

Reaction with dimethyl disulphide

Dimethyl disulphide was condensed into a reaction tube at −196°C and warmed to 0°C when it liquified. Phosphorus pentafluoride gas was now passed onto the dimethyl disulphide but no absorbtion occurred and no solid was deposited. After a short time the solution gradually became yellow. The liquid was then heated with a warm water bath and a little yellow solid was deposited. The volatile materials were removed under vacuum and the yellow solid was transferred to the dry box. It gradually darkened in colour until it was orange. The infrared spectrum showed a strong broad absorbtion at $840 cm^{-1}$ which indicate a hexafluoro phosphate salt or a phosphorus pentafluoride complex. The gas infrared spectrum of the volatile products showed the presence of phosphorus pentafluoride and traces of other compounds (e.g. phosphorus oxyfluoride) which were believed to be formed by reaction of the phosphorus pentafluoride with the glass apparatus.

Dimethyl disulphide and phosphorus pentafluoride were condensed into a large breakseal tube at −196°C and were allowed to react at room temperature over a period of 10 mont During this period a yellow crystalline solid was deposited. The infrared spectrum of the volatile products showed both phosphorus pentafluoride and dimethyl disulphide were present. The solid was handled in the dry box but it was not possible to identify it satisfactorily.

Reaction with bis-dimethylamino sulphide

Bis-dimethylamino sulphide and trichloro fluoro methane were condensed into a reaction tube and warmed until the solid sulphide just dissolved. Phosphorus pentafluoride was absorbed by the sulphide and a pale yellow solid was deposited. When no further absorbtion of the phosphorus pentafluoride occurred the volatile products were removed to leave a dry solid.

Analysis %C=18.3 %H=5.4 %N=8.7 %P=14.1
%F=43.1 %S=9.7

$3(PF_5)2(SN_2C_4H_{12})$ requires %C=18.6 %H=3.9 %N=9.1 %P=15.1
%F=44.7 %S=10.4

CHAPTER V

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH SOME ORGANO LITHIUM COMPOUNDS

Introduction

The methods of preparing organo non-metal fluorides have recently been summarised by Winfield[70]. He tried to prepare phenyl derivatives of non-metal fluorides by reacting the fluoride with tetraphenyl tin in a bomb under pressure at 100-150°C. for 12-24 hours.

The reaction

$$MF_x + \emptyset_4Sn \longrightarrow \emptyset MF_{x-1} + \emptyset_3SnF$$

was expected to proceed to the right because of the high lattice energy of the triphenyl tin fluoride formed. Using this method, he obtained phenyl difluoro borane and phenyl tetrafluoro phosphorane from boron trifluoride and phosphorus pentafluoride respectively. However he did not obtain the expected products with silicon tetrafluoride, sulphur tetrafluoride, sulphur hexafluoride, arsenic pentafluoride or trimeric phosphonitrilicfluoride. He suggested that this might be due to the presence of moisture since benzene was formed in these reactions. He supported this by showing that when tetraphenyl tin reacted with phosphorus pentafluoride in a bomb from which moisture had not been excluded, benzene was formed instead of phenyl tetrafluoro phosphorane. It was hoped that the reaction between organo lithium compounds and non-metal fluorides would lead to a general method of preparing substituted non-metal fluorides as follows.

$$MF_x + LiR \longrightarrow RMF_{x-1} + LiF$$

Discussion

General

The reactions between tetraphenyl tin and non-metal fluorides only proceed under extreme experimental conditions. The mixtures were heated in a bomb at 100-150°C for 12-24 hours under pressure so that, if a thermally unstable compound was formed, its decomposition under these conditions would prevent its isolation. This was particularly likely when the non-metal fluoride was a vigorous fluorinating agent such as sulphur tetrafluoride or arsenic pentafluoride as attack on the aromatic ring would lead to decomposition products. The non-formation of phenyl trifluoro silane was surprising as the other phenyl fluoro silane derivatives have been easily prepared by the reaction of silicon tetrafluoride with phenyl magnesium bromide[71].

The only reaction of organo lithium compounds with a non-metal fluoride which has been reported results in the formation of substituted phosphonitrilic fluorides when phenyl, butyl or pentafluorophenyl lithium were reacted with trimeric phosphonitrilic fluoride[78]. This work formed the first part of a detailed investigation into the reaction of non-metal fluorides with organo lithium compounds.

Phosphorus pentafluoride was used in this initial investigation because it was readily available without purification. The alkyl and aryl fluoro phosphoranes are thermally stable so that the conditions required to initiate reaction between the organo lithium compound and phosphorus pentafluoride could be examined closely without fear of the decomposition of the organo fluoro phosphorane.

Reaction with propyl lithium

Propyl lithium was prepared in ether solution according to the method of Coates[75]. The ether was removed and the propyl lithium dissolved in pentane to separate it from the lithium bromide. Phosphorus pentafluoride gas was rapidly absorbed by the propyl lithium solution and a white solid was deposited. When absorbtion ceased, the volatile products were removed and a white powdery solid was obtained. Analysis indicated the powder was lithium propyl pentafluoro phosphate $Li^{+}PF_5C_3H_7^{-}$ containing a trace of lithium hydroxide as impurity (from hydrolysis of the propyl lithium solution) . The lithium propyl pentafluoro phosphate had not been reported previously although Schmutzler[78] had prepared dialkylammonium phenyl pentafluoro phosphate by decomposing the dialkylamine phenyl tetrafluoro phosphorane complex. The decomposition can be represented by the equation.

$$2R_2NHC_6H_5PF_4 \longrightarrow R_2NPF_3C_6H_5 + R_2NH_2^{+}C_6H_5PF_5^{-}$$

The present method of preparation is much less complicated than previous ones and does not require the alkyl tetrafluoro phosphorane as starting material. The infrared spectrum of lithium propyl pentafluoro phosphate in nujol was recorded and the details are given below. Absorbtions occurred at (cm^{-1})

1280, 1175, 1080, 940, 840, 740, 735

The strong broad absorbtion at 840 cm^{-1} is due to the phosphorus-fluorine stretching vibrations of the pentafluoro phosphate group while the other absorbtions are attributed to the propyl part of the molecule.

The lithium propyl pentafluoro phosphate decomposed on heating to 180°C and a dark coloured residue remained . The volatile products were phosphorus pentafluoride together with a little phosphorus oxyfluoride and silicon tetrafluoride which was probably obtained from the attack on the glass. No propyl tetrafluoro phosphorane or other compounds containing organo-groups were obtained. The non-formation of propyl tetrafluoro phosphorane was surprising since the high lattice energy of lithium fluoride was expected to ensure its formation.

The corresponding potassium methyl trifluoro borate loses methyl difluoro borane rather than boron trifluoride when it is heated to 250°C[76]. This difference is difficult to explain as the variation in bond energies between boron and phosphorus atoms bonded to nitrogen and fluorine is not great. The difference in decomposition may be due to the different crystal structures of the potassium methyl trifluoro borate and lithium propyl pentafluoro phosphate as the smaller lithium ion is surrounded by larger propyl pentafluoro phosphate anion.

The compound, nitrosyl phenyl pentafluoro phosphate yields only tarry products on heating[74]. This is probably due to attack by the nitrosonium ion(NO^+) on the aromatic ring which causes the formation of complex products.

Reaction with dimethylamino lithium

The surprising stability of the propyl pentafluoro phosphate ion suggested that other lithium pentafluoro phosphate derivatives might exist. Dimethylamino lithium was prepared from propyl lithium and dimethylamine in pentane solution and was isolated as a white powder. It was reactedwith phosphorus pentafluoride in ether solution and , after the volatile products had been removed, a cream coloured solid was obtained. The solid was identified by analysis as lithium dimethylamino pentafluoro phosphate.

The infrared spectrum was recorded and is compared with the spectrum of phosphorus pentafluoride dimethylamine complex(which was prepared in Chapter II) in Table 10.

As the dimethylamino pentafluoro phosphate ion is isoelectronic with the dimethylamine phosphorus pentafluoride complex, the comparison of their infrared spectra may help in assigning the phosphorus-nitrogen stretching vibration.

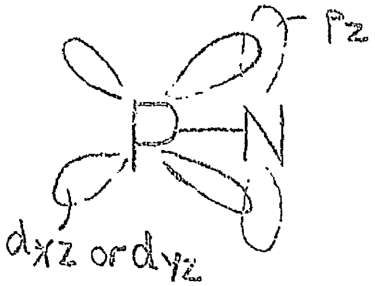
The spectra were found to have similar absorbtions in the region 1500-650 cm^{-1} except those at 1011cm^{-1} and 702cm^{-1} in the dimethylamine phosphorus pentafluoride complex which move to 967 and 745 cm^{-1} respectively in the dimethylamino pentafluoro phosphate ion. The variations in the infrared spectra can be explained by assuming that the dimethylamino group in the dimethylamino pentafluoro phosphate ion is planar with the nitrogen lone pair of electrons occupying the

TABLE 10

Infrared spectra of the dimethylamine phosphorus pentafluoride complex and the dimethylamino pentafluoro phosphate ion.

PF_5NMe_2H	$PF_5NMe_2^-$
1351	1348
1149	1171
1050	1055
1011	967
860	838
813	
702	745

p_z orbital of the nitrogen atom and partially overlapping with the unfilled d_{xz} or d_{yz} orbital on the phosphorus atom as shown below.



The phosphorus nitrogen bond is then strengthened by partial $p_{\pi} - d_{\pi}$ overlap and the infrared stretching vibration associated with this bond moves to a higher frequency. The band at 702 cm^{-1} which moves to 745 cm^{-1} is therefore assigned to the phosphorus-nitrogen stretching vibration. Bellamy suggests that phosphorus-nitrogen stretching vibrations normally occur in this region[26]. The band at 1011 cm^{-1} in the dimethylamine phosphorus pentafluoride complex is believed to be associated with the symmetric $N-C_s$ stretching vibration of the dimethylamino group.(See Chapter I). In the complex, the donation of the lone pair of electrons to form the phosphorus-nitrogen bond causes a small positive charge to be centred on the nitrogen atom. This positive charge causes a movement of electrons in the carbon-nitrogen bonds towards the nitrogen atom. The infrared stretching vibration associated with this bond then moves to higher frequency compared with a similar vibration in the dimethylamino pentafluoro phosphate ion as the nitrogen atom in this ion has a lone pair of electrons in the p_z orbital.

Lithium diethylamino pentafluoro phosphate was also prepared in a similar manner. Unfortunately it was contaminated with a little diethylamine phosphorus pentafluoride complex (the infrared spectrum contained a sharp absorbtion at 3370 cm^{-1}) so that conclusionsregarding the infrared spectrum of the ion can only be drawn with caution. The strong absorbtion at 745 cm^{-1} agrees with the absorbtion at 745 cm^{-1} in the dimethylamino pentafluoro phosphate ion.

Reaction with lithium ethoxide

The lithium ethoxide reacted with phosphorus pentafluorid in ether solution at -50°C to form a feathery white solid which quickly dissolved on warming to deposit a yellow oil. The volatile materials were removed after pumping under vacuum for twelve hours and a dirty white powder was obtained. The powder was identified by analysis as lithium hexafluoro phosphate.

The infrared spectrum in nujol was very simple and consisted of three absorbtions at 1274 cm^{-1}, 1163 cm^{-1}, and

838 cm^{-1}. The infrared spectrum in fluorolube showed no absorbtion in the region 3000-2800 cm^{-1} which confirmed the absence of an ethoxy group.

Lithium hexafluoro phosphate is a rather unstable compound and usually contains lithium fluoride as impurity. Russell[76] obtained a pure specimen by reacting lithium fluoride with phosphorus pentafluoride in liquid hydrogen fluoride at 50°C in a steel bomb. The Xray powder photograph of this sample was identifical to that of the sample prepared above.

The simplicity of preparing lithium hexafluoro phosphate using the above method renders it more useful than the methods of preparation previously described.

The white solid which was formed by the reaction of lithium ethoxide with phosphorus pentafluoride is believed to be lithium ethoxy pentafluoro phosphate $Li^+(EtOPF_5)^-$. However it readily reacted with the excess phosphorus pentafluoride (which was present in the solution as its diethyl ether complex) to form lithium hexafluoro phosphate and the unstable diethoxy trifluoro phosphorane.

The formation of lithium hexafluoro phosphate from lithium ethoxy pentafluoro phosphate probably occurs because of the higher lattice energy of the symmetrical hexafluoro phosphate salt combined with the high bond energy of the P=O bonds which are probably present in the decomposition products of diethoxy trifluoro phosphorane.

The reactions of phosphorus pentafluoride with the lithium compounds described above have produced a new aspect of its chemistry. Further reactions of phosphorus pentafluoride and other non-metal fluorides with a variety of lithium compounds will be investigated in the near future.

Experimental

Preparation of propyl lithium

A diagram of the apparatus used to prepare propyl lithium is shown in Fig. 10 as

The apparatus was flushed with dry nitrogen before use. 50 mls. of dry pentane were poured into the conical flask and ~ 1g. of lithium metal was cut into very small pieces and dropped onto the pentane under a stream of dry nitrogen. N-propyl bromide (8 gs.) was added to the flask which was then cooled under nitrogen. Any oxygen which was present in the system was removed at this stage so that decomposition of the propyl lithium was kept to a minimum. The mixture in the flask was now warmed to room temperature and the

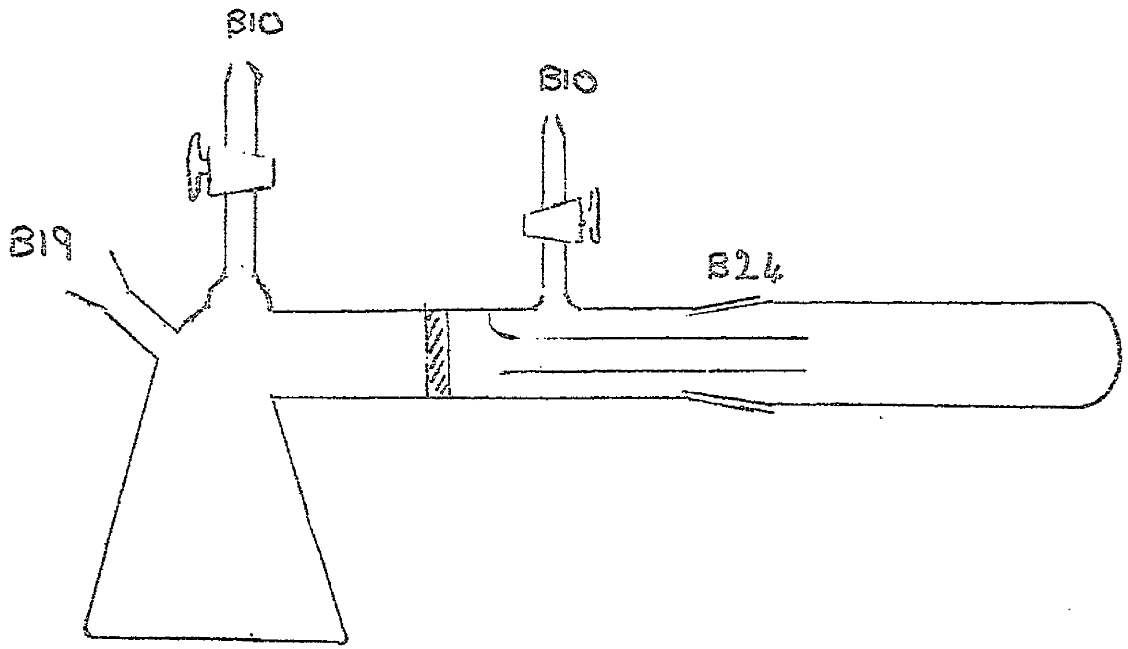


Fig. 10. Apparatus for the preparation and reaction of propyl lithium.

formation of the propyl lithium occurred under an atmosphere of pentane vapour. When the reaction was complete the apparatus was rotated through 90°C so that the pentane solution dropped into the round bottomed flask. The lithium bromide and any excess lithium were removed by the sintered disc leaving the propyl lithium solution as a clear liquid.

Reaction with phosphorus pentafluoride with propyl lithium

Phosphorus pentafluoride was passed via the vacuum line into the apparatus. The solution which was cooled to -78°C rapidly absorbed the phosphorus pentafluoride vapour and deposited a white solid. When absorbtion of phosphorus pentafluoride ceased the volatile materials were removed by pumping under vacuum leaving the lithium propyl pentafluoro phosphate as a dry white powder.

Analysis	%C=19.7	%H=4.5	%P=16.8	%F=51.5
$LiC_3H_7PF_5$ requires	%C=20.6	%H=4.0	%P=17.7	%F=54.3

Ratio of number of atoms C: P: F

3 1 5

Preparation of dimethylamino lithium

Dimethylamine was passed via the vacuum line into the apparatus containing the propyl lithium solution in pentane. The gas was rapidly absorbed and a white solid was deposited.

When absorbtion ceased the volatile products were removed and the dimethylamino lithium was obtained as a white powder.

Reaction of phosphorus pentafluoride with dimethylamino lithium.

The dimethylamino lithium prepared above was reacted directly with phosphorus pentafluoride in the same apparatus so that no hydrolysis could occur. Ether was condensed onto the dimethylamino lithium and the mixture was cooled to -78°C. Phosphorus pentafluoride was rapidly absorbed by the ether and a white solid was formed. When excess of the phosphorus pentafluoride was present the mixture was warmed so that the dimethylamino lithium could react with the phosphorus pentafluoride diethyl ether complex. After a few minutes the volatile products were removed by pumping under high vacuum to leave a cream coloured solid. This was pumped at 40°C under high vacuum for three hours to remove the final traces of the diethyl ether phosphorus pentafluoride complex which dissociates under vacuum.

Preparation of lithium ethoxide.

Finely divided pieces of lithium metal were added to absolute ethanol when reaction occurred in which hydrogen was evolved and a cloudy solution was obtained. The solution was poured into a large excess of ether and left overnight when a white solid was deposited. The liquid was poured off and the lithium ethoxide was obtained as a white solid by pumping it under vacuum.

Reaction of phosphorus pentafluoride with lithium ethoxide

The lithium ethoxide was placed in a reaction flask and attached to the vacuum line. Ether was condensed onto the solid at -196°C and the mixture warmed to -78°C. Phosphorus pentafluoride (in excess) was absorbed by the ether and the mixture was warmed to -50°C when a white feathery solid was formed. This rapidly dissolved and a yellow oily layer then separated. The volatile materials were removed under vacuum at 20°C and the solid obtained was pumped for a further 12 hours to remove traces of ether. The lithium hexafluoro phosphate was obtained as a dirty white powder.

Analysis $\%P = 20.0$ $\%F = 74.6$

$LiPF_6$ requires $\%P = 20.4$ $\%F = 75.0$

The Xray powder photograph of the lithium hexafluoro phosphate was identical to that which was obtained and indexed by Russell[76].

CHAPTER VI

PREPARATION OF SOME METAL CARBONYL FLUOROSULPHATES

Introduction

Although the chemistry of metal carbonyls has advanced rapidly during the past decade, no one has reported the isolation of a carbonyl compound bonded to a complex fluoroacid. In particular no compounds or derivatives of metal carbonyl fluorosulphates have been reported in the literature.

Nuttall[77] reacted dimanganese decacarbonyl with fluoro sulphuric acid and isolated a small quantity of yellow crystals which he identified by analysis as manganese pentacarbonyl fluorosulphate $Mn(CO)_5SO_3F$. This compound is moderately stable in the atmosphere but it decomposes to dimanganese decacarbonyl on heating to 50°C under vacuum. It is soluble in the common organic solvents and is also soluble in hot water. The infrared spectrum in nujol showed two absorbtions in the carbonyl region similar to dimanganese decacarbonyl while the remaining absorbtions were similar to those of silver fluorosulphate.

The reaction of other metal carbonyls with fluorosulphuric acid did not give stable metal carbonyl fluoro sulphates. Tungsten and molybdenum hexacarbonyls were recovered unchanged from fluoro sulphuric acid solution while dimeric cyclopentadienyl iron dicarbonyl $[C_5H_5Fe(CO_2)]_2$, cyclopentadienyl ion dicarbonyl iodide $C_5H_5Fe(CO)_2I$. and bis-triphenyl phosphine nickel dicarbonyl $(\O_3P)_2Ni(CO)_2$ gave decomposition products.

Shreeve[78] studied the reaction between peroxydisulphuryl difluoride $(SO_3F)_2$ and molybdenum hexacarbonyl. Quantitative evolution of carbon dixoide was observed and a white solid dioxo bis-fluorosulphanato molybdenum VI $MoO_2(SO_3F)_2$ was obtained.

Discussion

The reaction of silver fluorosulphate with metal carbonyl halides seemed to be a promising method of preparing metal carbonyl fluorosulphates. Silver fluorosulphate, unlike fluorosulphuric acid and peroxydisulphuryl difluoride is not a powerful oxidising agent so that the decomposition of the metal carbonyl halide should be reduced. Since silver fluorosulphate is also readily soluble in diethyl ether, the precipitation of the silver iodide and the removal of the solvent are possible without using extreme conditions, such as strong heating, which would destroy the carbonyl compounds in solution.

The reaction between silver fluorosulphate and cyclopentadienyl from dicarbonyl iodide $C_5H_5Fe(CO)_2I$ produced an orange solution and a yellow solid. The solid was identified as silver iodide by its insolubility in both water and concentrated ammonia solution and by its instability to light. The orange solution, on removing the solvent, deposited an orange-brown solid which recrystallized from a methylene chloride-light petroleum mixture as a dark brown wax.

The infrared spectrum of the wax in nujol is given in Table 11 in which it is compared with the spectra of cyclopentadienyl iron dicarbonyl iodide, manganese pentacarbonyl fluorosulphate and silver fluorosulphate.

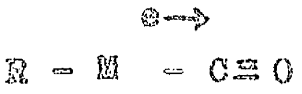
The infrared spectrum of the wax clearly indicates that it is cyclopentadienyl iron dicarbonyl fluorosulphate $C_5H_5Fe(CO)_2SO_3F$. The carbonyl stretching absorbtions at 2070 cm^{-1} and 2020 cm^{-1} in cyclopentadienyl iron dicarbonyl fluorosulphate are at higher frequencies than those in the corresponding iodide (2030, 1965 cm^{-1}) and chloride (2053, 1994 cm^{-1}). This shift to higher frequencies is consistent with carbonyls being part of a compound containing a strongly electronegative group and is explained as follows. When the carbon monoxide coordinates to the metal, the metal becomes slightly negatively charged. The charge is neutralised by back bonding of the unshared electrons from the metal

TABLE 11

Infrared spectrum of cyclopentadienyl iron dicarbonyl iodide and related compounds (cm^{-1})

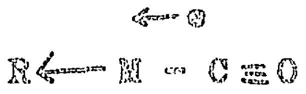
$C_5H_5Fe(CO_2)I$	$C_5H_5Fe(CO)_2SO_3F$	$Mn(CO)_5SO_3F$	$AgSO_3F$ [80]
2030(s)	2070(s)	2080(s)	
1998(s)			
1968(s)	2020(s)	2035(s)	
		1642(w)	1631(s)
		1355(w)	1282(s)
	1218(s)	1235(s)	1235(s)
	1178(s)		
	1074(m)	1062(s)	1057(s)
	990(s)	980(w)	975(w)
840(m)	848(m)		
	769(s)	760(s)	780(s)
			767(s)

d orbitals into the carbon monoxide antibonding orbitals (Fig. i). When an electronegative group such as fluorosulphate is attached to the metal, the electrons in the metal d orbtials move towards this group. The electrons in the π orbitals which are centred on the carbonyl move towards the carbon atom so that the carbonyl stretching vibrations move to higher frequencies (Fig. ii)



$$R - M \overset{\ominus\longrightarrow}{-} C \equiv O$$

(i)



$$R \longleftarrow \overset{\longleftarrow\ominus}{M} - C \equiv O$$

(ii)

The infrared spectrum of the cyclopentadienyl iron dicarbonyl fluorosulphate below 2000 cm^{-1} is very similar to the spectra of the other fluorosulphates shown in Table II. The absorbtion at 848 cm^{-1} is not present in the other fluorosulphates but is observed at 840 cm^{-1} in the spectrum of cyclopentadienyl iron dicarbonyl iodide and is assigned to the carbon-hydrogen deformation of the cyclopentadienyl ring.

The wax was dissolved in water and the orange brown reineckate salt precipitated by adding a solution of ammonium reineckate $NH_4Cr(NH_3)_2(NCS)_4$.

All of the compounds prepared gave low values in carbon analysis which were probably due to incomplete combustion of the organometallic compounds.

The reaction between silver fluorosulphate and manganese pentacarbonyl bromide $Mn(CO)_5Br$ was only attempted on a small scale because of the small quantity of carbonyl starting material available. The reaction product had a complex infrared spectrum suggesting that several carbonyl compounds were present. The compounds could not be separated from each other and were not satisfactorily identified.

The identification of fluorosulphates is now possible using ^{19}F nuclear magnetic resonance spectroscopy. At the time of this work no spectrometer was available so that the re-examination of the reactions using this technique should be much more productive.

Experimental

Silver fluorosulphate was prepared by the method of Woolf[79]. The fluorination of a mixture of nitrosyl persulphate $(NO)_2S_2O_7$ and silver powder with bromine trifluoride produced silver fluorosulphate which was isolated as a white solid. The cyclopentadienyl iron dicarbonyl iodide was prepared by Mr. T.W. Boyle in these laboratories by the reaction of iodine with dimeric cyclopentadienyl iron dicarbonyl $(C_5H_5Fe(CO)_2)_2$[85].

Reaction of silver fluorosulphate with cyclopentadienyl iron dicarbonyl iodide

Silver fluorosulphate (3.9 gs.) was placed in a 500 ml. flask and 250 mls. of diethyl ether were added. The mixture was surrounded by a warm water bath and refluxed until a clear solution was obtained. An ethereal solution of cyclopentadienyl iron dicarbonyl iodide (5.9 gs.) was slowly added to the silver fluorosulphate solution. The colourless solution immediately turned bright pink and gradually darkened to orange-brown as more of the iodide was added. The mixture was then refluxed for 30 minutes to complete the reaction. The diethyl ether was removed by distillation under vacuum and a dark brown solid was deposited. Part of the solid dissolved in methylene chloride to give an orange solution. This solution was filtered to remove the silver iodide and was poured into light petroleum (60-80°C) so that on cooling a dark brown solid was deposited. The solvents were poured off and the product dried under vacuum when it was obtained as a dark brown wax. Several attempts to crystallize the compound by precipitating it from a mixture of solvents proved to be unsuccessful.

Analysis $\%C = 24.8$ $\%H = 3.2$

$C_5H_5Fe(CO)_2SO_3F$ requires $\%C = 30.4$ $\%H = 1.8$

The wax dissolved in water to give an orange solution and the addition of ammonium reineckate $NH_4Cr(NH_3)_2(NCS)_4$) precipitated an orange brown solid. This was dried under vacuum.

Analysis $\%C=20.9$ $\%H=2.2$ $\%N=15.2$

$C_5H_5Fe(CO)_2Cr(NH_3)_2(NCS)_4$ requires $\%C=26.4$ $\%H=2.2$ $\%N=16.8$

Reaction of silver fluorosulphate with manganese pentacarbonyl bromide

Silver fluorosulphate was dissolved in diethyl ether and slowly added to an ethereal solution of manganese pentacarbonyl bromide. A white solid (silver bromide) was deposited and the orange yellow solution became pale yellow. The ether was removed by distillation to leave a brown oil and a white solid in the flask. The oil was dissolved in methylene chloride, filtered, and added to light petroleum (60-80°C). The methylene chloride was removed under vacuum and the orange solid which gradually precipitated was filtered off, washed with light petroleum and dried under vacuum in a desiccator.

The infrared spectrum in the carbonyl region (2200-1800cm^{-1}) showed absorbtions at 2095, 2040, 2005, 1965, and

1940 cm^{-1}). The complexity of the spectrum indicated that a mixture was present. The separation of these products could not be achieved on the small quantity of material available.

APPENDIX

Appendix

Structural determination of compounds containing phosphours and fluorine by nuclear magnetic resonance spectroscopy.

Since the phosphorus (^{31}P) and fluorine (^{19}F) nuclei both have spins of $\frac{1}{2}$, compounds containing both phosphorus and fluorine usually have very simple nuclear magnetic resonanse spectra. The coupling which occurs between these nuclei (J_{P-F}) and the chemical shift of the fluorine resonance (δ_F) (with reference to trifluoro methyl benzene) are very sensitive to substition by organic groups so that their values often indicate the degree of substitution which has taken place.

The replacement of fluorine atoms in phosphorus pentafluoride by methyl groups is an example of this change.

Compound	J_{P-F}	δ_F
PF_5	916	
$MePF_4$	967	-16
Me_2PF_3	820^x	-31^x
Me_3PF_2	545	-58

$$^x\ J_{P-F} = \frac{2J_{P-Fa} + J_{P-Fe}}{3} \qquad \delta_F = \frac{2\delta_{Fa} + \delta_{Fe}}{3}$$

In addition the coupling of the hydrogen nuclei to both the phosphorus and fluorine nuclei is of great importance in the determination of their structures. The couplings (J_{P-H} and J_{F-H}) also decrease as the number of atoms between the coupled nuclei increase as shown below.

Compound	J_{P-H}	J_{H-F}
F–P–H	950[68]	120
F–P–C–H	20	6
F–P–O–C–H	10	0.5
F–P–N–C–H	10	2

This observation is particularly important in the case of fluoro phosphorus esters since the presence of a methyl or methoxyl group is quickly recognized from the nuclear magnetic resonance spectra of these compounds.

The structures of many of the compounds which were prepared in this thesis were unequivocally determined from the nuclear magnetic resonance spectra. The detailed account of the determination of the structures of the new compound methoxy difluoro phosphine oxide is given below.

Methoxy difluoro phosphine oxide

The ^{1}H nuclear magnetic resonance spectrum of this liquid consisted of two quartets. The ^{19}F spectrum consisted of two triplets while the ^{31}P spectrum consisted of a triplet of quartets. These spectra showed the compound contained three hydrogen atoms, two fluorine atoms and one phosphorus atom. The four possible structures are, methyl difluoro phosphine CH_3PF_2 methoxy difluoro phosphine CH_3OPF_2, methyl difluoro phosphine oxide CH_3POF_2 and methoxy difluoro phosphine oxide CH_3OPOF_2. Methyl difluoro phosphine is reported to be unstable and decomposes to methyl tetrafluoro phosphorane[24]. The nuclear magnetic resonance data on methoxy difluoro phosphine and methyl difluoro phosphine oxide are given below together with the data of the new compound.

Compound	J_{P-F}	J_{P-H}	J_{H-F}	δ_H	δ_F	$\delta_{P(H_3PO_4)}$
CH_3OPF_2	1290	10	0.5	-4.0	-13	-111
CH_3POF_2	1105	20	6	-1.9	-2	-27
CH_3OPOF_2	1004	12	0.5	-4.1	+25	+19

The comparison of the spectral data of the new compound shows that it is not methoxy difluoro phosphine or methyl difluoro phosphine oxide. The hydrogen data suggests that the compound contains methoxy group while the data which is obtained from the phosphorus and fluorine spectra indicate the compound is a derivative of phosphorus oxyfluoride.

The compound was therefore identified as methoxy difluoro phosphine oxide.

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ABSTRACT

The reaction of phosphorus pentafluoride with a variety of ligands has been studied using standard high vacuum-line techniques. Thermal decomposition of the complexes formed produced several new compounds containing phosphorus-fluorine bonds; the structures of which were investigated using Infrared and Nuclear Magnetic Resonance Spectroscopy.

Phosphorus pentafluoride was found to form new compound with dialkylamines. Thermal decomposition of these complexe produced the new compounds dialkylamino tetrafluoro phosphoranes, PF_4NR_2, and bis dialkylamino trifluoro phosphora $PF_3(NR_2)_2$. Infrared and Nuclear Magnetic Resonance spectroscopy show these compounds are monomeric in the gaseo and liquid states and that the amino groups occupy the equatorial positions of the trigonal bipyramid. Reaction of phosphorus pentafluoride and primary alkyl amines was comple yielding non-stoichiometric mixtures. Thermal decomposition produced a solid liquid mixture which was not identified.

The reaction of phosphorus pentafluoride with phosphoru ligands was investigated to obtain information on the strengt of the novel phosphorus-phosphorus bond produced. Complexes were prepared with trialkyl phosphines, biedialkylamino

phosphines and trialkyl phosphites. The stability of the complexes were found to fall in the following order:-

$$PR_3 > P(NR_2)_3 > P(OR)_3$$

Possible explanations for this stability order are discussed on the basis that the fluorine lone pairs are overlapping with the trivalent phosphorus unfilled 'd' orbitals.

Thermal decomposition of the tris dimethylamino phosphine complex yielded the compounds dimethylamino tetrafluoro phosphorane, PF_4NMe_2, bis dimethylamino trifluoro phosphorane $PF_3(NMe_2)_2$, as well as dimethylamino difluoro phosphine, PF_2NMe_2, and bismethylamino fluoro phosphine, $PF(NMe_2)_2$, while the trimethyl phosphite complex decomposed to give the new compounds methyl difluoro phosphate, CH_3OPOF_2, and methyl trimethoxy phosphonium hexafluoro phosphate, $(CH_3O)_3\overset{+}{P}CH_3\overset{-}{P}F_6$. The kinetics of the decomposition of this salt, (which is an Arbuzov Rearrangement intermediate), in acetone and acetonitr solution, were observed from Nuclear Magnetic Resonance spectroscopy and electrical conductivity measurements. As the behaviour in these two solvents is so different the solvent must play a major part in the kinetic interpretations

The reaction of a variety of lithium salts with phosphorus pentafluoride and other non-metal fluorides in ether and pentane solution were investigated. Several new lithium salts including the novel propyl pentafluoro-phosphate salt were prepared while simpler methods of producing pure lithium hexafluoro phosphate than these described in the literature were developed.

The use of some of the new amino phosphorus fluorine compounds, as ligands to transition metal salts and metal carbonyls, confirmed the belief that the nitrogen lone pairs are π bonded into the vacant 'd' orbitals of the phosphorus and complexes can only be obtained under specific conditions.

Attempts to prepare metal carbonyl fluorosulphates from the metal carbonyl halides and silver fluorosulphate produced impure gluey compounds which could not be obtained crystalline. The ready solubility in water of the carbonyl compounds formed suggested the existence of the carbonyl fluorosulphate although only in the impure state.