THESIS.

"SOME ASPECTS OF PHOSPHORUS HALOGEN CHEMISTRY"

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by

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T.K.

NOMENCLATURE NOTE.

The nomenclature of phosphorus (V) compounds as derivatives of the hypothetical compound phosphorane, $P H_5$ has been recommended by the Chemical Society (a). Accordingly, the compound $P Cl_3 F_2$ would be named trichlorodifluorophosphorane. In the case of ionic compounds the system commonly used can be illustrated as follows: The solid, $(P Cl_4)^+(P F_6)^-$ would be described as tetrachlorophosphonium hexafluorophosphate (V). As these names are cumbersome and at times inconvenient their use has been avoided as far as possible in this thesis. The common names phosphorus pentabromide, pentachloride and pentafluoride are retained. The covalent mixed halides of phosphorus (V) are described as halophosphoranes (e.g. chlorofluorophosphoranes), and the individual members of the covalent phosphorus (V) compounds and the ionic solids are represented as formulae, thus: $(P Cl_4)^+ F^-$, $(P Cl_4)^+ (P F_6)^-$, $(P Cl_4)^+(P Cl_5 F)^-$, $P Cl_3F_2$ and $P F_3 Cl_2$.

The term "phosphine dihalides" (e.g. $Ph_3 P I_2$, triphenyl phosphine diiodide) had been used in the past to describe compounds of phosphines obtained by the addition of halogen, but in this thesis a slightly different form of nomenclature has been adopted. For example, the compound $Ph_3 P I_2$ is now named as triphenyl phosphorus diiodide following the method of Kosolapoff (b). The above description refers only to the stoichiometry of the compound. Whenever the compound is to be described in terms of its structure a more systematic form of nomenclature is followed. The compound $(Ph_2 P I_2)^+ I^-$, for example, would be described as diiododiphenylphosphonium iodide.

(a) Editorial report on Nomenclature,
J. Chem. Soc., 1952, 5122.

(b) Kosolapoff, "Organophosphorus compounds",
Wiley, New York, 1950, p.4.

CONTENTS.

PART I

A STUDY OF PCl_3F_2.

INTRODUCTION

Interest in phosphorus halogen chemistry began as early as the beginning of the nineteenth century. Developments in the initial phase of this branch of chemistry are largely attributable to the works of Davy, Dumas, Gay Lussac and Thenard (1) and they were followed by other chemists of distinction such as Balard, Gladstone and Wurtz (1) who also made notable contributions. The synthesis of compounds of the type PX_3, PX_5 and POX_3, where X is Cl or Br had been accomplished by the late eighteenforties and another development was the discovery of P_2I_4 as early as 1813 by Gay Lussac and Wurtz (2). This latter compound represents the beginning of an interest in halogen compounds containing P-P linkages. But to date this potentially interesting field has not been investigated with the thoroughness it, perhaps, deserves. Although P_2I_4 and P_2Cl_4 are well characterised, further investigations on P_2F_4 which has been reported only in a preliminary communication (3) are necessary and this is true of the bromine analogue which so far has not been synthesised.

The latter half of the nineteenth century saw much more rapid progress in the chemistry of phosphorus halides. The isolation of the fluorides of phosphorus which earlier, Davy and Dumas failed to achieve, was accomplished by Moissan (4) in the year 1884. The most significant event of this time was the preparation or attempted preparation of mixed fluorides of phosphorus, that is PF_3Cl_2, PF_3Br_2 and PF_3I_2 by Moissan (5), which opened a new field of research that has given rise to many exciting ideas in the way of chemical thinking in recent times. Following Moissan's work the syntheses and studies of certain of the properties of the three well-developed series of compounds, that is PX_3, PX_5 and POX_3 where X is a halogen, had been completed excepting the isolation of PI_5 and POI_3, compounds still not prepared and characterised. A great deal of physical and chemical information about the halides of phosphorus stems from these early works, even though in some cases it can not be accepted without critical examination and perhaps further investigation. Among the important chemical reactions (1) studied by these early workers decomposition by heat and electric discharge, reactions with hydrogen, oxygen, water, alkalies, halogens, hydrogen chloride, sulphur, ammonia, metals like sodium, copper, mercury, aluminium, iron, cobalt and nickel, transition metal chlorides and oxides are worth noting although only in a very few instances have the reactions been fully studied and conclusive results obtained.

Apart from the PX_3, P_2X_4, PX_5 and POX_3 type of phosphorus halides, another series of compounds in which there are seven or more halogen atoms per phosphorus atom can be recognised. The first of these polyhalides, PCl_6I, was prepared by Baudrimont (6) in 1864 by the reaction between PCl_5 and ICl. Other compounds of this series so far recognised are PCl_5 BrI, PCl Br_5I (7), PCl_3Br_4 (8), PBr_7 (9) and PBr_6I (10), whilst solids of formulae PCl_2Br_7, PCl_3Br_8 (11), PCl_5Br_{10} (12), PBr_{17} (13) and PCl_3Br_{18} (8) have been either isolated or identified indirectly. Crystal structure studies (14) on PCl_6I have shown that it is based on $(PCl_4)^+$ and ICl_2^- units. The solid liquid phase systems of phosphorus (III) halides and halogen have been extensively studied by many workers without significant advances (15). Conductance and transport number measurements (16) have shown that these polyhalides can be viewed as based on $(PX_4)^+$ and X_3^- or more complex anionic units. Spectrophotometric investigation (10) of PCl_6I and PBr_6I have been interpreted in terms of dissociation taking place into the pentahalide and the interhalogen in nonpolar solvents, and ionisation taking place with the formation of $(PX_4)^+$ cations and XIX^- anions in polar solvents.

After the investigations by Moissan on the mixed fluorohalides of phosphorus (V), this subject remained neglected until Booth and coworkers prepared PCl_2F PF_2Cl (17), PBr_2F and PF_2Br (18) in 1939. Even before the isolation of these compounds they had been detected spectroscopically (19) in heated mixtures of the appropriate phosphorus trihalides in which they are formed by a halogen exchange mechanism. In this way PCl_2Br and $PClBr_2$ (20) as well as PF_2Cl and PCl_2F (21) have been prepared. The synthesis of these compounds in pure form is a major achievement of the practical chemist as they have since been shown to undergo reorganisation reactions very readily making the study of the pure species inherently difficult.

Direct addition of halogen to the mixed trihalides of phosphorus offered a convenient method for the preparation of the mixed halides of phosphorus (V) and this technique led for example to the isolation of PCl_3F_2 and PCl_4F (17). More recently PCl_4F has been again prepared by Kolditz (22), by the pyrolysis of $(PCl_4)^+ (PF_6)^-$.

The first structural study on phosphorus (V) halides was undertaken independently by Brockway and Beach (23) and by Rouault (24). So far only PF_5, PF_3Cl_2 and PCl_5 have been studied by electron diffraction.

In the vapour state these molecules possess trigonal bipyramidal structures in agreement with the results obtained from studies on the Raman spectra (25) and these structures can be readily described in terms of sp^3d-hybridisation of the phosphorus atom. On the basis of electron diffraction studies (23) the two chlorine atoms in PF_3Cl_2 were thought to occupy axial positions with the three fluorine atoms in the equatorial sites. However, this has been shown to be incorrect in the light of recent F^{19} n.m.r. (26) and infrared (27) spectral studies. Holmes and his co-workers have interpreted this data to show that in PF_3Cl_2 and PCl_3F_2, the axial positions of the trigonal bipyramid are occupied by fluorine atoms, and in PCl_4F, one of the axial positions is occupied by fluorine and the other by chlorine. This is because fluorine in comparison with the less electronegative chlorine is capable of more effective overlap with the axial orbitals of phosphorus which can be concisely described in terms of d-p hybrids whereas the equatorial orbitals of phosphorus possess more s-p character (43, 28). The crystal structures of phosphorus pentachloride (29) and phosphorus pentabromide (30) have been worked out in considerable detail. Phosphorus pentachloride has the ionic structure $(PCl_4)^+$ $(PCl_6)^-$

in which the phosphorus can be described as being in sp^3- and sp^3d^2- hybridised states in the cation and the anion respectively. X-ray powder diagrams of phosphorus pentachloride show two distinct patterns (this thesis, Appendix) presumably due to a molecular form in addition to the ionic form. In polar solvents phosphorus pentachloride is present as the ions $(PCl_4)^+$ and $(PCl_6)^-$ (31) whereas in nonpolar solvents like carbon tetrachloride the molecular form is recognised (32). $(PBr_4)^+ Br^-$ exists in solid phosphorus pentabromide. In polar solvents phosphorus pentabromide undergoes ionisation to $(PBr_4)^+$ and $(PBr_6)^-$ species (33). The existence of $(PX_4)^+$ and $(PX_nX^1_{6-n})^-$ units in which X and X^1 may be the same or different is a general feature of phosphorus (V) halides. For example the following are known in the solid state: $(PCl_4)^+F^-$, $(PBr_4)^+F^-$, $(PCl_4)^+(PF_6)^-$, $(PCl_4)^+(PCl_5F)^-$, $(PCl_4)^+ (PBr_5F)^-$, $(PBr_4)^+$-$(PF_6)^-$ and $(PBr_4)^+Br^-$.

Structural investigations of the halides of phosphorus (V) opened up many unforeseen points such as the ionic chemistry and possible isomerism of these compounds. The number of compounds included within the phosphorus (V) halides is large when mixed halide complexes are considered and is still further increased if the possibility of positional isomerism in the trigonal bipyramidal, tetrahedral or octahedral structure units is considered. The potentialities, both synthetic, and chemical and structural, of this large group of compounds would be well enough illustrated by an investigation of the chlorofluorides and it was to this end that the work described was directed.

Of the compounds in the chlorofluoride series that is PCl_4F, PCl_3F_2, PF_3Cl_2 and PF_4Cl, only one was well known when this work was begun namely PF_3Cl_2 (61). In the course of the work details of PCl_4F, PCl_3F_2 and PF_4Cl (26, 34) became available, although not before considerable time had been already spent in the investigation.

For a systematic approach to the chemistry of phosphorus (V) halides it is essential to discuss a few relevant features concerning the chemical bonding in these compounds. Recently Van Wazer (35) has dealt with this subject in great detail and the treatment presented here is derived largely from his presentation. It is convenient to explore this topic under four classes depending on the usual structural entities encountered in phosphorus chemistry.

a) <u>Three-connected phosphorus</u>. In these cases a naive analysis sees the achievement of a stable octet arrangement around the phosphorus atom with an electron pair filling a nonbonding orbital. The shape thus obtained is a triangular pyramid with the phosphorus atom situated at the apex. The halogen - phosphorus - halogen angle decreases from 104 ± 4° in PF_3 through 101 ± 2° in PCl_3 and 100 ± 2° in PBr_3, to 98 ± 4° in PI_3. The relatively large drop in the bond angle as we go from PF_3 to PCl_3 has been attributed to the partial delocalisation of the electron pairs on the fluorine atom into the partly unoccupied d-orbitals of phosphorus, thus forming a multiple bond (36). The increased electron density in the multiple bond causes repulsion of the other bonds and hence the large angle. This phenomenon is characteristic of fluorine since its valence shell is complete with four electron pairs. On the other hand the repulsion between the electron pairs in the valence shells of the higher halogens with incomplete shells is not so significant. Consideration of the size of ligands coupled with the greater lone pair - bond pair repulsion than the bond pair - bond pair repulsion (37) explains the gradual drop in bond angle. The lone pair - bond pair repulsion in phosphorus trihalides also accounts for the values of the halogen - phosphorus - halogen bond angles which lie between those required for sp^3 hybridised and p^3 hybridised orbitals and hence the shape of these molecules as well.

b) <u>Four-connected phosphorus</u>. The frequent occurrence of $(PX_4)^+$ cations in phosphorus halides is an important feature as mentioned earlier. The phosphorus atom, in these cases, is tetrahedrally surrounded corresponding to sp^3hybridisation. These structures have been shown, by van Wazer (35), to consist of four σ-bonds with 0.2-0.5 π-bonds per σ-bond. In the case of the tetrahedral molecules of phosphorus oxyhalides molecular constants obtained from electron diffraction studies (24) and microwave spectra (38) show that P-Cl bond in all these compounds has very little π-character whereas P-F and P-Br bond lengths correspond to about $\frac{1}{3}$ π-bond per σ-bond. In $POCl_3$ the P-O bond has a large amount of π-character (approximately one π-bond per σ-bond); the lack of π-bond character in the P-Cl bonds is thus made up by an increase in the amount of π-bonding in the P-O bond. The exceptional stability of ions of the

$(PX_4)^+$ -type could be accounted for by the multiple bonding present in the P-X bonds. π-bonding in these cases serves to prevent undue accumulation of positive charge on the phosphorus atom which would otherwise happen due to the electronegativity difference between the phosphorus and the ligands.

Five-connected phosphorus. The stability of five-connected phosphorus compounds appears to be relatively restricted although the number has been added to recently and many more examples of this stereochemistry will undoubtedly be found. The recent preparations (39, 40) of alkyl, aryl and hydrogen substituted halophosphoranes indicates that the stability of five coordinate phosphorus is greater than was once thought from studies of simple halides. With the exception of phosphorus pentafluoride the pentahalides contain five-connected phosphorus only under special conditions, for example, phosphorus pentachloride has PCl_5 units only in vapour, liquid and nonpolar solvents (25, 41, 32). The vapour of phosphorus pentabromide is completely dissociated to PBr_3 and Br_2 (42), and PBr_5 units have not been detected; however they are presumed to be present in solutions in non-polar solvents. Both of these pentahalides are ionic in solid. However, the two distinct forms of solid phosphorus pentachloride observed in the present work presumably correspond to ionic and molecular lattices. The chlorofluorophosphoranes are molecular at low temperature, but they tend to transform to ionic species at room temperature. All these covalent molecules have a trigonal bipyramidal shape which is the expected one as a consequence of lone pair-bond pair repulsions. This stereochemistry is also readily described in terms of sp^3d-hybridisation. In the five connected phosphorus compounds there is apparently little π-bonding. The use of low energy d-orbitals for σ-bond formation might possibly account for the absence of π-bonding in these compounds. Siebert (25) has shown that the axial bonds are longer than the equatorial ones in the case of molecular PCl_5 that is in the vapour state. Certainly the axial positions and the equatorial positions are not geometrically equivalent. The elongation of the axial bonds has been explained as being due to the extra repulsion exerted on the bonding pairs in the axial sites relative to those in the equatorial positions. Incomplete hybridisation leading to three sp^2 equatorial orbitals and two dp axial orbitals has been offered as another explanation (43) since overlap with the higher energy-dp-hybrid orbitals would be expected to be less effective than with the sp-hybrid orbitals.

Six-connected phosphorus. The most favourable shape expected in a six-connected environment is octahedral on account of electron pair repulsion effects. The alternative approach involving sp^3d^2 hybridisation leads to the same result. The complex anions of the type $(PX_6)^-$ are thus frequently present in phosphorus (V) halide systems. In these ions there is little amount of π-character; the lack of π-character in these units may be given a similar explanation as in the case of the five-connected phosphorus compounds.

One striking feature that emerges is the predominance of five-connected and six-connected phosphorus molecules with halogens of high electronegativities. This is in accordance with the conclusions reached by Craig etal (43) from their theoretical studies on the use of d-orbitals of phosphorus for bond formation. Thus PF_5, PCl_5 and the chlorofluorides of phosphorus (V) are known to exist in molecular form. $(PF_6)^-$ ion is fairly common whereas $(PCl_6)^-$ ion exists only in solid phosphorus pentachloride and its solutions in nonaqueous polar solvents. $(PBr_6)^-$ appears to be much less common and so far has been recognised only in solutions of PBr_5 in nonaqueous polar solvents. (33). The absence of $(PBr_6)^-$ ion in the solid state may well be a steric consequence even though there is sufficient room for six bromine atoms around a phosphorus atom. Recent F^{19} nuclear magnetic resonance studies (28) on phosphoranes of the type R_nPF_{5-n} (R=alkyl or aryl group, n=1, 2 or 3) are consistent with a trigonal bipyramidal model in which the R groups always occupy equatorial sites. This again is in agreement with the argument based on the "electronegativity effect" of the ligands on the 3d-orbitals of phosphorus.

Quantum mechanical reasoning (43) supports the existence of π-bonding in quadruply connected phosphorus. This type of bonding is more or less restricted to compounds containing four-connected phosphorus and there is little or no π-bonding in the three -, five - and six-connected phosphorus compounds. The dissipation of positive charge that might accumulate on the triply connected phosphorus systems with strongly electronegative ligands can be effected by the lone pair electrons on the phosphorus atom, and this might account for the absence of any significant amount of π-bonding in them. The exceptionally frequent occurrence of $(PX_4)^+$ cations in many compounds has been well established and this has important consequences in the chemistry of phosphorus (V) halides. For example fluorination of $(PCl_4)^+(PCl_6)^-$ by arsenic trifluoride results in $(PCl_4)^+(PF_6)^-$ (44) indicating the relative inertness of $(PCl_4)^+$ to fluorination compared to the $(PCl_6)^-$ group. Similarly it has been shown by exchange studies (45) involving chloride ion that the chlorine atoms in $(PCl_6)^-$ are far more labile than those in $(PCl_4)^+$. Closely connected with this is the inherent instability of molecular chlorofluorophosphoranes with respect to reorganisation processes leading to the formation of stable lattices involving $(PX_4)^+$ and $(PX_6)^-$ units. Thus it is quite clearly established that the four-connected and six-connected species are more stable than the five-connected phosphorus compounds. A possible mechanism for the transformation of covalent PF_3Cl_2 to the ionic form has been suggested by Kennedy (46) to involve a reorganisation through the presence of halogen bridges in phosphorus (V) halides. Such bridged structures which represent an interesting bond type have been observed in the vapour phases of $(PCl_4)^+$ $(PCl_5F)^-$ and phosphorus pentachloride (47).

Another important aspect of the chemistry of phosphorus pentahalides is their Lewis acid behaviour and this has been the subject of recent investigations (48, 49, 50, 51, 52). For example phorphorus pentafluoride, apart from the well known $(PF_6)^-$ anion, forms in general, 1:1 adducts with a wide variety of donor molecules like amines, amides, nitriles, ethers, esters and sulphoxides (52). F^{19} nuclear magnetic measurements are consistent with an octahedral structure for these complexes. Similar compounds are known in the case of the other pentahalides of phosphorus. More will be said later on the stability of these complexes.

In conclusion it is appropriate to include a few comments on the chemical reactivity of phosphorus halides. On account of their high reactivity under certain conditions this has caused these compounds to be generally spoken of as "unstable". In the first instance the readiness with which they undergo hydrolysis has been a long recognised fact. The polar nature of the phosphorus halogen bond makes it very susceptible to nucleophilic attack and the sensitivity to hydrolysis increases with increasing size of the halogens bound to the phosphorus atom. As a class, phosphorus (V) compounds also undergo reorganisation processes rather readily. However, the reactivity is not great enough for any rearrangement to take place while the substance is being characterised. This could be illustrated, for example, in the case of the mixed chlorofluorophosphoranes. The covalent forms are fairly stable at low temperatures. At room temperature the transformation to ionic species takes place slowly. The actual mechanisms of these processes are likely to be complex, involving many reorganisation processes. Among the mixed trihalides, the presence of fluorine tends to stabilise them with respect to reorganisation processes (53).

The reactive nature of phosphorus halides makes at once obvious the necessity for handling these materials with great care. Techniques involving the use of vacuum lines, dry boxes etc. have, however, overcome many of the handicaps and made accessible reliable chemical information on these compounds.

RESULTS AND DISCUSSION

THE PREPARATION OF PCl_3F_2 - SOME PRELIMINARY CONSIDERATIONS.

Historical note.

Booth and coworkers (17) were the first to report the isolation of PCl_3F_2. The compound was prepared by the chlorination of PF_2Cl which was obtained by the controlled fluorination of phosphorus trichloride by antimony trifluoride or calcium fluoride.

$$PF_2Cl + Cl_2 \longrightarrow PCl_3F_2$$

The reaction was found to be exothermic in nature and the PCl_3F_2 was obtained as an unstable liquid which slowly changed to a white solid. This transformation was complete in about six days. The liquid had a vapour pressure of 387 mm at 32°C.

At the time the present investigation was started there was no further information regarding the properties of PCl_3F_2 and it was the aim of this work to prepare this compound and study it thoroughly. However, while work was in progress Holmes and coworkers (26, 27) reported the preparation, infrared spectra and F^{19} nuclear magnetic resonance spectra of a series of chlorofluorides of phosphorus (V) including PCl_3F_2. Their method of preparation of PCl_3F_2 and the other members of the family was also based on the chlorination of the appropriate mixed phosphorus trihalide.

General methods of preparation of mixed halophosphoranes.

(i) Halogenation of phosphorus trihalides.

The addition of halogen to a suitable phosphorus trihalide has been used in the past for the preparation of the mixed halides of phosphorus (V). This is a very convenient route for direct access to these compounds. In fact, Moissan (5) isolated the earliest known chlorofluoride of phosphorus (V) that is PF_3Cl_2 by the chlorination of PF_3. The process is somewhat cumbersome when the preparation of mixed trihalides of phosphorus as the starting materials becomes necessary. However, the experimental difficulties involved in the synthesis of the mixed phosphorus (III) halides have been reduced considerably by recent investigators (26). Even though this is at the cost of the yield of the products the simplicity of the experimental procedure more than compensates for it. The following equations summarise the syntheses of some mixed halides of phosphorus (V) which have been carried out by the halogen addition procedure:

$$PF_3 + Cl_2 \longrightarrow PF_3Cl_2 \quad (5, 61)$$
$$PF_2Cl + Cl_2 \longrightarrow PCl_3F_2 \quad (17, 26)$$
$$PFCl_2 + Cl_2 \longrightarrow PCl_4F \quad (17, 26)$$
$$PBr_2F + Br_2 \longrightarrow PBr_4F \quad (54)$$

(ii) Pyrolysis of the mixed halides of phosphorus (V).

Kolditz (22) reported the formation of PCl_4F by the pyrolysis of $(PCl_4)^+(PF_6)^-$ under reduced pressure:

$$(PCl_4)^+(PF_6)^- \longrightarrow PCl_4F + PF_5$$

On the other hand pyrolysis of $(PCl_4)^+(PF_6)^-$ at 100°C under reduced pressure was found to give PF_3Cl_2 by Kennedy and Payne (47). The same authors observed that the action of heat on $(PCl_4)^+(PF_6)^-$ suspended in boiling carbon tetrachloride led to PF_5, PF_3Cl_2 and the solid $(PCl_4)^+(PCl_5F)^-$.

(iii) Halogen exchange reactions.

Holmes and Carter (34) reported the preparation of PF_4Cl very recently. They obtained this compound by the controlled low temperature fluorination of PF_3Cl_2

with antimony trifluoride. This is the only example of this type of synthesis appearing in the literature so far.

Fluorine addition as a method of preparation of Chlorofluorophosphoranes.

Of all the methods outlined above halogen addition to a phosphorus trihalide appears to be the most direct and clear cut route to the synthesis of mixed halophosphoranes. By analogy, at least on a formal basis, with the reaction of chlorine, the reaction of fluorine with phosphorus trihalides also should lead to the formation of addition compounds, thus,

$$PCl_3 + F_2 \longrightarrow PCl_3F_2$$
$$PFCl_2 + F_2 \longrightarrow PF_3Cl_2$$
$$PF_2Cl + F_2 \longrightarrow PF_4Cl$$

In the case of chlorine addition takes place without exchange reactions if the trihalide contains only chlorine and fluorine whereas substitution of chlorine by fluorine can occur when addition by fluorine is attemped, the main reason for this being that the P-F bond energy (117K Cals/mole in PF_3) is much greater than the P-Cl bond energy (76 K Cals./mole in PCl_3).

The heat of reaction of the process

$$F_2 + 2\ P\text{-}Cl \longrightarrow 2\ P\text{-}F + Cl_2$$

can be approximately evaluated taking the heat of dissociation of molecular chlorine and fluorine to be 57 K cals and 60 K cals per mole respectively (55). In the same manner the heat of reaction for the fluorine addition reaction can be estimated and here the assumption is made that the P-Cl and P-F bond energies of the pentavalent phosphorus molecules do not differ from the corresponding values in the tri halides namely 76 K cals and 117 K cals per mole respectibely (56). This is known not to be so but the use in the calculation of P^{V}-Cl and P^{V}-F bond strengths as opposed to P^{III}-Cl and P^{III}-F bond strengths is not possible as the data is not at present completely available. It would appear likely that the differences whilst not insignificant would not be such as to alter completely the energetics of the reaction. An estimate made in this way for the reaction

$$PCl_3 + Cl_2 \longrightarrow PCl_5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.$$

using the known P-Cl bond strengths (57) in PCl_3 and PCl_5 shows a difference of 81 K cals for the heat of reaction (ΔH calculated by the approximate method:

95 K cals; ΔH calculated allowing for the difference between the P-Cl bond strengths in PCl_3 and PCl_5: 14 K cals.). Using the approximation the energy changes involved in reactions between phosphorus trichloride and fluorine may be represented as follows:

$$PCl_3 + F_2 \longrightarrow PClF_2 + Cl_2, \Delta H = -79 \text{ K cals} \quad \ldots\ldots 2$$

$$PCl_3 + F_2 \longrightarrow PCl_3F_2 \quad , \Delta H = -174 \text{ K cals} \quad \ldots\ldots 3$$

$$PCl_{5-n}Fn + F_2 \longrightarrow PCl_{3-n}F_{n+2} + Cl_2, \Delta H = -79 \text{ K cals} \quad \ldots\ldots 4$$

It will be observed that ΔH for the reaction given by equation 3 is likely to be considerably lower than the value given above by analogy with the addition reaction between PCl_3 and Cl_2. However, the heat of reaction in the former case would be expected to be greater than in the latter case considering the greater P-F bond energies relative to the P-Cl bond energies.

Trivalent phosphorus compounds are, by virtue of the lone pair electrons on the phosphorus, susceptible to electrophilic attack. This inherent reactivity is likely to be an important driving force in favour of the addition of fluorine to phosphorus trichloride rather than the displacement reaction. In practice this addition involves the loss of energy before the molecule breaks up or halogen exchange occurs. The absence of excess fluorine, reasonable dilution of the reactants as an effective means of dissipating the heat of reaction and removal of the addition product from the reaction zone soon after it is formed are essential to minimise side reactions. The balance between reactions represented by equations 3 and 4 is probably a question of mechanism rather than thermodynamics.

The successful preparation of PCl_3F_2 by the addition of fluorine to phosphorus trichloride is of interest because this is the first instance studied of the addition of fluorine to a compound containing less electronegative halogens. Further there is the advantage that the starting materials are readily available. The reaction between phosphorus trichloride and elementary fluorine was first reported by Moissan (58). He identified chlorine and phosphorus pentafluoride as the products. The lack of success of previous attempts to use fluorine for addition reactions must be attributed to its highly reactive nature, however it is clearly not incapable of addition to a lower valency state halide in the same way as the other halogens.

In the following pages are given the attempted experimental methods designed to establish suitable conditions under which the addition of fluorine to phosphorus trichloride would be possible.

THE VAPOUR PHASE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT ROOM TEMPERATURE

A dry nitrogen stream carrying phosphorus trichloride vapour was brought in contact with elementary fluorine in a horizontal copper reactor at room temperature The reactants were mixed in 1:1 mole ratio. During the reaction the inlet end of the reactor became slightly warm and a thin film of white deposit was formed gradually in the tubes joining the traps (cooled to -78°C) directly connected to the reactor. A yellowish white solid along with some liquid appeared in the first trap. During the experiment the yellow colour disappeared gradually. As the reaction proceeded white fumes issued from the outlet of the moisture guard trap where the nitrogen stream carrying material not condensed entered the atmosphere.

When the reaction was complete the copper reactor was opened and a white solid was found on its walls at the inlet end. It gave the following analysis: Cl, 71.4%; F, 12.4%; P, 15.8%, (total 99.6%) corresponding to the composition $PCl_{3.93}F_{1.23}$. An X-ray powder photograph of this compound (Fig. 1 and Table 1) was found to be almost identical to that of $(PCl_4)^+F^-$ (22).

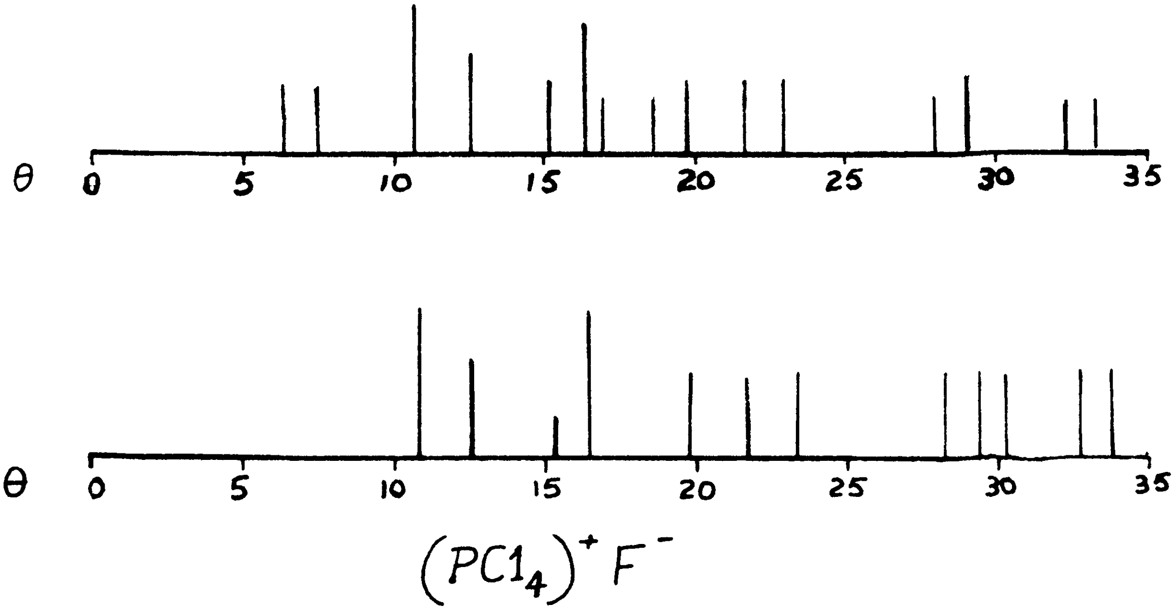
There were, however, a few additional weak lines not present in $(PCl_4)^+F^-$. The presence of $(PF_6)^-$ ion in the hydrolysate of the compound was shown by precipitating the Nitron-$(PF_6)^-$ compound (59) which was found to have a melting point of 228-230°C (Kolditz: Nitron-(PF_6^-) compound, M.P. 229°C). On the basis of these results the solid product can be considered to be a mixture of 91.8% of $(PCl_4)^+F^-$ and 8.2 % $(PCl_4)^+(PF_6)^-$.

Analysis of the white solid from the first trap (at -78°C) connected to the reactor gave Cl, 74.7%; P, 15.4%; calculated for $(PCl_4)^+F^-$, Cl, 73.8%; P, 16.15%. Again a mixture is indicated, however the composition is much closer to $(PCl_4)^+F^-$ than in the case of the material from the reactor. The volatile products from the traps at -78°C were separated into two fractions condensing at -78°C and -180°C by fractional distillation in a vacuum line. The identification of the volatiles was always done by means of their I.R. spectra. The -180°C fraction was found to contain POF_3, POF_2Cl, $POCl_2F$, PF_3Cl_2 and a compound showing a new band at 865 cm^{-1}. Small amounts of POF_2Cl and a compound showing a strong absorption at 865 cm^{-1} were present in the -78°C fraction. This new

Table 1. The X-ray Powder Data for the Product of Reaction between PCl_3 and F_2 at Room Temperature

θ	strength	$(PCl_4)^+F^-$	strength
6.4	w		
7.4	w		
10.6	vs	10.8	s
12.5	m	12.5	m
15.1	w	15.3	vw
16.4	s	16.5	s
17.1	vw		
18.6	vw		
19.7	w	19.9	m
21.6	m	21.9	w
23.0	w	23.4	w
28.0	vw	28.3	w
29.1	w	29.5	m
		30.3	w
32.3	vw	32.8	w
33.4	vw	33.9	w

Fig. 1. X-Ray Powder Diagram of the Solid Product of the Reaction between PCl_3 and F_2 at Room Temperature.



band is in the region where P-F absorption appears and the absence of all the then known fluorides, chlorofluorides and oxychlorofluorides of phosphorus which have P-F absorption in this region suggested that this peak at 865 cm^{-1} was due to the expected product PCl_3F_2. Further the $-78^{\circ}C$ fraction slowly deposited a white solid, a feature which is characteristic of the chlorofluorophosphorane which readily undergoes transformation to ionic solid as has been mentioned. This liquid fraction was sealed in a tube fitted with a break seal and left at room temperature for a week when nearly all of it had changed to a solid. The small amount of liquid present (POF_2Cl impurity) was pumped off and the white solid obtained analysed for chlorine and phosphorus: Cl, 61.6%; P, 16.7%; calculated for PCl_3F_2, Cl, 60.7%; P, 17.7% The composition of the solid was thus close to that of P: Cl_3: F_2. It appeared probable that covalent liquid PCl_3F_2 had transformed to an ionic analogue (the nature of which is discussed later) as in the case of covalent PCl_4F (22) which transforms to $(PCl_4)^+F^-$.

The details of the reaction are summerised in Table 2.

Table 2.

Reactants	Millimoles reacted	Products	Millimoles formed	% Conversion with respect to phosphorus
		$(PCl_4)^+F^-$	28.2	24.6
		$(PCl_4)^+(PF_6)^-$	1.0	1.8
PCl_3	114.5	PCl_3F_2	2.6	2.2
F_2	114.5	POF_3,) POF_2Cl)	traces	-
Total phosphorus accounted for				28.6%

The above mass balance is by no means complete since attention has been paid only to products which are not volatile at -78°C under atmosphere pressure. An attemped study of the products not condensed at -78°C encountered experimental difficulties which could not be readily overcome and was not therefore followed up in detail. However, a qualitative experiment concerning the material volatile at -78°C in reactions of this type is described later.

THE LIQUID - VAPOUR PHASE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT - 78° C. I.

The formation of $(PCl_4)^+F^-$ as a product of the reaction between phosphorus trichloride and fluorine appeared to be the result of a thermal breakdown of the addition compound, PCl_3F_2 formed initially. Instances of such decomposition are known from recent work (22, 46) on the chlorofluorides of phosphorus (V).

If yields of PCl_3F_2 were to be increased it appeared necessary to minimise the effect of the heat of reaction; this could be achieved by cooling the reactor to sufficiently low termperature.

In the first experiment fluorine diluted with dry nitrogen was passed through liquid phosphorus trichloride cooled at -78°C. It was hoped that the presence of phosphorus trichloride in excess over the amount of fluorine and the expected decrease in the reactivity of fluorine at low temperature would facilitate the addition reaction. As in the previous experiment shortly after the reaction was started white fumes appeared at the exit end of the moisture guard trap and small amounts of a white solid were formed in the exit and inlet tubes of the traps. After running for about twenty minutes the nitrogen flow commenced to fall, however, when the phosphorus trichloride was allowed to warm up the nitrogen flow increased slowly, but again fell on cooling. It was presumed that this was due to a viscosity effect. However, the application of higher pressures to induce the flow of nitrogen was not possible since the fluorine cell can not operate with an excess pressure of more than a few inches of water pressure. The experiment had therefore to be discontinued; although in the initial stages it appeared that a reaction occurred it was not possible to study it further. Some white solid was found at the bottom of the trap containing phosphorus trichloride, however, since the reaction had not gone to any significant extent no attempt was made to work up the products.

THE LIQUID VAPOUR PHASE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT -78°C . II.

In this experiment phosphorus trichloride was allowed to drop into an atmosphere of fluorine diluted with dry nitrogen in a pyrex glass reaction flask cooled to -78°C. White fumes were formed inside the flask and a white solid was deposited on its walls. The region immediately below the neck of the flask not covered by the freezing mixture was found to be hot (+70°C) and in the later stages of the experiment the rate of dropwise addition of phosphorus trichloride could not be observed visually because of the deposit of white solid on the flask walls. For this reason the rate of the reactants entering the reaction flask could not be adjusted in the latter stages of the reaction. The experiment was completed by the addition of the stoichiometric amount of phosphorus trichloride although the rate of addition could not be controlled.

The white solid from the reaction flask had a chlorine content of 70.5%; the X-ray powder diagram was found to be identical to that of $(PCl_4)^+F^-$, but the presence of $(PF_6)^-$ ion also, in the compound, was shown by precipitation with Nitron reagent in the way previously mentioned. The solid can accordingly be considered to be a mixture of 88.5% $(PCl_4)^+F^-$ and 11.5% $(PCl_4)^+(PF_6)^-$.

The I.R. spectrum of the volatile products from the reaction in the region 2000 - 650 cm^{-1}, showed only the presence of traces of POF_3. No indication of the presence of any chlorofluorophosphoranes was obtained. This suggested that only unreacted phosphorus trichloride was present in the volatiles, it was verified by vapour pressure check also. The experimental results are shown in Table 3.

Table 3.

Reactants	Millimoles	Products	Millimoles	% Conversion with respect to phosphorus
PCl_3	114.5	$(PCl_4)^+F^-$	45.8	56.0
F_2	114.5	$(PCl_4)^+(PF_6)^-$	2.5	6.2
		PCl_3 (unreacted)	32.7	-
Total phosphorus accounted for				62.2%

THE VAPOUR PHASE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT -78°C. III.

The previous experiment (II in this series) showed about a 50% increase in the yield of impure $(PCl_4)^+F^-$ over that obtained in the vapour phase reaction between phosphorus trichloride and fluorine carried out at room temperature in a copper reactor. If it is accepted that $(PCl_4)^+F^-$ is formed as a result of a thermal breakdown of the desired addition compound PCl_3F_2, then the twofold increase in yield of $(PCl_4)^+F^-$ can be explained in terms of the generation of heat observed experimentally inside the reaction flask. For this reason a vertical copper reactor which would conduct away heat efficiently was used in this experiment. The phosphorus trichloride was introduced into the reaction vessel in a nitrogen stream which presumably lead to a mist of fine droplets, and fluorine was added through another inlet tube.

A few minutes after the reaction was commenced white fumes appeared at the outlet of the moisture guard tube and this continued throughout the experiment as has been described previously. These white fumes gave a test for free halogen (potassium iodide paper darkened). A thin film of a white solid deposited in the traps (at -78°C) and the tubes connecting them whilst only small amounts of liquid collected in these traps. After the reaction was over the cooling bath around the reactor was removed and the flow of dry nitrogen through the apparatus was increased slightly. A considerable amount of liquid product from the reactor was found to condense in the glass traps (cooled at -78°C) which were suitable for attachment to the vacuum system.

A white solid was found at the bottom of the copper reactor. This contained Cl, 75.2%; P, 16.1%; calculated for $(PCl_4)^+F^-$, Cl, 73.8%; P, 16.2%. The higher chlorine content may be due to small amounts of PCl_5, though this was not shown in the X-ray powder diagram which was very closely similar to that of $(PCl_4)^+F^-$ except for a few weak additional lines as have been observed before.

Analysis of the white solid deposited in the traps (at -78°C) gave a value of 68.6% for the chlorine content. This suggested that the material is possibly a mixture of $(PCl_4)^+F^-$ and the solid formed from liquid

PCl_3F_2. The latter solid obtained by the transformation of liquid PCl_3F_2 will be referred to later. An equimolar mixture of $(PCl_4)^+F^-$ and the solid of the composition PCl_3F_2 would contain 68.2% of chlorine.

The volatiles collected at -78°C at atmospheric pressure were fractionated in a vacuum line through traps held at -40°C, -78°C and -180°C. The main fraction obtained in the trap at -78°C showed in the I.R. spectrum a strong absorption at 865 cm^{-1} and the presence of small amounts of POF_2Cl which could not be removed even on extended fractionation. The contents of the trap at -180°C was found to contain POF_3, POF_2Cl and PF_3Cl_2.

A new absorption in the I.R. spectrum at about 780 cm^{-1} was observed in the case of the -40°C fraction along with absorptions attributable to $POCl_2F$, of medium intensity. However, the low vapour pressure of this fraction (35 mm at 20°C) showed that the amount of $POCl_2F$ was small. The absorption at 780 cm^{-1} is in the P-F region and the gradual transformation of the liquid to solid suggested the presence of a chlorofluorophosphorane. The liquid product was therefore allowed to solidify and the solid obtained after $POCl_2F$ was removed, was found to contain Cl, 74.7%; P, 16.3%; calculated for $(PCl_4)^+F^-$, Cl, 73.8%; P, 16.15%. Since PCl_4F was known to undergo transformation to the ionic form $(PCl_4)^+F^-$ (22) it was concluded that the -40°C fraction is PCl_4F, which thus has the P-F absorption at 780 cm^{-1}. This was subsequently found to be in agreement with the results of Holmes and coworkers (27).

Vapour density determination on the -78°C fraction gave a molecular weight of 177 which is very close to the theoretical value for PCl_3F_2 (175.4). Further, analysis of the compound gave Cl, 61.5%; P, 17.7%; F, 20.8% (by difference); calculated for PCl_3F_2, Cl, 60.7%; P, 17.7%; F, 21.7%.

The transformation of PCl_3F_2 (-78°C fraction) to the ionic solid appeared much slower than that of PCl_4F (-40°C fraction) as obtained in this reaction. As referred to earlier a sample of PCl_3F_2 transforms completely to the solid over a period of one week at room temperature compared to about three to four hours for the conversion of PCl_4F to $(PCl_4)^+F^-$. Both these transformations can be retarded to a very great extent but not eliminated by storing the samples at low temperature (-78°C) and in this respect are similar to the known behaviour of PF_3Cl_2 (61).

[illegible] °C and the [illegible] arrangement [illegible] possible to condense the [illegible] escaping the trap [illegible] found necessary to raise and lower [illegible] the experiment in order [illegible] in the system. This operation [illegible] entailed the inevitable loss of pure [illegible] products so that a quantitative investigation [illegible] not possible in this case. The details of the [illegible] spectrum of the condensate in the range 2000 [illegible] cm^{-1} are given below:

cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
1431m	997vs	906s	[illegible]
1421s	963m	891s(Sh)	673w
1408m	953m	876s	[illegible]
1033m	935m	868s(Sh)	
1025m	[illegible]	834m	

IDENTIFICATION OF THE PRODUCTS (FROM THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT -78°C)

VOLATILE AT -78°C

The use of a liquid exygen trap between the set of traps cooled to -78°C and the moisture guard trap in the experimental arrangement (see experimental section) made it possible to condense the products of the reaction escaping the traps held at -78°C. However, it was found necessary to raise and lower the liquid oxygen trap during the experiment in order to avoid blockage in the system. This operation, unfortunately, entailed the inevitable loss of part of the products so that a quantitative investigation was not possible in this case. The details of the I.R. spectrum of the condensate in the range 2000-650 cm^{-1} are given below:

cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
1431m	997vs	900s	693w
1421s	963m	891s(Sh)	673w
1408m	953m	876s	664w
1033m	935m	868s(Sh)	
1025m	908m	834m	

The presence of POF_3, SiF_4, PF_5 and presumably the recently synthesised compound PF_4Cl (34) in the mixture is indicated in the spectrum. The appearance of absorptions at 834 cm^{-1} (m) and 900 cm^{-1} (s) along with other peaks common to PF_4Cl and PF_5 supports the idea that PF_4Cl is present in the system. At the time this experiment was carried out the presence of PF_4Cl was not in fact recognised since the details of the I.R. spectrum was not then available and its presence was not suspected until results from the study of the transformation of PCl_3F_2 in the vapour phase were available. Appreciable amounts of chlorine in the gaseous mixture was shown by the greenish yellow colour of the sample and by the displacement if iodine from potassium iodide. This suggested that PF_2Cl is likely to be among the products. However, the overlap of P-F absorptions of POF_3 and PF_2Cl made it difficult to detect it in the I.R. spectrum.

THE DISTRIBUTION OF PRODUCTS FROM THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE AT -78°C

The detailed data on the quantitative yields of the various products formed in the vapour phase reaction between phosphorus trichloride and fluorine at -78°C are presented in Tables 4 and 5. The percentage yield Y of a product "with respect to X" given in Table 5 has been calculated using the expression

$$Y = \frac{\text{amount of X in the product}}{\text{total amount of X in the reactants}} \times 100.$$

Yields calculated in this way are a convenient means of assessing the mass balance of the individual elements present in the system. The low total yield based on fluorine thus indicates the loss of large amounts of fluorine as possibly PF_3, PF_2Cl, $PFCl_2$, PF_4Cl and PF_5, in this case PF_3Cl_2 is not included since it was not indicated in the I.R. spectrum of the material not condensed at -78°C under atmospheric pressure. Similarly about 50-60% of the total chlorine is in the fraction condensing at -78°C under atmospheric pressure, without being displaced by fluorine.

Table 4.

The Distribution of Products from the Reaction between PCl_3 and F_2 at -78°C

Run No.	Millimoles of reactants used		Millimoles of products not volatile at -78°C under atmospheric pressure						Total no. of millimoles of phosphorus in the products
	PCl_3	F_2	Crude PCl_3F_2	Pure PCl_3F_2	PF_3Cl_2	PCl_4F	$(PCl_4)^+F^-$	POF_3	
1.	572.5	572.5	132.0	74.8	11.4	5.2	117.0	1.1	266.7
2.	687.0	687.0	168.0	86.6	14.5	5.7	167.6	1.6	357.4

Table 5.

The Distribution of Products from the Reaction between PCl_3 and F_2 at -78°C

Run No.	% yield with respect to	Products not volatile at -78°C under atmospheric pressure					Total % yield based on	
		Crude PCl_3F_2	Pure PCl_3F_2	PF_3Cl_2	PCl_4F	$(PCl_4)^+F^-$	Crude PCl_3F_2	Pure PCl_3F_2
1.	Phosphorus	23.1	13.1	2.0	1.0	20.5	46.6	36.6
	Chlorine	23.1	13.1	1.3	1.2	27.3	52.9	42.9
	Fluorine	23.1	13.1	3.0	0.5	10.2	36.8	26.8
2.	Phosphorus	24.5	12.6	2.1	0.8	24.4	51.8	39.9
	Chlorine	24.5	12.6	1.4	1.1	32.5	59.5	47.6
	Fluorine	24.5	12.6	3.2	0.4	12.2	40.3	28.4

By "crude" PCl_3F_2 is meant the volatiles condensed in the traps at -78°C under atmospheric pressure. From the tables the amount of purified PCl_3F_2 is found to be nearly half that of the crude material, though the impurities such as PCl_4F, PF_3Cl_2 and the oxychlorofluorides do not account for this completely. Purification of the products into various fractions requires several cycles of low temperature vacuum distillation and during this process significant amounts of solid products are formed in the fractionation traps. The observed loss of material can thus be explained on this basis. Since the amounts of oxychlorofluorides present in the crude PCl_3F_2 were comparatively small (1%) they are not included in Table 5 along with the other products.

For reasons outlined earlier it was not possible to get quantitative data on the volatiles not retained at -78°C under atmospheric pressure. About 3.5 g of these low boiling products from an experiment using 115 millimoles (15.8 g) of phosphorus trichloride, were obtained by condensing them in a liquid oxygen trap. This fraction was found to contain 16.6 millimoles of free chlorine (9.3% of the total chlorine). This would correspond to about 14% of the phosphorus trichloride being converted

Table 5.

The Distribution of Products from the Reaction between PCl_3 and F_2 at -78°C

Run No.	% yield with respect to	Products not volatile at -78°C under atmospheric pressure					Total % yield based on	
		Crude PCl_3F_2	Pure PCl_3F_2	PF_3Cl_2	PCl_4F	$(PCl_4)^+F^-$	Crude PCl_3F_2	Pure PCl_3F_2
1.	Phosphorus	23.1	13.1	2.0	1.0	20.5	46.6	36.6
	Chlorine	23.1	13.1	1.3	1.2	27.3	52.9	42.9
	Fluorine	23.1	13.1	3.0	0.5	10.2	36.8	26.8
2.	Phosphorus	24.5	12.6	2.1	0.8	24.4	51.8	39.9
	Chlorine	24.5	12.6	1.4	1.1	32.5	59.5	47.6
	Fluorine	24.5	12.6	3.2	0.4	12.2	40.3	28.4

DISCUSSION OF THE EXPERIMENTAL RESULTS ON THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND FLUORINE.

The experimental results on the investigation of the reaction between phosphorus trichloride and fluorine in the vapour phase have shown that the addition of fluorine to phosphorus trichloride is possible under suitable conditions. The yield of over 20% of crude PCl_3F_2 obtained is a reasonable figure in view of the side reactions which are possible. Although a direct comparison is not quite relevant a few yields from controlled fluorination by exchange reactions may be quoted. Booth and coworkers (17) have reported yields as high as 60% in the preparation of $PClF_2$ and PCl_2F by the fluorination of phosphorus trichloride with antimony trifluoride. However these authors used a very complex carefully designed experimental arrangement to achieve such a high yield. Control of the reaction temperature, fractionation column temperature and pressure in the system were the significant features which made it possible to isolate the desired product efficiently without further fluorination occurring. By employing a less complicated experimental set-up Holmes and coworkers (26) have reported yields of PCl_2F and PF_2Cl around 35-40% for the same reactions.

The same authors have even more recently obtained PF_4Cl (34) in 20% yield by the controlled fluorination of PF_3Cl_2 with antimony trifluoride.

The relatively low yield of PCl_3F_2 in the preparation described in the present work could be explained if we consider the other products of the reaction. The formation of $(PCl_4)^+F^-$ in about 20-25% yield is quite significant. It is quite reasonable to suppose that $(PCl_4)^+F^-$ is formed as a result of the breakdown of PCl_3F_2 caused by the highly exothermic nature of the reaction. Even though the reactor was kept cooled at -78°C the local heat of reaction in the interior of the reactor is not likely to be removed sufficiently quickly. The occurrence of a breakdown process is supported by the analogous behaviour of PF_3Cl_2 at high temperature. The pyrolysis of PF_3Cl_2 (46) has been studied in detail and it has been shown that a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$ in the solid phase, and SiF_4, PF_5 and POF_3 in the vapour phase are the products. Kolditz (22) has observed the pyrolysis of $(PCl_4)^+F^-$ leading to the formation of PCl_5 and $(PCl_4)^+(PF_6)^-$ and that of $(PCl_4)^+(PF_6)^-$ leading to the formation of PCl_4F and PF_5. In the light of this evidence similar decomposition processes can be conceived for PCl_3F_2:

$$2\ PCl_3F_2 \longrightarrow PCl_4F + PF_3Cl_2$$

and then the following reactions can occur:

$$2\ PF_3Cl_2 \longrightarrow PCl_4F + PF_5$$

$$PCl_4F \longrightarrow (PCl_4)^+F^-$$

$$(PCl_4)^+F^- + PF_5 \longrightarrow (PCl_4)^+(PF_6)^-$$

The observed yield of PF_3Cl_2 is relatively small, which would mean that most of it has been decomposed as indicated above. However, the compound $(PCl_4)^+(PF_6)^-$ is present in the solid product from the reaction only in small amounts, which apparently runs contrary to the above scheme. But it must be emphasised that in the investigations on the pyrolysis of PF_3Cl_2 the experiments were done in closed systems, which could lead to the absorption of PF_5 by $(PCl_4)^+F^-$ resulting in the formation of $(PCl_4)^+(PF_6)^-$ and this may not necessarily occur if we are dealing with an open system like the one used in the reaction between phosphorus trichloride and fluorine. It is possible therefore that the low boiling phosphorus pentafluoride was continuously flushed out of the system thus preventing its build-up and hence its combination with $(PCl_4)^+F^-$ and this is supported by the appearance of fumes beyond the moisture guard tube.

The reaction between phosphorus trichloride and fluorine in a pyrex flask cooled at -78°C led to the formation of about 56% yield of $(PCl_4)^+F^-$ which is significant compared with the figures (20-25%) obtained in the other experiments. Further no trace of any chlorofluorophosphoranes was observed in the volatiles. The development of heat in the reaction flask in spite of cooling at -78°C has been mentioned earlier. It seems likely, therefore, that the chlorofluorophosphoranes formed in this reaction must have been completely decomposed thermally, thus providing some experimental support for the elucidation of the formation of $(PCl_4)^+F^-$, PCl_4F and PF_3Cl_2 in the system.

An important observation was the formation of $(PCl_4)^+F^-$ at the bottom of the vertical copper reactor as a uniformly thick layer. Only small amounts of white solid were found on the walls of the reactor at the inlet side. This appears to suggest that initially liquid PCl_4F collects at the bottom of the copper reactor and that it transforms to the solid later on. The transformation of PCl_4F to $(PCl_4)^+F^-$

has been observed to be much faster (in about two to three hours at room temperature nearly complete transformation takes place) than that of PF_3Cl_2 or PCl_3F_2, in the present work.

If only solid $(PCl_4)^+F^-$ were present in the reactor this is likely to be covered by liquid PCl_3F_2 and the small amounts of PF_3Cl_2 present with the result that $(PCl_4)^+F^-$ is unlikely to come into contact readily with PF_5. Since the reactor is kept at -78°C during the experiment and until all the traces of fluorine are flushed out of the system after the experiment it is more likely that PCl_4F formed is in the covalent liquid form and perhaps along with slight amount of ionic solid form at this stage. In such a case the formation of $(PCl_4)^+(PF_6)^-$ is not likely since PCl_4F and PF_5 would not interact even if they were in contact. It is to be expected that the transformation $PCl_4F \longrightarrow (PCl_4)^+F^-$ might take place later, when the reactor is allowed to warm up and the volatiles are being transferred to the -78°C traps by a stream of dry nitrogen. The low vapour pressure of PCl_4F observed in the present work (35 mm at 20°C) suggests that evaporation of PCl_4F from the reactor by the nitrogen stream must be slow. This would explain why only small amounts of PCl_4F were present in the fraction of the volatiles which condensed at -78°C under atmospheric pressure. The inevitable exposure of the contents of the reactor to room temperature for about three to four hours required for the complete transfer of the volatiles would thus tend to accelerate the transformation of the molecular to the ionic form.

On the basis of the breakdown process outlined above the yield of PCl_3F_2 formed if no decomposition were taking place can be estimated as around 50%. This is a fairly good yield considering the reactivity of fluorine which as has been mentioned earlier is likely to lead to side reactions. The thermal decomposition of PCl_3F_2 could possibly be lessened still further if the apparatus were suitably designed to reduce the effect of local heating inside the reactor.

Even though no quantitative data were obtained for the products volatile at -78°C under atmospheric pressure many useful conclusions may be drawn by examining their infrared spectrum. The occurence of reorganisation and displacement reactions is evidenced by the presence of PF_5, possibly PF_4Cl, PF_2Cl, $PClF_2$ and chlorine. A great variety of reactions may be taking place such as

$2\,PCl_3 + 3F_2 \longrightarrow 2\,PF_3 + 3Cl_2$ 5
$PF_3 + F_2 \longrightarrow PF_5$ 6
$PF_3 + Cl_2 \longrightarrow PF_3Cl_2$ 7
$PCl_3 + F_2 \longrightarrow PF_2Cl + Cl_2$ 8
$PF_2Cl + F_2 \longrightarrow PF_4Cl$ 9
$PF_2Cl + Cl_2 \longrightarrow PCl_3F_2$ 10
$2PCl_3 + F_2 \longrightarrow 2PCl_2F+Cl_2$................11
$PCl_2F + F_2 \longrightarrow PF_3Cl_2$ 12
$PCl_2F + Cl_2 \longrightarrow PCl_4F$ 13
$PCl_3 + Cl_2 \longrightarrow PCl_5$ 14

The formation of chlorofluorphosphoranes by the addition of chlorine to the phosphorus trihalides (equations 7, 10, and 13) appears to be small from the experimental results observed. One piece of evidence in favour of this hypothesis is the absence of any significant amount of phosphorus pentachloride formed in any of the solid products obtained. Reaction between chlorine and phosphorus trichloride is very rapid at room temperature in the gaseous phase, however, the corresponding addition of chlorine to PCl_2F, PF_2Cl and PF_3 possibly takes place less readily, especially at low temperature. In the case of PF_3 the vapour phase reaction $PF_3 + Cl_2 \longrightarrow PF_3Cl_2$ is known to be slow (61) although it is rapid in the liquid phase. The addition of fluorine to the phosphorus trihalides is the expected reaction and is favoured. Since the amount of fluorine is not allowed to be in excess of the 1:1 mole ratio of the reactants the extent to which the fluorine addition to the trihalides other than phosphorus trichloride takes place is thus very restricted.

It would be of interest to follow the course of the reaction if it is carried out with increasing amounts of fluorine for ratios of $F_2: PCl_3 > 1:1$ but this has not been done. This might shift the reaction towards the formation of chlorofluorophosphoranes containing more fluorine especially PF_4Cl which is a compound of some synthetic interest in view of its recent preparation by an alternative route. However, further investigations are necessary to explore this subject more thoroughly and time was not available to do so.

An extension of the vapour phase addition of fluorine to phosphorus trichloride would be the application of this procedure to systems like

$$PF_2Cl + F_2 \longrightarrow PF_4Cl$$
$$PBr_3 + F_2 \longrightarrow PBr_3F_2$$
$$(C_2H_5)_3P + F_2 \longrightarrow (C_2H_5)_3PF_2 \text{ etc.}$$

In the case of less volatile compounds, for example PBr_3 and $(C_2H_5)_3P$, the use of a suitable solvent which is resistant to fluorination, as a dispersing medium would be worth trying. The addition of fluorine by halogen fluorides like ClF_3 and BrF_3 might turn out profitable. There is also the possibility of the addition of halogen fluorides, and this might yield very significant results. Some of the following reactions would be extremely interesting from this point of view:

$$ClF_3 + PCl_4F \longrightarrow (PCl_4)^+(ClF_4)^-$$
$$BrF_3 + PF_5 \longrightarrow (BrF_2)^+(PF_6)^-$$
$$IF_5 + PF_3 \longrightarrow (PF_4)^+(IF_4)^- \quad (?)$$
$$IF_5 + PF_5 \longrightarrow (PF_4)^+(IF_6)^- \quad (?)$$
$$\longrightarrow (IF_4)^+(PF_6)^-$$

THE INFRARED SPECTRUM OF PCl_3F_2 VAPOUR

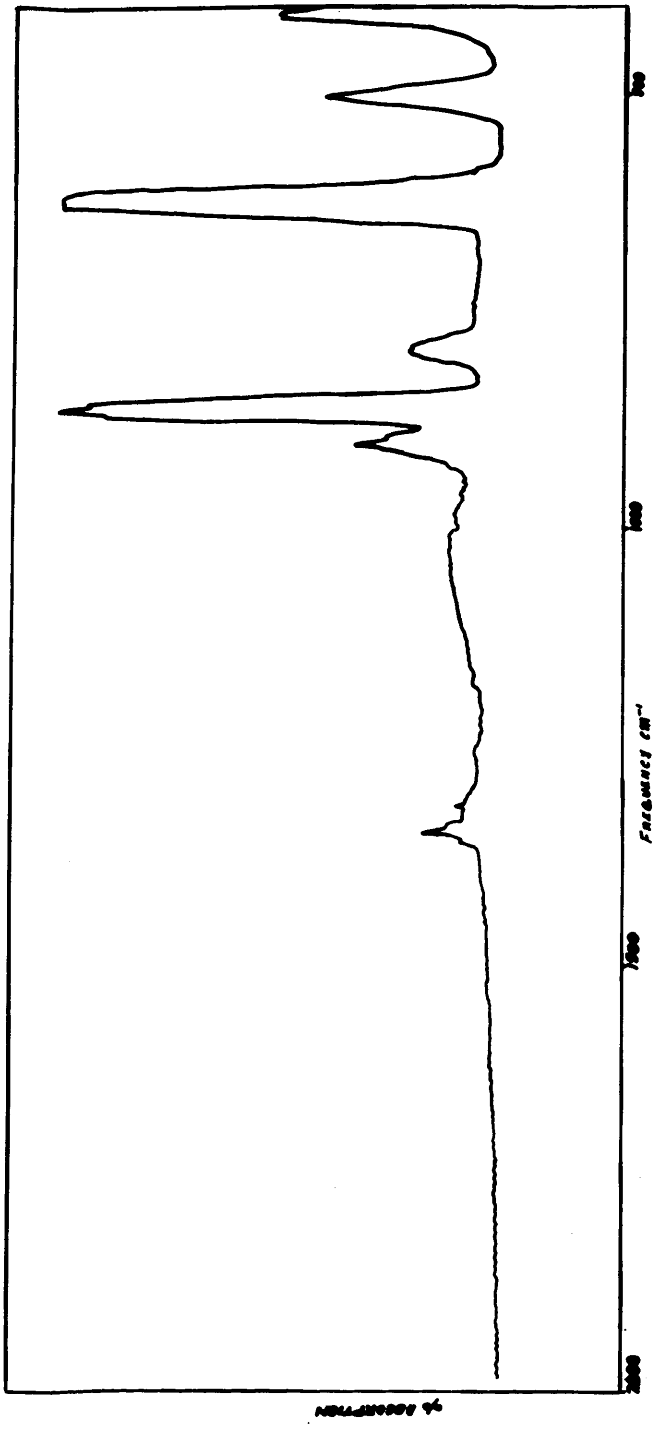
The infrared spectrum of PCl_3F_2 vapour at 10 mm pressure was recorded in the range 400 - 2000 cm^{-1}. The details of the spectrum are given in Table 6.

Holmes and coworkers (27) have given the infrared and low temperature Raman spectra of all the chlorofluorophosphoranes. The details of their infrared spectrum of PCl_3F_2 also are presented in Table 6 for comparison. There is good agreement between the two spectra as can be seen from the table. The only notable difference is the peak at 1500 cm^{-1} which is not present in our spectrum up to a pressure as high as 50 mm. This is perhaps a question of the pressure employed since the above authors observed it at a pressure of 200 mm. Two weak bands appearing in our spectrum at 1320 cm^{-1} and 1353 cm^{-1} are due to the presence of traces of $POFCl_2$ and POF_2Cl (60) respectively, which could not be eliminated completely by vacuum distillation.

Table 6. THE INFRARED SPECTRUM OF PCl_3F_2 VAPOUR

Spectrum reported by Holmes and coworkers		Spectrum obtained in the Present Work	
cm^{-1}	Intensity	cm^{-1}	Intensity
328	m		
404	vs	408	m
		412	m (sh)
498	w	506	m
522	w		
		605	vw (sh)
625	vs	628	vs
742	w		
797	m	800	vw
		861	vs (sh)
867	vs	865	vs
		872	vs (sh)
		898	vw (sh)
903	w	907	w
1017	w	1018	w
1255	w		
		1320	vw($POFCl_2$ impurity)
		1353	vw(POF_2Cl impurity)
1382	w		
1500	m		

Fig. 2. The Infrared Spectrum of PCl_3F_2 Vapour.



The infrared and low temperature Raman spectral studies have been interpreted to show that PCl_3F_2 has a trigonal bipyramidal symmetry with the two fluorine atoms in the axial positions and the three chlorine atoms in the equatorial sites. The reason for the preferential occupation of the axial sites by the fluorines in molecules of this type has already been discussed in the introduction.

THE VAPOUR PRESSURE, BOILING POINT, MELTING POINT AND ELECTROLYTIC CONDUCTANCE OF PCl_3F_2

The vapour pressure of a sample of PCl_3F_2 (98.5% pure) was measured using a mercury manometer over the temperature range -20.5° to $20.5^\circ C$. Table 7 shows the experimental results. Pressures were measured for both ascending and descending temperatures in order to check reproducibility. The plot of $\log_{10} p$ mm versus $\frac{1}{T}$, where p is the vapour pressure of the sample and T the absolute temperature, shows a linear relationship (Fig. 3).

The variation of vapour pressure with temperature follows the equation

$$\log_{10} p_{mm} = -1369\, T^{-1} + 6.95$$

This relationship was obtained by the application of the method of least squares. The molar heat of vaporisation and Trouton's constant for the liquid, deduced from the above equation were found to be 6.27 K Cals. and 18.6 respectively.

It appears from the value of the Trouton's constant that PCl_3F_2 is not associated. The boiling point of the liquid was determined from the vapour pressure equation by extrapolation and was found to be $63.4^\circ C$. This is very close to the boiling point of PCl_4F

Table 7

THE VAPOUR PRESSURE OF PCl_3F_2

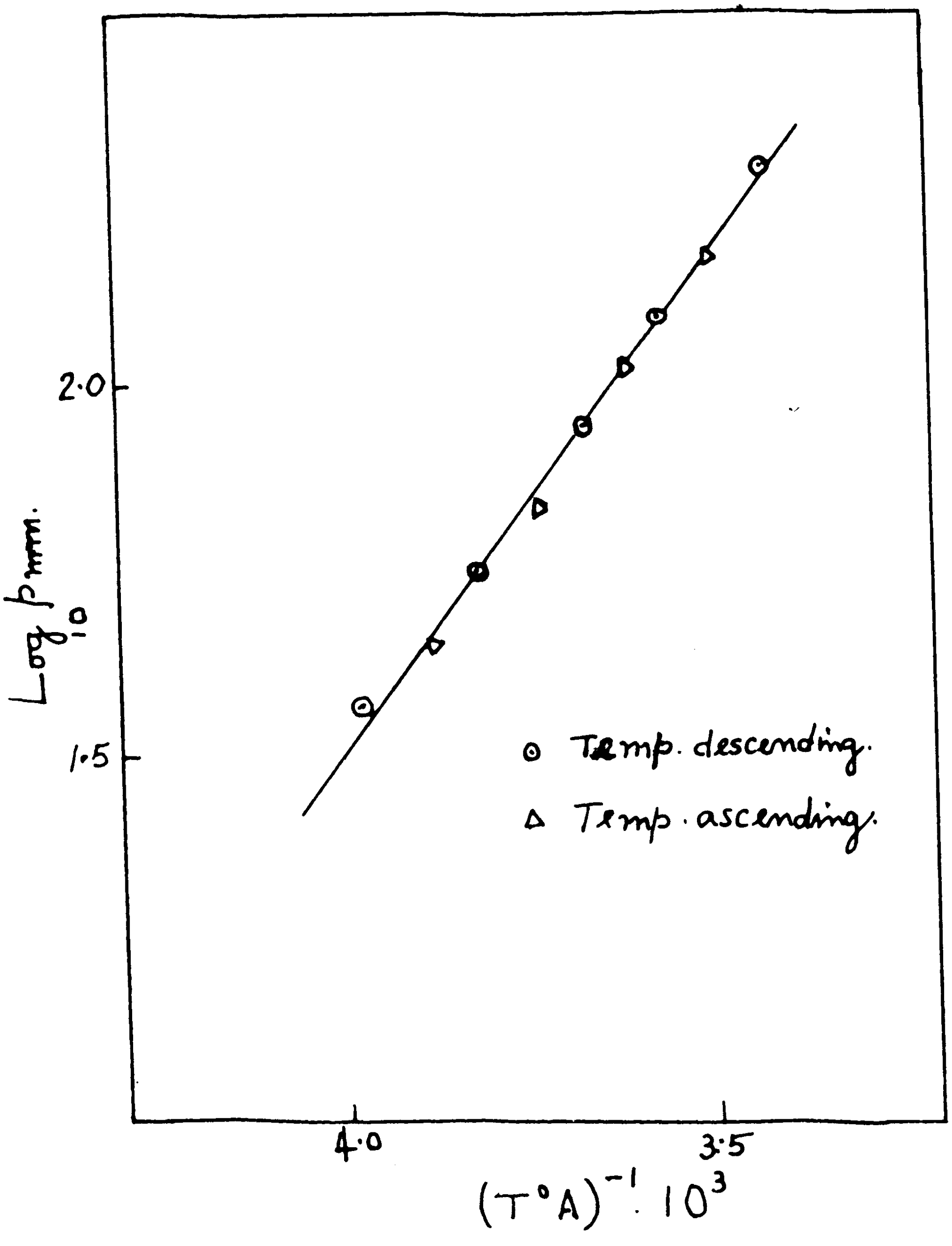
Temp. °C	Press. mm	$\log_{10}p_{mm}$	$\log_{10}p_{mm}$ Calcd.	$\Delta \log_{10}p_{mm}$
20.50	198.65	2.298	2.286	+0.012
13.00	145.63	2.163	2.164	+0.005
8.50	123.55	2.092	2.087	+0.003
4.00	104.20	2.018	2.008	+0.024
0.25	87.69	1.943	1.940	+0.063
-5.00	67.36	1.828	1.842	+0.005
-11.00	56.10	1.749	1.725	-0.014
-15.00	44.57	1.649	1.644	+0.010
-20.50	37.18	1.570	1.507	-0.001

SOME PHYSICAL CONSTANTS OF THE CHLOROFLUOROPHOSPHORANES

Table 8

Compound	M.P.	B.P.	Molar Heat of Vaporisation	Trouton's Constant	Ref.
PCl_4F	-63	67.0	-	-	(22)
	-59				(26)
PCl_3F_2	-65 to -70	63.4	6.54 K.Cals	18.6	(Present Work)
	-63				(26)
PF_3Cl_2	-125 to -130	7.1	5.66 "	20.2	(61)
	-124				(26)
PF_4CL	-132 ±3	-43.4	5.16 "	22.5	(34)

Fig. 3. The Vapour Pressure of PCl_3F_2.



(67°C) reported by Kolditz (22). However, no analytical figures were given for liquid covalent PCl_4F supposed to be formed by the pyrolysis of $(PCl_4)^+(PF_6)^-$ under reduced pressure, and in arsenic trichloride. The boiling point was given on the basis that a volatile product formed in the system had a condensation point of 67°C. This compound was presumed to be covalent PCl_4F since the solid, $(PCl_4)^+F^-$, was obtained from the arsenic trichloride solution in which the pyrolysis was carried out. Further examination of the pyrolysis of $(PCl_4)^+(PF_6)^-$ (46) in arsenic trichloride showed the formation of PF_5, PF_3Cl_2 and a solid of the composition PCl_3F_2 which was identified as a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$. It is known from the present work that covalent PCl_3F_2 transforms to a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$ of identical composition. This appears to show that covalent PCl_3F_2 is also likely to be formed in the system and the boiling point of 67°C reported by Kolditz may well be that of PCl_3F_2. It may be noted that covalent PCl_3F_2 was found to be the main product of the pyrolysis of $(PCl_4)^+F^-$ in arsenic trichloride (this thesis, Appendix)

The vapour pressure of PCl_4F reported by Booth and coworkers (17) is 275 mm at 75-80°C. This would suggest a much higher boiling point for PCl_4F than that given by Kolditz. In the light of these results it appears necessary that the physical constants of covalent PCl_4F should be reinvestigated.

Ideally the vapour pressure of compounds like PCl_3F_2 which may be attacked by mercury should be measured in an apparatus like a spiral gauge system which does not permit contact between the vapour and mercury. However, the results of vapour pressure measurements using a mercury manometer at descending and ascending temperatures show reasonably good reproducibility. Thisperhaps implies that the reaction of the mercury with PCl_3F_2 is not significant over the period of measurement that is about five to six hours. It is probable that a thin film of mercuric chloride or fluoride formed protects the mercury from further attack.

The vapour density of PCl_3F_2 vapour was measured by determining the mass of a known volume of vapour at known temperatures and pressures. This gave a value of 177 (theoretical value 175.4) which confirms the monomeric nature of the compound in the vapour phase.

The melting point of PCl_3F_2 was determined by a dropping weight apparatus and was found to be in the range -65 to -70°C (literature value, -63°C).

Liquid PCl_3F_2 was found to have a very low electrolytic conductance, the specific conductance being $< 10^{-7}$ ohm^{-1} cm^{-1} showing the molecular nature of the compound in the liquid phase.

Some physical constants of PCl_3F_2 are given in Table 8 along with those of the other members of the series for comparison.

TRANSFORMATION OF COVALENT PCl_3F_2 TO THE IONIC FORM

(a) **Transformation in the liquid phase.** Liquid PCl_3F_2 slowly deposits a white solid at room temperature and the transformation goes to completion in about three to four days. However, this process is very slow at low temperature and hence PCl_3F_2 is always preserved by storage at -78°C. This temperature was found to be satisfactory to prevent the formation of the solid to any appreciable extent.

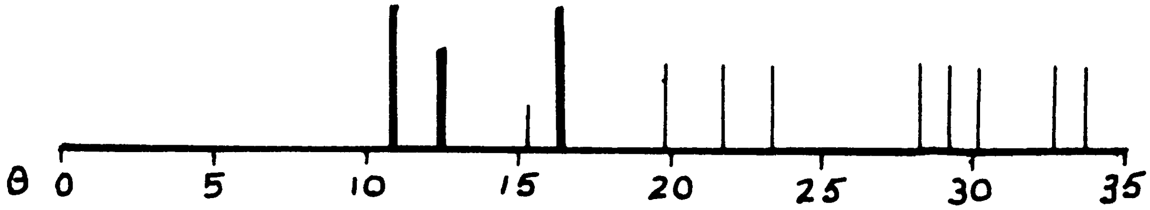
A sample of liquid PCl_3F_2 was stored in a sealed tube and kept at room temperature until the whole of it changed to solid form. The tube was then broken open under vacuum without exposure to moisture. Small traces of volatiles were obtained shown by I.R. examination to be only POF_2Cl and $POCl_2F$. The compound has thus completely transformed into a white solid product which was examined by chemical analysis and X-ray powder technique.

Table 9.

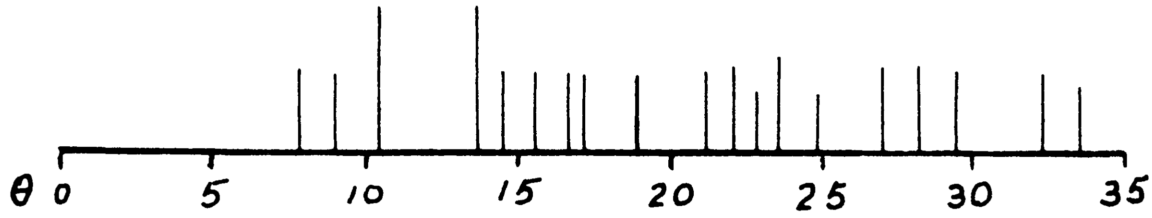
X-RAY POWDER DIAGRAM OF THE WHITE SOLID OBTAINED BY STORAGE OF $POCl_3F_2$

θ	Intensity
6.5	w
7.5	w
8.9	w
10.2	s
10.7	vs
12.5	m
13.6	m
15.1	vw
15.6	vw
16.6	vs
17.1	w
18.7	w
19.9	w
21.8	m
23.2	w
28.2	w
29.3	w
32.4	w
33.8	w

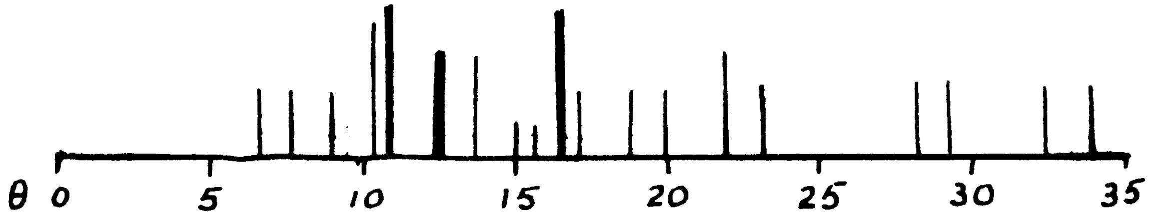
Fig.4. X-Ray Powder Diagram of the white Solid obtained by Storage of PCl_3F_2



$(PCl_4)^+F^-$



$(PCl_4)^+(PF_6)^-$



The phosphorus and chlorine content was found to be 17.6% and 61.3% respectively corresponding to a composition of PCl_3F_2 (Calcd. for PCl_3F_2, P, 17.7%; Cl, 60.7%). A solid of this composition could exist in one of the many ionic forms containing cations of the form $(PCl_nF_{4-n})^+$ and anions of the form $(PCl_nF_{6-n})^-$. The X-ray powder photograph of the solid showed it to be a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$ (Fig. 4). The presence of $(PF_6)^-$ ion was confirmed by precipitating it as the Nitron compound which gave a melting point of 230-231°C (literature value: 229°C). Further the I.R. spectrum of this material was identical to that of the Nitron-$(PF_6)^-$ compound reported earlier (46). In the light of these results the overall transformation can be represented by the equation

$$4\ PCl_3F_2 \longrightarrow 2(PCl_4)^+F^- + (PCl_4)^+(PF_6)^-.$$

It may be noted that the solid product obtained in similar circumstances from PF_3Cl_2 is also a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$. However, PF_5 is formed in the vapour phase whereas this is not present among the products from PCl_3F_2.

(b) Transformation in acetonitrile solutions. The formation of the ionic solid which is a mixture of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$, from liquid PCl_3F_2 on storage at room temperature suggested that the same mode of rearrangement might take place in a polar solvent. $(PCl_4)^+F^-$ (22) and $(PCl_4)^+(PF_6)^-$ (44) have been already shown by Kolditz to form conducting solutions in acetonitrile, the molar conductances of these compounds being 40 ohm^{-1} cm^2 $mole^{-1}$ in 0.06-0.1M solution and 90.9 ohm^{-1} cm^2 $mole^{-1}$ in 0.042M solution respectively. For this reason it was thought that conductometric measurements of solutions of PCl_3F_2 in acetonitrile at various time intervals would be a useful line of attack on the transformation of the compound to the ionic form.

Three separate solutions of PCl_3F_2 in acetonitrile of different concentrations were studied conductometrically at $18 \pm 1^\circ C$. A specially designed all-glass apparatus incorporating platinum electrodes was used for this purpose to enable the manipulation of solutions without coming into contact with moisture. The results of these experiments are summarised in Table 10 and the plots of molar conductance versus time are shown in Fig. 5. In all the three cases a slow increase in conductance reaching a saturation value was observed. The final steady value increased slightly with decreasing concentration of the solution. It may be noted that the time taken to attain the maximum value of conductance varies with the concentration of the solution that is increases with dilution. Similar studies on PF_3Cl_2 by Kennedy and Payne (46, 61) gave identical results except for the fact that in this case the time taken to reach the saturation conductance value increases with the concentration of the solution.

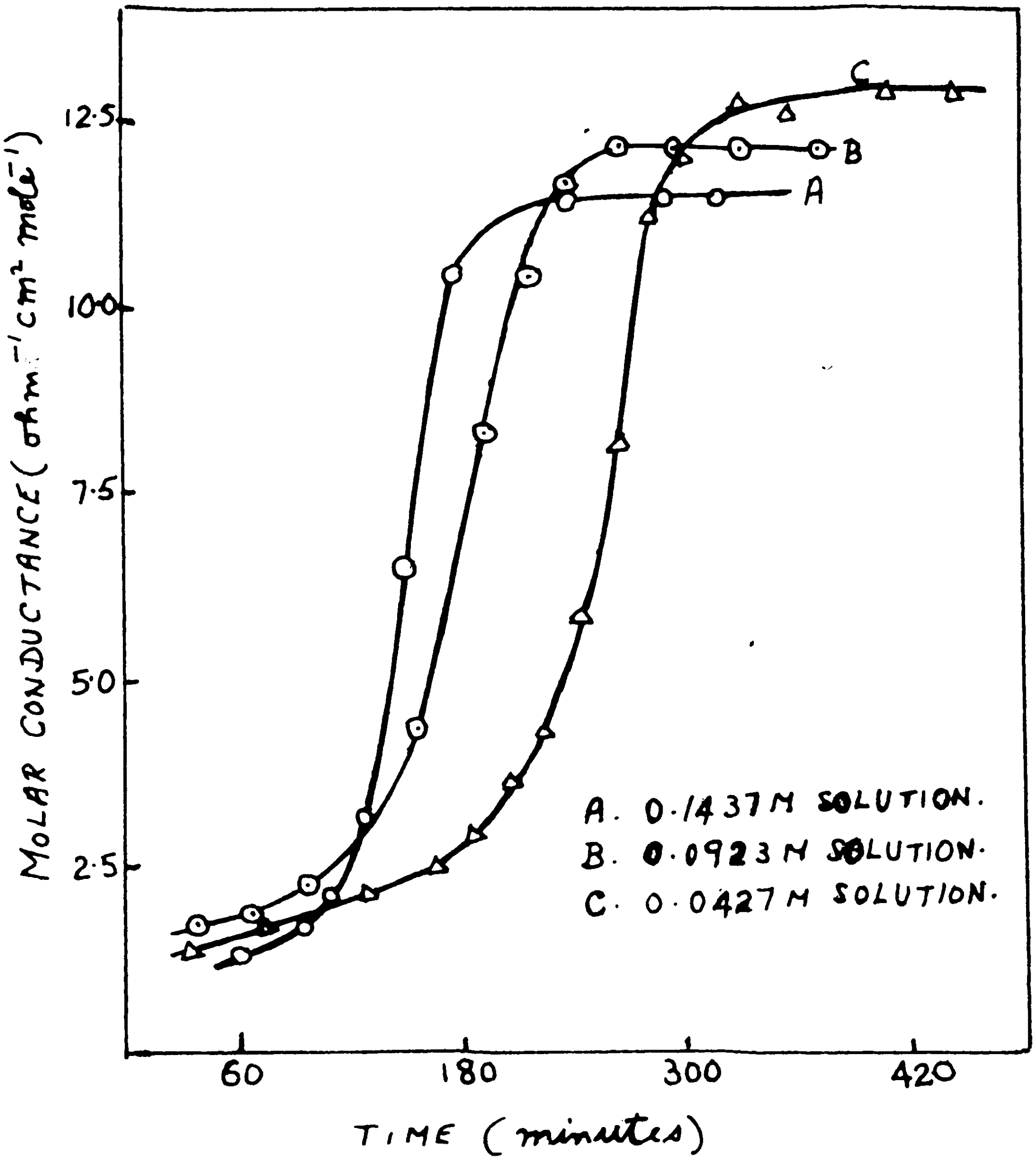
The magnitude of the steady value of molar conductance attained in acetonitrile solutions of PCl_3F_2 is very low when compared with the corresponding values of $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$ in the same solvent. This straightaway eliminates the possibility of a complete transformation to the above ionic species. An alternative process that could take place is a dissociation of the type

Table 10.

CONDUCTANCE OF PCl_3F_2 IN ACETONITRILE SOLUTIONS

0.1437M soln.		0.0837M soln.		0.04273M soln.	
Time (mins.)	Λ_m	Time (mins.)	Λ_m	Time (mins.)	Λ_m
15	0.56	15	0.69	10	1.03
21	0.77	25	1.21	20	1.22
36	1.08	41	1.68	35	1.35
63	1.34	70	1.91	60	1.49
80	1.43	100	2.22	76	1.60
95	1.60	159	4.29	105	1.79
112	2.11	195	8.33	133	2.02
129	3.08	220	10.41	168	2.49
152	6.46	240	11.65	187	2.98
177	10.40	265	12.16	208	3.64
241	11.44	298	12.06	225	4.34
290	11.44	330	12.06	244	5.85
320	11.44	375	12.06	266	8.16
				285	11.21
				301	11.91
				331	12.82
				358	12.24
				388	12.24
				413	12.80
				448	12.80

Fig. 5. Conductance of PCl_3F_2 in Acetonitrile Solutions.



$PX_5 \longrightarrow PX_3+X_2$. This has been considered by Kennedy (46) in the case of PF_3Cl_2 solutions in acetonitrile. However, the author observed that the conductance of PF_3 and halogens in acetonitrile is too low to account for the experimentally observed molar conductance of PF_3Cl_2 that is 9.63 ohm^{-1} cm^2 mole^{-1} at 0.05-0.09M. concentration in the same solvent. A similar argument rules out the possibility of a dissociation process operative in the case of PCl_3F_2.

Gradual drift in conductance with time in acetonitrile solutions has also been observed by Harris and Payne (33) in the case of phosphorus pentabromide, and by Popov and Skelly (63) in the case of interhalogen compounds. The "conductance drift effect" in acetonitrile solutions of iodine monochloride has been explained in terms of a slow ionic dissociation of the type.

$$2ICl \rightleftharpoons I^+ + ICl_2^-.$$

It is possible that in acetonitrile solutions of PCl_3F_2 a slow ionisation process leading to the establishment of a dissociation equilibrium exists.

This can be represented as follows,

$$4PCl_3F_2 \rightleftharpoons 2(PCl_4)^+F^- + (PCl_4)^+(PF_6)^-.$$

The rate of transformation of PCl_3F_2 in acetonitrile (as seen from the conductance-time graph) indicates a reaction of order greater than unity since the time taken to attain identical values of molar conductance varies inversely with the initial concentration of the solution.

(c) Transformation in the vapour phase. The vapour phase transformation of PF_3Cl_2 has been studied by Kennedy (46) who found it to be a zero order reaction initiated catalytically on the glass surface of the apparatus. It was of interest to investigate on similar lines the behaviour of PCl_3F_2.

A preliminary experiment was carried out by enclosing the vapour in a glass bulb carrying a mercury manometer to record pressure readings at suitable time intervals. The vapour was maintained at 25°C throughout the experiment. The results obtained are given in Table 11 and Fig. 6. It was observed that the pressure dropped more steeply in the initial stages, say over a period of twelve days and thereafter the change was much slower. After storage for about two months the pressure was reduced to about 65% of the original value and a white solid was deposited on the walls of the bulb. The residual vapour showed the presence of SiF_4, PF_5, PF_3Cl_2 and traces of PCl_2F, POF_2Cl and $POCl_2F$. Besides these some new peaks appearing at 998 cm^{-1} (vs), 992 cm^{-1} (s) and 695 cm^{-1} (m) were observed. POF_3 shows an absorption at 999 cm^{-1}, however, this appeared to be absent in the spectrum since the P-O absorption at around 1425 cm^{-1} was not observed. As will be mentioned later, these peaks are attributable to PF_4Cl.

One striking difference between PF_3Cl_2 and PCl_3F_2 in respect of the behaviour of their vapour phase transformation is the linear dependence of pressure on time in the former case and the non-linear curve obtained in the latter case. The presence of mercury in the second instance was thought likely to be responsible for this. For this reason the above experiment was repeated in an all glass apparatus incorporating a spiral gauge so that contact

Table 11

THE VAPOUR PHASE TRANSFORMATION OF PCl_3F_2

In the presence of mercury		In the absence of mercury	
Time hrs.	Pressure mm.	Time hrs.	Pressure mm.
6.0	97.5	5.0	117.8
13.0	95.5	20.5	112.9
23.5	91.5	48.5	107.3
34.2	90.0	72.5	103.7
37.0	89.5	98.0	101.1
49.0	88.5	150.5	97.6
73.5	84.0	222.0	93.4
97.5	82.0	287.5	89.2
122.0	80.3	341.0	86.7
146.0	78.0	386.0	84.8
169.5	76.5	457.0	82.5
218.5	74.3	530.0	80.6
274.5	72.5		
411.0	70.0		
515.0	68.5		
960.0	66.5		
1500.0	64.5		

Fig. 6. The Vapour Phase Transformation of PCl_3F_2.

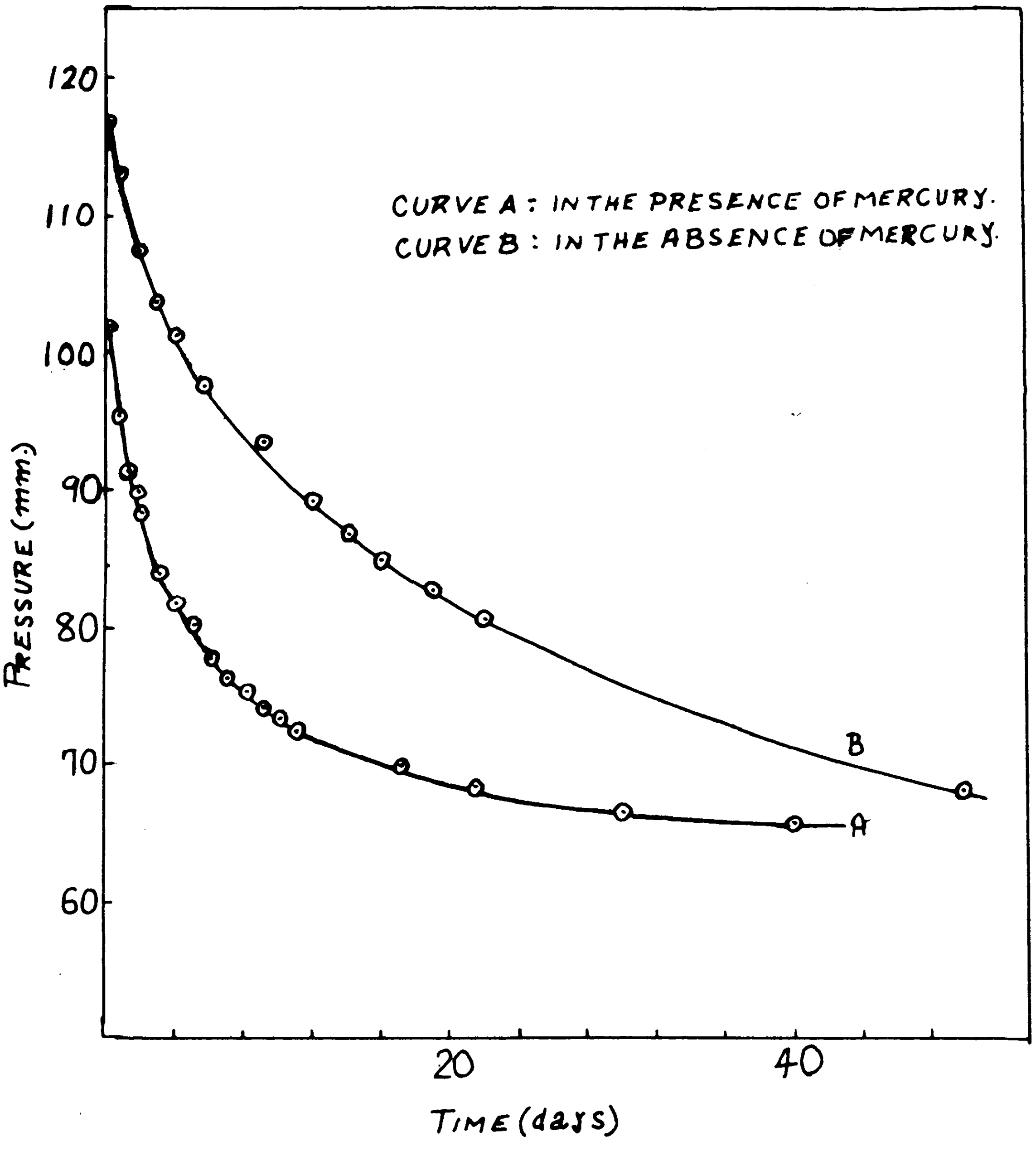
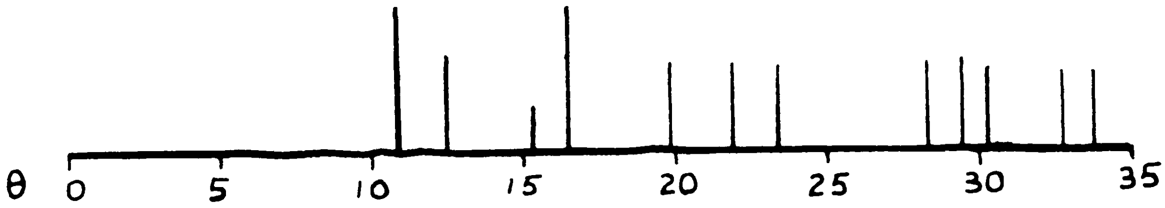
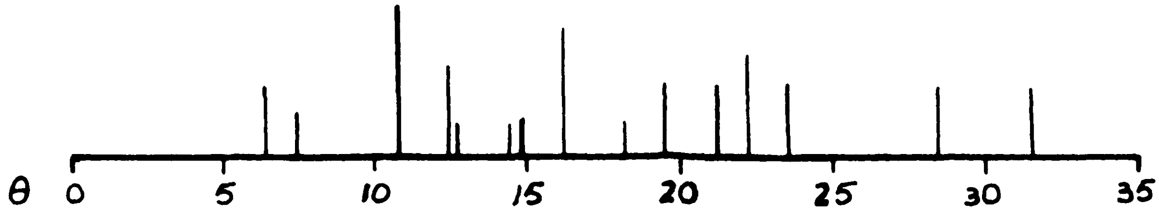


Fig. 7. X-Ray Powder Diagram of the white Solid obtained by Storage of PCl_3F_2 Vapour.



$(PCl_4)^+F^-$



between PCl_3F_2 vapour and mercury was prevented. Table 11 shows the pressure readings at various intervals of time. The pressure-time curve is plotted in Fig. 6. Even though there is no close quantitative agreement between the two curves obtained in the presence and absence of mercury the qualitative picture is the same in both cases. About 56% drop in pressure was observed in the second experiment as compared to about 65% drop in pressure in the first experiment. The deposition of a white solid on the walls of the storage vessel occurred as before.

The amount of solid formed was small. Hence it was possible to get only an X-ray powder photograph which was almost identical to that of $(PCl_4)^+F^-$ (Fig. 7).

The infrared spectrum of the residual vapour showed the presence of SiF_4, PF_5, PF_3Cl_2 and traces of POF_2Cl. As in the last experiment some new peaks at 998 cm^{-1} (s), 992 cm^{-1} (m, sh) and 695 cm^{-1} (w) were observed. The sample was then fractionated through traps maintained at -78°C, -98°C, -160°C and -196°C. The -196°C fraction gave an I.R. spectrum with absorption at the following frequencies:

Spectrum I.

cm^{-1}	cm^{-1}	cm^{-1}
1032 vs	950 vs	825 w
1025 vs	942 vs(sh)	702 w
998 s	928 s(sh)	695 w
991 m(Sh)	907 s	674 w
958 vs	900 s	660 w

The above spectrum resembles that of PF_5 except for the additional bands around 1000 cm^{-1} and 900 cm^{-1} and the absence of the strong PF_5 peak at 875 cm^{-1} (the band at 1032 cm^{-1} is due to SiF_4). This points to the fact that the spectrum is not due to PF_5. Thus the appearance of new peaks in the P-F region suggests the presence of a chlorofluorophosphorane which could be only PF_4Cl since the I.R. spectra of the other members of the series are well established (27).

In a private communication Holmes and Carter have given the details of the I.R. spectrum of PF_4Cl which they synthesised recently, as shown below:

Spectrum II

cm^{-1}	cm^{-1}	cm^{-1}
1606 w	945 s	859 m
1415 w	927 vs (sh)	817 w
1063 w	921 vs	692 s
1026 s	903 vs	672 m
993 vs	895 vs	665 m
954 w	869 m	

A comparison of spectra I and II shows a great deal of similarity between them. However, there are some notable disagreements as well. For example the absorption at 958 cm^{-1} (s) in spectrum I is not present in spectrum II. Similarly spectrum I does not contain peaks at 869 cm^{-1} (m) and 859 cm^{-1} (m) which are present in spectrum II. Further the absorption at 695 cm^{-1} is weak in spectrum I whereas there is a strong peak at 692 cm^{-1} in spectrum II. Holmes and Carter suggested the peak at 993 cm^{-1} as being due to POF$_3$ impurity. However, our spectrum shows no indication of the presence of POF$_3$ and the strong peak at 998 cm^{-1} is still present in it. The variation of the nature of the spectrum with pressure could not be studied since the compound in question was available only in small amounts.

The results of the storage experiment may be summarised as follows:

PCl_3F_2 (2.002 m.moles)
Storage for two months

Solid
$(PCl_4)^+F^-$
(0.849 m.moles, by difference)

Volatile Compounds
(1.173 m.moles)

PF_4Cl (?) 0.1109 m.moles
$POF_3+PF_3Cl_2+PF_5$ 0.078 m. moles
PCl_2F 0.5834 m.moles
POF_2Cl 0.3 m.moles

Identification of PCl_2F was based on the absorption at 830 cm^{-1} (60) and the temperature (-95°C) at which it is retained under vacuum (26). The appearance of PCl_2F would be expected to be accompanied by the formation of ClF or F_2 as follows:

$$PCl_3F_2 \longrightarrow PCl_2F+ClF$$
$$PF_3Cl_2 \longrightarrow PCl_2F+F_2$$

Out of these only ClF can be detected in the I.R. spectrum and it has been found to absorb at 786 cm^{-1} (64). In the present work however, ClF was not detected in the I.R. spectrum of the residual vapour from the storage experiment. This may be a question of pressure which could not be increased beyond 10 mm. whereas in the reported spectrum of ClF measurement was made at pressures of 10-15 cm. of mercury in a cell of the same path length.

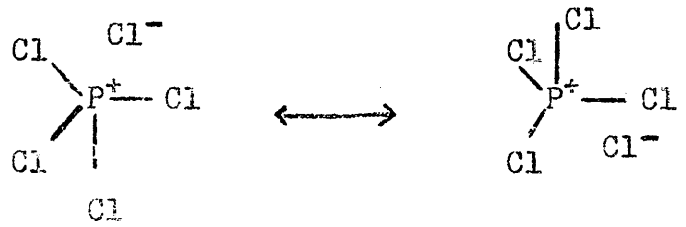
It may be mentioned that a strong band at 830 cm^{-1} was observed by Kennedy (46) in the I.R. spectrum of the residual vapour obtained on storage of PF_3Cl_2 at room temperature even though this was not assigned to PCl_2F. Surprisingly in the present work PCl_2F appears to be the major component of the residual vapour. This can not be explained unless it is assumed that the halogen formed is consumed by a reaction of some kind. Since the system is completely devoid of mercury or tap grease the only reaction which appears possible is attack on glass by the halogen to form compounds like $SiCl_4$, SiF_4 and oxygen.

Discussion of the experimental results. The transformation of liquid chlorofluorides of phosphorus(V) to solids was first noticed by Booth and coworkers (17) when they obtained PCl_3F_2 and PCl_4F by the chlorination of $PClF_2$ and PCl_2F respectively. Similar observations have been made by other workers (22, 26, 61).

Kolditz (65) studied the kinetics of transformation of PCl_4F and the results were interpreted in terms of first order kinetics. However, these results are suspect since the compound he studied may not in fact have been PCl_4F. This suspicion is confirmed by the repetition of the method of preparing PCl_4F used by Kolditz (65), which showed PCl_3F_2 as the main fraction of the products with only very small amount of PCl_4F being formed (this thesis, Appendix). Kennedy (46) studied the stability of PF_3Cl_2 at room temperature by methods analogous to those used in the present work.

The mechanism operative in the transformation of the covalent chlorofluorides of phosphorus (V) to the ionic modifications are likely to be very complex in nature. No direct experimental evidence has been obtained so far, which might allow us to predict with certainty any mechanism as exclusively the most probable. However, some of the following mechanisms may be considered.

(i) Ionisation mechanism. Kolditz (65) considered an ionisation mechanism for the transformation of covalent PCl_4F to the ionic solid $(PCl_4)^+F^-$. This was based on the formulation of phosphorus pentachloride molecule as the resonance hybrid



by Siebert (25) who thus explained the greater bond lengths of the axial bonds relative to those in the equatorial position. According to Kolditz a similar ionisation process takes place in the case of PCl_4F, the molecular form of which has fluorine in an axial position (27). Kolditz who expressed his views before the structure of PCl_4F was known assumed that fluorine was in an equatorial site but underwent migration to an axial position before ionisation.

Transformation of PCl_3F_2 can not be as direct and must involve several steps, displacement reactions as well as ionisations being involved. A possible scheme is the following:

$$
\begin{array}{lcl}
PCl_3F_2 & \rightleftharpoons & (PCl_3F)^+F^- \\
PCl_3F_2+F^- & \rightleftharpoons & PF_3Cl_2+Cl^- \\
(PCl_3F)^++Cl^- & \rightleftharpoons & PCl_4F \\
PCl_4F & \longrightarrow & (PCl_4)^+F^- \\
PF_3Cl_2+F^- & \rightleftharpoons & PF_4Cl+Cl^- \\
PF_4Cl+F^- & \rightleftharpoons & PF_5+Cl^- \\
(PCl_4)^+F^-+PF_5 & \rightleftharpoons & (PCl_4)^+(PF_6)^-
\end{array}
$$

In the above picture ionisation of the molecular PCl_3F_2 giving rise to Cl^- ions was not considered since ionisation should be favoured at the axial sites which are occupied by fluorine atoms. However, an intramolecular exchange leading to exchange between fluorine and chlorine followed by ionisation of chloride ion should not be completely overruled in view of the labile nature of groups attached to five-connected phosphorus atom. The ionisation scheme outlined above is by no means complete. Various other interactions, for example between the cations and molecular phosphorus chlorofluorides may be considered to take place as alternative routes to the final products.

It has been shown by I.R. examination that on storing liquid PCl_3F_2 at -78°F for periods over a week traces of PF_3Cl_2 and PCl_4F are formed and it is worth noting that these appear as intermediates in the above scheme.

The presence of traces of moisture has been found to have a catalytic effect on the covalent ionic transformation of PF_3Cl_2 (46). This may be true of PCl_3F_2 as well. The result of the reaction between moisture and the phosphorus (V) chlorofluoride is to produce HCl or HF, and the Cl^- and F^- ions thus formed can take part in the type of reactions described above, catalysing the process. In the absence of any externally introduced ions, the transformation is slow possibly because the equilibrium concentrations of the ionic species formed in the system under such conditions are small.

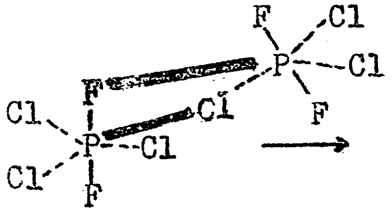
(ii) Molecular mechanism. This has been considered by Kennedy (46) as a possible mechanism for the transformation of PF_3Cl_2 to $(PCl_4)^+F^-$ and $(PCl_4)^+(PF_6)^-$. A similar approach may be used in the case of PCl_3F_2. This would involve the decomposition of PCl_3F_2 to molecular species which recombine to form other chlorofluorophosphoranes. The process repeats itself until stable products result. In the transformation of PCl_3F_2 the following reactions may be considered:

$$\begin{array}{rcll}
PCl_3F_2 & \rightleftharpoons & PCl_3+F_2 & \ldots\ldots\ldots\ldots 15 \\
 & \rightleftharpoons & PCl_2F+ClF & \\
 & \rightleftharpoons & PClF_2+Cl_2 & \\
PCl_3+Cl_2 & \longrightarrow & PCl_5 & \\
PCl_2F+Cl_2 & \longrightarrow & PCl_4F & \\
PCl_4F & \longrightarrow & (PCl_4)^+F^- & \\
PClF_2+ClF & \longrightarrow & PF_3Cl_2 & \\
PF_3Cl_2 & \longrightarrow & PF_3+Cl_2 & \\
PF_3+F_2 & \longrightarrow & PF_5 & \\
PF_3Cl_2+ClF & \longrightarrow & PF_4Cl+Cl_2 & \\
PF_4Cl+ClF & \longrightarrow & PF_5+Cl_2 & \\
(PCl_4)^+F^-+PF_5 & \longrightarrow & (PCl_4)^+(PF_6)^-. &
\end{array}$$

In the liquid phase PF_3Cl_2 and PCl_4F have been identified as products of transformation of PCl_3F_2 and there is reason to believe that PF_4Cl is formed in the vapour phase. However, PCl_5 has never been identified among the products. This could mean that the dissociation scheme represented by equation 15 does not take place. Since the fluorine atoms are at the apices of the trigonal bipyramidal molecule of PCl_3F_2 any intramolecular dissociation may not yield fluorine readily, unless some exchange takes place within the molecule itself between chlorine and fluorine atoms. It is signigicant that PCl_2F has been observed in the I.R. spectrum of the residual vapour obtained on storage of PCl_3F_2 at 25°C.

Mass spectrometric evidence for the existence of dimeric units of phosphorus pentachloride and $(PCl_4)^+(PCl_5F)^-$ in the vapour phase led Kennedy (46) to postulate a different form of molecular mechanism involving associated species of trigonal bipyramidal molecules containing mixed halogen bridges which could give rise to the desired products by repeated dissociation and association. The following scheme may be suggested for PCl_3F_2:

$2\,PCl_3F_2 \longrightarrow$



$\longrightarrow PCl_4F + PF_3Cl_2$

$$2PF_3Cl_2 \longrightarrow P_2F_6Cl_4 \longrightarrow PCl_3F_2 + PF_4Cl$$

$$2PF_4Cl \longrightarrow P_2F_8Cl_2 \longrightarrow PF_3Cl_2 + PF_5$$

$$PCl_4F \longrightarrow (PCl_4)^+F^-$$
$$(PCl_4)^+F^- + PF_5 \longrightarrow (PCl_4)^+(PF_6)^-.$$

The dotted lines in the above spatial description of PCl_3F_2 molecule signify the equaterial bonds. The halogen bridges are denoted by thick lines. The chlorofluorophosphoranes that is PCl_3F_2, PF_3Cl_2 and PF_4Cl formed undergo further aggregation and breakdown until the whole of the material changes over to the end products. Studies on the vapour phase stability of PCl_3F_2 show that PF_3Cl_2, PF_5 and perhaps PF_4Cl are among the products.

The ionic and molecular mechanisms considered here show that they lead to identical intermediate products thus making it difficult to choose between the two alternatives. The effect of traces of moisture in catalysing the transformation process favours an ionic mechanism or at least a mechanism involving polar species and this is further supported by the extreme tendency to form species in which phosphorus is quadruply connected. The ease with which reorganisation processes take place among phosphorus compounds might play a significant role in the formation of cations of various compositions by the ionisation process. On the other hand the identification of PCl_2F among the products formed on storage of PCl_3F_2 vapour at room temperature and the evidence for the existence of dimers of $(PCl_4)^+(PCl_5F)^-$ and PCl_5 in the vapour phase favour a molecular mechanism.

It is more probable that the ionic mechanism operates in the liquid phase. As regards the molecular mechanisms it is difficult to make any distinction between the liquid phase and the gaseous phase. The formation of the observed products by the molecular mechanism involving dimers requires the incidence of mixed halogen bridges. This is however a novel phenomenon and it is open to question until further evidence is available.

THE REACTION BETWEEN PCl_3F_2 AND DIMETHYL AMINE.

The reaction between PF_3Cl_2 and ammonia leading to the formation of $PF_3(NH_2)_2$ was reported by Moissan (5) and this was reinvestigated by Kennedy(46) quite recently. Only solid products were obtained, which consisted of a mixture of ammonium chloride and other nonvolatile material, no ammonium fluoride being present. No definite conclusions were reached as to the exact nature of the other components of the mixture, however it appeared to establish the difference in reactivity of the fluorine and chorine in the PF_3Cl_2 molecule.

A similar reaction between PCl_3F_2 and ammonia might lead to more complex materials although $(PNF_2)_n$ polymers could result if the condensation went sufficiently far. It was thought that the use of a secondary amine in this reaction would make the picture less complicated because of the presence of only one replaceable hydrogen provided, of course, that no migration of the substituent groups on the nitrogen atom took place. Further, reactions of the above type with mixed chlorofluorophosphoranes have not so far been looked at. An investigation of the reaction between PCl_3F_2 and dimethyl amine was therefore carried out.

It was desired that only one halogen atom on the phosphorus was replaced by the amino group and for this purpose the amine to phosphorus mole ratio was kept at 2:1. The reactants were condensed together using liquid nitrogen as coolant and then allowed to warm up slowly. A white solid resulted and there was only a very small residual pressure corresponding to about 1% of the original amount of amine added, after completion of the reaction; the amount of material volatile in vacuum was very small indeed.

The X-ray powder diagram of the solid is set out in Table 12. It was found that lines due to $(CH_3)_2 NH.HCl$ were present in it. Thus the chlorine atom of the PCl_3F_2 molecule is displaced by the amino group rather than a fluorine atom. The extra lines in the powder diagram of the solid must arise from other components in the mixture. The overall reaction may be represented by the following equation:

$$PCl_3F_2 + 2\,(CH_3)_2\ NH \longrightarrow (CH_3)_2\,N\,PCl_2\,F_2 + (CH_3)_2\,NH.\,HCl.$$

Further, rearrangements of the following type are conceivable:

TABLE 12. X-RAY POWDER DIAGRAM OF THE SOLID PRODUCT OF THE REACTION BETWEEN PCl_3F_2 AND $(CH_3)_2NH$.

θ	$(CH_3)_2NH.HCl$	θ	$(CH_3)_2NH.HCl$
5.8 vw		18.6 vw	
7.5 m			19.1 vw
8.2 s		19.6 vw	19.6 w
8.9 s	8.9 s	20.0 vw	20.1 vw
10.6 vw	10.8 vw	20.7 vw	20.7 vw
11.2 vw	11.2 vw	21.2 vw	21.3 vw
11.7 vw		22.0 vw	21.9 vw
12.2 vs	12.2 vs	22.6 vw	22.6 vw
13.4 vw	13.3 vw	23.9 vw	24.0 vw
14.4 vw	14.2 vw	24.4 vw	24.4 vw
15.2 s	15.2 s	24.9 vw	25.0 vw
15.6 vw		25.4 vw	25.5 vw
16.0 m	16.0 m	26.2 vw	26.4 vw
16.3 vw	16.3 vw	28.1 vw	28.0 vw
17.4 m	17.3 m	30.6 vw	30.7 vw
17.9 vw	18.0 vw	33.5 vw	33.5 vw

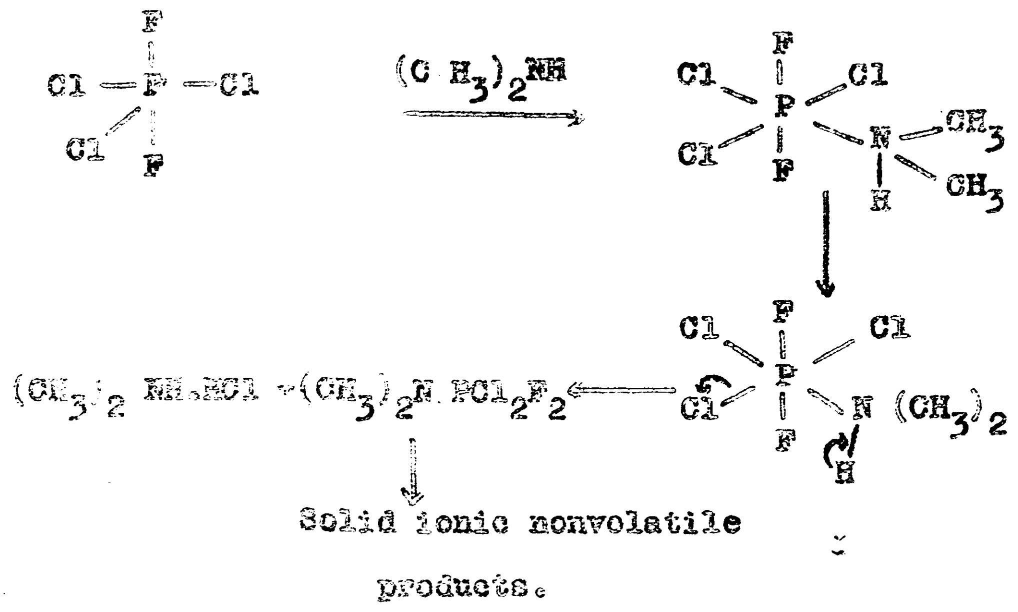
$$2(CH_3)_2NPCl_2F_2 \longrightarrow \left[\left\{(CH_3)_2N\right\}_2PCl_2\right]^+ \left[PCl_2F_4\right]^- .$$

$$3(CH_3)_2NPCl_2F_2 \longrightarrow \left[(CH_3)_2N - PCl_3\right]^+ \left[PF_6\right]^- + \left[(CH_3)_2N\right]_2PCl_3 \quad \text{---------} \quad 16$$

$$\left[(CH_3)_2N\right]_2PCl_3 \longrightarrow \left[\left\{(CH_3)_2N\right\}_2PCl_2\right]^+ \quad Cl^-$$

which would account for the absence of other volatile products. The presence of $(PF_6)^-$ ion was detected in the solid product and this would suggest a rearrangement such as that given by equation 16; however, in reactions of this type a number of processes usually occur together and it is rarely that a single product is encountered.

The displacement of chlorine from PCl_3F_2 by the dimethyl amino group runs parallel to the observation in the case of the reaction between ammonia and PF_3Cl_2; that is no simple volatile compounds are formed. It is tempting to explain the substitution for chlorine rather than fluorine observed in the above reactions on the basis of the greater strength of P-F bonds over that of P-Cl bonds, but this is not likely to be the controlling factor since other bonds are formed and the nature of the halogen displaced may be determined by the ability of an attacking group to form a suitable transition complex; this might favour the equatorial position since an octahedral intermediate complex could be visualised:



However, in the case of PF_3Cl_2 the effect of the greater bond strength of the P-F bond relative to that of the P-Cl bond is emphasised because one fluorine is present in the equatorial position.

No attempts were made to separate the solid into its components by sublimation or any other procedure such as the use of a solvent. Further investigation of this reaction is required to establish the nature of the products.

REACTIONS BETWEEN PCl_3F_2 AND DONOR MOLECULES.

The Lewis acid behaviour of phosphorus pentafluoride and phosphorus pentachloride has been the subject of considerable investigation. Combination of PF_5 with various bases containing nitrogen, oxygen and sulphur donor groups such as amines, nitriles, ethers, esters and sulphoxides has been well established (48, 52). In most instances a 1 : 1 complex is formed. The formation of an interesting set of compounds in the series $PF_5 \cdot (NH_3)_n$ where n= 1,2 and 3 has been postulated from evidence based on manometric measurements but their nature has not been established (48). The stability of PF_5 complexes has been found to be dependent on steric factors (52) and direct evidence for effects of steric hindrance has been obtained. For example $PF_5 \cdot O(C_2H_5)_2$ is largely dissociated at 25°C whereas $PF_5 \cdot O(CH_2)_4$ can be distilled at 116°/0.15 mm pressure. Similarly complexes with triethyl amine and 2,4,6-trimethyl pyridine showed only partial association at 25°C. F^{19} nuclear magnetic resonance measurements on the 1 : 1 complexes of PF_5 with Lewis bases are fully consistent with an octahedral model.

The situation with PCl_5 is somewhat less clear.

Trost (49) first reported the formation of $PCl_5 . 2.5 (C_2H_5)_3N$ and $PCl_5 . (C_2H_5)_3N$. A reinvestigation of this system by Holmes and Bertaut (50) showed, however, that no addition compound was formed. On the other hand PCl_5 was reduced to PCl_3 by reaction with both triethyl amine and trimethyl amine. These authors formulated the other products formed as $(C_2H_5)_3NCl_2$ and $[(CH_3)_3N]_2 Cl_2$ respectively in the two cases although no direct evidence for these species was obtained. Beattie and Webster (51) carried out the reaction between PCl_5 and $(C_2H_5)_3N$ in Carbon disulphide solution and obtained a solid which was identified as $(C_2H_5)_3N.HCl$. A direct addition compound was obtained by the reaction between phosphorus pentachloride and trimethyl phosphine in bromobenzene solution. This has the composition $PCl_5.1.97(CH_3)_3P$ (50). Reactions of a similar type have been carried out in the case of chlorofluorophosphoranes by Holmes and Gallagher (26). They prepared the 1 : 1 pyridine adducts of PCl_4F, PCl_3F_2 and PF_3Cl_2 and by calorimetric measurements (66) of these complexes in nitrobenzene solution the order of Lewis acid strength was given along with those of $SbCl_5$ and PCl_5 as $SbCl_5 > PCl_3F_2 > PCl_4F > PCl_5$. The F^{19} n.m.r. spectra of the complexes $C_5H_5N.PCl_4F$ and $C_5H_5N.PCl_3F_2$ in nitrobenzene showed a doublet arising from spin - spin coupling between phosphorus and fluorine. Increased upfield shifts relative to those of the pure phosphoranes suggested electron pair donation from nitrogen to phosphorus (26).

In view of the acceptor ability of PCl_3F_2 to form stable complexes with bases like pyridine, it was considered worthwhile exploring similar reactions with other donor molecules. The addition of triethyl amine and triethyl phosphine was chosen as it offered the possibility of comparing a $N \rightarrow P^{V}$ to $P^{III} \rightarrow P$ bond, and these bases are readily available as moderately volatile liquids at room temperature, which should favour the investigation.

1. Reaction between PCl_3F_2 and triethyl amine.

a) Reaction between PCl_3F_2 and excess triethyl amine.

Preliminary work showed that direct reaction between PCl_3F_2 and triethyl amine in the absence of any solvent was exothermic. For this reason an excess amount of the amine was employed to reduce the effect of the heat of reaction. Thus PCl_3F_2 was condensed in several stages at $-78^{\circ}C$ into an excess of triethyl amine to give an overall 1 : 3·5 moleratio. Repeated warming up and cooling at $-78^{\circ}C$ resulted in the formation of a white solid. The excess amine was removed by pumping at room temperature when a buff coloured solid product was obtained; however this was contaminated with a small amount of a yellow material. From the weight of the solid product, assuming that all the PCl_3F_2 had reacted, a ratio of 1 : 1.01 was obtained for $PCl_3F_2:(C_2H_5)_3N$. The analysis of the solid gave Cl, 26.8%; P, 5.5%; calculated for $PCl_3F_2 \cdot (C_2H_5)_3N$, Cl, 38.5%; P, 11.2%; calculated for $PCl_3F_2 \cdot 2(C_2H_5)_3N$, Cl, 28.2%; P, 8.2%. Thus on the basis of analysis the composition of the solid does not correspond to any addition compound, although the weight of product was correct for a 1 : 1 compound. The volatiles from the reaction were not investigated.

b) Reaction between PCl_3F_2 and triethyl amine in 1 : 2 mole ratio. In this experiment the reactants were mixed at −78°C to give a white solid. The reaction flask was held at −78°C for about three hours and then allowed to warm up slowly to room temperature over a period of four hours. The presence of volatile material was noticed by the development of pressure in the system on warming up and this was condensed in a trap cooled by liquid nitrogen under vacuum. The pale buff coloured product thus obtained gave the following analysis: Cl, 33.2%; P, 7.3% and again this does not indicate the composition of a 1 : 1 or 1 : 2 adduct, however it differs considerably from the previous result (Cl, 26.8%; P, 5.5%).

The volatile products were vacuum fractionated and this led to the recovery of unreacted triethyl amine together with PF_2Cl and traces of PF_3. PF_3 is presumed to be derived from traces of PF_3Cl_2 present in the PCl_3F_2 used.

c) Reaction between PCl_3F_2 and triethyl amine in 1 : 1 mole ratio. The reactants were mixed at -78°C and as in previous experiments a white solid was formed. The reaction flask was left at -78°C overnight and later allowed to warm up gradually to room temperature over a period of about four to five hours. Some volatile products were formed and were collected separately in a trap under vacuum. The solid obtained was of a light buff colour. It analysed to give Cl, 38.8%; P, 8.5%.

The volatile products were separated by vacuum fractionation and identified as unreacted triethyl amine and PF_2Cl.

In none of the above three experiments was it observed that a pure adduct between PCl_3F_2 and $(C_2H_5)_3N$ was formed. As the ratio of the reactants, that is PCl_3F_2 : $(C_2H_5)_3N$, was increased from 1 : 1 through 1 : 2 to 1 : 3.5 a decrease in the chlorine content of the solid product was found. If we assume the formation of two addition compounds namely $PCl_3F_2 \cdot (C_2H_5)_3N$ and $PCl_3F_2 \cdot 2(C_2H_5)_3N$ in the system it would be reasonable to suppose that more of the former compound would be formed at lower PCl_3F_2 : $(C_2H_5)_3N$ ratios, the reverse being true of the latter. In fact the chlorine content of the solid formed is consistent with this, although clearly the product is not the simple adduct. It was observed that the chlorine content of the solid formed in reaction (a) that is when a 3.5 fold excess of $(C_2H_5)_3N$ was reacted with PCl_3F_2, is very close to that of $PCl_3F_2.2(C_2H_5)_3N$. Similarly the solid from reaction (c) has a chlorine content which is very near that of $PCl_3F_2.(C_2H_5)_3N$ whereas the solid from reaction (b) has a % chlorine value which is midway between those for the solids from reactions (a) and (c). However, the phosphorus content in all the three cases is lower than that required for both the adducts considered. Evidence was obtained in reactions (b) and (c) for the reduction of PCl_3F_2 to PF_2Cl. This must be true of reaction (a) too even though the volatiles from this reaction were not investigated. It is clear that triethyl amine has abstracted chlorine from PCl_3F_2 to form a compound which would then be present in the solid products. This would lead to a drop in the % phosphorus content of the solid compounds formed from those expected for $PCl_3F_2.(C_2H_5)_3N$ and $PCl_3F_2.2(C_2H_5)_3N$.

The formation of compounds $(C_2H_5)_3NCl_2$ and $\left[(CH_3)_3N\right]_2Cl_2$ was postulated by Holmes and Bertaut (50) in the reactions between the corresponding amines and phosphorus pentachloride. Bohme and Krause (67) obtained a trimethyl amine - chlorine adduct as white needles in carbon tetrachloride medium but it was found to be unstable at room temperature decomposing with the liberation of chlorine. One mole of the compound gave 0.5 mole of chlorine in this manner. The position with regard to an adduct between $(C_2H_5)_3N$ and chlorine is uncertain, substitution of the alkyl group is possible and a compound like $(C_2H_5)_2N(C_2H_4Cl).HCl$ might be formed. As mentioned earlier Beattie and Webster (51) obtained a compound which they showed was largely composed of $(C_2H_5)_3N.HCl$ by reacting $(C_2H_5)_3N$ and phosphorus pentachloride in carbon disulphide, thus evidence for HCl as a product has been obtained. They suggested that dehydrogenation of the amine must have taken place in this process to give this HCl. However, a test for unsaturation in the amine was negative so that the source of the HCl in their experiments is uncertain. Addition of chlorine to triethyl amine in approximately 1 : 1 mole ratio at -78°C showed the formation of a white solid which decomposed violently on warming up to room temperature and a charred residue was obtained in no way similar to the behaviour of the products of the reaction with PCl_3F_2 or PCl_5. However, when the product was allowed to warm up to room temperature slowly over a period of four to five hours a light buff coloured solid product was obtained. Hydrolysis of the compound gave on analysis, a chlorine content (as chloride) of 28.7% whereas microanalysis gave a higher value of 30.5%. On exposure to air the compound changed colour to reddish brown, became sticky, and dissolved in the water it absorbed. A melting point determination in a closed tube showed that the material started darkening at about 80°C, at which temperature it shrank in size gradually becoming darker at the same time. No melting was noticed until 270°C. A black residue was left behind and a small amount of a white deposit was formed. Analysis of the compound gave the following results:

Description	%C	%H	%N	%Cl
Unknown sample	47.8	10.8	10.0	30.5
Calcd. for $(C_2H_5)_3N.HCl$	52.4	11.6	10.2	25.8
Calcd. for "$(C_2H_5)_2N\ (C_2H_4Cl).HCl$"	41.9	8.7	8.1	41.3
Calcd. for $(C_2H_5)_3N.HCl$, 65% + "$(C_2H_5)_2N(C_2H_4Cl).HCl$, 35%"	48.7	10.6	9.5	31.2

It is possible that the solid product is a mixture of 65% $(C_2H_5)_3N.HCl$ and 35% "$(C_2H_5)_2N(C_2H_4Cl).HCl$" (the inverted comas signify the uncertainty regarding the molecular formula of the compound since polymeric materials of the same composition could result in similar reactions as will be mentioned later). On this basis the amount of hydrolysable chlorine in the compound

"$(C_2H_5)_2N(C_2H_4Cl).HCl$" may be empirically deduced to be 83% of the total chlorine since the ethylamine - chlorine compound contains 28.7% of chlorine available as Cl^- ion on treatment with water.

A preliminary analysis of the experimental data on the reaction between PCl_3F_2 and $(C_2H_5)_3N$ may be made on the assumption that the nonvolatile products of the reaction are composed of $PCl_3F_2.(C_2H_5)_3N$, $PCl_3F_2.2(C_2H_5)_3N$, $(C_2H_5)_3N.HCl$ and "$(C_2H_5)_2N(C_2H_4Cl).HCl$", the relative proportions of which vary with the mole ratio of the reactants. The reduction of PCl_3F_2 would result in equimolar amounts of PF_2Cl and Cl_2. The chlorine would be abstracted by the amine and therefore the amount of amine hydrochlorides formed could be calculated from the amount of PF_2Cl formed. Total amine used for the reaction minus (amine present in the amine hydrochlorides + unreacted amine) gives the amount of amine associated with the phosphorus present in the solid product, this phosphorus being assumed to be either in the form of $PCl_3F_2.(C_2H_5)_3N$ or $PCl_3F_2.2(C_2H_5)_3N$. The relative amounts of the two adducts can therefore be calculated. Tables 13, 14a, 14b and 15 summarise the results thus obtained.

In the reaction between PCl_3F_2 and triethyl amine in 1 : 3.5 mole ratio the loss in phosphorus (total phosphorus

Table 13. Reaction between PCl_3F_2 and excess $(C_2H_5)_3N$.

Description	Millimoles present	
	Reactants	Products
PCl_3F_2	11.8	0.00
$(C_2H_5)_3N$	41.3	excess.
Phosphorous in the solid product	-	5.85
PF_2Cl (loss in phosphorus)	-	5.95 (11.8 - 5.85)
Chlorine in the solid product	-	12.37
$(C_2H_5)_3N\cdot HCl$	-	11.90 (5.95 x 2)
$PCl_3F_2\cdot 2(C_2H_5)_3N$	-	5.85

% Cl in the solid product (calculated) : 27.3
% Cl in the solid product (observed) : 26.8

Table 14a. Reaction between PCl_3F_2 and $(C_2H_5)_3N$ in 1 : 2 mole ratio.

Compound	Millimoles of compound present		Analysis of compounds in the products (values in millimoles)		
	Reactants	Products	Cl	P	F
PCl_3F_2	11.99	0.00	-	-	-
$(C_2H_5)_3N$	21.33	6.82	-	-	-
PF_2Cl	-	2.93	1.47	2.93	2.93
PF_3	-	0.66	-	0.66	0.99
$(C_2H_5)_3N \cdot HCl$	-	7.18	3.59	-	-
$PCl_3F_2 \cdot (C_2H_5)_3N$	-	7.18	10.77	7.18	7.18
Total number of millimoles in the products: " " by theory:			15.83 17.98[a]	10.77 11.99[a]	11.10 11.99[a]
% chlorine in the solid product (calculated) :			34.4		
" " (observed) :			33.3		

[a] expected from the amount of PCl_3F_2 used.

Table 14b. Reaction between PCl_3F_2 and $(C_2H_5)_3N$ in 1 : 2 mole ratio.

Compound	Millimoles of compound present		Analysis of compounds in the products (values in millimoles).		
	Reactants	Products	Cl	P	F
PCl_3F_2	11.99	0.00	-	-	-
$(C_2H_5)_3N$	21.33	6.82	-	-	-
PF_2Cl	-	2.93	1.47	2.93	2.93
PF_3	-	0.66	-	0.66	0.99
$(C_2H_5)_2N(C_2H_4Cl)\cdot HCl$	-	3.59	3.57	-	-
$PCl_3F_2\cdot(C_2H_5)_3N$	-	3.44	5.16	3.44	3.44
$PCl_3F_2\cdot 2(C_2H_5)_3N$	-	3.74	5.61	3.74	3.74
Total number of millimoles in the products :			15.81	10.77	11.10
" " by theory :			17.98[a]	11.99[a]	11.99[a]
% Cl in the solid product (calculated) : 32.7					
" " (observed) : 33.30					

[a] expected from the amount of PCl_3F_2 used.

Table 15. Reaction between PCl_3F_2 and $(C_2H_5)_3N$ in 1 : 1 mole ratio.

Compound	Millimoles of compound present		Analysis of compounds in the products (values in millimoles)		
	Reactants	Products	Cl	P	F
PCl_3F_2	12.36	0.00	-	-	-
$(C_2H_5)_3N$	11.75	0.99	-	-	-
PF_2Cl	-	3.75	1.88	3.75	3.75
$(C_2H_5)_2N(C_2H_4Cl).HCl$	-	3.75	3.75	-	-
$PCl_3F_2.(C_2H_5)_3N$	-	7.76	11.64	7.76	7.76
Total number of millimoles in the products :			17.27	11.51	11.51
" " " by theory :			18.54^a	12.36^a	12.36^a
% Cl in the solid product (calculated) :		37.5			
" " (observed) :		38.5			

[a] expected from the amount of PCl_3F_2 used.

in the reactants minus phosphorus in the solid product) was attributed to the amount of PF_2Cl formed (the volatile products of this reaction were not investigated). The solid product could be represented only as a mixture of $(C_2H_5)_3N.HCl$ and $PCl_3F_2.2(C_2H_5)_3N$. The calculated and observed values of the percentage of chlorine in the solid are in good agreement with each other. It will be noted that the theoretical amount of the total chlorine in the products (17.7 m. moles) is higher than the experimental value (15.3 m. moles, calculated from the amount of PCl_3F_2 used for the reaction). An explanation of this is given later.

The two distributions of products calculated for the reaction between PCl_3F_2 and triethyl amine in 1 : 2 mole ratio appear to be equally acceptable. The percentage chlorine in the solid product was calculated on the assumption that only 83% of the chlorine in $(C_2H_5)_2N(C_2H_4Cl).HCl$ is available as chloride ion on hydrolysis with dil. alkali(this was empirically deduced earlier). The slightly lower experimental values for the total amounts of the respective elements present in the products may be attributed to the formation of small amounts of solid in the initial stages when the volatiles from the reaction flask were condensed in fractionating traps, this material not being accounted for in the calculations. The origin of this solid is not quite clear. If it is assumed that this material is of the same composition as the solid product from the reaction flask the analytical figures for the elements present in the products can be recalculated; the weight of solid formed in the traps is equal to the total weight of reactants minus the total weight of the products that is 2.3364 g.(PCl_3F_2)+2.155g. ($(C_2H_5)_3N$) - [3.0364 g. (solid product from the reaction flask) + 1.129 g.(volatiles)] = 0.326 g. Accounting for the contributions from 0.326g. of the solid the new values (in m. moles) for the total amounts of the individual elements in the products turn out to be Cl, 17.37; P, 11.54 and F, 11.87. These are very close to the theoretical values. The lower experimental value for the total chlorine present in the products of the reaction between PCl_3F_2 and $(C_2H_5)_3N$ in 1 : 1 mole ratio might arise for the same reasons.

The details regarding the calculated amounts of products likely to be formed in the reaction between PCl_3F_2 and $(C_2H_5)_3N$ in 1 : 1 mole ratio show that the quantities involved do not permit the inclusion of $(C_2H_5)_3N.HCl$ and $PCl_3F_2.2(C_2H_5)_3N$ among the products. The formation of small amounts of solid products from the volatiles was observed in this case also and the lower experimental values for the total amounts of the respective elements present in the products may be attributed to this. The amount of solid thus formed was estimated to be 0.178g. by the difference between the total weights of the reactants and the products [2.170g.(PCl_3F_2)+ 1.193g.($(C_2H_5)_3N$) -

{2.573g. (solid product from the reaction flask)+ 0.612g. (volatiles)}]. The recalculated values (in m. moles) for the individual elements present in the products are Cl, 18.32; P, 12.05 and F, 12.05, in better agreement with the theoretical values.

Further investigations of the solid products showed the presence of $[PF_6]^-$ ion in them. Quantitative results could not be obtained, but qualitatively it appears that there is a significant amount of $[PF_6]^-$ ion formed indicating that reorganisation processes are taking place. Consequently the simple 1 : 1 and 1 : 2 adducts considered so far must be described in terms of a complex mixture of products. The following schemes involving the migration of alkyl groups and halogen atoms may be suggested to account for this:

$$3\,PCl_3F_2\cdot(C_2H_5)_3N \longrightarrow [(C_2H_5)_2N - PCl_3]^+\;[PF_6]^- + (C_2H_5)_4NCl + (C_2H_5)_3N + PCl_5 \ldots\ldots\ldots\ldots 17$$

$$\longrightarrow [(C_2H_5)_4N]^+\;[PF_6] + (C_2H_5)_2N\;PCl_4 + (C_2H_5)_3N + PCl_5 . \ldots\ldots\ldots\ldots 18$$

$$\longrightarrow [(C_2H_5)_3N - PCl_2]^+\;[PF_6]^- + (C_2H_5)_4NCl + (C_2H_5)_2NCl + PCl_5 \ldots\ldots\ldots\ldots 19$$

$$\longrightarrow [(C_2H_5)_4N]^+\;[PF_6]^- + (C_2H_5)_2N\;PCl_4 + 2(C_2H_5)_4NCl + [(C_2H_5)_2N]_2\;PCl_3 .$$

The reaction between phosphorus pentachloride and triethyl amine has been reported (50) to be very slow (0.2 - 0.3 millimoles of

PCl_5 were attacked by the amine on standing for two days at room temperature even though excess amine was present in the system). Considering the time intervals used in the experiments in the present work negligible reaction must have taken place before the triethyl amine formed according to equations 17, 18 and 19 is removed from the solid product. In reaction (c) although the amount of PCl_3F_2 taken was slightly more than required for PCl_3F_2: $(C_2H_5)_3N$ to be 1 : 1 about one millimole of $(C_2H_5)_3N$ was recovered unreacted. It may be noted that $(C_2H_5)_3N$ is also a product of the reactions postulated by equations 17, 18 and 19. Diethyl N-chloramine (68) has been described as a yellowish sticky oil. No evidence for the formation of such a compound was obtained and hence the disproportionation reaction indicated by equation 19 is probably not taking place.

The reduction of PCl_3F_2 by triethyl amine is possibly more complex than indicated earlier although the mechanism of reduction by tertiary amines is not properly understood yet. Antler and Laubengayer (69) have suggested two mechanisms for the observed reduction of $TiCl_4$ by trimethyl amine to form $TiCl_3 \cdot (N\,Me_3)_2$:

(i) reduction of the metal halide is accompanied by the formation of $(CH_3)_2N(CH_2Cl)$ or more chlorinated products and the HCl liberated can combine with trimethyl amine and the chlorinated amine products to form quaternary salts. Further trimethyl amine and the chlorinated amine products can combine to form quaternary ammonium salts of the type  $C_5H_5\underset{Cl}{N}-\underset{Cl}{N}C_5H_5$ suggested by Wardlow and Webb (70) to explain the reduction of $MoCl_5$ by pyridine.

(ii) free radicals of the type $(CH_3)_2N\,CH_2\cdot$ are produced during the process of reducing the metal halide liberating HCl. Combination of free radicals results in polymeric units which form quaternary ammonium salts with HCl. If excess trimethyl amine is present trimethyl amine hydrochloride also would be expected among the products.

The infra-red spectra of a chloroform solution of the solid products of the reaction between PCl_3F_2 and triethyl amine did not aid in recognising the nature of the products and investigations of the proton resonance spectra in chloroform solution showed only ethyl type of protons. Further, it was observed that the proton resonance spectra of $(C_2H_5)_4NCl$ in aqueous solution, and $(C_2H_5)_3N.HCl$, the product obtained by the reaction between triethyl amine and chlorine and also the solid products from the reaction between PCl_3F_2 and triethyl amine in chloroform solutions were identical. Mass spectrometric investigation was unsuccessful as the compound could not be transferred to the electron beam satisfactorily.

The sensitivity of the compound to reaction with moisture further prevented the use of chromatographic techniques of separation. Even under dry box conditions exposure of the compound resulted in slow decomposition over a period of a few hours. However, chromatographic separation under carefully controlled conditions in specially designed apparatus and separation by vacuum-sublimation might prove fruitful techniques.

2. The reaction between PCl_3F_2 and triethyl phosphine.

When PCl_3F_2 was condensed on to triethyl phosphine in 1 : 1 mole ratio at -78°C a white solid product was formed, which on allowing to warm up changed with the evolution of heat to a red solid which was contaminated with traces of a white solid. In subsequent experiments the temperature of the reaction vessel was raised slowly from -78°C over a period of four to five hours in order to control the effects of the exothermic reaction. When PCl_3F_2 and $(C_2H_5)_3P$ were reacted in petroleum ether (40-60°) as a solvent the solid product obtained was similar in appearance and composition (phosphorus and chlorine content)to that formed in the absence of a solvent. Extraction with dry acetonitrile or chloroform followed by evaporation of the solvent yielded a white crystalline material which gave Cl, 36.3%; P, 2.7%; calcd. for $PCl_3F_2.(C_2H_5)_3P$, Cl, 36.3%; P, 10.6% (the phosphorus in $(C_2H_5)_3P$ is not available as

PO_4^{3-} ion on simple treatment with alkali or acid); calcd. for $(C_2H_5)_3PCl_2$, Cl, 37.5%; P, 0.0%. A yellowish red amorphous material remained behind as the insoluble component which gave P, 84.8%; C, 5.4%; H, 2.4%. The volatile products of the reaction were identified as PF_3, PF_2Cl, PCl_2F, $POCl_2F$ (traces) and PCl_3.

The analysis of the white solid compound obtained does not conform to either $PCl_3F_2 \cdot (C_2H_5)_3P$ or $(C_2H_5)_3PCl_2$. However it may be considered as a mixture of $(C_2H_5)_3PCl_2$ and another compound containing hydrolysable phosphorus. The presence of $[PF_6]^-$ ion in the white solid was demonstrated by precipitation with Nitron reagent. It would be reasonable to assume that the compound is $[(C_2H_5)_3PCl]^+ [PF_6]^-$, the $[PF_6]^-$ ion in which yields phosphate ion on hydrolysis. However, in order to account for the chloride content the presence of a third component namely $(C_2H_5)_3P \cdot PCl_3F_2$ also has to be postulated. On this basis the white solid could be considered as a mixture of $(C_2H_5)_3PCl_2$ (74.4%), $PCl_3F_2 \cdot (C_2H_5)_3P$ (21.7%) and $[(C_2H_5)_3PCl]^+ [PF_6]^-$ (3.9%) and the calculated and experimental values are in fairly good agreement as shown in Table 16. The formation of PF_3, PCl_2F and PCl_3 in addition to PF_2Cl indicates that the reaction is not simply one of reduction. Pyrolytic decomposition could account for PF_3, PCl_2F and PCl_3 in the products. The following processes are postulated as taking place in the system:

Table 16. Reaction between PCl_3F_2 and $(C_2H_5)_3P$ in 1 : 1 mole ratio.

Description	Millimoles present		Analysis of compounds in the products (values in millimoles)			
	Reactants	Products	P	Cl	F	$(C_2H_5)_3P$
PCl_3F_2	15.57	-				
$(C_2H_5)_3P$	14.80	-				
PF_3	-	2.40	2.40	-	3.60	-
PF_2Cl	-	7.05	7.05	3.53	7.05	-
PCl_2F	-	0.34	0.34	0.34	0.17	-
PCl_3	-	1.70	1.70	2.55	-	-
P in the red material	-	1.96	1.96	-	-	-
$PCl_3F_2\cdot(C_2H_5)_3P$	-	2.32	4.64	3.48	2.32	2.32
$[(C_2H_5)_3PCl]^+[PF_6]^-$		0.41	0.82	0.21	1.23	0.41
$(C_2H_5)_3PCl_2$	-	12.34	12.34	12.34	-	12.34
Total number of millimoles in the products:			31.25	22.45	14.37	15.07
" " " by theory :			30.37[a]	23.35[a]	15.57[a]	14.80[a]

[a] expected from the amounts of reactants taken.

$$PCl_3F_2 + (C_2H_5)_3P \longrightarrow (C_2H_5)_3PCl_2 + PF_2Cl$$

$$PCl_3F_2 + (C_2H_5)_3P \longrightarrow PCl_3F_2\cdot(C_2H_5)_3P.$$

$$2PF_2Cl \xrightarrow{\text{pyrolysis}} PF_3 + PCl_2F \text{........}20$$

$$2PCl_2F \xrightarrow{\text{pyrolysis}} PF_2Cl + PCl_3 \text{........}21$$

$$3PCl_3F_2\cdot(C_2H_5)_3P \longrightarrow [(C_2H_5)_3PCl]^+[PF_6]^- + 2(C_2H_5)_3PCl_2 + P_2Cl_4$$

$$3P_2Cl_4 \longrightarrow 4PCl_3 + 2P \text{.........}22$$

The interconversion of mixed trihalides of phosphorus by heat is quite well established (19, 20, 21) and therefore the pyrolytic disproportionations represented by equations 20 and 21 are justifiable. The transformation of the initially white product obtained by the low temperature interaction between PCl_3F_2 and $(C_2H_5)_3P$ needs some comment. The solid product left in the reaction flask when it was slowly warmed up to room temperature was pale reddish in colour and only after standing for six to seven hours at room temperature did the colour gradually deepen. The behaviour of P_2Cl_4 which decomposes at room temperature to phosphorus trichloride and red phosphorus as given in equation 22 is similar to this. However, the relative amounts of phosphorus trichloride and the red phosphorus obtained in the present reaction do not conform to the stoichiometry expected for the decomposition reaction of P_2Cl_4.

Proton resonance spectrum of the white solid in deuterochloroform indicated the presence of only one type of proton consistent with an ethyl group linked to a phosphorus atom. The F^{19} signal was found to be weak. This gave a doublet structure and had a P-F coupling constant of 712 cps which indicated the presence of $[PF_6]^-$ ion. The reported P-F coupling constant for $[PF_6]^-$ is 710 cps (52). However, there was no evidence for $PCl_3F_2 \cdot (C_2H_5)_3P$ since the P-F coupling constant in this case would be expected in the region of 1000 cps by comparison with those observed for PCl_3F_2 and $PCl_3F_2 \cdot C_5H_5N$ (26). This would suggest that the major amount of fluorine present in the solid must be in the form of $(PF_6)^-$ which could arise by some form of rearrangement of the addition compound as indicated by the following possibilities:

$$3\ PCl_3F_2 \cdot (C_2H_5)_3P \longrightarrow [(C_2H_5)_3P{-}PCl_2]^+ [PF_6]^- + 2(C_2H_5)_3PCl_2 + PCl_3.$$

$$\longrightarrow [(C_2H_5)_2P{-}PCl_3]^+ [PF_6]^- + (C_2H_5)_4PCl + (C_2H_5)_3PCl_2 + PCl_3$$

$$\longrightarrow [(C_2H_5)_4P]^+ [PF_6]^- + (C_2H_5)_2PPCl_4 + (C_2H_5)_3PCl_2 + PCl_3$$

$$\longrightarrow [(C_2H_5)_3P{-}PCl_2]^+ \ [PF_6]^- + (C_2H_5)_4PCl + (C_2H_5)_2PCl_3 + PCl_3.$$

It is significant that phosphorus trichloride formed according to the above schemes has been observed among the products.

The amorphous red solid formed in the system contains carbon and hydrogen in addition to phosphorus which constitutes the major amount as mentioned earlier. The presence of carbon in the material is not understood. However, it has been recognised that the formation of amorphous red phosphorus in an organic solvent is accompanied by the incorporation of the organic groups, which behaving as catalysts, form terminal groups in the polymerised structure.(71). A similar explanation is possibly relevant in the present case.

Discussion of the reaction of PCl_3F_2 with triethyl amine and triethyl phosphine. The most striking feature about the reactions of PCl_3F_2 with triethyl amine and triethyl phosphine is that it was not possible to obtain the simple addition compounds. In both reactions reduction of the phosphorane to the trihalide takes place. PF_2Cl is the reduction product; the small amounts of PF_3 and PCl_2F observed in the reaction between PCl_3F_2 and triethyl phosphine are likely to be formed by the pyrolysis of PF_2Cl. The abstraction of chlorine instead of fluorine by the amine and phosphine once again emphasises that reactivity lies in the P-Cl bonds rather than in the P-F bonds. Triethyl phosphine appears to be a stronger reducing agent than triethyl amine by comparing the relative extent of reduction taking place in the two reactions. A similar trend has been observed with trimethyl arsine and trimethyl stibine in their reactions with the tri- and penta-chlorides of group $\bar{V}$ b elements (72). In these cases trimethyl stibine exhibits stronger reducing properties than trimethyl arsine.

Even though no addition compound of PCl_3F_2 and $(C_2H_5)_3N$ or $(C_2H_5)_3P$ has been isolated it seems that at low temperatures at least an adduct is formed as indicated by the appearance of a white solid at -78°C. As the temperature rises the adduct presumably decomposes via two competitive processes namely (i) reduction of the phosphorane and (ii) disproportionation leading to stabler products. The presence of $[PF_6]^-$ ion in the solid products in both the triethyl amine and the triethyl phosphine cases point out the tendency, in general, of chlorofluorophosphorane systems to rearrange to form compounds containing stable anions particularly the $[PF_6]^-$ ion.

Steric factors may be significant in determining the stability of the adducts between triethyl amine (phosphine) and PCl_3F_2 as has been suggested by earlier workers. The weak association between PF_5 and Lewis bases like diethyl ether, triethyl amine and 2, 4, 6, - trimethyl pyridine compared to the stable complexes $PF_5.O(CH_2)_4$ and $PF_5.C_5H_5N$ has been considered by Muetterties etal (52) to support this hypothesis. Holmes

(73) suggested that $PCl_3.(CH_3)_3N$ is isolable whereas $PCl_3.(C_2H_5)_3N$ is not, is due to steric effects. Yet another example is the existence of the stable compound $PCl_5.C_5H_5N$ while $PCl_5.(C_2H_5)_3N$ has not been obtained although this may be a question of base strength. Steric hindrance has been again considered as one of the factors responsible for the inhibition of acceptor properties and the instability of Lewis acid - base complexes formed in a study on organofluorophosphoranes (74).

If steric factors are really important in deciding the stability of the type of compound considered above it would be interesting to pursue studies on the Lewis acid behaviour of PCl_3F_2 using donor molecules which are less likely to cause steric hindrance. From this point of view the reactions with trimethyl amine, trimethyl phosphine and tetrahydrofuran are especially worth investigating.

PART II

THE REACTION OF BIS (DIPHENYL PHOSPHINO) ETHYL AMINE WITH IODINE.

INTRODUCTION.

The ability of organophosphines and phosphites, and their halogen substituted derivatives to undergo halogen addition had been long recognised and has been the subject of many investigations. This reactivity arises from the lone pair of electrons on the phosphorus atom, available for further bond formation. The addition of one molecule of halogen or interhalogen to one molecule of the phosphine or the phosphite is a general feature of these reactions; however in the case of bromine or iodine or the interhalogen compounds of chlorine, bromine and iodine this ratio can be exceeded because of the formation of polyhalides. The compounds formed between halogens and phosphines can be represented by the general 'formula R_nPX_{5-n} Where X is halogen and n=1,2 or 3. The further addition of halogen usually gives rise to compounds of the series $R_n\ PX_{7-n}$.

The addition of halogen to phosphines is an exothermic reaction and the resulting halides are invariably sensitive to attack by moisture. This reactive nature renders their preparation and characterisation difficult and accounts for their slow development. However, the investigation of these compounds has been carried out successfully in recent years using the techniques currently available.

The chemistry of the halogen addition compounds of phosphines can be said to have started with the extensive synthetic contributions of Michaelis (75,79) in the field of organo-phosphines, - arsines and - stibines. He isolated a series of halogen and mixed halogen addition compounds of triphenyl-, chlorodiphenyl - and dichlorophenyl-phosphines as well as the mono-alkyl phosphine derivative as the ethyl derivative $C_2H_5 PCl_4$. Further synthesis of alkyl phosphine - halogen adducts of the type $RP Cl_4$ and $R_3 PX_2$ were carried out by Cahours and Hoffmann (76), and Guichard (77) during much the same period. In 1930 Jackson, Davies and Jones (78) reported the bromine adducts of some mixed alkyl aryl substituted phosphines. Although the reactions of triphenyl phosphine with bromine and iodine were reported by Michaelis and von Soden (79) the products were not fully characterised. Triphenyl phosphorus dichloride and dibromide were again prepared by Jensen(80) and the dichloride originally described as an oil was obtained as a white solid. Many more trialkyl and triaryl phosphorus dihalides including the hitherto less investigated diiodides were prepared by Issleib and coworkers (81,82) in the last decade. Very recently the interaction of interhalogen compounds with triphenyl phosphines to form addition products has been investigated by Beveridge and Harris (83).

Initial work in the area of phosphine - halogen Chemistry was mostly concerned with synthetic aspects. Not much was known about the structure of the resulting compounds until recently. The first ideas about the structure of phosphine-halogen adducts were largely based on a consideration of their physical properties. Thus the solubility in organic solvents and the low melting points of the primary and secondary derivatives ($R\ PX_4$ and $R_2\ PX_3$) led Rochow, Hurd and Lewis (84) to suggest covalent structures for them. On the other hand Van Wazer (85) considered these compounds to be ionic in nature by analogy with the behaviour of phosphorus pentahalides. This view was shared by Kosolapoff (86) as well. For the ionic structures Van Wazer suggested that the organic groups would be present in the cation as far as possible. The ionisation scheme could be represented as follows:

$$R\ P\ Cl_4 \longrightarrow (R\ P\ Cl_3)^+ + Cl^-$$

however, Van Wazer emphasised the need for physico - chemical investigations to establish this point conclusively.

The addition of halogens to the dihalides of primary, secondary and tertiary phosphines is suggestive of the presence of quaternary phosphonium group in these compounds since this behaviour is shown by quaternary salts. For example tetraalkyl ammonium halides take up halogens to form compounds containing polyhalide ions (87) which may arise from interaction between the added halogen and a halide ion present in the original compound which must therefore contain a quaternary ammonium type ion. Such formation of polyhalide ions need not, however, involve a quaternary ammonium type ion. This is well illustrated by the behaviour of triphenyl arsenic dibromide which is largely covalent in acetonitrile (in fact it behaves as a weak electrolyte) but at the same time takes up iodine bromide to form $(Ph_3\ As\ Br)^+\ (I\ Br_2)^-$ (88).

Recently Kuchen and Strolenburg (89) have shown that diethyl and dipropyl phosphorus trichlorides and the pentabromides are soluble in polar solvents and that these solutions show appreciable conductance. Accordingly these authors formulate the trichlorides and the pentabromides as $(R_2\ P\ Cl_2)^+\ (R_2\ P\ Cl_4)^-$ and $(R_2\ PBr_2)^+\ Br_3^-$ respectively.

Jensen (80) has suggested a covalent trigonal bipyramidal structure for triphenyl phosphorus dichloride by analogy with the corresponding compounds of antimony and bismuth from dipole moment measurements. Mann (90) also expressed similar views in favour of a covalent structure for the tertiary phosphorus dibromides rather than a quaternary salt structure. Conductometric studies by Issleib and Seidel (82) on the complexes of trialkyl and triaryl phosphorus dihalides with $Sb\ Cl_5$, $Sb\ Br_3$, $Hg\ Br_2$ and $Hg\ I_2$ showed that they behave like binary electrolytes in nitrobenzene solutions and on these grounds the complexes have been formulated as containing phosphonium ions

$(R_3\ PX)^+$, (R = alkyl or aryl group, X = halogen) and anions like $(Sb\ X_6)^-$, $(Sb\ X_4)^-$, $(Hg\ X_3)^-$ and $(Hg_3\ X_7)^-$ as the case may be. The existence of $(R_3\ PX)^+$ ions in these complexes could be taken as an evidence for its presence in the triaryl and trialkyl phosphorus dihalides. However, these authors observed that the diiodides of tertiary phosphines form conducting solutions in polar solvents whereas the corresponding chlorides and bromides behaved differently suggestive of weak electrolytes or even of non-electrolytes. It has been further suggested that these latter two groups of compounds are however likely to exist as ions in the solid state even if they do not behave as strong electrolytes in solution. Very recently Beveridge and Harris (83) found that $Ph_3\ PCl_2$ and $Ph_3\ PBr_2$ are good conductors in acetonitrile. Vibrational structural studies on trimethyl phosphorus dichloride, dibromide and diiodide by Goubeau and Baumgartner (91) have supported the view that these compounds possess the structure $[(CH_3)_3\ PX]^+\ X^-$.

More direct evidence for the ionic nature of the dihalides and tetrahalides of tertiary phosphines stems from the work of Beveridge and Harris (83). The mode of ionisation in solution of these compounds has been established by transport experiments in acetonitrile solutions.

Some of these ionisation schemes are given below:

$$2\,Ph_3PCl_2 \rightleftharpoons [Ph_3PCl]^+ + [Ph_3PCl_3]^-$$

$$Ph_3PBr_2 \rightleftharpoons [Ph_3PBr]^+ + Br^-$$

$$Ph_3PI_2 \rightleftharpoons [Ph_3PI]^+ + I^-$$

$$2\,Ph_3PI_2 \rightleftharpoons Ph_3P + [Ph_3PI]^+ + I_3^-$$

$$Ph_3PBrI_3 \rightleftharpoons [Ph_3PBr]^+ + I_3^-$$

A very important observation that emerges from the studies on the ionisation of the compounds in the tetrahalide series $Ph_3PBr_nI_{4-n}$ is that in the compounds containing two different halogens the cation is always associated with bromine.

X-ray structure studies (92) on $Ph_3AsI_2Br_2$ and Ph_3AsIBr_3 have shown that they are built up from tetrahedral $[Ph_3\,P\,As\,Br]^+$ units and linear trihalide ions. the corresponding phosphine compounds may have similar structures.

By simple analogy with the behaviour of phosphines, amines also might be expected to react with halogens in a similar fashion to form haloammonium halides, the nitrogen attaining its maximum co-ordination number of four. However, the absence of π bonding in the case of nitrogen may limit the formation of nitrogen - halogen bonds. Halogen addition to amines has been studied by many workers (93). In several instances typical products from the amine reactions are loosely bound "molecular complexes" in which the halogen is readily detached - this is as might be expected in view of the bonding limitations of nitrogen. These studies have been stimulated by the work of Mulliken (94) who proposed the idea of "molecular complexes" and discussed the resulting charge transfer spectra. Hassel and coworkers(95) have elucidated the structural details of some of these compounds From these results there is no evidence to suggest that a halogen substituted quatermary nitrogen atom occurs in the solid amine - halogen adducts. The N-X-X (X') bond has been shown to be linear with some elongation of the X-X(X') bond present in the original halogen or interhalogen molecule. The N-X bond length suggests that it is covalent in character. However, in solution the nature of the species may be different since the dielectric of the medium and solvation effects can not be ignored (96). There is evidence for a chloroammonium ion, $[\mathrm{Et\ NH_2\ Cl}]^+$, from kinetic data on the reaction of ethyl chloramine with the phenoxide ion (97), but this apparently refers only to a transient reaction species. More substantial evidence for haloammonium ions comes from the work of Böhme and Krause (67) on the reaction of halogens with trimethyl amine. They obtained a solid which was formulated as $(Me_3N\ Br)^+\ Br^-$. However, a rearrangement reaction occurred readily in aqueous solution. Similar halogeno - trimethyl ammonium ions can be postulated for the corresponding chlorine and iodine adducts. These latter examples apart, molecular complexes appear to be the most usual form, particularly of the iodine adducts of amines. Iodine forms complexes with nitrogen substituted phosphazenes (98), for example $N_4\ P_4\ (N\ Me_2)_8 \cdot 2\ I_2$, which are characterised by charge transfer bands at around 370 mμ. and are similarly to be regarded as "molecular complexes." In these cases the ring nitrogen atoms are involved in complex formation.

The first example of the reaction between a system containing both trivalent phosphorus and nitrogen together in the same molecule, and a halogen, is the behaviour of bis-(trifluoromethyl) amino phosphine with chlorine, reported by Harris (3). However, the reaction was complex leading to a mixture of products, which possibly included the direct addition compound $(C\ F_3)_2\ P(N\ H_2)\ Cl_2$ but this was not isolated. It is relevant to note the greater base strength of phosphorus compared to that of nitrogen in this compound. Similar instances reported are the reactions of methyliodide with dimethyl amino dimethyl phosphine (99) and phenyl bis (diethyl amino) phosphine (100). The availability of further aminophosphines has enabled their reactions with halogens to be re-examined in greater detail and a study of the reaction between bis (diphenylphosphino) ethylamine and iodine has been undertaken to clarify the position.

RESULTS AND DISCUSSION.

CONDUCTOMETRIC ANALYSIS OF THE SYSTEM.

$Ph_2PN(Et)PPh_2 - I_2$.

The reaction between $Ph_2PN(Et)PPh_2$ (bis-(diphenyl phosphino)ethyl amine) and iodine was followed conductometrically in acetonitrile solutions. The experimental results are given in table 17. Fig. 8 shows the conductometric titration curve in which molar conductance Λ_m (based on the $Ph_2PN(Et)PPh_2$ present) is plotted against the added iodine (that is the mole ratio of $I_2 : Ph_2PN(Et)PPh_2$).

Manipulation of solutions in the absence of moisture was facilitated by the use of a specially designed apparatus. The solution of $Ph_2PN(Et)PPh_2$ in acetonitrile, initially colourless, acquired gradually a pale yellow colour on the addition of iodine until a mole ratio of 1:1 was reached. Thereafter it became pale brown in colour which deepened further as more and more iodine was added. Towards the end of the titration a dark brown solution was obtained.

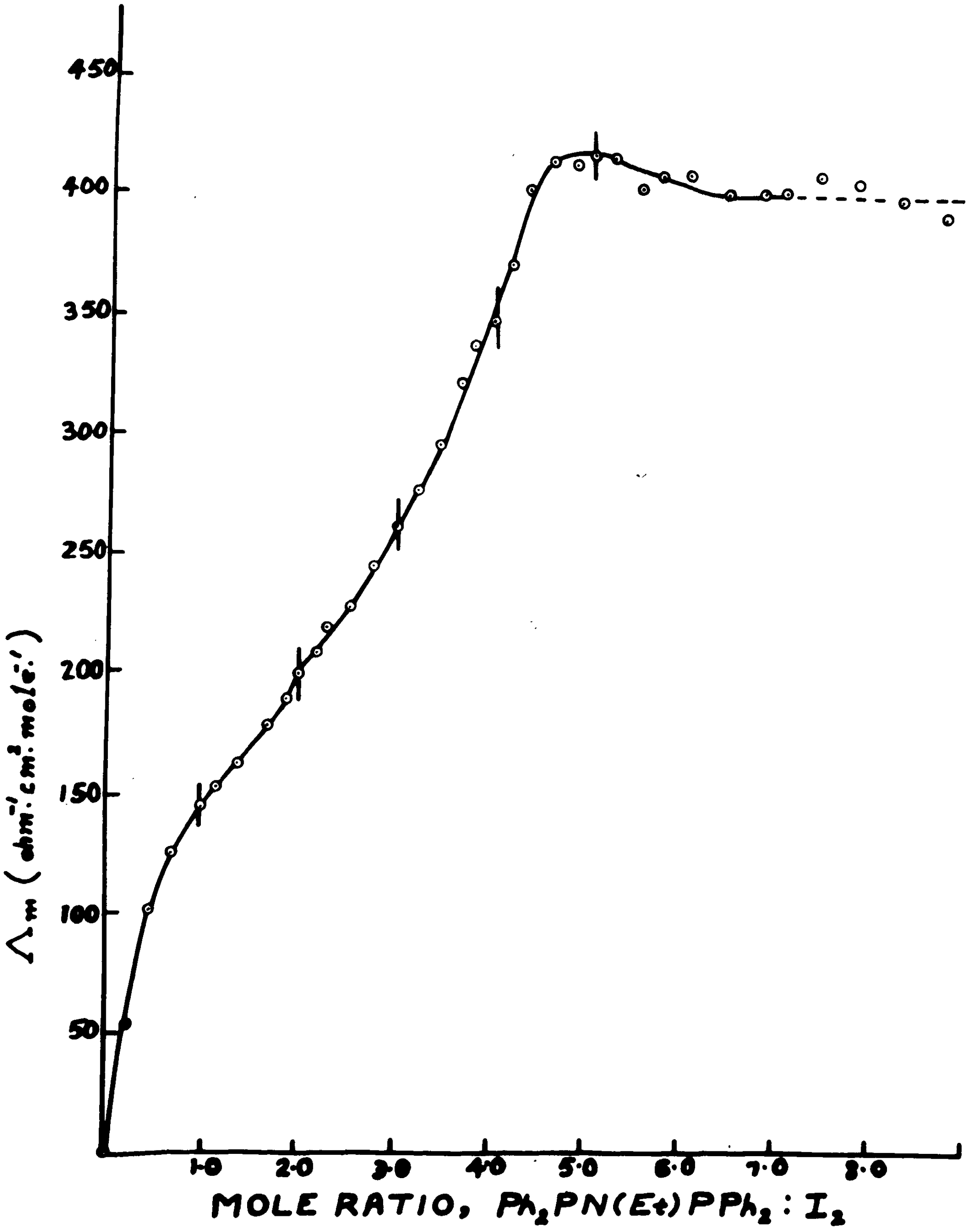
Two inflections appearing in the curve at the mole ratios of 1:1 and around 1:5 might indicate the formation of the two compounds $Ph_2PN(Et)PPh_2.I_2$ and $Ph_2PN(Et)PPh_2.5I_2$ which

TABLE 17. CONDUCTOMETRIC ANALYSIS OF THE SYSTEM Ph_2 PN (Et) P Ph_2 — I_2 IN ACETONITRILE SOLUTION.

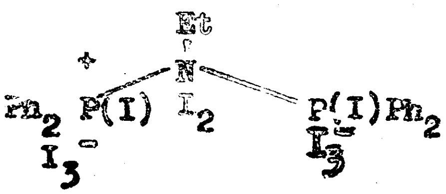
Mole Ratio I_2:$Ph_2PN(Et)PPh_2$	Λ_m $ohm^{-1}.cm^2.mole^{-1}$.	Mole Ratio I_2:$Ph_2PN(Et)PPh_2$	Λ_m $ohm^{-1}.cm^2$ $mole^{-1}$.
0.00	0.35	4.36	400.10
0.23	53.76	4.58	412.90
0.46	100.60	4.81	411.70
0.69	124.60	5.00	416.40
1.00	144.50	5.23	415.40
1.37	162.40	5.50	402.40
1.69	178.30	5.73	407.80
2.00	198.30	6.00	408.00
2.29	217.50	6.42	399.20
2.52	225.80	6.78	401.50
2.75	242.40	7.00	400.60
3.00	258.30	7.38	408.60
3.21	274.90	7.79	405.90
3.44	293.80	8.25	399.00
3.67	318.90	8.71	392.60
3.81	335.90	9.67	396.00
4.00	344.90	10.00	397.10

Fig.8. Conductometric Analysis of the System

Ph_2 PN(Et)P Ph_2 - I_2 in Acetonitrile Solution.



undergo ionisation in solution. There is no clear cut evidence for the existence of any compounds with intermediate mole ratios in the solution. This was not to be expected if only the two phosphorus atoms are involved unless an I_8^{2-} ion is present; however if the three reactive sites on the molecule Ph_2 PN(Et)P Ph_2 that is, the two phosphorus atoms and one nitrogen atom are considered to take part in the reaction a compound could be formulated as



It may be noted that at the mole ratio of 1:5 a molar conductance of 400 ohm^{-1} cm^2 $mole^{-1}$ is obtained if it is assumed that the compound formed is Ph_2PN (Et)P $Ph_2 . 5\ I_2$. This value is too high for electrolytes so far encountered in this type of system.

ISOLATION OF THE PRODUCTS FROM THE SYSTEM

Ph_2 PN (Et) P Ph_2 — I_2.

As the next step to understanding the reaction between Ph_2PN (Et) P Ph_2 and iodine further, the possibility of isolating the adducts formed was considered. For this purpose nearly saturated solutions of Ph_2PN(Et) P Ph_2 and iodine in acetonitrile were mixed in 1:1, 1:2, 1:3, 1:4, and 1:5, mole ratios. In the 1:1 case when the solution was concentrated by removing part of the solvent under vacuum followed by cooling in ice, pale yellow crystals of the composition Ph_2PN (Et) P Ph_2. I_2 were obtained. The same compound was obtained as a pale yellow precipitate when petroleum ether (40 — 60°) was used as the solvent. An orange yellow compound of the composition Ph_2PN(Et)P Ph_2. 3.1 I_2 crystallised out of the solution in the case of the reactants mixed in a 1:2 mole ratio. In the case of the reactants in 1:3, 1:4 and 1:5 ratios dark violet materials, all approximately identical, crystallised out of the solution with iodine analysis corresponding to Ph_2PN (Et)P Ph_2. 5.3 I_2, soon after mixing.

Similar results were obtained from reactions in methylene chloride solutions, however in this case the solutions had to be concentrated by freeze drying before the products crystallised out.

The attempted preparation of the compounds, except $Ph_2PN(Et)PPh_2 . I_2$, from petroleum ether ($40 - 60^{\circ}$), diethyl ether and benzene always resulted in the precipitation of a dark gummy substance.

The three materials thus prepared will hereafter be referred to as the 1:1, 1:3 and 1:5 "adducts", although later their true nature will be discussed and the composition interpreted suitably. The formation of the 1:5 "adduct" from solutions in which this stoichiometry is not originally present shows that there is an overlap of equilibria leading to a common product.

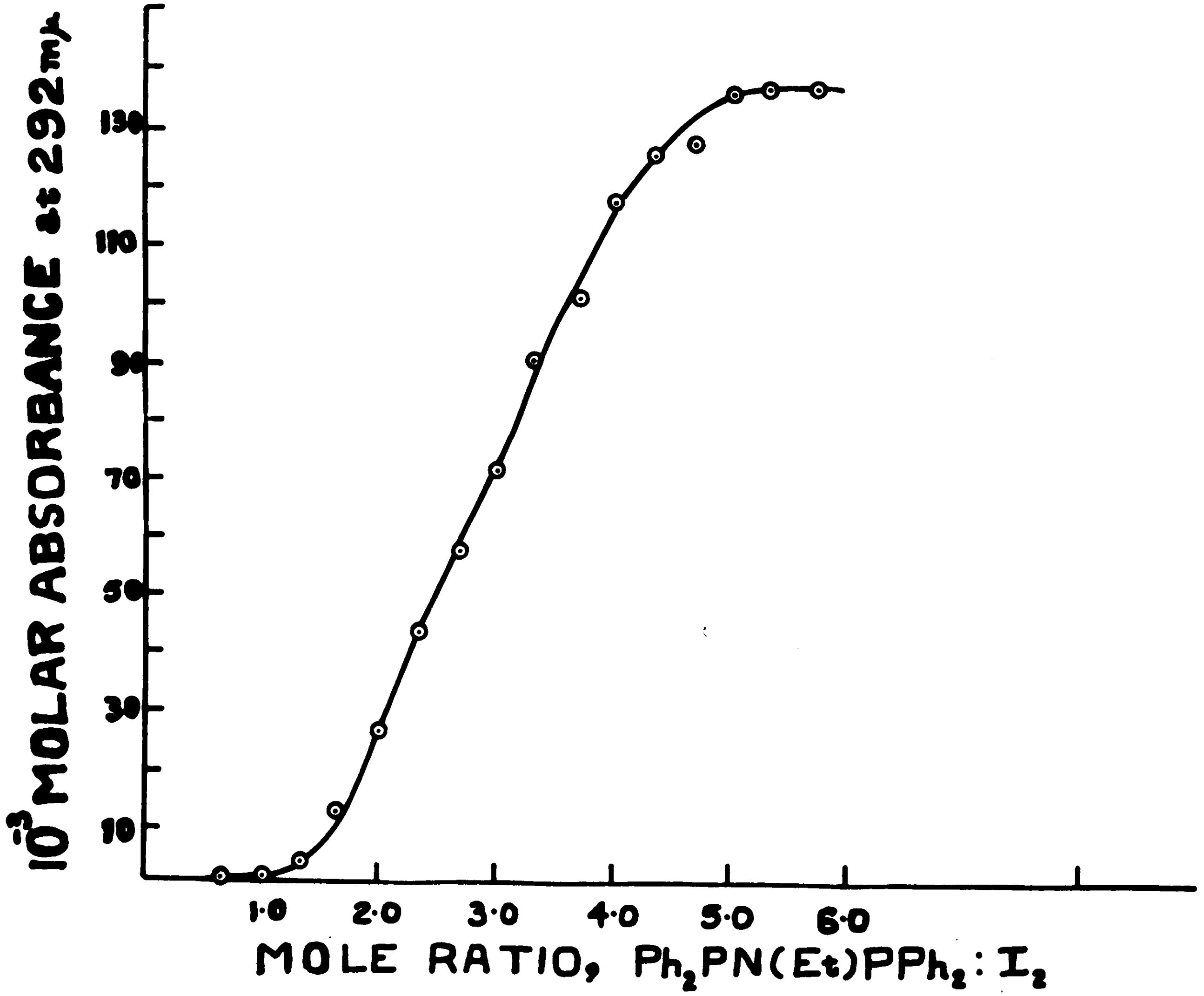
It was observed that all the three compounds isolated were very susceptible to attack by moisture, and the sensitivity to hydrolysis decreased as the iodine content of the compound increased. During all operations the compounds were handled with careful exclusion of moisture in a nitrogen filled drybox.

ULTRAVIOLET SPECTRA OF THE PRODUCTS FROM THE SYSTEM Ph_2 PN (Et) P Ph_2-I_2

Popov and Swensen (101) have studied the ultraviolet spectra of polyhalogen complexes in acetonitrile solutions and characteristic absorption bands due to these species have been observed. Thus the triiodide ion, for example, absorbs at 291 mμ and 360 mμ. The presence of polyiodide ions in the 1:3 and 1:5 "adducts" obtained by the reaction between Ph_2 PN(Et) P Ph_2 and iodine was suggested by their composition and in order to confirm this their ultraviolet spectra in the region 190 to 390 mμ. in acetonitrile solutions were recorded. These showed absorptions characteristic of the phenyl groups and of the triiodide ion (292 mμ and 360 mμ) in the case of the 1:3 and 1:5 "adducts", whereas the 1:1 "adduct" showed only the presence of phenyl groups.

The formation of triiodide ion in the system was followed up in greater detail by examining the ultraviolet absorption of acetonitrile solutions of Ph_2PN (Et)P Ph_2 and iodine mixed in various mole ratios at 292 mμ and 360 mμ. The results obtained are shown graphically in Fig. 9. It will be observed that the formation of the triiodide ion begins only beyond a mole ratio of 1:1. Thereafter the molar extinction coefficient increases

<u>Fig. 9.</u> Photometric Titration of Ph_2 PN(Et) P Ph_2 with Iodine in Acetonitrile Solution.



slowly up to about a mole ratio of 1:1.7. From this it is clear that once the 1:1 "adduct" is formed only part of the iodine added is used up to form, say, a second $>\overset{+}{P}-I$ site indicating thereby an equilibrium between this process and another process involving the build-up of the I_3^- ion. Beyond the 1:1.7 ratio there is a faster and almost linear growth of the I_3^- ion in the system until a mole ratio of 1:4 is attained. Further build - up of I_3^- ions is slower up to a mole ratio of 1:5 beyond which the curve levels off. The results of this experiment would appear to correlate with those obtained in the conductometric titration. The conductance measured in the region between 0.0 and 1:1 mole ratios is due to the iodide and the phosphonium ions formed. Beyond this point the conductance should be due to phosphonium, iodide and triiodide ions. The relatively greater amount of triiodide ions formed in the system during the final stage of the titration would account for the steeper rise in conductance towards the latter half of the region between 1:1 and 1:5 mole ratios since it has been shown in the case of quaternary ammonium salts that their polyhalides are stronger electrolytes in acetonitrile solutions than the corresponding halides because of increased solvation of polyhalide ions (102.)

TABLE 18.

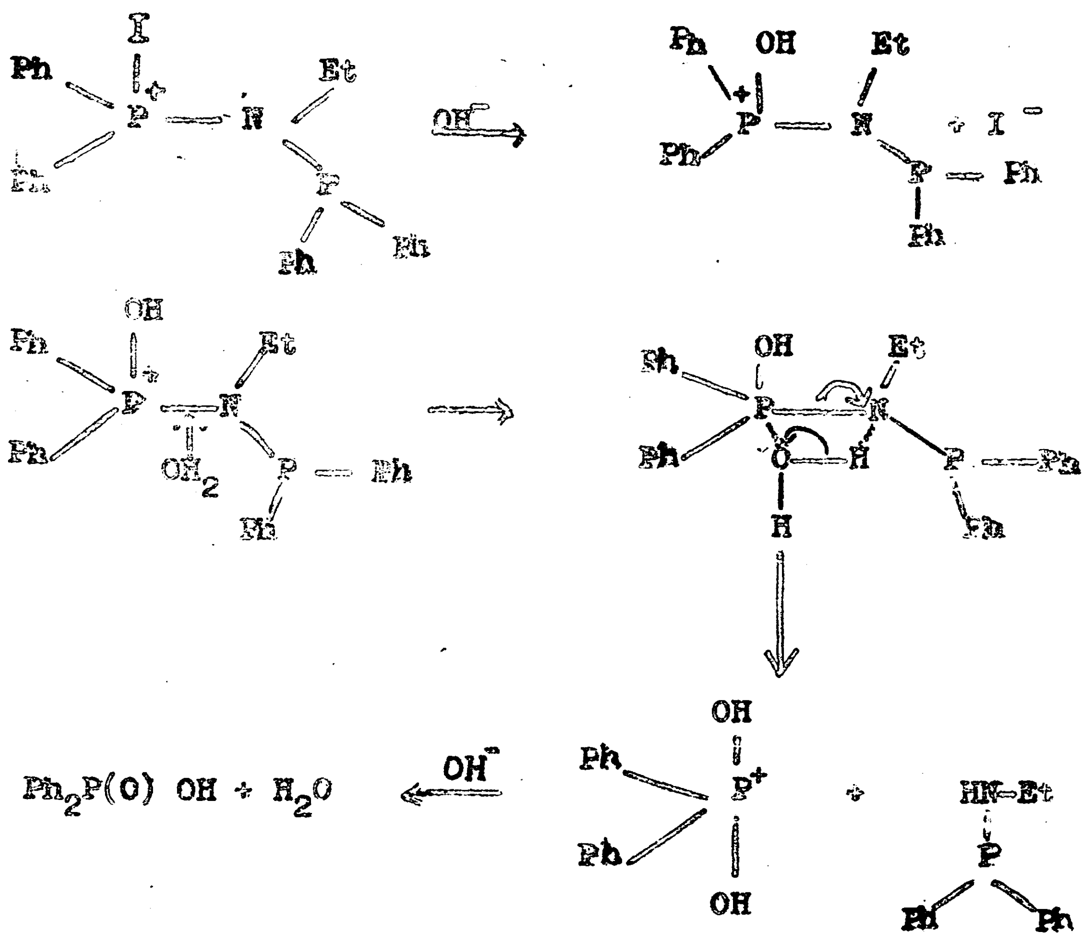
Compound	$\epsilon_{292\ m}$	$\epsilon_{360\ m}$
$Ph_3PI^+I_3^-$	68,000	34,300
$Ph_3AsI^+I_3^-$	57,700	31,000
1:3"adduct"	91,370	50,880
1:5"adduct"	141,800	78,720

The molar extinction coefficient ϵ at 292 mμ and 360 mμ obtained for the 1:3 and 1:5 "adducts" by direct measurements on these compounds are given in Table 18 along with the corresponding values for the known compounds triphenyl iodophosphonium triiodide (83) and triphenyl iodoarsonium triiodide (88). The latter two compounds are known to contain one triiodide ion per formula weight. On this basis a comparison of the values in the table would suggest the presence of one triiodide ion in the 1:3 compound and two triiodide ions in the 1:5 compound per formula weight based on Ph_2 PN (Et) P Ph_2 originally present.

HYDROLYSIS OF THE PRODUCTS FROM THE SYSTEM $Ph_2 PN (Et) P Ph_2 - I_2$

It has been already mentioned that the 1:1, 1:3 and 1:5 "adducts" obtained from the system $Ph_2PN(Et)P Ph_2 - I_2$ are very sensitive to hydrolysis. On exposure to moist air the materials rapidly acquire a dark brown colour and form a sticky mass. Decomposition using dil. sodium hydroxide solution in the cold gave diphenyl phosphinic acid $Ph_2 P(O) OH$ on acidification in all the three cases. In this way the 1:1 "adduct" gave diphenyl phosphinic acid in 40 - 45% yield. This is consistent with the scission of one P - N bond leading to the formation of one molecule of diphenyl phosphinic acid and presumably one molecule of diphenyl phosphino ethyl amine. The latter compound was not isolated. Hydrolysis of the other two compounds gave diphenyl phosphinic acid in over 90% yield consistent with the cleavage of both P - N bonds in the P - N - P skeleton.

The oxidation of phosphorus (III) to P(V) in $Ph_2P(O)OH$ as a result of hydrolysis can be explained only on the assumption that the phosphorus has reacted with iodine to form phosphonium ion which undergoes a nucleophilic attack by hydroxyl ions since the original compound $Ph_2 PN(Et)P Ph_2$ found to be stable to hydrolysis under similar conditions. The hydrolytic process may therefore be represented as follows:



The resulting diphenyl phosphino ethylamine is water soluble and stable to further hydrolysis.

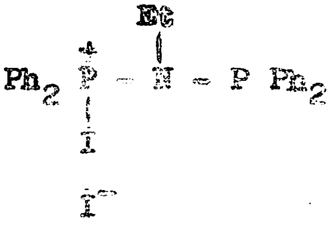
The above results show (i) that the phosphorus atoms in $Ph_2PN(Et)PPh_2$ are attacked by iodine to form the "adducts" and (ii) that only one phosphorus atom in the 1:1

"adduct" is attached to iodine whereas both phosphorus atoms are bound to iodine in the other two "adducts". On this basis it was thought that a mild hydrolysis of the compounds without rupturing the P-N bond might lead to the formation of the monoxide $Ph_2P(O)N(Et)PPh_2$ in the case of the 1 : 1 "adduct" and the dioxide $Ph_2P(O)N(Et)P(O)Ph_2$ in the case of the other two "adducts and this would give a more direct proof as regards the structure of the iodine adducts. To this end the following experiments were carried out:

1. Hydrolysis by dil. sodium bicarbonate solution, pH 8.0 to 9.0.
2. Hydrolysis by dil. aqueous trimethyl amine solution.
3. Hydrolysis by aqueous potassium iodide solution.
4. Hydrolysis by shaking melthylenechloride solution of the adduct with dil. sodium bicarbonate solution (the dioxide and monoxide are soluble in methylene chloride).
5. Hydrolysis by the addition of damp acetone to methylene chloride solution of the adduct.

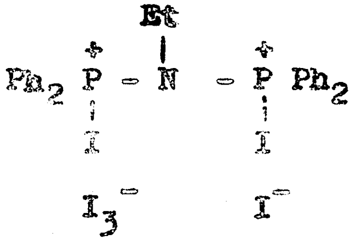
However, in all the above cases dipenyl phosphinic acid was obtained in nearly quantitative yield.

Correlating the results of the hydrolysis experiments and the investigations on the ultraviolet spectra which throw light on the number of phosphorus atoms undergoing quaternisation and the number of I_3^- ions present in the 1 : 1, 1 : 3 and 1 : 5 "adducts" of $Ph_2PN(Et)PPh_2$ with iodine the following structures could be assigned to these "adducts":



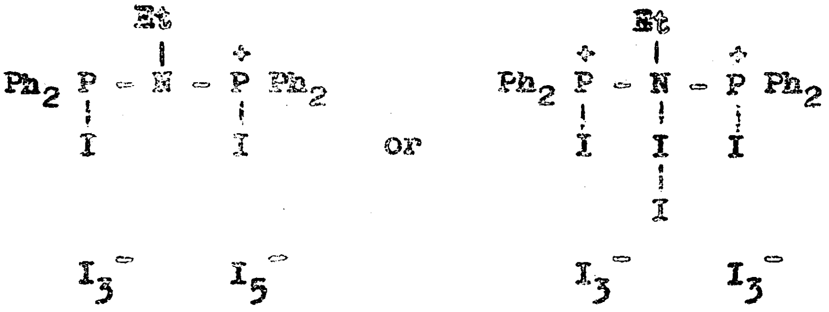
$$\mathrm{Ph_2\underset{\underset{I}{\vdots}}{\overset{+}{P}}-\overset{\overset{Et}{|}}{N}-P\,Ph_2}\qquad \mathrm{I^-}$$

1 : 1 "adduct"



$$\mathrm{Ph_2\underset{\underset{I}{\vdots}}{\overset{+}{P}}-\overset{\overset{Et}{|}}{N}-\underset{\underset{I}{\vdots}}{\overset{+}{P}}Ph_2}\qquad \mathrm{I_3^-}\quad \mathrm{I^-}$$

1 : 3 "adduct".



$$\mathrm{Ph_2\underset{\underset{I}{\vdots}}{P}-\overset{\overset{Et}{|}}{N}-\underset{\underset{I}{\vdots}}{\overset{+}{P}}Ph_2}\qquad \mathrm{I_3^-}\quad \mathrm{I_5^-}$$

or

$$\mathrm{Ph_2\underset{\underset{I}{\vdots}}{\overset{+}{P}}-\overset{\overset{Et}{|}}{\underset{\underset{\underset{I}{\vdots}}{I}}{\vdots}{N}}-\underset{\underset{I}{\vdots}}{\overset{+}{P}}Ph_2}\qquad \mathrm{I_3^-}\quad \mathrm{I_3^-}$$

1 : 5 "adduct"

The postulate of the presence of an I_5^- ion in the 1 : 5 "adduct" is justifiable since both I_5^- and I_3^- ions absorb at the same wavelenghts and cannot be thus distingiushed. The second structure suggested for the 1 : 5 "adduct" involves a nitrogen - halogen - halogen linkage similar to that found in "molecular complexes" as mentioned earlier in the introduction. If the above structures given were true the iodine present in the form of polyiodide ions can be estimated by titrating the iodine liberated on acidification of the alkaline hydrolysate of the compound concerned. This can be represented by the following equation:

$$I_3^- + 2OH^- \Longrightarrow OI^- + 2I^- + H_2O$$
$$OI^- + I^- + 2H^+ \Longrightarrow I_2 + H_2O$$

However, no molecular iodine was obtained from the 1 : 3 adduct whereas the 1 : 5 compound gave only two moles of molecular iodine from each formula weight containing ten iodine atoms. Even if the second structure for the 1 : 5 "adduct" is accepted approximately three moles of molecular iodine should be obtained per "mole" since almost all of the iodine present in the 1 : 1 molecular complexes of amines with iodine has been found to be liberated on acidification of the alkaline hydrolysate. The liberation of molecular iodine from I_3^- ion in phosphonium polyhalides was tested in the case of $(Ph_3PI)^+ I_3^-$ which gave 90%of the expected amount of molecular iodine.

The above disparity between the spectral and hydrolytic behaviour was, however, in part resolved in the case of the 1 : 3 adduct when a solution of the compound in acetonitrile was shaken up with aqueous alkali. The alkaline hydrolysate gave molecular iodine on acidification. This suggested that although the "adduct" in the solid state does not contain any I_3^- ion or atleast iodine in such a form that it reacts with OH^- to give OI^-, in acetonitrile solution it undergoes an ionisation giving rise to the I_3^- ion observed in the U.V. spectrum. Analogous behaviour has been noticed in the case of Ph_3PI_2(83) which may ionise in the following manner,

$$Ph_3\,PI_2 \rightleftharpoons (Ph_3PI)^+ + I^-$$
$$2Ph_3\,PI_2 \rightleftharpoons Ph_3P + (Ph_3PI)^+ + I_3^-$$

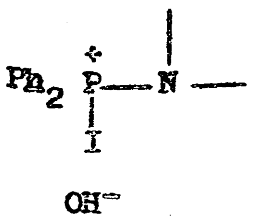
to give a complex equilibrium situation involving several species including I_3^-.

It is evident that the information so far available does not lead to any definite conclusions regarding the nature of the products obtained from the system $Ph_2PN(Et)\,PPh_2 - I_2$ except for the 1 : 1 "adduct" which appears to conform to the structure suggested. On the other hand the structures proposed for the 1 : 3 and 1 : 5 adducts are clearly incorrect on the basis of the molecular iodine available on hydrolysis.

THE INFRA RED SPECTRA OF THE PRODUCTS FROM THE SYSTEM $Ph_2PN(Et)PPh_2 - I_2$.

The infra-red spectra of $Ph_2PN(Et)PPh_2$ and its iodine "adducts" were recorded in the region 4000 - 650 cm^{-1} as Nujol and Hexachlorobutadiene mulls. The details of the spectra are shown in Table 19. Probable assignments (103, 104, 105) to the absorption peaks observed with $Ph_2PN(Et)PPh_2$ are also given for comparison with the spectra of the "adducts".

The weak bands at 3656 cm^{-1} and 3443 cm^{-1} observed for the 1 : 1 "adduct" were found to be due to hydrolysis since they became more intense on exposing the mull to moist atmosphere before the spectrum was run and are therefore probably due to O-H and N-H stretching frequencies. Only the hydroxyl ion (106) has been found to give a sharp peak in the region 3700 - 3500 cm^{-1}. The observed peak at 3656 cm^{-1} might thus arise from a hydroxyl ion in the structure



The N-H stretch in a secondary amine (107) could account for the bond at 3443 cm^{-1} which is possibly due to species like H - N-

(Et) - PPh_2. The origin of the broad absorption in the region 3200 - 3100 cm^{-1} present in the 1 : 1 "adduct" is not clear. Associated N-H gives a stretching frequency in this range (107).

Most of the aromatic absorption peaks appearing in $Ph_2PN(Et)$-PPh_2 are present in the iodine "adducts" also, however with change in position and intensity in some cases. The aryl C-H stretching frequencies between 3000 cm^{-1} and 3100 cm^{-1}, for example, steadily decrease in intensity in the "adducts", being very weak or scarcely discernible in the 1 : 5 "adduct" presumably due to "dilution" of the sample with iodine. The appreciable shifts in the positions of the bands at 1067 cm^{-1} and 925 cm^{-1} to 1050 cm^{-1} and 950 cm^{-1} respectively in the 1 : 1 "adduct" and their absence in the other two "adducts" are worth noting. It was observed earlier by Jones etal (104) that in phosphonium compounds the "X" sensitive band moves to higher frequencies than in the corresponding phosphines possibly due to an increase in the P-C bond order resulting from $d\pi - p\pi$ overlap. Similar trends are observed in the 1 : 1 and 1 : 3 adducts to a small degree.

The only bands clearly attributable to alkyl groups (107) are found in the range 2850 - 3000 cm^{-1} in $Ph_2PN(Et)PPh_2$. These are definitely present in the 1 : 1 "adduct" while the very low intensity of the corresponding bands in the 1 : 3 and

Table 19. The I.R. Spectra of $Ph_2PN(Et)P\ Ph_2$ and its Iodine "Adducts".

$Ph_2PN(Et)P\ Ph_2$ (cm-1)	Probable assignments	1 : 1"adduct" (cm-1)	1 : 3 "adduct" (cm-1)	1 : 5 "adduct" (cm-1)
		3656w		
		3443w		
		3240 - 3100 (m, broad)		
3135w		3100s	3120w	
3065s	aryl C-H stretch	3075m	3060w	
3045s	" "	3050m	3045m	3050vw
			3025w (sh)	
3005m(sh)		3003m	3010w	
2985m		2986m	2990w	
2965s		2967m	2978w	
2955m				
2923m	aliphatic C-H stretch	2925w		
2895w(sh)		2887w		
2875w(sh)		2863w		
2860w				

Table 19. The I.R. Spectra of $Ph_2PN(Et)P\ Ph_2$ and its Iodine "Adducts" (contd.).

$Ph_2PN(Et)P\ Ph_2$ (cm-1)	Probable assignments	1 : 1 "adduct" (cm-1)	1 : 3 "adduct" (cm-1)	1 : 5 "adduct" (cm-1)
		2835w		
1960w	overtone and combination bands arising from substituted aromatics	1975w	1978vw	1995w
			1955vw	
		1915w	1930w	1920w
1885w			1902w	
1880w			1880vw	1880w
1815w		1825w		
			1785vw	1795w
			1770vw	
				1730w
1587w	aryl C-C stretch	1590w	1580w	1582w
			1568w	1570w
				1560w
1477vs	aryl C-C stretch	1481w	1482w	1473w
1454m	$C-CH_3$ asymm.bend?	1464m	1472m	1465w(sh)
			1462w(sh)	1460m
1450m	C-H déformation in CH_2-N?	1450w(sh)	1450w	1448w(sh)

Table 19. The I.R. Spectra of $Ph_2PN(Et)P\ Ph_2$ and its Iodine "Adducts" (contd.).

$Ph_2PN(Et)P\ Ph_2$ (cm-1)	Probable assignments	1 : 1 " adduct" (cm-1)	1 : 3 "adduct" (cm-1)	1 : 5 "adduct" (cm-1)
1435vs	aryl C-C stretch	1441vs	1435vs	1438w(sh)
		1432s(sh)		1433m
		1400w(sh)	1408w	
1372s	$C-CH_3$ symm. deformation?	1380m	1390w	1388vw
			1382w	
			1378vw	1375vw
1347w	aryl C-C stretch?	1352vw	1340vw	1340vw
1327w	overtones arising from substituted aromatics or in plane aryl C-H deformation? or twisting and wagging vibrations of methylene group?		1322vw	1330w
1307w		1307m	1308m	1310w
				1303w
1297w				1295vw
1277w		1274w	1280vw	1285w
1257vw			1260w	1260vw
1207w		1195w	1190w	1195w
1177vw	in plane aryl C-H deformation	1185w	1185w	

Table 19. The I.R. Spectra of $Ph_2PN(Et)P\ Ph_2$ and its Iodine "adducts" (contd.)

$Ph_2PN(Et)P\ Ph_2$ (cm-1)	Probable assignments	1 : 1 "adduct" (cm-1)	1 : 3 "adduct" (cm-1)	1 : 5 "adduct" (cm-1)
			1162w	1162w
1150m	in plane aryl C-H deformation	1150m	1140w	1145w
		1138m		
1122w		1120w		
		1100s(sh)		
		1095s	1090s	
1087vs	"X"-sensitive band	1085m	1085m	1086s
1067vs		1070w	1068w	1062vw(sh)
	in plane aryl	1050s		
1025w	C-H deformation	1030w(sh)	1026w	1026w
			1020w	
		1000m	1007w	
997w	Ring breathing	992w(sh)	997s	999s
974mw	aryl C-H out of plane deformation	978w	968w	967vw
964vw		950s		

Table 19. The I.R. Spectra of $Ph_2PN(Et)P\ Ph_2$ and its Iodine "Adducts" (contd.).

$Ph_2PN(Et)P\ Ph_2$ (cm-1)	Probable assignments	1 : 1 "adduct" (cm-1)	1 : 3 "adduct" (cm-1)	1 : 5 "adduct" (cm-1)
925m	aryl C-H out of plane deformation		920vw	938w
				920vw
907w				892vw
882vs		872s		
852w	aryl C-H out of plane deformation	852w	850vw	
847w(sh)		843w	839w	832vw
		788vw(sh)		
767s		779s		
755vs	aryl C-H out of plane deformation	751s	758m	753vs
747vs		745s	743s	742m
742s(sh)				
705vs	out of plane ring deformation characteristic of mono substituted benzene	721m	715m	712w
700vs		695s(sh)	695w	699m
670w(sh)		690s	687m	690s
			682s	682s
659w(sh)		655w	662w	670w(sh)

1 : 5 "adducts" makes the presence of ethyl group in them doubtful. The assymmetric CH deformation vibrations of the CH_3 -C group (107) appear to be present only in the 1 : 1 "adduct". The corresponding symmetric mode possibly gives rise to the band at 1372 cm^{-1}. However, the high intensity of this band compared to weak absorptions observed in the case of $(Ph_3PEt)^+$ compounds (103) is not in accord with this suggestion. It may be noted that this band steadily decreases in intensity in the iodine "adducts". One of the bands at 1454 cm^{-1} and 1450 cm^{-1} may be attributed to C-H bending in CH_2-N (108) since it has been found to occur in the range 1475 - 1440 cm^{-1}. On the other hand if this band occurs at some other frequency in this range it is likely to be masked by the strong peaks due to aryl groups present. The absorptions at 882 cm^{-1} (vs) and 767 cm^{-1} (s) in $Ph_2PN(Et)PPh_2$ are present in the 1 : 1 "adduct" at 872 cm^{-1} (s) and 779 cm^{-1} (s), but are absent in the 1 : 3 and 1 : 5 "adducts". These absorptions have been taken as characteristic of the P^{III}-N skeleton (109). It is worth noting that a new band appears at 721 cm^{-1} (m), 715 cm^{-1} (m) and 712 cm^{-1} (w) in the 1 : 1, 1 : 3 and 1 : 5 "adducts" respectively.

In the present investigation no efforts were made to identify a C-N stretching frequency in the infra-red spectra studied. Aliphatic amines give only weak C-N absorption bands and then over a wide frequency range often obscured by the many other skeletal vibrations which occur alongside thus making any correlations not of much direct value (107).

On balance, the infra-red spectral evidence supports the presence of an unchanged $N(C_2H_5)$ group in the 1 : 1 "adduct" and gives only ambiguous evidence for the other "adducts". The fact that the skeletal frequencies due to $P^{III}-N$ are present only in the case of the 1 : 1 "adduct" suggests that, at this stage, the molecule still contains this structural unit, presumably as $P^{III}-N-P^{V}$, whereas at the 1 : 3 and 1 : 5 stages either the skeleton is $P^{V}-N-P^{V}$ or no P-N bond is present.

It will be observed that on the basis of all the evidence so far reported it is not possible to formulate the 1 : 1 "adduct" other than as $\left[Ph_2PN(Et)P^+(I)Ph_2\right]I^-$, without making unfounded assumptions as to structure. On the other hand the nature of the 1 : 3 and 1 : 5 "adducts" is not clear.

THE PROTON RESONANCE SPECTRA OF THE SOLID PRODUCTS FROM THE SYSTEM Ph_2 PN (Et) P Ph_2 – I_2

The lack of evidence for the ethyl group in the 1:3 and 1:5 "adducts" on the basis of infrared investigation led to an n.m.r. investigation of these "adducts" in the hope of obtaining more conclusive evidence. Solutions of the compounds in dry pyridine were investigated as no other solvents tried were capable of giving solutions of sufficiently high concentration. The frequencies associated with the ethyl group were found to be absent in both the 1:3 and 1:5 "adducts." Under comparable conditions Ph_2 PN (Et) P Ph_2 showed the characteristic pattern of absorption due to ethyl group.

The n.m.r. investigation thus provided confirmatory evidence for the absence of ethyl groups and hence presumably of the Et – N – group, in the 1:3 and 1:5 "adducts." The implications of this conclusion are now discussed.

FROM THE SYSTEM $Ph_2\ PN\ (Et)\ P\ Ph_2 - I_2$.

FROM THE SYSTEM $Ph_2\ PN\ (Et)\ P\ Ph_2 - I_2$.

The evidence for the presence of ethyl group in the 1:3 and 1:5 "adducts" being negative, these compounds may be considered to possess either a P - N - P skeletal structure in which the ethyl group originally attached to the nitrogen is replaced by a substituent non protonic group, or a structure in which the P - N bonds are absent due to the complete removal of the Et-N - group from the system. The acceptance of the existence of a P-N-P structure is difficult to justify in the case of the 1:3 and 1:5 "adducts" on the basis of the experimental results so far presented. The scission of the P-N bonds implied by the second alternative proposed should lead to the formation of $Ph_2\ PI_3$, $Ph_2\ PI_5$ and $Et\ NI_2$, and the $Ph_2\ PI_3$ and $Ph_2\ PI_5$ might be expected to appear as solid whilst any nitrogen containing material would remain in solution. The composition of Ph_2PI_3 and $Ph_2\ PI_5$ gives I, 67.3% and 77.4% respectively and correspond with the values found for the 1:3 "adduct", I, 66.9% and the 1:5 "adduct", I, 76.9% respectively. The two phosphorus compounds would be expected to ionise in acetonitrile to yield I_3^- ions:

$$Ph_2PI_3 \rightleftharpoons (Ph_2PI_2)^+ + I^-$$

$$2\,Ph_2PI_3 \rightleftharpoons Ph_2PI + (Ph_2PI_2)^+ + I_3^-$$

(by analogy with Ph_3PI_2).

$$Ph_2PI_5 \rightleftharpoons (Ph_2PI_2)^+ + I_3^-$$

Further, only in the case of Ph_2PI_5 would the alkaline hydrolysate yield molecular iodine on acidification, which is in agreement with the experimental results.

In order to prove the above hypothesis Ph_2PI_3 and Ph_2PI_5 were synthesised and their properties compared with those of the products obtained from the system $Ph_2PN(Et)PPh_2 - I_2$. The compounds were prepared by the reaction between $Ph_2P(O)PPh_2$ and iodine, which takes place as follows:

$$Ph_2P(O)PPh_2 + 2I_2 \longrightarrow Ph_2P(O)I + Ph_2PI_3$$

$$Ph_2PI_3 + I_2 \longrightarrow Ph_2PI_5.$$

When solutions of iodine in acetonitrile and $Ph_2P(O)PPh_2$ in methylene chloride were mixed an orange yellow compound and a dark violet compound precipitated out depending on the mole ratio of the reactants. These compounds were found to be Ph_2PI_3 and Ph_2PI_5 respectively, by analysis: (orange yellow compound, C.25.2%; H,1.8%, P,5.7%; I,66.7%;

TABLE 20.

COMPOUND	M. P. °C	MIXED M.P. °C	Λ_m $ohm^{-1} cm^2 mole^{-1}$ at 22°C	ϵ_{292} m μ	ϵ_{360} m μ
Ph_2 PI_3	146-147	144-145	147 $(C_m=2.70 \times 10^{-3}M)$	45,280	24,960
1:3 "adduct"	144-146		142 $(C_m=2.00 \times 10^{-3}M)$	44,000	24,500
Ph_2 PI_5	137-138	137-138	195 $(C_m=2.27 \times 10^{-3}M)$	70,920	41,850
1:5 "adduct"	134-136		199 $(C_m=1.36 \times 10^{-3}M)$	69,070	38,350

calcd. for $Ph_2 PI_3$, C, 25.5%; , 1.8% ; P, 5.5% ; I, 67.3%; Dark violet compound, C, 17.6%; H, 1.2% ; P, 3.9% ; I, 76.3%; calcd. for $Ph_2 PI_5$, C, 17.6%; H, 1.2%; P, 3.8%; I, 77.4%).

Table 20 gives the physical properties of $Ph_2 P I_3$ and $Ph_2 PI_5$ along with those of 1:3 and 1:5 "adducts". In the case of the latter two substances the molar extinction coefficients and molar conductances have been recalculated on the assumption that they are $Ph_2 PI_3$ and $Ph_2 PI_5$ respectively. It will be observed that there is good agreement between the two sets of results showing the compounds so far considered as 1:3 and 1:5 "adducts" of $Ph_2 PN (Et)P Ph_2$ with iodine, to be in fact $Ph_2 PI_3$ and $Ph_2 PI_5$ respectively. This is also supported by a complete analysis of the elements present in the compounds (1:3 "adduct", C, 25.5%; H, 1.9%; P, 5.5%; I, 66.9%; 1:5 "adduct", C 17.3%; H, 1.6%; P, 3.7%; I, 76.9%).

The infrared spectra of the 1:3 and 1:5 "adducts" in the range 4,000 to 650 cm^{-1} as Nujol and Hexachlorobutadiene mulls were found to be identical to those of Ph_2PI_3 and $Ph_2 PI_5$ respectively.

Unfortunately attempts at complete analysis of the 1:1 "adduct" were not satisfactory since the material was very sensitive to hydrolysis. However, the presence of nitrogen was confirmed (Found, 3.3%; Calcd. for $Ph_2PN(Et) P Ph_2.I_2$, 2.1%).

The high value is understandable if iodine is lost by hydrolysis as hydrogen iodide. The iodine analysis is, however, quite acceptable (Found, 38.1%; Calcd., 38.1%).

Knowing the nature of the solid products from the system Ph_2 PN (Et) P Ph_2 — I_2 it should be possible to discuss the experimental results obtained in the light of the chemistry of the reactions involved. The inflections in the conductometric titration curve which might be taken as indicative of compound formation is substantiated only in the case of the mole ratio 1:1. The isolation of solid Ph_2PI_3 and Ph_2 PI_5 from the system implies also their formation in the solution and shows that the inflection at the 1:5 mole ratio only represents the final break - down of the P-N-P skeletal structure to form ionic species. The following sequence of reactions may be considered to take place:

$$\begin{tikzcd} Ph_2PN(Et)PPh_2 + I_2 \arrow[r] & Ph_2PN(Et)P(I_2)Ph_2 \arrow[d, shift left] \\ & {[Ph_2PN(Et)\overset{+}{P}(I)Ph_2] + I^-} \arrow[u, shift left] \end{tikzcd}$$

$$Ph_2PN(Et)P(I_2)Ph_2 + 2I_2 \longrightarrow Ph_2P(I_2)N(Et)I + Ph_2PI_3 \quad \ldots\ldots\ldots\ldots 23$$

$$Ph_2P(I_2)N(Et)I \rightleftharpoons [Ph_2\overset{+}{P}(I)N(Et)I] + I^-$$

$$Ph_2PI_3 \rightleftharpoons [Ph_2PI_2]^+ + I^-$$

$$\begin{tikzcd} Ph_2PI_3 + I_2 \arrow[r, dash] & Ph_2PI_5 \arrow[d, shift left] \\ & {[Ph_2PI_2]^+ + I_3^-} \arrow[u, shift left] \end{tikzcd}$$

$$\begin{tikzcd} Ph_2P(I_2)N(Et)I + I_2 \arrow[r, dash] & Ph_2P(I_4)N(Et)I \arrow[d, shift left] \\ & {[Ph_2\overset{+}{P}(I)N(Et)I] + I_3^-} \arrow[u, shift left] \end{tikzcd}$$

The reaction represented by equation 23 may also be thought to proceed in two stages as shown below:

$$\begin{tikzcd} Ph_2PN(Et)P(I_2)Ph_2 + I_2 \arrow[r] & Ph_2PN(Et)I + Ph_2PI_3 \arrow[d, shift left] \\ & {[Ph_2PI_2]^+ + I^-} \arrow[u, shift left] \end{tikzcd}$$

$$\begin{tikzcd} Ph_2PN(Et)I + I_2 \arrow[r] & Ph_2P(I_2)N(Et)I \arrow[d, shift left] \\ & {[Ph_2\overset{+}{P}(I)N(Et)I] + I^-} \arrow[u, shift left] \end{tikzcd}$$

This implies that the P - N bond is susceptible to scission by iodine. However, this is not in accord with the formation of $Ph_2P(I_4)N(Et)I$ which can be postulated in order to account for the break at a mole ratio of 1:5 in Fig. 8 and 9. The rupture of P-N bond in this compound would entail another mole of iodine and in this case the inflection would have been at a mole ratio of 1:6 instead of 1:5. Further, it would be expected that tervalent phosphorus in the compound $Ph_2PN(Et)P(I_2)Ph_2$ would be reactive enough for electrophilic attack by iodine to take place instead of the scission of the P-N bond. But consequent on the attack of the second phosphorus atom by iodine it is possible that steric hindrance might affect the situation causing the P-N bond to undergo cleavage. The importance of steric factors in these cases must be expected since the P-N-P bond angle is found to be about 120° from X-ray structural analysis on related compounds (110). The mechanism of the reaction implied by equation 23 may therefore be represented as follows:

$$Ph_2PN(Et)P(I_2)Ph_2 + I_2 \longrightarrow Ph_2P(I_2)N(Et)P(I_2)Ph_2$$

(transient species)

$$\downarrow I_2$$

$$Ph_2P(I_2)N(Et)I + Ph_2PI_3.$$

The existence of the compounds $Ph_2P(I_2)N(Et)I$ and $Ph_2P(I_4)N(Et)I$ appears to be supported by the fact that

Ph_2PI_3 and Ph_2PI_5 were obtained in low yields ($\approx$35 - 40%) in all preparations. Evaporation of the solvent from the filtrate yielded a dark thick liquid which was not further worked up.

The indistinct break at a mole ratio of 1:3 in the conductometric titration curve (Fig. 8) suggests that the processes taking place in the region 1:1 to 1:3 mole ratio are predominantly those represented by equation 23. The appearance of I_3^- ion in this region (Fig. 9) can be explained on the basis of the mode of ionisation of Ph_2PI_3 already observed.

The molar extinction coefficients (Table 20) for the triiodide ion obtained from measurements on Ph_2PI_5 in acetonitrile solution are much higher than those reported (101) for tetramethyl ammonium triiodide in the same solvent ($[(CH_3)_4N]^+I_3^-$: $\epsilon_{291\,m\mu}$ 38,800; $\epsilon_{360m\mu}$ 25,500). On the other hand the values for Ph_2PI_5 are in better agreement with those of triphenyl phosphorus tetraiodide ($\epsilon_{291\,m\mu}$ 68,000; $\epsilon_{360\,m\mu}$ 34,300) and on this basis the molar extinction coefficients $\epsilon_{292\,m\mu}$ 45280 and $\epsilon_{360m\mu}$ 24960 for Ph_2PI_3 indicate partial ionisation giving rise to I_3^- ion. The reason for significant increase in the ultraviolet absorption by the I_3^- ions present in these compounds is obscure at this stage. Abnormal values of molar conductance for the compounds $Ph_2PN(Et)P(I_2)Ph_2$, Ph_2PI_3 and Ph_2PI_5

are also to be noted. In the case of $Ph_2PN(Et)P(I_2)Ph_2)Ph_2$ (Λ_m = 144 $ohm^{-1}cm^{2}.mole^{-1}$. (C_m = 1.08 x 10^{-2} M) $d\pi - p\pi$ $p\pi$ bonding between the phosphorus and the nitrogen would tend to stabilise the cation thus facilitating the ionisation to go to completion. New modes of ionisation, even though without any direct evidence, have to be postulated in order to account for the behaviour of Ph_2PI_3 and Ph_2PI_5 in this respect. For example, ionisation schemes like

$$(Ph_2PI_2)^{+} I^{-} \rightleftharpoons (Ph_2P)^{+} + I_3^{-}$$

would be expected to increase considerably the conductance that would have been observed otherwise since polyhalides have been found to be better conductors than the corresponding halides in acetonitrile solutions (102). Acetonitrile is a good solvent for polyhalides ions and might therefore favour an ionisation of the type given above. The existence of a Ph_2P^{+} ion is an interesting postulate since it would correspond to a linear ion and might be expected to have a high molecular mobility. Further investigations are clearly warranted to check the existence or otherwise of this mode of ionisation.

The results of the present investigation have demonstrated the greater base strength of phosphorus (III) over that of nitrogen when they are linked together, in agreement with observations made earlier (99,100). Burg and

Slota (99) attributed this to the interaction of the lone electron pair on the nitrogen atom with an appropriately directed 3d orbital of phosphorus thus weakening the donor bonding power of nitrogen. The lone pair on the phosphorus can not interact with nitrogen in this way and hence its base action would be enhanced by the inductive effect of the electrons on the nitrogen atom.

Closely similar to the cleavage of the P - N bond in Ph_2 PN (Et) P Ph_2 by the action of iodine, are the reactions of tetraaryl diphosphines with halogens (bromine and iodine) and alkyl halides leading to the scission of the P - P bond (111,112). In the case of tetraalkyl diphosphines, however, addition takes place with alkyl halides to form monoquaternised phosphonium compounds with the P - P bond intact.

Investigations of the behaviour of the lower members of the halogen series towards Ph_2 PN (Et) P Ph_2 can possibly reveal the part played by steric factors in these reactions. The use of bis-(dialkyl phosphino) ethylamine for similar reactions is also important from this point of view. Addition of alkyl iodide to Ph_2 PN (Et) P Ph_2 gives only a 1:1 adduct. It would be interesting to examine the nature of the corresponding reactions with aryl iodides. Systems involving P - N - P rings and chains offer many more possibilities.

1. X-RAY POWDER DIAGRAMS OF PHOSPHORUS PENTACHLORIDE.

In a study of phosphorus pentachloride Kennedy (46) observed that the X-ray powder diagram of the compound varied depending on the method of purification used. Further there was no agreement with the reported powder diagrams which are reproduced in Fig. 10. An experimental study of the X-ray powder patterns of phosphorus pentachloride obtained by different purification methods was, therefore, undertaken in an attempt to clarify the position.

The following samples of phosphorus pentachloride were prepared and their X-ray powder diagrams examined:

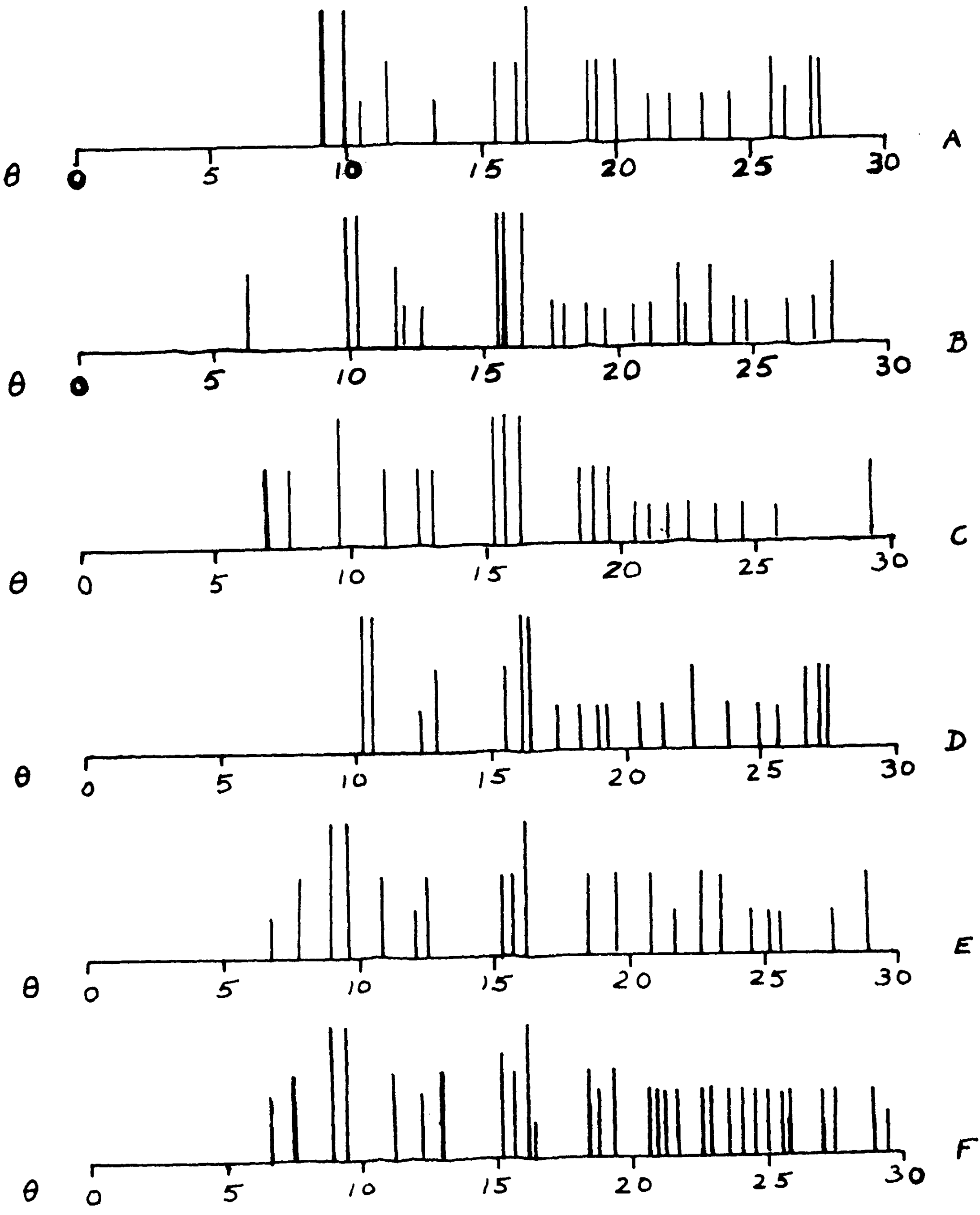
(i) Phosphorus pentachloride recrystallised from nitrobenzene.

(ii) Phosphorus pentachloride recrystallised from nitroethane.

(iii) Phosphorus pentachloride recrystallised from carbon tetrachloride.

(iv) Phosphorus pentachloride sublimed under vacuum.

Fig. 10. X-Ray Powder Diagrams of Phosphorus Pentachloride.



A. KOLDITZ (44) D. KENNEDY: SUBLIMED (46)
B. POPOV : NORMAL (120) E. CLARK et al : RECRYST. FROM (29)
C. POPOV : SUBLIMED (120) F. PRESENT WORK : NITROBENZENE

Table 21. **X-ray powder diagrams of phosphorus pentachloride (present work).**

PCl$_5$ recrystallised from nitrobenzene		PCl$_5$ recrystallised from nitroethane	
θ		θ	
6.7 w	21.7 w	6.6 w	21.7 w
7.6 m	22.6 w	7.6 m	22.6 w
9.0 vs	22.8 w	9.0 vs	22.8 vw
9.5 vs	23.5 w	9.5 vs	23.5 w
11.2 m	23.9 w	11.3 m	23.9 vw
12.2 w	24.4 w	12.2 w	24.4 w
12.8 m	24.9 w	12.9 m	24.9 w
15.1 s	25.4 w	15.1 s	25.5 w
15.6 m	25.7 w	15.6 m	25.7 w
16.1 vs	26.9 vw	16.1 vs	27.2 vw
16.3 vw	27.5 vw	16.3 vw	27.4 vw
18.4 m	28.8 w	18.4 m	28.8 w
18.7 w	29.3 w	18.7 w	29.3 w
19.4 m	31.2 w	19.4 w	
20.5 w	31.5 w	20.5 w	31.5 w
20.9 w	32.8 vw	20.8 w	32.9 w
21.2 w		21.2 vw	

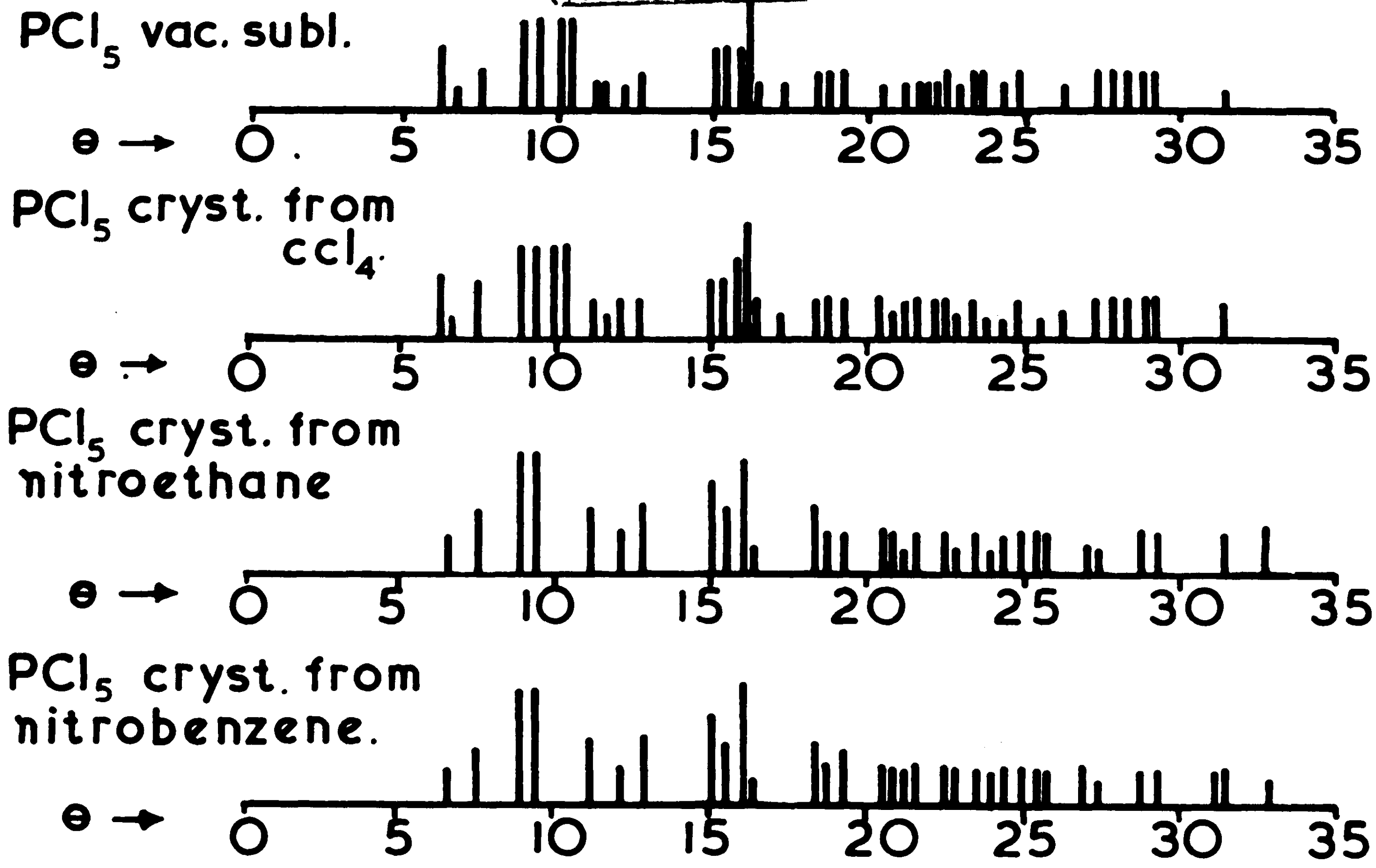
Table 22. X-ray powder diagrams of phosphorus pentachloride (present work).

PCl_5 recrystallised from carbon tetrachloride.		PCl_5 vacuum sublimed.	
θ		θ	
6.3 m	20.8 vw	6.3 m	
6.7 vw	21.2 w	6.7 vw	21.2 vw
7.6 m	21.7 vw	7.6 w	21.7 vw
9.0 s		9.0 s	22.0 vw
9.5 s	22.2 w	9.5 s	22.2 w
10.0 s	22.5 w	10.0 s	22.6 w
10.4 s	22.9 vw	10.4 s	23.1 vw
11.3 w	23.5 w	11.2 vw	23.5 w
11.7 vw	23.8 vw	11.7 vw	23.7 w
12.1 w	24.4 vw	12.2 vw	24.5 vw
12.8 w	24.8 w	12.7 w	24.9 w
15.1 m	25.6 vw	15.1 m	
15.5 m	26.4 vw	15.5 m	26.4 vw
15.8 m	27.3 w	15.8 m	27.4 w
16.1 vs	27.9 w	16.1 vs	27.9 w
16.4 w	28.4 w	16.4 vw	28.4 w
17.3 vw	28.8 w	17.3 vw	28.8 w

Table 22 continued.

PCl_5 recrystallised from carbon tetrachloride.		PCl_5 vacuum sublimed.	
θ		θ	
18.4 w	29.2 w	18.4 w	29.3 w
18.8 w	31.5 w	18.8 w	31.6 vw
19.3 w	32.8 vw	19.3 w	
20.5 w		20.5 vw	

Fig.11. X-Ray Powder Diagrams of Phosphorus Pentachloride.
(present work.)



The results are set out in Tables 21 and 22, and diagramatically represented in Fig. 11 from which it is readily observed that there are two distinct types of pattern: (i) and (ii); (iii) and (iv). This distinction can also be noted in the appearance of the samples: samples obtained by methods (i) and (ii) are pale yellow in colour whereas those from methods (iii) and (iv) are white. It would seem therefore that solid phosphorus pentachloride exists in atleast two crystalline forms.

Application of the usual analytical methods (113) showed that the X-ray powder data of both forms of phosphorus pentachloride did not accord with either cubic or tetragonal symmetries; other crystal systems were not examined since the calculations were more complicated in these cases. X-ray structure studies on single crystals of phosphorus pentachloride recrystallised from nitrobenzene by Clark, Powell and Wells (29) showed tetragonal symmetry for the unit cell which is made up of $[PCl_4]^+$ and $[PCl_6]^-$ ions. A method of calculating the d spacings from the unit cell parameters obtained in this work has been given by Kennedy (46). The powder diagram constructed accordingly was found to have some resemblance with those of (i) and (ii), but the powder lines in the two cases were not exactly matched (Fig. 10). It has been shown by Payne (31) that phosphorus pentachloride exists as $[PCl_4]^+$ and $[PCl_6]^-$ ions in nitrobenzene solutions also. Molecular phosphorus pentachloride has been recognised in nonpolar solvents (32) and in the vapour state (24). These observations would suggest an ionic lattice for (i) and (ii), and a molecular lattice for (iii) and (iv). Further work directed towards the confirmation of this interpretation of the X-ray powder photographs of phosphorus pentachloride is required and the results of this would be of great interest.

2. THE PYROLYSIS OF $(PCl_4)^+ F^-$

a) The Pyrolysis of $(PCl_4)^+F^-$ in Carbon tetrachloride.

During a study of the reaction between $(PCl_4)^+ F^-$ and iodine in carbon tetrachloride observations were made that some kind of transformation of $(PCl_4)^+F^-$ occurs when a suspension of $PCl_4^+ F^-$ in carbon tetrachloride is heated (to about 80°). The pyrolysis of phosphorus (V) chlorofluroides in general has been found to give a variety of products depending on the experimental conditions. A typical instance is the behaviour of $(PCl_4)^+ (PF_6)^-$ (22, 47) which has been already discussed in Part I of this thesis in connection with the general methods of preparing chlorofluorophosphoranes. In the light of these results it was of interest to investigate the changes in $(PCl_4)^+ F^-$ which occur when its suspensions in carbon tetrachloride are heated to above room temperature (80° C).

$(PCl_4)^+ F^-$ is sparingly soluble in carbon tetrachloride in the cold. On warming to about 80° C it dissolved gradually with the evolution of gas, and it was observed that no solid came out of solution on cooling to room temperature. The solution thus prepared gave phosphorus pentachloride in the residue (analysis: Cl, 84.4%; Calcd. for PCl_5, Cl, 85.1%) when the solvent was removed by freeze drying; part of the phosphorus pentachloride was found to pass over into the distillate. The distillation was done quantitatively and the following observations were made:

$(P\ Cl_4)^+ F^-$ (14.86 m. moles) was dissolved in carbon tetrachloride (~50 ml) by heating to 80° C under reflux in an atmosphere of dry nitrogen. Part of the $P\ Cl_5$ (4.86 m. moles) formed was obtained as a solid residue on removal of the solvent. $P\ Cl_5$ (7.03 m. moles) present in the distallate was hydrolysed with dil. alkali followed by estimation of the chloride (17.5 m. moles of chlorine) in the aqeous layer. The mole ratio of $(P\ Cl_4)^+ F^-$ (originally present) to the total amount of $P\ Cl_5$ formed was found to be 5: 3.94.

During the above pyrolysis of $(P\ Cl_4)^+ F^-$ in carbon tetrachloride white fumes appeared at the outlet of the apparatus. In a separate experiment these volatiles were passed through traps at -78° C (to collect $C\ Cl_4$) and then one at liquid oxygen temperature to collect the remaining volatiles. The I. R. spectrum of the volatiles collected in the liquid oxygen trap showed the presence of SiF_4, PF_5 and $P\ O\ F_3$. $Si\ F_4$ and POF_3 were presumed to be formed as a result of the attack on the glass by PF_5. The mole ratio of $(P\ Cl_4)^+ F^-$ (20.96 m. moles) originally present to the amount of PF_5 (3.89 m. moles, by phosphorus estimation) formed was found to be 5: 0.93.

The overall distribution of reactants and products thus assumes the ratio, $[(P\,Cl_4)^+ F^-] : [P\,Cl_5] : [P\,F_5]$ :: 5: 3.94: 0.93 which is close to 5:4:1. The reaction occuring can, therefore, be represented as follows:

$$5(P\,Cl_4)^+ F^- \longrightarrow 4\,P\,Cl_5 + P\,F_5.$$

b) <u>The Pyrolysis of $(P\,Cl_4)^+F^-$ in arsenic trichloride.</u>

Kolditz (65) reported the preparation of covalent $P\,Cl_4\,F$ by the pyrolysis of $(P\,Cl_4)^+ F^-$ in arsenic trichloride at about 90°C, however, no analytical data on the product were given. For this reason as well as the apparently different pyrolytic behaviour of $(P\,Cl_4)^+ F^-$ in carbon tetrachloride it was thought worthwhile to reinvestigate the system in order to confirm the exact nature of the products.

$(P\,Cl_4)^+ F^-$ (296 m. moles, 57.0 g) was suspended in arsenic trichloride (30 ml) and pyrolysed at about 90°C for approximately 7-8 hrs. in an atmosphere of dry nitrogen. The volatiles formed were collected in traps cooled to -78°C and - 196° C. On fractionation of the - 78°C fraction in a vacuum line the products were found to be $P\,Cl_3\,F_2$ (85.7 m. moles), $P\,F_3\,Cl_2$ (25.2 m. moles) and $P\,Cl_4\,F$ (5.0 m.moles) $P\,F_5$, $Si\,F_4$ and $PO\,F_3$ were found to be present in the volatiles condensed at - 196°C. This fraction (5.2 m. moles) could not be collected quantitatively since part of it was likely to have been lost when the trap was occasionally allowed to warm up to prevent blockage in the system due to the formation of solid.

A white solid crystallised out of the arsenic trichloride on cooling to room temperature. When a small amount of this product was pumped under vacuum for about six hours the compound lost its crystallinity and became powdery. This is possibly due to a solvate, for example X.n $AsCl_3$ losing solvent under vacuum (P_2Cl_{10}. 5 $As\ Cl_3$ is known to lose $As\ Cl_3$ on being pumped under vacuum (114)). The material on analysis gave Cl, 79.0%; calcd. for $P\ Cl_5$, Cl, 85.1% ; calcd. for $(P\ Cl_4)^+\ F^-$, Cl, 73.8%; Calcd. for $(P\ Cl_4)^+\ (P\ Cl_5\ F)^-$, Cl, 79.8%. The X - ray powder photograph of the sample appeared to indicate a mixture of $(P\ Cl_4)^+\ F^-$ and $P\ Cl_5$; that is the sample consists of unchanged $(P\ Cl_4)^+\ F^-$ and $P\ Cl_5$ formed by pyrolysis.

On the basis of these results the reactions taking place may be represented as follows:

$$2\ (P\ Cl_4)^+\ F^- \longrightarrow P\ Cl_5\ +\ P\ Cl_3\ F_2$$

$$3\ (P\ Cl_4)^+\ F^- \longrightarrow 2P\ Cl_5\ +\ P\ F_3\ Cl_2$$

$$5\ (P\ Cl_4)^+\ F^- \longrightarrow 4P\ Cl_5\ +\ P\ F_5$$

The main reaction occuring in the system is that leading to the formation of $P\ Cl_3\ F_2$ which is obtained in about 57% yield (based on fluorine).

The dependence of the nature of the products formed by the pyrolysis of phosphorus (V) chlorofluorides on the medium in which the reaction is carried out is very interesting. A complete explanation of this is, however, difficult at this stage although it can be partly attributed to the difference in the nature of the species present in the different media. It is important to note that pyrolysis reactions offer further possible routes for the preparation of chlorofluorides of phosphorus (V).

3. I.R. SPECTRA.

Details of the I.R. spectra used for the identification of compounds in this research are given in the following pages.

a) PF_5 at 10mm. pressure (46).

535 s, 568 s, 578 s,
590 s, 875 s, 940 s,
950 s, 960 s, 1025 vs. cm^{-1}
($2000 - 400$ cm^{-1})

b) PF_3Cl_2 at 5 mm. pressure (46).

930 s, 920 s, 904 s,
899 s, 870 s, 675 s,
668 s, 635 s, 564 m,
492 m, 432 w. cm^{-1}
($2000 - 400$ cm^{-1}).

c) POF_3 at 8 mm. pressure (46).

480 s, 875 m, 999 vs,
1410 m, 1425 m, 1430 m. cm^{-1}
($2000 - 400$ cm^{-1})

d) POF_2Cl (60).

1358 m 895 m cm^{-1}
($2000 - 650$ cm^{-1})

e) $POFCl_2$ (60).

1331 m., 894 m., cm^{-1}

(2000 - 650 cm^{-1})

f) PF_3 at 10 mm. pressure (46).

855 s., 864 s., 894 s.,

900 w. cm^{-1}

(2000 - 400 cm^{-1})

g) PF_2Cl (60).

860 s. cm^{-1}

(2000 - 650 cm^{-1})

h) $PFCl_2$ (60).

827 m. cm^{-1}

(2000 - 650 cm^{-1})

i) PCl_3 at 10 mm. pressure (present work).

508 vs. cm^{-1}

(2000 - 400 cm^{-1})

j) SiF_4 (46).

1032 vs. cm^{-1}

(2000 - 400 cm^{-1})

k) **Nitron $(PF_6)^-$ complex as Nujol mull.**

688 m, 698 m, 712 m,

740 m, 755 s, 777 m,

820 - 888 shoulder (vs).

967 m, 1008 w, 1022 w,

1041 w, 1063 w, 1080 w,

1161 w, 1214 m, 1230 m,

1296 w, 1338 w, 1488 s,

1557 s, 1593 s, 1620 s. cm^{-1}.

EXPERIMENTAL PART

GENERAL TECHNIQUES

The compounds studied in the present work were found to be extremely sensitive to decomposition by moisture. For this reason a vacuum system which provided the best working conditions was used extensively for handling volatile materials and in the case of non volatile compounds the manipulation was done in a nitrogen filled dry box. The special techniques involved in these operations are described in the following pages.

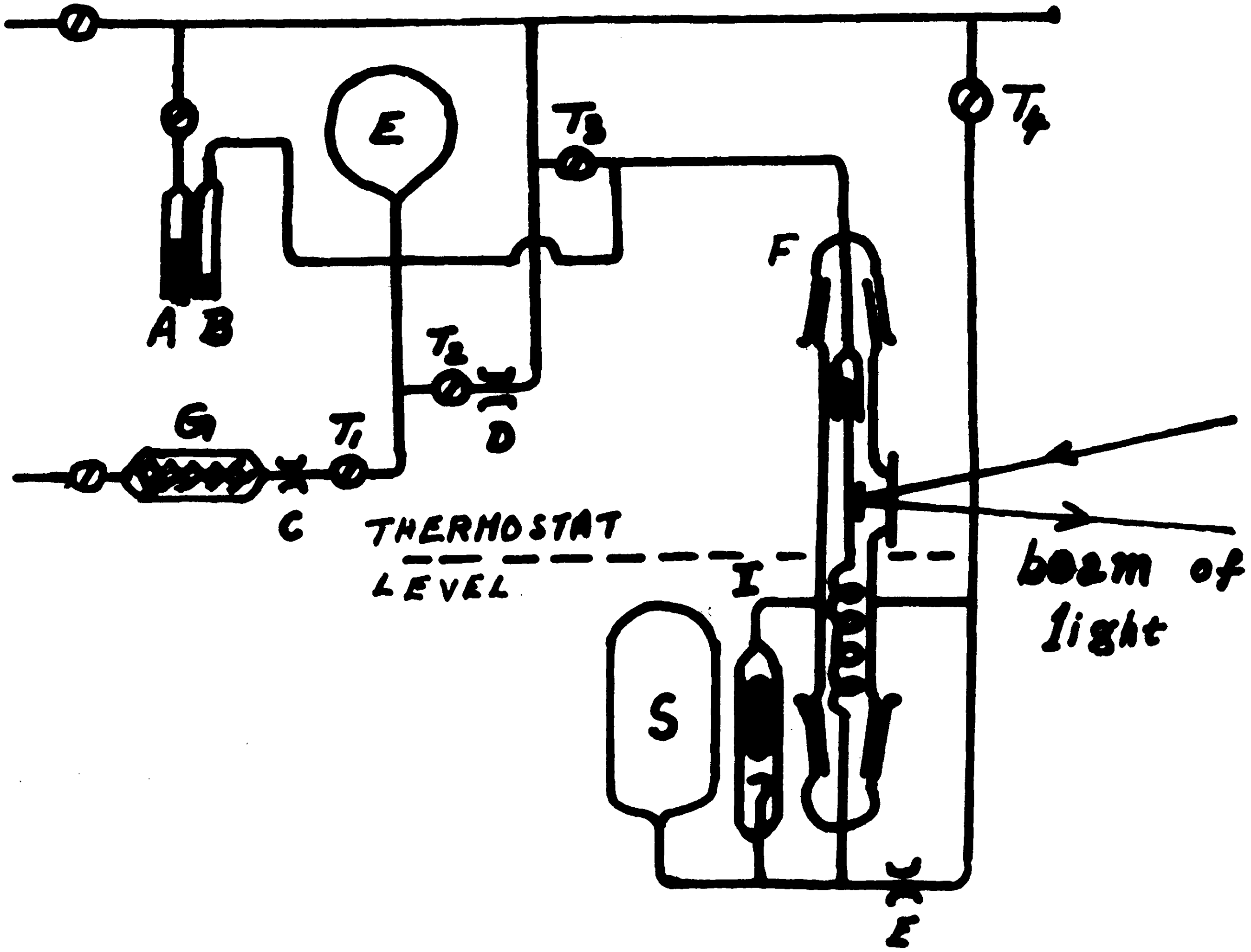
Vacuum system. This consisted of a pumping unit (incorporating a mercury diffusion pump backed by a rotary oil pump) connected to a main line through two protective sludge traps. Various special units of apparatus designed for operations like fractionation, vapour pressure measurement, I.R. measurement, storage of gases, molecular weight determination and temporary attachment of apparatus to the vacuum system, branched off from the main line.

Fractionation. A series of U-tube traps interconnected by taps and which could be operated independently of each other were used for vacuum fractionation. The individual traps were held at the desired temperatures by immersion in Dewar flasks containing suitable coolants and the volatile material to be separated was passed through the train of traps when fractional condensation took place. In the course of the work the following coolants were used: "Drikold" and acetone (-78°C), methanol slush (-98°C), isopentane slush (-161°C), liquid oxygen (-183°C) and liquid nitrogen (-196°C). Intermediate temperatures in the range 0° - -78°C were obtained by adding suitable amounts of "Drikold" to acetone.

Pressure measurement. The vapour pressure of PCl_3F_2 was measured using wide-bore (10 mm) mercury manometers. During the study of the vapour phase transformation of PCl_3F_2 pressure measurements were made in the all glass apparatus *shown in Fig. 12. The spiral gauge in the system was used as a null instrument in which the deflection of the spiral was magnified by the optical lever principle. The pointer extending from the spiral carried a mirror which underwent deflection as a result of the movement of the spiral and the mirror was allowed to reflect a parallel beam of light on to a scale situated at a distance of about one metre. A pressure differential of 1 mm. caused the spot of light on the scale to move through a distance of 5 mm.

The vapour was admitted into the storage bulb S from the main vacuum line through tap T_4 and the constriction E was sealed off. The instrument was brought back to the null position by admitting dry air into the chamber F through the drying tube G by opening the tap T_1. The fine constriction C and the air

Fig.12. Apparatus for Pressure Measurement.

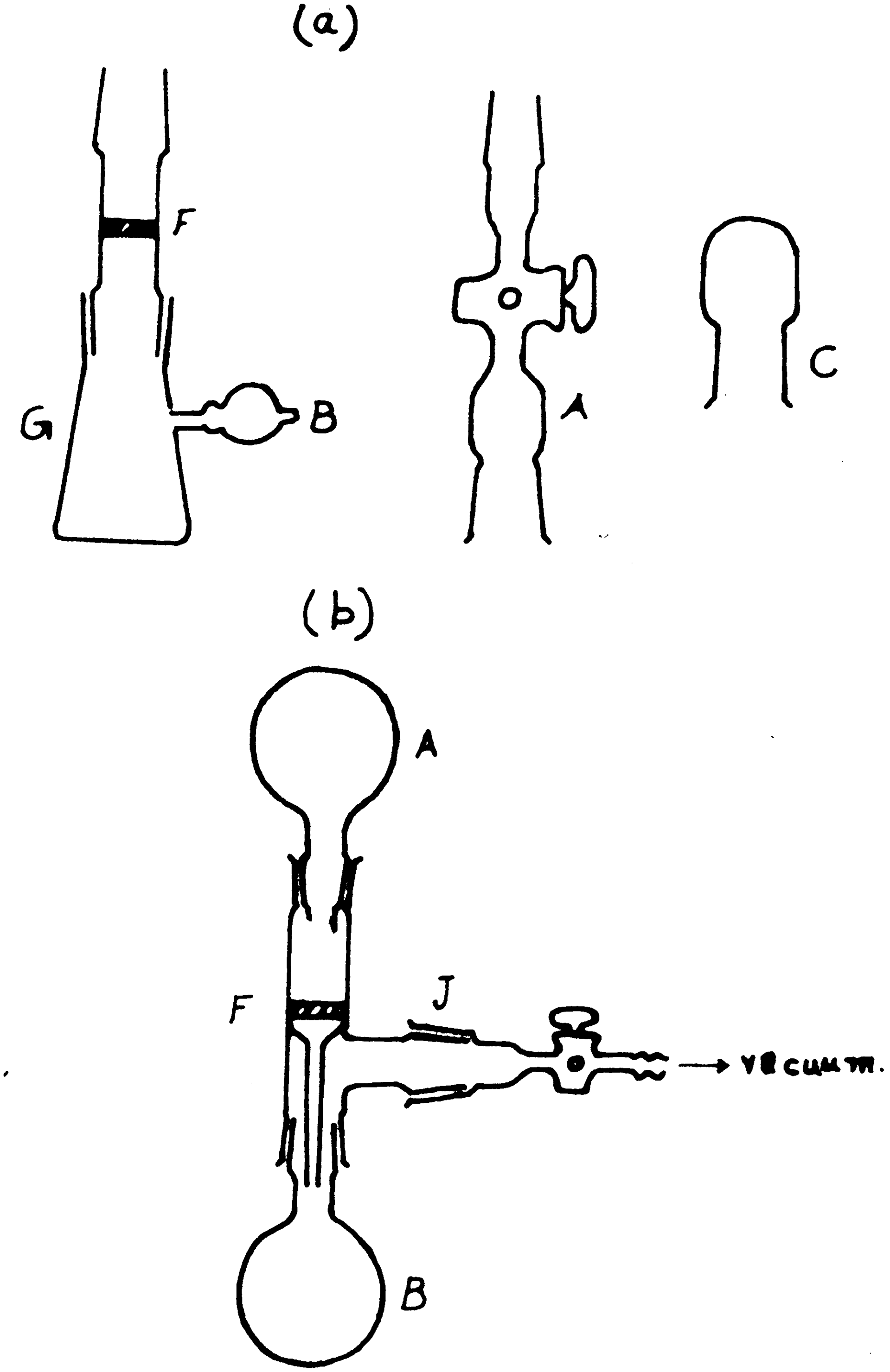


surge chamber E facilitated fine control of this operation. If necessary the pressure in the chamber F was reduced by connecting this section of the apparatus to the vacuum line via tap T_2 and the fine constriction D. Once the pressures on either side of the spiral were balanced the pressure of the vapour could be obtained from the difference in the mercury levels in the wide - bore manometers A and B arranged close together and immersed in the same mercury reservoir. The manometer A functioned as an ordinary barometer. The mercury levels in A and B were read with the aid of a cathetometer (least count, 0.01 mm.). The storage bulb and the spiral gauge system were immersed in a water thermostat the temperature of which was controlled using a toluene thermoregulator and a Sunvic Relay (Type F 102/3). After the experiment was over the vapour was taken out of the system for examination via the break seal I.

Molecular weight determination. This was carried out by Regnaults' method. The weight of a known volume (~ 300 ml) of vapour contained in a light bulb (~ 64 g) was found out at known temperatures and pressures and the molecular weight could be computed from this with an accuracy of 1.0%.

Melting point determination. The melting point of PCl_3F_2 was found out by means of a dropping weight apparatus. A glass rod incorporating an iron core was raised magnetically inside an

Fig. 13. Filtration Apparatus.

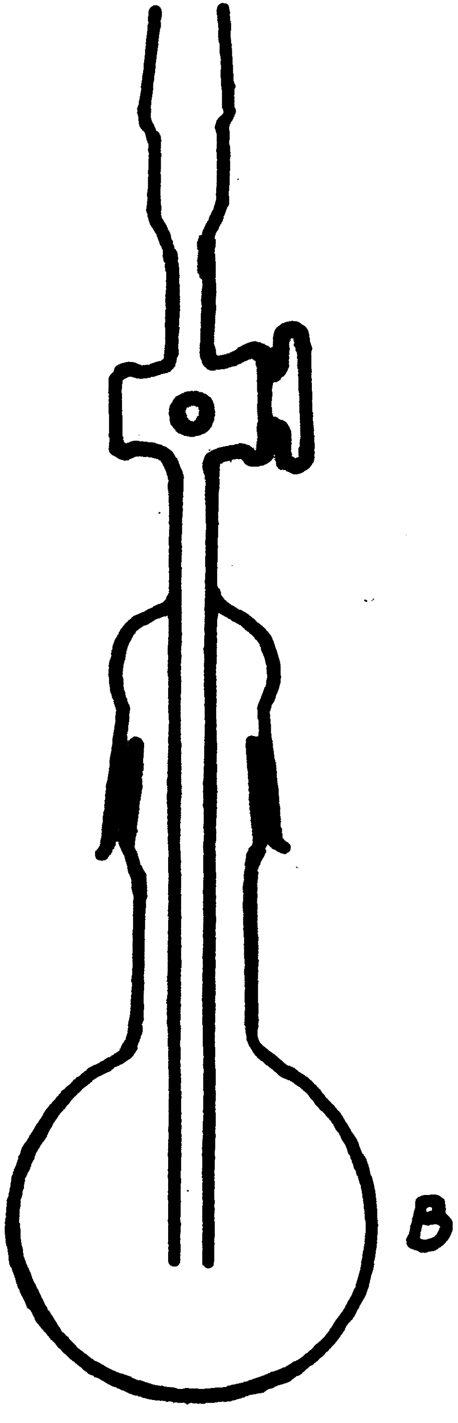


evacuated glass tube and the vapour was condensed below it to form a ring of solid material (projecting from the wall of the tube) which supported the rod when the magnet was removed. The tube was then surrounded by a suitable bath the temperature of which could be raised slowly. The melting of the solid was indicated by a downward movement of the visible part of the rod and the temperature of the bath at that instant was noted by means of a pentane thermometer.

Filtration and drying of moisture-sensitive solids. The filtration of moisture sensitive solid compounds inside a dry box was carried out using the filter funnel F in conjunction with the filter flask G and the rubber bulb B which was used to apply suction (Fig. 13a). After washing the filtered compound the funnel was closed at the top and the bottom by the adaptor A and the cap C respectively and the apparatus attached to the vacuum line for pumping.

Fig. 13b shows the apparatus used for filtration on the vacuum line. The apparatus was assembled in the dry box and afterwards connected to the vacuum line and evacuated with the tap closed. Initially the flask A containing the liquid + solid mixture was kept at the bottom. This was brought in the position shown in the figure by rotation about the joint J. The tap was partially opened when the liquid passed through the fil-

Fig. 14. Apparatus for Hydrolysis.



ter disc F to the flask B.

Hydrolysis. The solid and liquid chlorofluorides of phosphorus (V) were hydrolysed using the apparatus shown in Fig. 14. Solid materials were introduced into the detachable bulb B (~ 100 ml capacity) in a dry box and the bulb was then evacuated for about thirty minutes. The tap was closed and the apparatus was detached from the vacuum system. The bulb B was cooled in crushed "Drikold" and 0.5N sodium hydroxide was introduced into it from the top by manipulating the tap, care being taken not to cause a violet reaction by overaddition. After the reaction was over the apparatus was set aside for two to three hours in order that all the hydrogen halides formed were absorbed by the alkali. In the case of liquid materials they were condensed in the bulb under vacuum and hydrolysed as described above. The apparatus was weighed under vacuum before and after the introduction of the material so that the amount of material hydrolysed could be determined.

The solid products of the reaction between $Ph_2PN(Et)\ P\ Ph_2$ and iodine were hydrolysed as follows: a suitable amount of the material was transferred into a conical flask inside a dry box. The flask was stoppered and taken out of the dry box. A sufficient amount of 0.5N sodium hydroxide solution was added quickly and the flask immediately stoppered and kept overnight to enre complete hydrolysis.

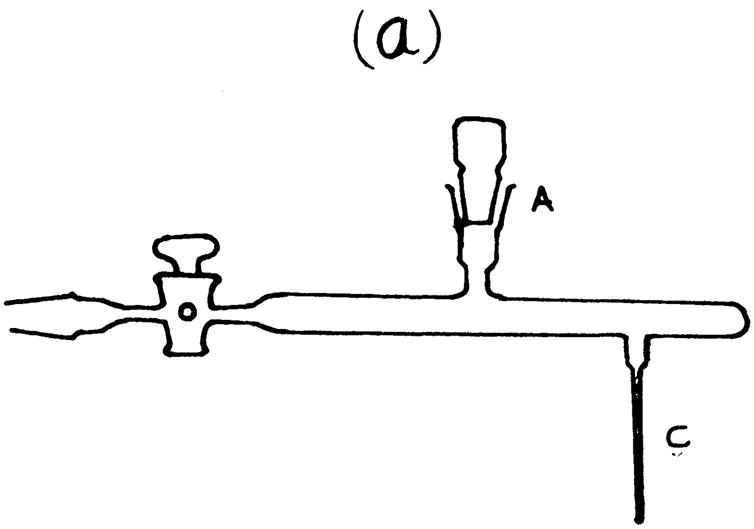
Analysis. Chloride and iodide ions in solution were estimated gravimetrically as silver chloride and by Volhard's method respectively. Fluoride present in solution was converted to fluosilicic acid by distillation from a sulphuric acid solution containing soft glass beads in a specially designed apparatus (115). The distillate was titrated with thorium nitrate solution on an EEL UNIGALVO PHOTO-ELECTRIC TITRATOR, TYPE 20 using sodium alizarin sulphonate as indicator (116). The end point was detected by extrapolation since the titration curve did not give a sharp break. The fluoride concentration was determined from a calibration curve obtained by titrating known amounts of fluoride with thorium nitrate solution.

Phosphate in solution was estimated volumetrically by the ammonium molybdate method. Solutions suspected of containing $(PF_6)^-$ ion were treated with nitric acid and the mixture (6N in acid) was evaporated to dryness on a steam bath in order to effect hydrolysis to PO_4^{3-} ion, before analysis.

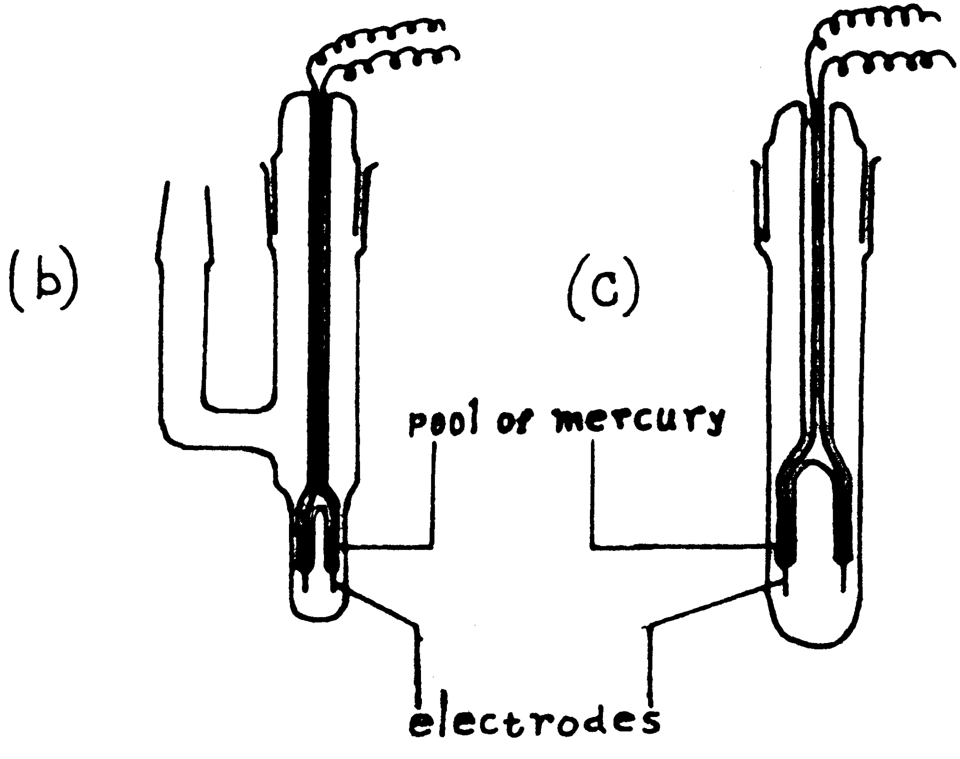
Carbon, hydrogen, nitrogen and phosphorus in organophosphorus compounds were determined by microanalytical methods. The- were carried out commercially by A. Bernhardt, Mikroanalyti- Laboratorium im Max - Planck - Institut für Kohlenforschung,

Fig. 15.

Apparatus for filling Sample Tubes for X-Ray Powder Photography.



Conductance Cells.



Hohenweg.

X-ray powder photography. The filling of capillary tubes for x-ray powder photography was achieved using the apparatus shown in Fig. 15a. The well powdered sample was introduced into the apparatus (through socket A) inside a dry box and after stoppering, the apparatus was evacuated. The fine capillary C was filled with the sample by gentle tapping. It was then sealed at the top by means of a microburner. The powder photographs were taken with Philips PW 1024 model powder camera. Very fast, high contrast film (Ilford - Industrial G) was used. The radiation employed was Cu K_α and the exposure time of each film was about 40 hrs. at 35 kv and 13 mA.

Conductance measurements. The conductance of liquid PCl_3F_2 was measured using the cell shown in Fig. 15b. The side limb carrying a B 14 cone was attached to the vacuum line, evacuated and flamed out. PCl_3F_2 was condensed in the cell under vacuum and the cell was isolated from the vacuum line by means of a tap. The contents were allowed to warm up and liquify and the conductance of the liquid was measured at the required temperature.

The conductance of PCl_3F_2 in acetonitrile solutions was measured in an apparatus incorporating a pipette cell which can be ached to the vacuum line by the cone at C (Fig. 16). The

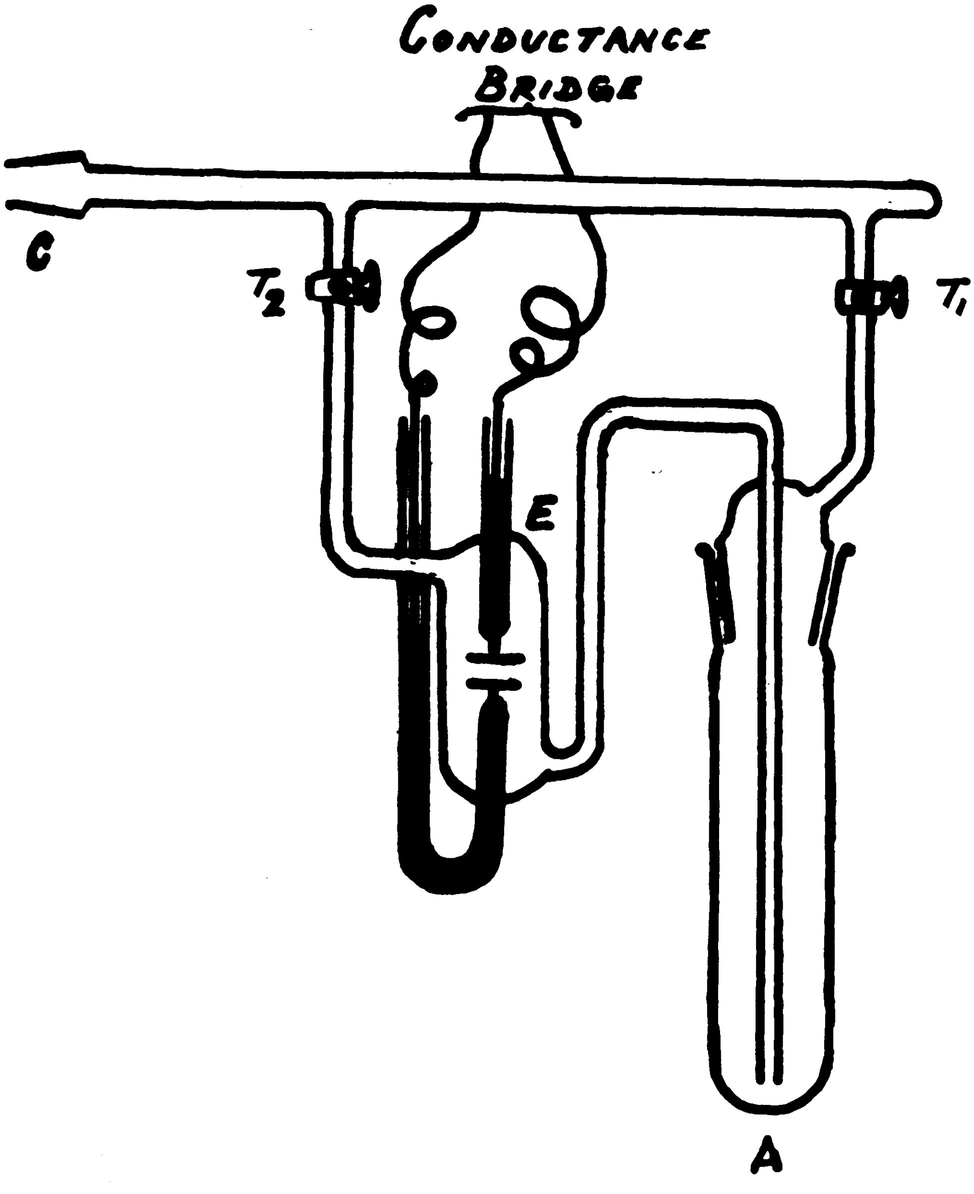


Fig. 16. Apparatus for Measuring the Conductance of PCl_3F_2 in Acetonitrile solutions.

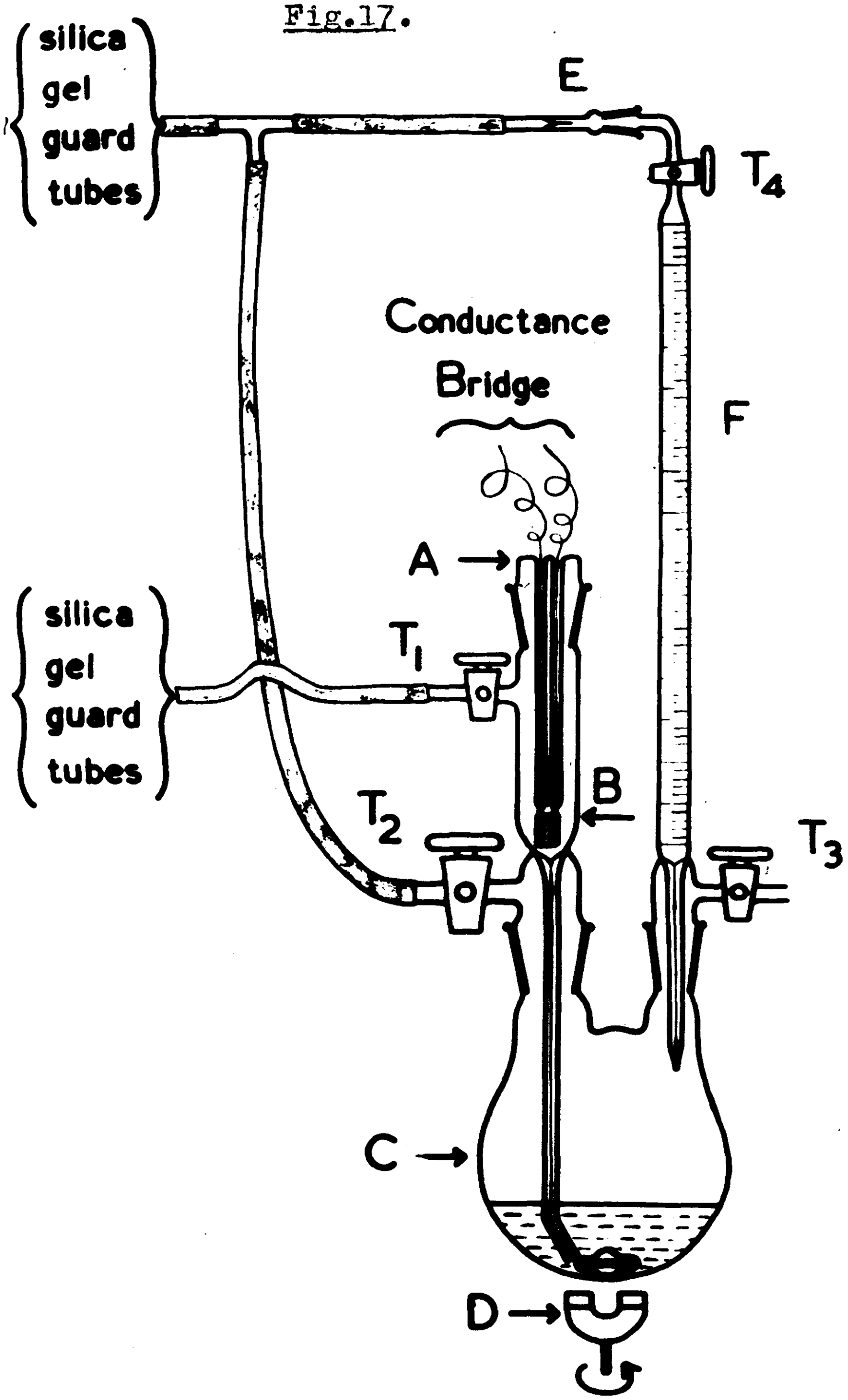
apparatus was evacuated, and PCl_3F_2 and acetonitrile were condensed in the tube A. The taps T_1 and T_2 were closed and the material was allowed to warm up and liquify. A slow stream of dry nitrogen was admitted into the vacuum system and by opening the tap T_2 the gas was allowed to bubble through the contents of the tube A in order to stir the solution. The solution was then sucked up into the electrode chamber E by gently reducing the pressure on that side. The electrode chamber E was surrounded by a water bath maintained at the required temperature and the conductance of the solution was measured at various intervals until it was constant.

In the case of Ph_2PI_3 and Ph_2PI_5, solutions of suitable concentration were made up and the cell (Fig. 15c) was filled inside a dry box prior to measurement of the conductance.

The conductometric titration apparatus used to study the system $Ph_2PN(Et)PPh_2 - I_2$ is shown in Fig. 17. This apparatus was found to be very efficient for dealing with anhydrous systems. The various parts of the apparatus were well baked at 110°C for 4-5 hrs. before use. The reactants of known concentration in acetonitrile were prepared inside a dry box. The burette F was attached to the flask containing the titrant and filled by gently applying suction through tap T_4, the tap T_3 being kept exposed to the atmosphere through drying tubes. The solution to

Conductometric Titration Apparatus.

Fig.17.



be titrated was introduced into the flask C and the apparatus was assembled. The tap T_3 was kept closed thereafter. The burette solution was run into the flask by opening the tap T_4. The narrow capillary E gave fine control over the addition. The solution was mixed well by means of the magnetic stirrer D. The conductance of the solution at various stages of the titration was measured by running the solution into the electrode chamber B via the capillary tube applying gentle suction through the silica gel guard tube connected to the tap T_1. The solution was held in the electrode chamber by closing the tap T_1. After noting the conductance the solution was returned to the flask C and the titration continued.

A pair of smooth platinum electrodes was used in all the types of cells described above. The conductance was measured by the Philips conductance bridge (type PR 9500/01).

Infra-red spectra. A Unicam double beam instrument (type S.P. 100) and a Perkin Elmer model 237 double beam instrument were used to study the infra-red spectra of the compounds in the regions 3700 - 375 cm^{-1} and 4000 - 650 cm^{-1} respectively. Gaseous samples were contained in a 10 cm. cell with potassium bromide or sodium chloride windows. Solid compounds were examined as Nujol and Hexachlorobutadiene mulls dispersed between sodium chloride plates. Moisture sensitive compounds were mulled in a dry box.

Ultraviolet spectra. The ultra violet spectra of solutions were studied by means of a Unicam S.P. 500 spectrophotometer. Solutions of moisture - sensitive compounds were prepared in a dry box and contained in standard 0.5 cm. or 1.0 cm. quartz cells with ground glass stoppers.

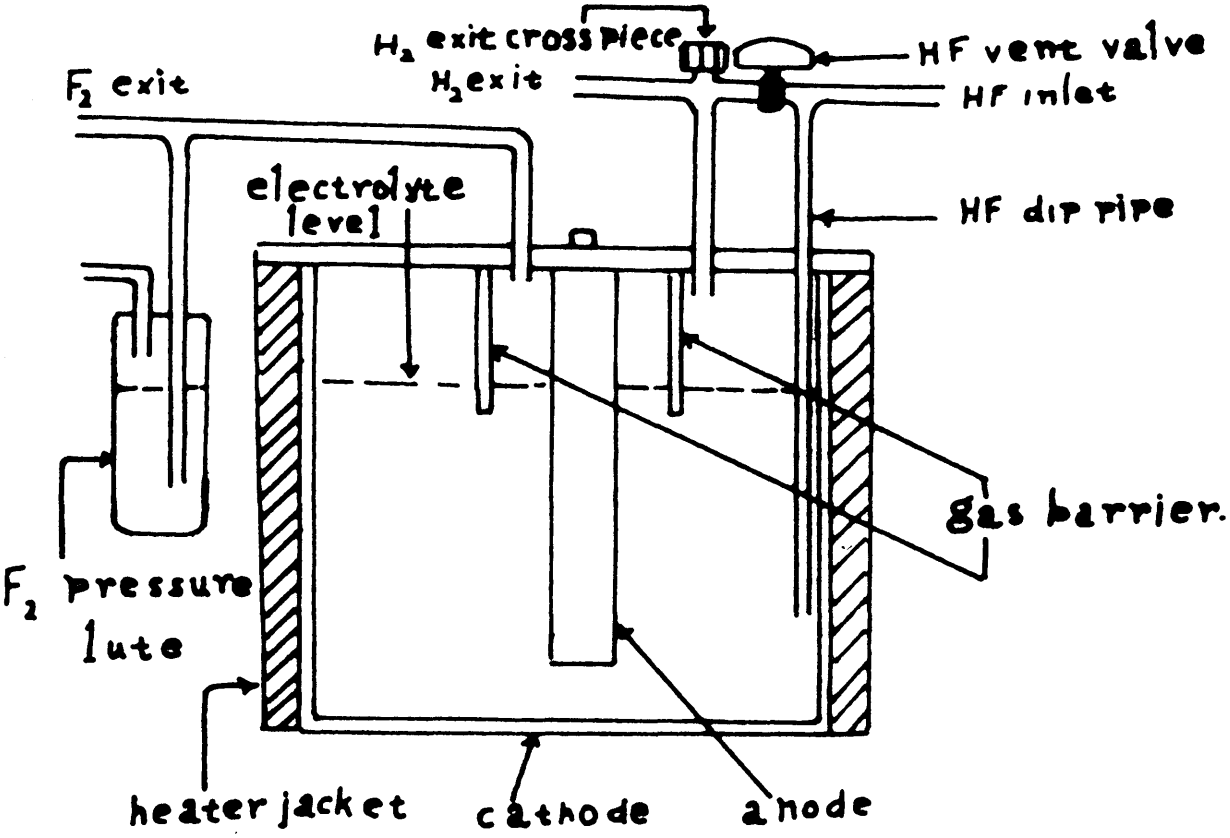
Nuclear Magnetic Resonance spectra. The proton resonance spectra were recorded on a Perkin Elmer R. 10 (60 MC) spectrometer. The compounds were examined in pyridine, chloroform or aqueous solutions as the case may be, and the samples were contained in closed pyrex glass tubes. Tetramethyl silane was used as an internal reference standard. The F^{19} resonance spectra of deuterochloroform solutions were recorded on a Perkin Elmer 40 MC spectrometer using CCl_3F as an internal reference standard.

The Fluorine cell. The fluorine cell used was a 10 amp. generator supplied on loan by I.C.I. Ltd.

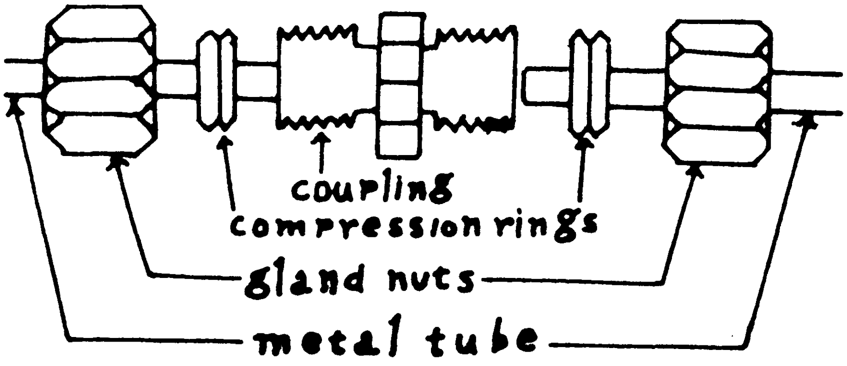
Fluorine is generated in the cell by the electrolysis of a material of the approximate composition KF.2HF. A schematic diagram of the cell is shown in Fig. 18a. The generator consists of an electrolyte container (cathode) surrounded by a jacket with thermostatically controlled heating units. The anode stem passes through the centre of the cover of the generator and

Fig. 18.

a) The Fluorine Cell.



b) Metal to Metal Joint.



is insulated from it. The fluorine exit is near the anode (carbon) and has a side connection to a fluorine pressure lute containing fluorine resistant oil with an outlet for vented fluorine. The skirt type gas barrier prevents mixing of fluorine and hydrogen. The hydrogen exit is through a cross piece fitted with an access plug for sampling the electrolyte and checking the depth of the electrolyte by means of a dip-stick. Hydrogen fluoride is added through a dippipe which is connected through a valve (HF vent valve) to the hydrogen exit. Pockets are provided for thermostatic control and a thermometer on the top of the cell; a junction box for heater connections is fitted to the base of the generator. The generator temperature (80± 2°C) is regulated by the thermostatic control, working with a relay between the supply and the heater junction box.

The operating voltage of the generator is variable in the range of 5-10 volts at 2 - 10 amperes.

<u>Glass to metal and metal to metal joints.</u> The use of fluorine made it necessary for those parts of the apparatus which are subjected to prolonged exposure to the gas to be made of metal resistant to serious corrosion damage. Copper was used for such constructions. In these cases glass to metal and metal to metal joints were made by means of brass compression unions of the type vailable in the "Instantator" range of fittings. A simple me-

tal to metal joint is illustrated in Fig. 18b. For the corresponding glass to metal joint a "Neoprene" ring was used instead of the metal compression ring.

The flanged metal to metal joints were provided with "Neoprene" washers and the two flanged ends were held together by screws.

PURIFICATION OF CHEMICALS.

Phosphorus Trichloride. Phosphorus trichloride (Albright and Wilson) was purified by fractional distillation before use. A one and a half foot fractionation column packed with Fenske rings was used for this purpose and the fraction distilling at 74 - 75°C was taken.

Dimethyl amine. Dimethyl amine (B.D.H., Laboratory reagent) was dried over sodium wire in a vacuum line and used without further purification.

Tri ethyl amine. Triethyl amine (Honeywell and Stein Ltd.) was fractionated in a vacuum line and the middle fraction obtained was dried over sodium wire.

Chlorine. Cylinder chlorine was fractionated through a - 78°C trap in a vacuum line in order to remove traces of moisture present.

Iodine. Commercial (Whiffen) resublimed iodine was further purified as follows (117); Iodine (10 g.) and potassium iodide (4 g.) which would retain any chlorine or bromine present as non - volatile potassium salts, were ground together and sublimed gently. The sublimate was resublimed without the addition of potassium iodide. The iodine so obtained was dried over calcium chloride.

Acetonitrile. Acetonitrile (Hopkin and Williams Ltd.) was further purified as follows: The solvent was left over freshly regenerated molecular sieve(B.D.H.Ltd.TYPE 4A (aluminium sodium silicate) 4-8 Mesh Beads) for about three days and was decanted off and distilled from a flask containing phosphorus pentoxide on to phosphorus pentoxide in a receiver. This procedure was repeated until on swirling the distillate the phosphorus pentoxide moved about freely in the solvent without sticking to the walls of the flask and no yellow colouration was produced shortly after the solvent came in contact with the phosphorus pentoxide. The purified material was stored over phosphorus pentoxide and distilled when required. The solvent thus obtained was freed from traces of phosphorus pentoxide sublimed over, by freeze drying. Acetonitrile purified in this manner gave a specific conductance of the order 10^{-7} ohm^{-1} cm^{-1}.

Nitrobenzene. "Analar" nitrobenzene was used without further purification for recrystallisation purposes.

Nitroethane. Nitroethane (L. Light and Co.Ltd.) was used directly for recrystallisation purposes.

Carbon Tetrachloride. The "Analar" reagent was dried by distillation from phosphorus pentoxide.

Chloroform. "Analar" chloroform was left over freshly regenerated silica gel to remove traces of alcohol present and the decanted liquid was distilled from phosphorus pentoxide.

Methylene Chloride. Methylene Chloride was dried over calcium hydride for about three days and the decanted solvent was purified by distillation.

Pyridine. Pyridine (Yorkshire Tar Distillers) was redistilled and the middle fraction obtained was stored over KOH pellets for a week. The solvent was finally purified by distillation in the vacuum line.

PREPARATIONS.

Nitron - $(PF_6)^-$ compound.

The $(PF_6)^-$ ion when present in the hydrolysate of the chlorofluorides of phosphorus (V) was precipitated by the method described by Kolditz (44). The hydrolysate (containing approximately 70 mg. of PF_6^- ion) was acidified with acetic acid and an equivalent amount of silver acetate was added in order to precipitate all the chloride present. To the filtrate about 0.5 g. of Nitron laboratory reagent (B.D.H.) in about 30 ml. dil. acetic acid was added. The complex formed was filtered off and dried at 110°C in an air oven for about three hours.

Triethyl phosphine. The preparation of triethyl phosphine has been described in the literature (118) and the same method was followed here. It was obtained by the reaction between the Grignard reagent C_2H_5 Mg Br and phosphorus tribromide (which was purified by fractional distillation.) The product obtained was kept dry by storage over potassium hydroxide pellets and distilled in a vacuum line when required.

Bis (diphenyl phosphino) ethyl amine, Ph_2PN (Et)P Ph_2.

The synthesis of Ph_2 PN (Et) P Ph_2 has been described by Ewart et al (109). The same method of preparation by the reaction between ethyl amine and chlorodiphenyl phosphine was used to obtain this compound which was thoroughly dried by pumping under vacuum for three to four hours. The purity of the compound was checked from its M.P.(99° C) and I.R. spectrum.

Diphenyl diiodophosphonium iodide, $(Ph_2P I_2)^+ I^-$.

This compound was prepared by the reaction between tetraphenyl diphosphine monoxide ($Ph_2 P (O) P Ph_2$) and iodine. The tetraphenyl diphosphine monoxide which had been obtained by the reaction between chlorodiphenyl phosphine and water in the presence of triethyl amine as hydrogen chloride acceptor (119) was supplied by Mr. W. Sim.

$Ph_2 P(O) P Ph_2$ (2 g., 5.2 m. moles) was dissolved in methylene chloride (15 ml) and to this a solution of iodine (2g., 7.9 m.moles) in acetonitrile (45 ml) was added slowly with stirring inside a dry box. An orange yellow precipitate was formed which dissolved on shaking. Towards the end of the addition of iodine orange yellow crystals started depositing and the amount increased on standing for a few minutes(further addition of iodine was found to give some dark violet crystals). The product (1.73 g. 3.0 m.moles) was filtered, washed thoroughly with acetonitrile and dried by pumping under vacuum for about two hours. Yield based on iodine, 77%.

Diphenyl diiodophosphonium triiodide. $Ph_2P (O)P Ph_2$ (2.0g., 5.2 m.moles) was dissolved in methylene chloride

(15 ml) and to this a solution of iodine (3.9g., 15.4 m.moles) in acetonitrile (90 ml) was added rapidly with stirring inside a drybox. Dark violet crystals of the compound separated out. The product (1.93g., 2.4 m.moles) was filtered, washed thoroughly with acetonitrile and pumped under vacuum for about two hours. Yield, 46%.

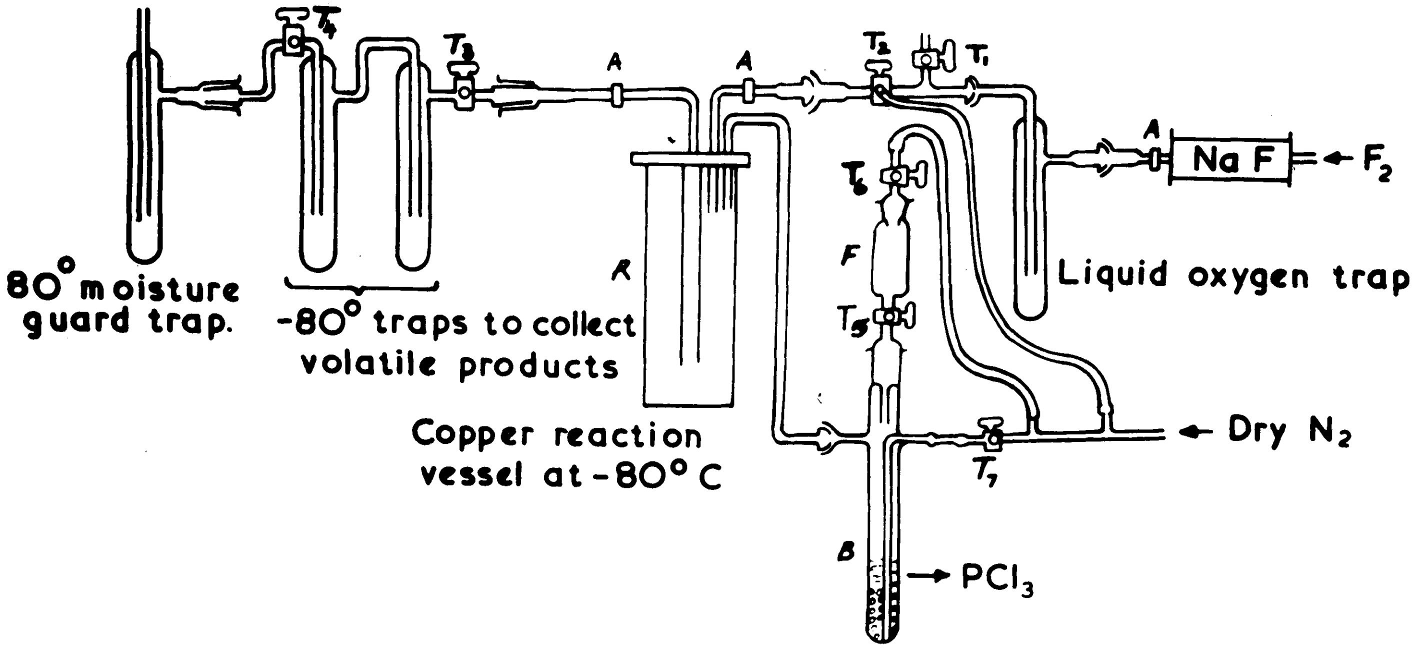
PART I.

Reaction between phosphorus trichloride and fluorine at room temperature. The apparatus used was similar to that shown in Fig. 19 except for the vertical reactor R which in this case was replaced by a horizontal reactor. This was fitted with two inlet tubes at one end and an outlet tube at the other end. The reactor and the tube containing NaF were made of copper. The metal to glass joints are marked"A". Fluorine - resistant KEL - F grease was used to lubricate the ground glass joints. Before assembling, the apparatus was thoroughly dried in an air oven at 110°C for about five hours.

The tap funnel F was filled with the required amount of phosphorus trichloride inside a dry box, the tap T_6 was closed and was attached to the apparatus as shown. The taps T_3, T_4, and T_7, were opened and the tap T_1 was closed. The "three way" tap T2 was opened to the liquid oxygen trap and the reactor and the fluorine cell was run at a high amperage (~8 amp.) for about an hour in a current of dry nitrogen through the apparatus. This procedure removed by electrolysis traces of water present in the electrolyte. The passage of nitrogen was continued until all the fluorine generated was expelled from the system. The taps T_3, T_4 and T_7 were closed and the tap T_2 was now opened to the nitrogen line and the liquid oxygen trap and the nitrogen was allowed to bubble through the fluoro-carbon oil in the pressure lute for a sufficiently long time to ensure that the fluorine cell was filled with dry nitrogen. The taps T_3, T_4 and T_7 were opened and the tap T_2 was opened to the liquid oxygen trap and the reactor and the nitrogen flow was maintained for about two hours at 0.2 litres/minute.

The traps were surrounded by suitable cooling baths and the phosphorus trichloride was run into the bubbler B containing glass beads from the tap funnel F. The taps T_5 and T_6 were closed and the nitrogen flow was maintained at 0.1 litre/minute. The fluorine generator was started at 2.5 amperes. Under these conditions the amount of phosphorus trichloride entering the reactor in the nitrogen stream and the amount of fluorine fed into the reactor were in the mole ratio of 1:1. The sodium fluoride in the copper tube served to trap the hydrogen fluoride present in the fluorine gas and the last traces of hydrogen fluoride were retained by the liquid oxygen trap. 10 ml of phosphorus trichloride were reacted in this way in three hours. After the reaction was over the fluorine generator was stopped and the apparatus was flushed out with dry nitrogen to remove the last traces of fluorine. The taps T_3, T_4 and T_7 were closed, and the tap T_2 was opened to the nitrogen line and the liquid oxygen trap. The tap T_1 was opened and the liquid

Fig.19. Apparatus for the Reaction between PCl_3 and F_2



oxygen bath was removed and the gases evolved were flushed out of the system. The traps containing the volatiles were attached to the vacuum line for separation and purification of the products. The copper reactor was opened (the two flanged ends are detachable) and the solid products formed were scraped out and transferred to storage tubes.

Reaction between phosphorus trichloride and fluorine at -78°C.

Experiments I and II in this series were carried out by connecting the appropriate reactor between the horizontal copper reactor and the set of cold traps in the apparatus used for the reaction between phosphorus trichloride and fluorine at room temperature. In this case the horizontal copper reactor served as a chamber for diluting the fluorine with nitrogen. The reactor used in experiment I was a bubbler type device (carrying a tap funnel containing phosphorus trichloride) similar to the phosphorus trichloride reservoir B shown in Fig. 19. In experiment II a three-necked round bottom flask (100 ml) with a tap funnel (containing phosphorus trichloride) fitted into the central neck was employed as the reactor. In both these experiments the reactor was cooled to -78°C during the reaction.

The apparatus used to carry out experiment III in this series is shown in Fig.19. The details of the experimental procedure are the same as those given for the reaction between phosphorus trichloride and fluorine at room temperature except for the fact that the vertical copper reactor was kept cooled to − 78°C during the reaction. Since the outlet of the reactor extended up to about one and a half inches from the bottom, efficient mixing of the reactants was attained in this system. About five continuous runs, each run consisting of a charge of 10 ml of phosphorus trichloride, were performed in order to get fairly reasonable quantities ($\sim$25 g.) of volatile products.

The volatile products of the reaction between phosphorus trichloride and fluorine were separated into individual components by fractional distillation under vacuum as follows: $P\,Cl_4\,F$, $P\,Cl_3F_2$ and $P\,F_3Cl_2$ were found to be stopped by traps cooled to −40°, −78° and −98° C respectively. Several cycles of distillation through the above traps gave the pure components. The last traces of POF_2Cl present in PCl_3F_2 could not be eliminated by this procedure. In spite of the fact that very drastic measures were taken to exclude moisture from the system the products were always contaminated with traces of oxyhalides of phosphorus ($PO\,F_3$, POF_2Cl and $PO\,F\,Cl_2$).

Reaction between $P\,Cl_3F_2$ and dimethylamine.

A round bottom flask with a B 19 cone neck was attached to the vacuum line by means of an adaptor fitted with a tap.

The apparatus thoroughly dried at 110°C was evacuated and flamed out. P Cl_3F_2 (12.5 m.moles) was condensed in the flask and dimethyl amine (25.0 m.moles) dried over sodium wire under vacuum, was condensed over the P Cl_3F_2 in small amounts. After each addition the reaction was allowed to proceed smoothly by alternate warming and cooling of the reaction vessel. At the end of the reaction only solid products were obtained and they were transferred from the reaction flask into a suitable storage tube inside a dry-box.

Reaction of P Cl_3 F_2 with triethylamine and triethyl phosphine.

The reactants were condensed in a reaction flask similar to that used for the reaction between P Cl_3F_2 and dimethyl amine, then they were allowed to warm up to room temperature very slowly (over a period of four to five hours)by surrounding the flask with cold acetone (-70°C) contained in a beaker the temperature of which was allowed to rise by itself. At the end of the reaction the volatile products were condensed in a separate trap under vacuum and examined. The solid products were removed from the reaction vessel to storage tubes inside a dry box.

In the reaction between P Cl_3F_2 and triethylamine the volatile products contained triethyl amine, P F_2Cl and traces of P F_3 which were stopped by traps cooled to -78°C, -160°C and − 196°C respectively. Repeated vacuum fractionation through these traps separated the mixture into its components.

PF_3, PF_2Cl, PCl_2F and PCl_3 present in the volatile products of the reaction between PCl_3F_2 and triethyl phosphine were separated by fractional condensation under vacuum in traps cooled to − 196°, −160°, −98° and − 78°C respectively.

PART II.

Reaction between $Ph_2PN(Et)PPh_2$ and iodine in the mole ratio of 1:1. A solution of iodine (61.5 mg., 0.24 m.mole) in 40 - 60°. petroleum ether was added with stirring to a solution of $Ph_2PN(Et)PPh_2$ (100 mg., 0.24 m.mole) in the same solvent (30 ml). A pale yellow precipitate consisting of the 1:1 adduct was obtained. This was filtered in the vacuum line and pumped dry. Yield, 76%.

Reaction between $Ph_2PN(Et)PPh_2$ and iodine in the mole ratio of 1:2.5. Iodine (4.7 g., 18.5 m.moles) in acetonitrile (120 ml) was added gradually with shaking to a solution of $Ph_2PN(Et)PPh_2$ (3.0g., 7.2 m.moles) in the same solvent (150 ml). At the end of addition the solution became slightly warm and a mixture of orange yellow and dark violet crystals separated out. The solution was stored at 0°C overnight when the amount of dark product became less. After about 48 Hrs. it was observed that all the dark product had disappeared leaving only an orange yellow compound (Ph_2PI_3) which was filtered and washed inside a dry box and pumped under vacuum for two hours. Yield based on iodine. 32%.

ratio of 1:3.
Iodine (5.6g., 22.0 m.moles) dissolved in acetonitrile(130ml)

ratio of 1:3.
Iodine (5.6g., 22.0 m.moles) dissolved in acetonitrile(130ml)

was added slowly with stirring to a solution of Ph_2 PN-(Et) P Ph_2 (3.0g., 7.3 m.moles) in acetonitrile (150 ml.) Soon after the addition was completed the solution became slightly warm and dark violet crystals separated out. The product (Ph_2 PI_5) was filtered and washed in a dry box, and vacuum dried. Yield based on iodine, 37%.

APPENDICES.

The pyrolysis of $(PCl_4)^+F^-$ in carbon tetrachloride.

$(PCl_4)^+F^-$ was suspended in carbon tetrachloride in a three necked round bottom flask (250 ml) which was fitted with a vertical water-cooled condenser. The latter was joined in series with three separate traps similar to those used in the reaction between phosphorus trichloride and fluorine. The apparatus was filled with dry nitrogen by connecting a supply of the gas to one of the side necks of the flask (the other side - neck was stoppered), and the current of dry nitrogen was maintained throughout the experiment. The first, second and third traps were cooled to -78°C, -196°C and -78°C respectively. The last trap served as a moisture guard tube. The flask was heated in an oil bath at about 80°C The $(PCl_4)^+F^-$ gradually went into solution with the evolution of gas bubbles. The pyrolysis was stopped when all the $(PCl_4)^+F^-$ went into solution. The -78°C trap retained the carbon tetrachloride carried over in the gas stream and the PF_5 evolved was collected in the - 196°C trap.

The pyrolysis of $(PCl_4)^+F^-$ in arsenic trichloride. The apparatus used in this case was similar to that employed for the pyrolysis of $(PCl_4)^+F^-$ in Carbon tetrachloride but with a few modifications. The pyrolysis flask was directly connected to two traps cooled to -78°C followed by another trap cooled in liquid nitrogen, which in turn was attached to a moisture guard tube. Precautions were taken to exclude moisture from the system by maintaining a flow of dry nitrogen through the apparatus. The suspension of $PCl_4^+ F^-$ in arsenic trichloride was heated in an oil bath at about 90°C. The volatile products formed were condensed in the cold traps. The liquid nitrogen bath was raised and lowered occasionally to prevent blockage in the system. The volatile products obtained were fractionated in a vacuum line. PCl_4F, PCl_3F_2 and PF_3Cl_2 condensing at -40°, -78° and -98°C were separated in this manner. The volatiles escaping the -98° trap contained POF_3, PF_5 and SiF_4 which were not further separated.

REFERENCES

(1) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans, Green and Co. Ltd., London, 1928, Vol. VIII.

(2) Gay Lussac, Ann.Chim. Phys., 1813, 88, 311, 319; Wurtz, Ibid., 1854, 42, 129.

(3) Harris, Ph.D. Thesis, Cambridge, 1958.

(4) Moissan, Compt.rend., 1884, 99, 655.

(5) Moisson, "Les Fluors et Ses Composes", Paris, 1900; Ann. Chim. Phys., 1885, 6, 433, 438.

(6) Baudrimont, Ibid., 1864, 2, 8.

(7) Muzyka and Fialkov, Doklady Akad. Nauk S.S.S. R., 1952, 83, 415.

(8) Fialkov and Kuźmenko, Zhur. Obshcheĭ Khim., 1951, 21, 433.

(9) Kastle and Beatty, Amer. Chem. J., 1899, 21, 392.

(10) Popov and Schmorr, J.Amer.Chem.Soc., 1952, 74, 4672; Gutmann, Monatsh., 1952, 83, 583.

(11) Prinvault, Compt. rend., 1872, 74, 868.

(12) Plotnikov and Yakubson, Z. physik. Chem., 1928, 138, 243.

(13) Biltz and Jeep, Z. Anorg. Chem., 1927, 162, 32.

(14) Zelenzy and Baenziger, J.Amer.Chem.Soc., 1952, 73, 6151.

(15) van Wazer, "Phosphorus and its Compounds", Interscience Publishers Inc., New York, 1958, Vol. I, p. 243 and references therein.

(16) van Wazer, Ibid., p. 244 and references therein.

(17) Booth and Bozarth, J. Amer. Chem. Soc., 1939, 61, 2927.

(18) Booth and Frary, Ibid., 1939, 61, 2934.

(19) van Wazer, op.cit., p. 221 and references therein.

(20) Renc, Roczniki Chem., 1934, 14, 69; Ibid., 1933, 13, 509; Mitobedzki, Chem. Listy, 1932, 26, 458; Mitobedzki and Krakowiecki, Roczniki Chem., 1928, 8, 563.

(21) Booth and Bozarth, J. Amer.Chem.Soc., 1933, 55, 3890.

(22) Kolditz, Z.anorg. Chem., 1956, 286, 307.

(23) Brockway and Beach, J.Amer.Chem.Soc., 1938, 60, 1836.

(24) Rouault, Ann.phys., 1940, 14, 78; Compt.rend.,1938, 207, 1620.

(25) Siebert, Z.anorg. Chem., 1951, 265, 303.

(26) Holmes and Gallagher, Inorg.Chem., 1963, 2, 433.

(27) Griffiths, Carter and Holmes, J.Chem.Phys.,1964, 41, 863.

(28) Muetterties, Mahler and Schmutzler, Inorg. Chem., 1963, 2, 613.

(29) Clark, Powell and Wells, J.Chem.Soc., 1942, 642.

(30) Van Driel and MacGillavry, Rec.trav.chim., 1943, 62, 167; Powell and Clark, Nature, 1940, 145, 971; de Ficquelmont, Wetroff and Moureu, Compt.rend., 1940, 211, 566.

(31) Payne, J.Chem.Soc., 1953, 1052; Gutmann, Monatsh., 1952, 83, 583.

(32) Trunel, Compt.rend., 1936, 202, 37; Simons and Jessop, J.Amer.Chem.Soc., 1931, 53, 1263.

(33) Harris and Payne, J.Chem.Soc., 1956, 4617.

(34) Holmes and Carter, Private communication; Holmes and Car-

ter, Inorg. Chem., 1965, 4, 738.

(35) van Wazer, op.cit., Ch. 1, 2 and 3.

(36) Schmutzler, Advan. Fluorine Chem., Vol. IV (in print).

(37) Gillespie and Nyholm, Quart.Revs., 1957, 11, 369.

(38) Williams, Sheridan and Gordy, J.Chem.Phys., 1952, 20, 164; Hawkins, Cohen and Koski, Ibid., 1952, 20, 528; Gordy, Ann. N.Y. Acad. Sci., 1952, 55, 774; Senatore, Phys.Rev. 1950, 78, 293.

(39) Kosolapoff, "Organophosphorus Compounds", Wiley, New York, 1950, pp. 58, 78, 325; Bennet, Emelius and Haszeldine, J.Chem.Soc., 1953, 1565; Emelius, Haszeldine and Paul, Ibid., 1955, 563;

(40) Blaser and Worms, Angew. chem., 1961, 73, 76; Ivanova and Kirsanov, Zhur. Obscheĭ. Khim., 1961, 31, 3991; Ibid, 1962, 32, 2592.

(41) Voigt and Biltz, Z. anorg. Chem., 1924, 133, 277.

(42) Harris and Payne, J.Chem.Soc., 1958, 3732.

(43) Craig, Maccoll, Nyholm, Orgel and Sutton, J.Chem.Soc., 1954, 342.

(44) Kolditz, Z. anorg.Chem., 1956, 284, 144.

(45) Kolditz and Hass, Ibid., 1958, 294, 191.

(46) Kennedy, Ph.D.Thesis, Glasgow, 1959.

(47) Kennedy and Payne, J.Chem.Soc., 1960, 4126.

(48) Johnson, Ph.D.Thesis, Purdue, 1953.

(49) Trost, Can.J.Chem., 1954, 32, 356.

(50) Holmes and Bertaut, J.Amer.Chem.Soc., 1958, 80, 2980.

(51) Beattie and Webster, J.Chem.Soc., 1961, 1730.

(52) Muettertíes Bither, Farlow and Coffmann, J. Inorg.Nucl. Chem, 1961, 16, 52.

(53) Delwaulle, Cras, Bridoux and Migeow, XVII th I.U.P.A.C. conference, Munich, 1959.

(54) Kolditz and Bauer, Z. anorg. Chem., 1959, 302, 241.

(55) "Fluorine Chemistry", Edited by J.H. Simons, Academic press inc., New York, 1950, Ch. 10, p. 325.

(56) Hartley, Holmes, Jacques, Mole and McCoubrey, Quart.Revs., Vol. XVII, 1963, 204.

(57) Van Wazer, op. cit., p. 33.

(58) Moissan, Ann.Chim.Phys., 1891, 24, 224.

(59) Lange and Muller, Chem.Ber., 1930, 63, 1058.

(60) Delwaulle and François, J.Chim.Phys., 1949, 46, 87.

(61) Kennedy and Payne, J.Chem.Soc., 1959, 1228.

(62) Harris, Ph.D.Thesis, Glasgow, 1956.

(63) Popov and Skelly, J.Amer.Chem.Soc., 1955, 77, 3722.

(64) Nielsen and Jones, J.Chem.Phys., 1951, 19, 1117.

(65) Kolditz, Z. anorg. Chem., 1957, 293, 147.

(66) Holmes, Gallagher and Carter, Inorg. Chem., 1963, 2, 437.

(67) Bohme and Krause, Chem. Ber., 1951, 84, 170.

(68) "Beilsteins Handbuch der Organischen Chemie" Vol. IV, p. 127.

(69) Antler and Laubengayer, J.Amer.Chem.Soc.,1955, 77, 5250.

(70) Wardlaw and Webb, J.Chem.Soc., 1930, 2100.

(71) van Wazer, op.cit., p. 114.

(72) Holmes and Bertaut, J.Amer.Chem.Soc., 1958, 80, 2983.

(73) Holmes, Ibid., 1960, 82, 5285.

(74) Muetterties and Mahler, Inorg. Chem., 1965, 4, 119.

(75) Michaelis, Chem.Ber., 1873, 6, 601, 816; Michaelis and Kohler, Ibid., 1876, 9, 519, 1053; Michaelis, Ann., 1876, 181, 265; Chem.Ber., 1877, 10, 627; Ibid., 1880, 2174.

(76) Cahours and Hoffmann, Liebigs Ann.Chem., 1869, 104, 1.

(77) Guichard, Chem.Ber., 1899, 32, 1572.

(78) Jackson, Davies and Jones, J.Chem.Soc., 1930, 132, 2298.

(79) Michaelis and Von Soden, Ann., 1885, 229, 295.

(80) Jensen, Z. anorg. Chem., 1943, 250, 257.

(81) Issleib and Brack, Ibid., 1954, 277, 258.

(82) Issleib and Seidel, Z. anorg. Chem., 1956, 288, 201.

(83) Beveridge and Harris, Private Communication.

(84) Rochow, Hurd and Lewis, "The Chemistry of Organometallic compounds", Wiley and Sons Ltd., New York, 1957, ch. 8, p. 216.

(85) van Wazer, op.cit., p. 263.

(86) Kosolapoff, op.cit., p. 71.

(87) Chattaway and Hoyle, J.Chem.Soc., 1923, 123, 654.

(88) Beveridge and Harris, Ibid., 1964, 6076.

(89) Kuchen and Strolenburg, Angew. Chem., 1962, 74, 27.

(90) Mann, J.Chem.Soc., 1945, 65.

(91) Goubeau and Baumgartner, Z. Electrochem., 1960, 64, 598.

(92) "Mc Ewen and Sim, Personal Communication", quoted by Beveridge, Ph.D.Thesis, Glasgow, 1964.

(93) Andrews, Chem.Revs., 1954, 54, 713; Orgel, Quart.Revs., 1954, 8, 422; Andrews and Keefer, Advan.Inorg.Chem. Radiochem., 1961, 3, 91; Reference (96).

(94) Mulliken, J.Amer.Chem.Soc., 1950, 72, 600; Ibid., 1952, 74, 811; J.Phys.Chem., 1952, 56, 801; J.Chem.Phys., 1955, 23, 397; Rec.trav.Chim., 1956, 75, 845.

(95) Hassel and Romming, 1956, Acta.Chem.Scand., 1956, 10, 696; Eia and Hassel, Ibid., 1956, 10, 139; Hassel, Proc.Chem. Soc., 1957, 250; Hassel, Mol.Phys., 1958, 1, 241.

(96) Schmulbach and Hart, J.Amer.Chem.Soc., 1964, 86, 2347.

(97) Brown and Soper, J.Chem.Soc., 1953, 3576.

(98) Das, Shaw, Last and Wells, Chem. and Ind., 1963, 866.

(99) Burg and Slota, J.Amer.Chem.Soc., 1958, 80, 1107.

(100) Payne, Ewart, Porte and Lane, J.Chem.Soc., 1962, 3984.

(101) Popov and Swensen, J.Amer.Chem.Soc., 1955, 77, 3724.

(102) Popov and Skelly, Ibid., 1954, 76, 5309.

(103) Deacon, Jones and Rogasch, Austr.J.Chem., 1963, 360.

(104) Deacon and Jones, Ibid., 1963, 499.

(105) Steger and Stopperka, Chem.Ber., 1961, 94, 3023.

(106) Nakamoto, "Infra-red Spectra of Inorganic and Coordination Compounds", John Wiley and Sons Inc., New York, 1963, p.73.

(107) Bellamy, "The Infra-red Spectra of Complex Molecules", Met-

huen, London, 1962.

(108) "Progress in Infra-red Spectroscopy", Edited by H. Szymanski, Plenum Press, New York, 1962, Vol I. p. 11.

(109) Ewart, Lane, McKechnie and Payne, J.Chem.Soc., 1964, 1543.

(110) Mokuolu, Private Communication.

(111) Issleib and Seidel, Chem.Ber., 1959, 92, 2681.

(112) Hoffmann, Grunewald and Horner, Ibid., 1960, 93, 861.

(113) D'eye and Wait, "X-Ray Powder Photography in Inorganic Chemistry", Butterworths, London, 1960.

(114) Kolditz, Z.anorg.Chem., 1957, 289, 118.

(115) Huckabay, Welch and Metler, Analyt.Chem., 1947, 19, 154.

(116) Nichols and Kindt, Ibid., 1950, 22, 785.

(117) Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, Green and Co., London, 1953, p. 185.

(118) "Methoden der Organischen Chemie, Phosphor Verbindungen", Edited by Eugen Müller, Georg Thieme Verlag, Stuttgart, 1963, Vol.I, p. 33.

(119) McKechnie, Payne and Sim, J.Chem.Soc., 1965, 3500.

(120) Popov, Geske and Baenziger, J.Amer.Chem.Soc., 1956, 78, 1793.