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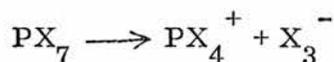
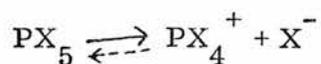
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ABSTRACT

The reactions of halogens (Br_2 , I_2 and IBr) with phosphorus tribromide, phosphorus triiodide, dibromophenylphosphine, diiodophenylphosphine, bromodiphenylphosphine and diphenyliodophosphine in methyl cyanide solution were investigated, using conductometric titrations to indicate the stoichiometry of compound formation. Ultra-violet spectrum studies showed that, in most of these systems, several overlapping equilibria, arising from extensive halogen rearrangement in methyl cyanide, were present. Members of the series $\text{PhPBr}_n\text{I}_{4-n}$ ($n = 0-4$), $\text{Ph}_2\text{PBr}_n\text{I}_{3-n}$ ($n = 0, 3$) PX_5 type compounds, $\text{PhPBr}_n\text{I}_{6-n}$ ($n = 0, 2, 4, 5$) and $\text{Ph}_2\text{PBr}_n\text{I}_{5-n}$ ($n = 0-4$) PX_7 type compounds were prepared and found to be strong electrolytes in methyl cyanide. From this and the ultra-violet spectrum results, the following ionisation modes were suggested:

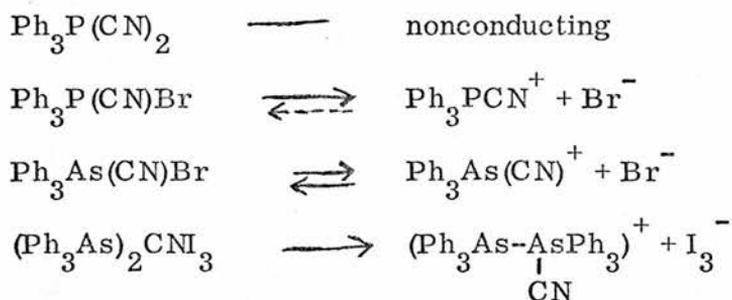


In addition to these, three other solid compounds of novel PX_6 , stoichiometry were isolated. These were Ph_3PBr_5 , Ph_2PBr_4 and PhPBr_4I .

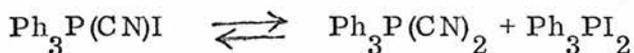
The Mass spectra of all the halogen adducts showed that they are hydrolytically and thermally unstable.

The interaction of cyanogen halides (CNBr and CNI) with triphenylphosphine and triphenylarsine in methyl cyanide were investigated using conductometric methods. The preparation of adducts from these systems was also attempted and those successfully isolated had the formulae,

$\text{Ph}_3\text{P}(\text{CN})_2$, Ph_3PI_2 , $\text{Ph}_3\text{P}(\text{CN})\text{Br}$, $(\text{Ph}_3\text{As})_2\text{CNI}_3$ and $\text{Ph}_3\text{As}(\text{CN})\text{Br}$. The electrolytic behaviour of these species can be summarised as follows,



Efforts to isolate the 1:1 adducts $\text{Ph}_3\text{P}(\text{CN})\text{I}$ and $\text{Ph}_3\text{As}(\text{CN})\text{I}$ have not met with success. The absence of $\text{Ph}_3\text{P}(\text{CN})\text{I}$ (even though it was indicated by conductometric titration) was believed to be due to its rearrangement as follows :



The infra-red spectra of these adducts are discussed and their mass spectra demonstrate their extreme lability.

The reactions of the halogens Br_2 , I_2 , and IBr with the biarsines, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$, were investigated using similar techniques. These studies, coupled with the behaviour of the solid adducts when dissolved in methyl cyanide, showed that ions containing only one arsonium centre were preferred. Conflicting results obtained from the infra-red and ^1H n.m.r. spectra of these adducts are also described.

To My Wife

NAJIBA

A STUDY OF
REACTIONS OF SOME PHOSPHINES AND ARSINES WITH
HALOGENS AND PSEUDOHALOGEN HALIDES

A Thesis

Presented for the degree of

Doctor of Philosophy

in the Faculty of Science of the

University of St. Andrews

by

Habib Abdulahad Aughsteen, B. Sc. (IRAQ)



May 1975

United College of
St. Salvator and St. Leonard
St. Andrews.

(II)

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Chemistry Department of the University of St. Andrews during the nine terms beginning 1st March 1973, under the supervision of Dr. G. S. Harris.

(III)

CERTIFICATE

I hereby certify that

Habib Abdulahad Aughsteen

has spent nine terms at research work under my supervision, has fulfilled the conditions of Ordinance General No. 12 and Resolution of the University Court, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

(IV)

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I N T R O D U C T I O N

INTRODUCTION

The reactive character and ready availability of elemental phosphorus made its reactions with halogens an obvious subject of study for early chemists. In 1808, Gay Lussac and Thenard¹ as well as Davy² discovered the three phosphorus halides - phosphorus trichloride, phosphorus pentachloride and phosphorus trifluoride. Nearly all of the other simple halides of phosphorus which are known today, were prepared and partially characterised in the nineteenth century. It has been well established that the reaction of elemental phosphorus with halogens gives two distinct series of compounds, the tri- and penta- halides. The existence of these two well-defined series of compounds, was of great general interest in the development of chemical ideas, particularly in connection with valency. The high reactivity of phosphorus halides with hydroxyl compounds enabled analysis to be undertaken readily and formulas to be firmly established. It is therefore of the greatest credit to the early chemists that they obtained, with the limited apparatus at their disposal, so much correct and valuable information on these very reactive materials.

A further development of phosphorus halide chemistry was the study of substituted pentahalides of the general formula $R_n P X_{5-n}$ ^{3,4}, (n = 1, 2, 3, 4 ; R = organic group). In 1871, Crafts and Silva⁵ were able to isolate $(C_2H_5)_3 PI_2$, the first compound of this type ; $(C_2H_5)_3 PI_4$ and $(C_2H_5)_4 PI_3$ were formed as a mixture by heating phosphorus and ethyl iodide in a sealed tube⁶.

The best known and best understood halides of the Group VB elements in general are the trihalides. All of the halogens from fluorine

to iodine form phosphorus, arsenic, antimony and bismuth - trihalides. With some exceptions, pentahalides of these elements are also known. A further type of halide sometimes found is the dihalide, MX_2 . Relatively few of these have been prepared and their properties are less well understood. Phosphorus di-iodide is the best known example of this type of compound. In the following sections a summary is given of the main features of the chemical and structural properties of the different types of halides of Group VB elements.

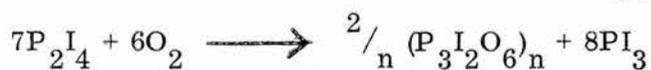
The Halides of Group VB Elements

The Dihalides (M_2X_4)

Several halogen compounds containing M-M bonds (M=P, As) are known. P_2I_4 , P_2Cl_4 , P_2F_4 and As_2I_4 are examples which have been prepared and characterised. No antimony compounds of this type have been isolated and the existence of analogous bismuth halides are not yet certain ¹¹.

Diphosphorus tetraiodide (P_2I_4) can be prepared by direct combination of red or white phosphorus and iodine in carbon disulphide ⁷.

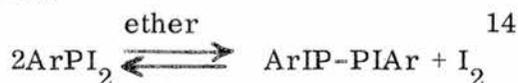
In this solvent P_2I_4 was reported ¹² to react with oxygen forming an amorphous insoluble adduct of stoichiometry $(P_3I_2O_6)_n$



However, Fishchenko et al. ¹³ have also isolated P_2I_4 from a diethyl ether solution of phosphorus triiodide, and they have shown that the solvent catalyses the reaction:

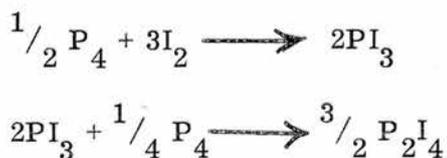


It is of interest to note that aryl diiodophosphines undergo a similar reaction.



In one study, the reaction between white phosphorus and iodine in carbon tetrachloride was investigated by means of iodine colour comparisons with standard solutions ¹⁵. It was shown that the product P_2I_4 had formed via several intermediates, without breaking and reforming the P-P bond. In contrast with this, a ^{31}P n. m. r. and spectrophotometric analysis ¹⁶ of this system demonstrated that in the

formation of P_2I_4 all of the P-P bonds were broken, and the mechanism proposed is :



The trans structure of P_2I_4 as shown by X-ray diffraction analysis¹⁷ (Figure 1) is essentially that found in PI_3 , each phosphorus being at the apex of a triangular pyramid.

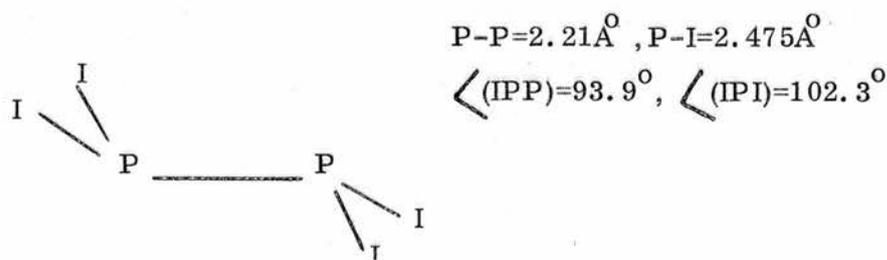


Figure 1. The structure of P_2I_4

The P-P distance corresponds to twice the single - bond radius; this observation suggests that the lone pair on each phosphorus atom is localised and is not involved in $d-p$ bonding. The gauche form of the structure of P_2I_4 has also been reported on the basis of dipole moment¹⁸ and infra-red spectrum^{19,20} results for solutions of P_2I_4 in carbon disulphide. Cowley²¹ therefore, suggested that the P_2I_4 initially formed probably possessed a gauche conformation but that the effect of crystal packing gives rise to the trans conformation in the solid. In contrast to this, other workers²² have established that the trans conformation of solid P_2I_4 persists in a variety of solvents which includes carbon disulphide. Diphosphorus tetrachloride (P_2Cl_4)²³ likewise has been shown to adopt a trans configuration in its various states. From

transforms to PI_3 and iodine when it contains 33mol% of P_2I_4 . ^{31}P n. m. r. and infra-red spectra of the $\text{P}_2\text{I}_4 - \text{Br}_2$ system offered evidence for the presence of PBr_2I and PBrI_2 . A thorough investigation of such systems involving different halogens, and using new physical and manipulative techniques, now available, would be of great value as a means of exploring possible new preparative methods for mixed phosphorus halides.

The Trihalides

The simple trihalides of the Group VB elements are well-known, but so far relatively little investigation of the mixed halides has been undertaken. Much of the early work done on these halides was preparative. The first two trihalides to be prepared were antimony trichloride and bismuth trichloride by Glauber (1649) and Boyle (1664)²⁹ respectively. All of the trihalides, except the fluorides, are formed by direct combination of the elements,



The fluorides are obtained indirectly by reacting the corresponding chloride or bromide with a suitable fluorinating agent, for example,



Table 1 overleaf contains the trihalides which have been isolated and whose individual properties have been recognised.

Table 1. The Trihalides of P, As, Sb and Bi

Phosphorus	Arsenic	Antimony	Bismuth
PF_3	AsF_3	SbF_3	BiF_3
PCl_3	AsCl_3	SbCl_3	BiCl_3
PBr_3	AsBr_3	SbBr_3	BiBr_3
PI_3	AsI_3	SbI_3	BiI_3

Although the number of possible mixed trihalides is large, so far relatively few have been isolated. They can be prepared either by re-organisation reactions, in which mixtures of different trihalides are heated together until an equilibrium mixture has been obtained, or by partial exchange of halogens with another halide.

The mixed trihalides which have been isolated and well-characterised are set out in Table 2, and others identified by various physical methods such as nuclear magnetic resonance (n. m. r.), mass spectrometry and Raman spectra, are collected in Table 3.

Table 2. The Isolated Phosphorus and Antimony - Mixed Trihalides

Phosphorus	Antimony
PF_2Cl 30	SbBrI_2 35
PFCl_2 30	
PF_2Br 31	
PBr_2 31	
PCl_2Br 32, 33, 34	
PClBr_2 32, 33, 34	

Table 3. The Mixed Trihalides (identified by physical methods)

Phosphorus	Arsenic	Bismuth
36, 37 PFCIBr	40 AsF ₂ Cl	42 BiCl ₂ I
38, 39 PCl ₂ I	40 AsFCl ₂	42 BiClI ₂
38, 39 PClI ₂	41 AsCl ₂ Br	43 BiBr ₂ Cl
38, 39 PBr ₂ I	41 AsClBr ₂	43 BiBrCl ₂
38, 39 PBrI ₂		

Van Wazer²⁵ has drawn attention to the principles of bonding in phosphorus compounds and these may quite appropriately be extended to the whole group. The phosphorus (III) halides are found to adopt triangular pyramidal structures. Results based on bond-length shortening and enthalpy data²⁵ suggest that in the case of phosphorus there are three pure σ -bonds, with little or no π -character. This has been confirmed from the results of nuclear magnetic resonance studies⁴⁴. The same almost certainly applies to the trihalides of the other elements of Group VB. The X-M-X bond angles in the pyramidal molecule lie between 90° and 109.5° (the tetrahedral angle) which on the Gillespie - Nyholm picture can be attributed to the variation in the interaction between the lone pair of electrons on the central atom and the bonding electron pairs depending on the particular elements involved.

The trihalides of Group VB elements exhibit many features of chemical interest. Re-organisation processes have been observed in phosphorus trihalide systems and several mixed phosphorus trihalides

found in this way have been characterised. A mixture of phosphorus trichloride and phosphorus tribromide was shown by ^{31}P n. m. r. ^{32, 38} to form PCl_2Br and PClBr_2 in less than fifteen minutes at 25°C in the equilibrium,

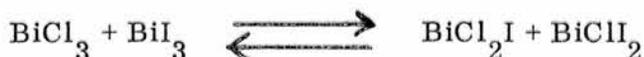
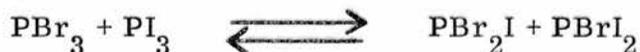


Mixed trihalides are also formed by exchange with halide - containing solvents. This happens in solutions of phosphorus trichloride in liquid hydrogen bromide and of phosphorus tribromide in liquid hydrogen chloride. ⁴⁵ Phosphorus triiodide is sparingly soluble in liquid hydrogen chloride, however, and does not exchange ³⁸.

Re-organisation reactions are also known for arsenic trihalides. It was shown by mass spectral and ^{19}F n. m. r. studies ⁴⁰ that the following exchange equilibria occur in the vapour phase,



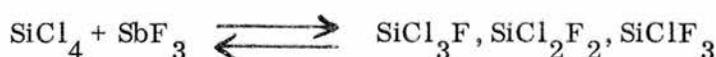
Spectrophotometric investigations of the $\text{PBr}_3 - \text{PI}_3$ and $\text{BiCl}_3 - \text{BiI}_3$ systems, by Gaizer and Beck ⁴² as well as ^{31}P n. m. r. studies of the former system, ³⁸ offered evidence for the formation of PBr_2I , PBrI_2 and BiCl_2I , BiClI_2 respectively in an equilibrium mixture.



In none of the above cases is equilibrium established instantaneously, the reaction being considerably slower when fluoride is present in one of the molecules involved. ³² For this reason isolation of mixed fluorophosphines is possible. It appears likely that this type of reaction

is general to this periodic group, and that the chemistry of the trihalides (particularly those of phosphorus) is dominated by these 'scrambling' reactions, in which halogen exchange occurs when two different trihalides are mixed.

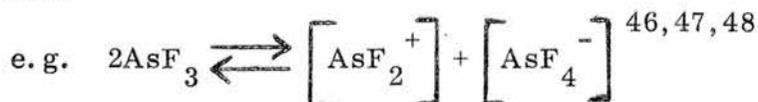
Another feature of the chemistry of the trihalides is their ability to add a mole of halogen to form pentahalides, and sometimes in the presence of excess halogen, polyhalides are formed (see later). The trihalides also, in some cases, act as halogenating agents, and this property is made use of in syntheses, such as in the fluorination of non-metal chlorides¹¹



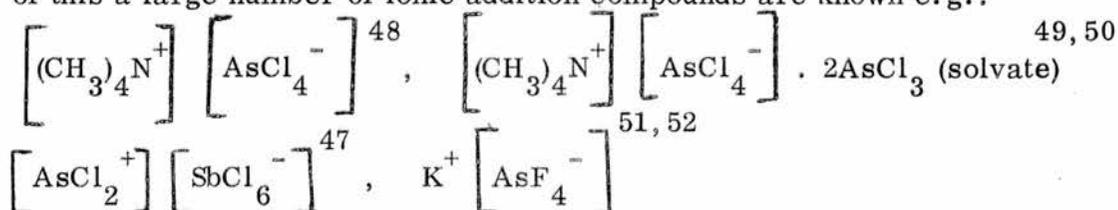
and



The trihalides, in the liquid phase, are generally poor electrical conductors. The observed low conductivity is attributed to weak self ionisation



The ionisation of AsF_3 , AsCl_3 , AsBr_3 , SbCl_3 and SbBr_3 is promoted by addition of compounds which can either donate halide ions (e.g. KF , $(\text{CH}_3)_4\text{NCl}$, TlBr) or accept them (e.g. SbF_5 , FeCl_3 , AlCl_3). As a result of this a large number of ionic addition compounds are known e.g.:



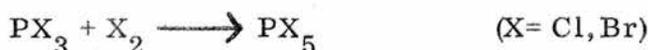
The trihalides of the Group VB elements are also able to behave as electron - pair donors and to a lesser extent as acceptors. Thus

they form numerous molecular addition compounds, e.g. $\text{Ni}(\text{PF}_3)_4$,
 $\text{Ni}(\text{PCl}_3)_4$, $\text{Ni}(\text{PBr}_3)_4$ (Phosphorus trihalide acting as a donor molecule)
 and $(\text{CH}_3)_3\text{N} \cdot \text{PBr}_3$, $(\text{CH}_3)_3\text{N} \cdot \text{AsCl}_3$, $(\text{CH}_3)_3\text{N} \cdot \text{SbCl}_3$ (Group VB
 trihalides acting as an acceptor molecules).

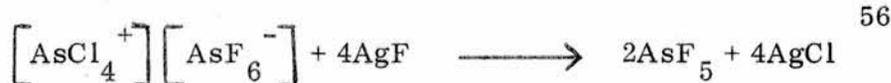
The Pentahalides of Group VB Elements

The pentahalides of type MX_5 ($\text{M}=\text{P, As, Sb, Bi}$; $\text{X}=\text{F, Cl, Br}$) which have been isolated so far are; PF_5 , PCl_5 , PBr_5 ; AsF_5 ; SbF_5 , SbCl_5 ; and BiF_5 .

The penta-chlorides and - bromides can be prepared by reaction of the elements, or by simple addition of a mole of halogen to the corresponding trihalide.



The pentafluorides of Group VB elements can be obtained by indirect fluorination methods:



Phosphorus pentaiodide has not been isolated or even observed. Its absence has been explained in terms of incompatibility of the 3d-orbitals of phosphorus atom with the 7s, 7p and 7d - orbitals of iodine ¹¹.

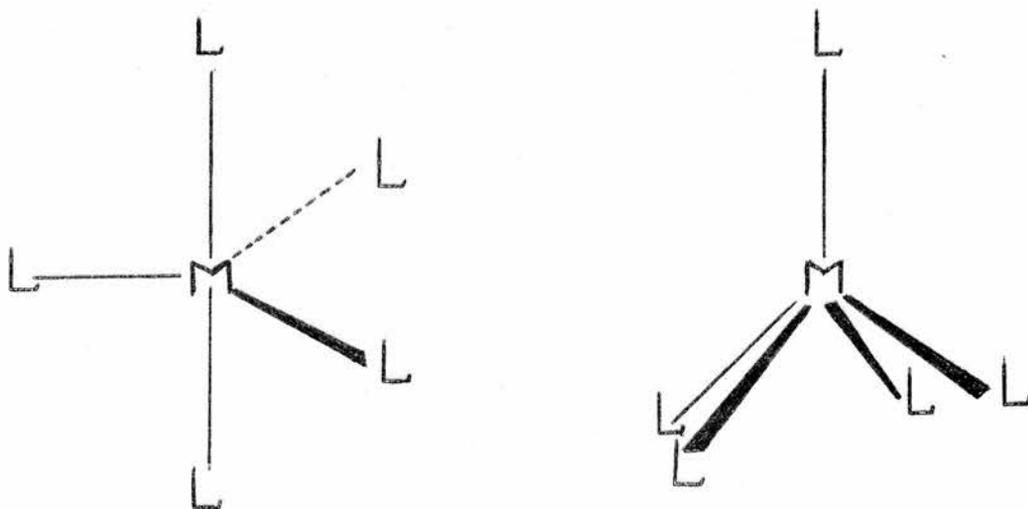
Although arsenic pentachloride is described as "unstable" at 25°C, ⁵⁸

it seems fairly certain that this compound is also entirely unknown ^{59, 60, 61}.

It was concluded by Gutmann that in AsSbCl_{10} and AsPCl_{10} (isolated from ⁶¹

the reaction between SbCl_5 or PCl_5 with excess $\text{AsCl}_3 + \text{Cl}_2$, the maximum co-ordination number of the arsenic (V) atom towards chlorine is less than five; each compound probably contains the As (V) atom as AsCl_4^+ .

The most favourable structure for a molecule in which five like ligands are bonded to a central atom is either the trigonal bipyramid (D_{3h}) involving $sp^3d_z^2$ hybridisation, or the tetragonal pyramid (C_{4v}) involving $sp^3d_{x^2-y^2}$ hybridisation of the phosphorus. The two configurations in question may be represented as in Figure 2.



(a) Trigonal bipyramid

(b) Tetragonal pyramid

Figure 2. The two possible configurations for ML_5

There is no evidence for the adoption of the square pyramidal structure by any covalent PX_5 compounds. This structure is however adopted by antimony pentaphenyl (SbPh_5)⁶². The basic trigonal bipyramidal framework is now well established as being the normal ground

state configuration for five-co-ordinated phosphorus (V) compounds ⁶³. Indeed, all recent investigations, based on spectroscopic (n.m.r., i.r., Raman, etc.), X-ray, and electron diffraction methods, confirm this. It might be mentioned at this point that a square pyramidal structure is believed to occur as the intermediate in the interconversion of axial and equatorial positions of certain trigonal bipyramidal molecules ('Berry' Pseudorotation - discussed later ⁶⁴).

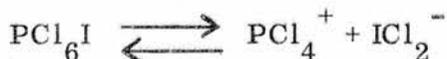
Phosphorus pentachloride (PCl_5) is known to show a varied structural nature which depends upon its phase and the environment in which it is found. In the molten ⁶⁵ and vapour phase ^{66, 67} PCl_5 consists of molecules with the trigonal bipyramidal structure, whilst in the solid state it has been shown by X-ray analysis ⁶⁸ to be ionic, composed of tetrahedral $\left[\text{PCl}_4^+\right]$ and octahedral $\left[\text{PCl}_6^-\right]$ units. A similar structure has been reported for the crystalline phosphorus pentabromide (PBr_5) except that the ions present in the solid phase are $\left[\text{PBr}_4^+\right]$ and $\left[\text{Br}^-\right]$ ^{69, 70}. The other pentahalides of known structure, PF_5 ⁷¹, AsF_5 ⁷² and SbCl_5 ⁶⁶, possess trigonal bipyramidal structures in the vapour phase and in the case of SbCl_5 in the solid state also.

The influence of solvents on the behaviour of phosphorus pentachloride has been investigated by many authors. In polar solvents, such as methyl cyanide (CH_3CN) and nitrobenzene (PhNO_2), PCl_5 is found to be ionic, whereas in non-ionising solvents like carbon tetrachloride (CCl_4) and carbon disulphide (CS_2), the molecular species is present. Payne ⁷³ has shown, by transport number and electrolytic conductance measurements, that in CH_3CN and PhNO_2 , unionised phosphorus pentachloride molecules are in equilibrium with PCl_4^+ and PCl_6^- ions. This equilibrium

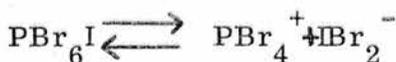
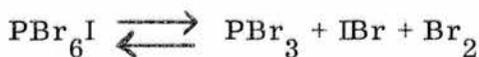
was further supported by the results obtained from conductance and spectral (i. r. and ^{31}P n. m. r.) studies of phosphorus pentachloride in methyl cyanide⁷⁴. Beattie and Webster's findings⁷⁵ were in agreement with the presence of the above ions, PCl_4^+ and PCl_6^- , but they claimed that phosphorus pentachloride was effectively fully ionised. Moreover, the addition reaction between phosphorus pentachloride and iodine monochloride (ICl) from which PCl_6I was isolated, offered further evidence for the existence of PCl_4^+ ions since this solid addition compound is reported to have the ionic structure $\text{PCl}_4^+ \cdot \text{ICl}_2^-$ ⁷⁶. Spectrophotometric analysis⁷⁷ of PCl_6I revealed that in carbon tetrachloride the complex dissociates into component molecules



and in ionising solvents, like methyl cyanide, the dissociation is ionic:



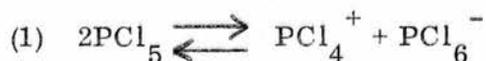
The corresponding adduct of phosphorus pentabromide and iodine monobromide is found to show a parallel solvent - dependent behaviour, the equilibria being,



in non-polar and polar solvents respectively.

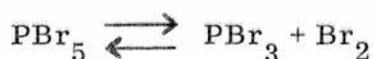
Shore et al.⁷⁸ have recently shown that the behaviour of these PX_5 type compounds is not only dependent on the nature of the solvent but is strongly influenced also by concentration. They have shown that the concentration of the solution affects the mode of ionisation of phosphorus pentachloride. On the basis of Laser Raman spectra and freezing point

depression results of phosphorus pentachloride solutions in the polar solvents: CH_3CN , CH_3NO_2 and PhNO_2 ; they have demonstrated the presence of two competing equilibria in solution, namely,

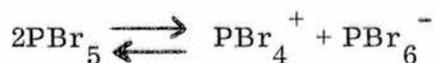


with (1) being predominant above about 0.03M and (2) being predominant at lower concentration. Thus, the solution behaviour of phosphorus pentachloride is more complicated than envisaged by Payne⁷³.

Like phosphorus pentachloride, phosphorus pentabromide exhibits two kinds of dissociation - molecular in non-polar solvents and ionic in polar solvents. In non-polar solvents, like benzene, it is reported by Kastle and Beatty⁷⁹ that phosphorus pentabromide (PBr_5) dissociates to phosphorus tribromide and bromine.



With regard to the behaviour of PBr_5 in solvents of high dielectric constant, Harris and Payne⁸⁰ have investigated the type of ions present in CH_3CN and PhNO_2 solutions of phosphorus pentabromide. They have shown by ion migration methods that the dissociation equilibrium in methyl cyanide is :



This is a slightly surprising result because although the cation found in solution is the same as that in the solid⁶⁹ the anion is not. This is the only report of the existence of the hexabromophosphate ion (PBr_6^-) which would not, on steric grounds, be expected to be very stable. It must be assumed that it owes its existence in methyl cyanide to

stabilisation by the solvent in some way. Negative ions of the type

PBr_4^- are more common. For example Dillon and Waddington⁸¹ have reported its existence in tetra-alkylammonium salts such as $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{PBr}_4^-$. The ^{31}P n.m.r. spectrum of these compounds in PhNO_2 suggested the presence of the equilibrium :



Thus, the PBr_4^- ions found in the solid compound must be stabilised by the limited solubility of the tetra-alkylammonium salts. Attempts made by the same authors to prepare the analogue PCl_4^- were unsuccessful even though it was expected to be more stable than PBr_4^- ion⁸².

The tetrahedral PBr_4^+ ion is relatively stable and common. As well as being found in phosphorus pentabromide its existence is known in a number of complexes e.g. $\text{PBr}_4^+\text{PF}_6^-$. The mode of preparation of this compound - fluorination of phosphorus pentabromide by arsenic trifluoride¹¹ - demonstrates its stability.

A recent infra-red study of antimony pentafluoride by Aljibury and Redington⁸³ using matrix isolation methods has led to the interesting suggestion that monomeric antimony pentafluoride (SbF_5) possesses the tetragonal pyramidal rather than the trigonal bipyramidal structure as reported by Gaunt and Ainscough⁸⁴. Furthermore, they have shown⁸³ that higher polymeric (condensed) species derived from SbF_5 namely $(\text{SbF}_5)_n$ are associated through Sb-F-Sb bridge bonds. This observation is in line with the temperature - dependent nuclear magnetic resonance spectrum results for liquid SbF_5 ⁸⁵, which suggested strong inter-molecular association through fluorine bridge bonds to form chains of pseudo - octahedral antimony pentafluoride molecules. Gillespie and

Moss⁸⁶, from nuclear magnetic resonance studies of SbF_5 dissolved in hydrogen fluoride, also pointed out the presence of an appreciable concentration of the fluorine-bridged $\text{Sb}_2\text{F}_{11}^-$ ions. The configuration of the $(\text{SbF}_5)_n$ species can be represented as in Figure 3.

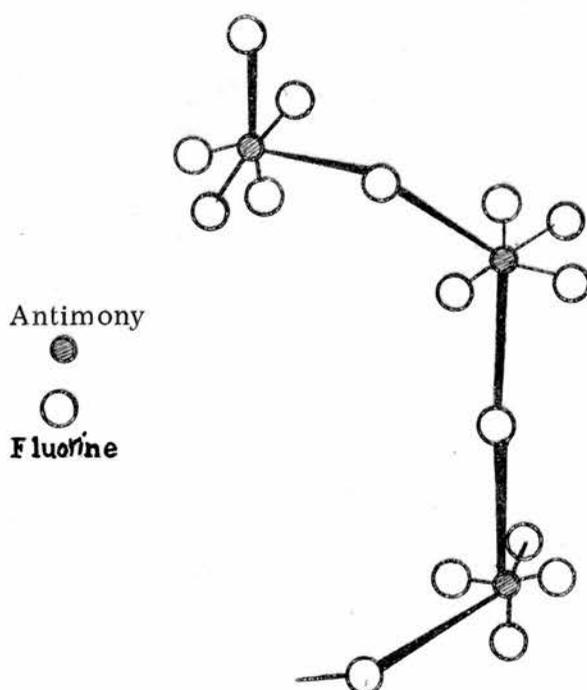


Figure 3. Schematic chain structure of SbF_5 polymer

Thus the structure differences between SbF_5 on the one hand and AsF_5 and PF_5 on the other, exactly parallel those of the solid Sb, As, and P pentaphenyl compounds (as determined by X-ray diffraction⁸⁷).

The Mixed Pentahalides of Group VB Elements

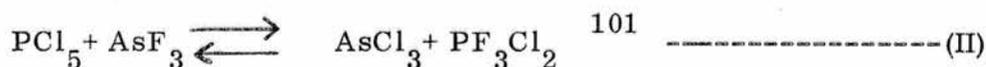
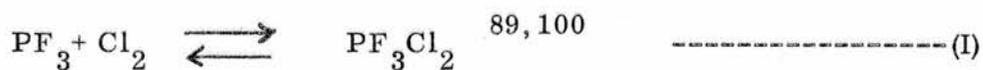
The number of possible species of the title compounds, even excluding stereoisomers, which might be obtained by allowing for simple and mixed fluorides, chlorides, bromides, and iodides of phosphorus,

arsenic and antimony, is over 200, only about a tenth having so far been recognised. The compounds which have been isolated and identified by various physical techniques are summarised in Table 4 below.

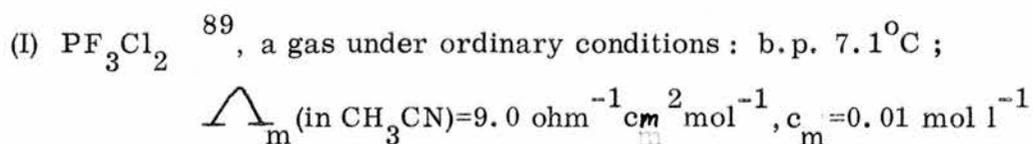
Table 4. The mixed pentahalides of phosphorus group elements

Phosphorus	Antimony
PF ₄ Cl 88	SbF ₃ Cl ₂ 96
PF ₃ Cl ₂ 89, 90	SbF ₂ Cl ₃ 97
PF ₂ Cl ₃ 91, 92	SbFCl ₄ 98
PFCl ₄ 91, 92	SbF ₃ Br ₂ 99
PF ₃ Br ₂ 93	
PF ₂ Br ₃ 35	
PFBBr ₄ 94	
PClBr ₄ 95	

The mixed phosphorus pentahalides (in particular chloride fluorides) can be obtained either by addition reactions, or by methods involving halogen exchange, for example :



The compound PF₃Cl₂ obtained in the above reactions is of special interest since that obtained from the addition reaction (I) differs in its physical properties from that obtained from the exchange reaction :



(II) PF_3Cl_2 ¹⁰¹, a solid sublimes at 135°C ;

$$\Lambda_m \text{ (in CH}_3\text{CN)} = 90.9 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}, c_m = 0.042 \text{ mol l}^{-1}$$

Thus the two reactions outlined above yield two different isomers of

PF_3Cl_2 . The former being virtually non-conducting in methyl cyanide⁸⁹

is molecular PF_3Cl_2 , i.e. dichlorotrifluorophosphorane, and the

latter being a strong electrolyte has the ionic formula $\left[\text{PCl}_4^+ \right] \left[\text{PF}_6^- \right]$ ¹⁰¹.

The analogous chloride fluoride of arsenic is known but it is

reported to exist solely as $\left[\text{AsCl}_4^+ \right] \left[\text{AsF}_6^- \right]$ and never as molecular

AsF_3Cl_2 ^{102, 103}. Some of the known mixed pentahalides of antimony

are listed in Table 4: A number of these exist in the ionic form whilst

others are covalent and as with phosphorus pentachloride, it is found

that the phase and environment of the compound determines the structure

adopted. The ionic form $\left[\text{SbCl}_4^+ \right] \left[\text{SbF}_6^- \right]$ is reported for the

crystalline product resulting from liquid SbF_3Cl_2 ¹⁰⁴. In case of

SbFCl_4 the Raman spectrum of the solid indicated the ionic form

$\text{SbCl}_4^+ \text{F}^-$ ¹⁰⁵; in contrast, the covalent trigonal bipyramidal structure

of this compound is believed to be present in solutions of it in non-polar

solvents¹⁰⁶ (see later). Kolditz and Mill¹⁰⁷ have recently reported the

existence of SbCl_3Br_2 as a very labile compound which they succeeded in

stabilising by forming 1:1 complexes with electron donor reagents like

$(\text{C}_2\text{H}_5)_2\text{O}$, THF, Ph_3PO and Ph_3PS . It is of interest to note that the

adduct $\text{SbCl}_3\text{Br}_2 \cdot \text{OPPh}_3$ gave $\text{SbCl}_3\text{Br}_2 \cdot \text{PhNO}_2$ on treatment with PhNO_2

which at room temperature transformed to a heteropolar compound of

the general formula $\left[\text{SbCl}_n \text{Br}_{4-n} (\text{PhNO}_2)_2^+ \right] \left[\text{SbCl}_m \text{Br}_{6-m}^- \right]$,

with $m+n=6$ and $n = 1-4$.¹⁰⁷

It should be noted however that early phase studies of the mixture

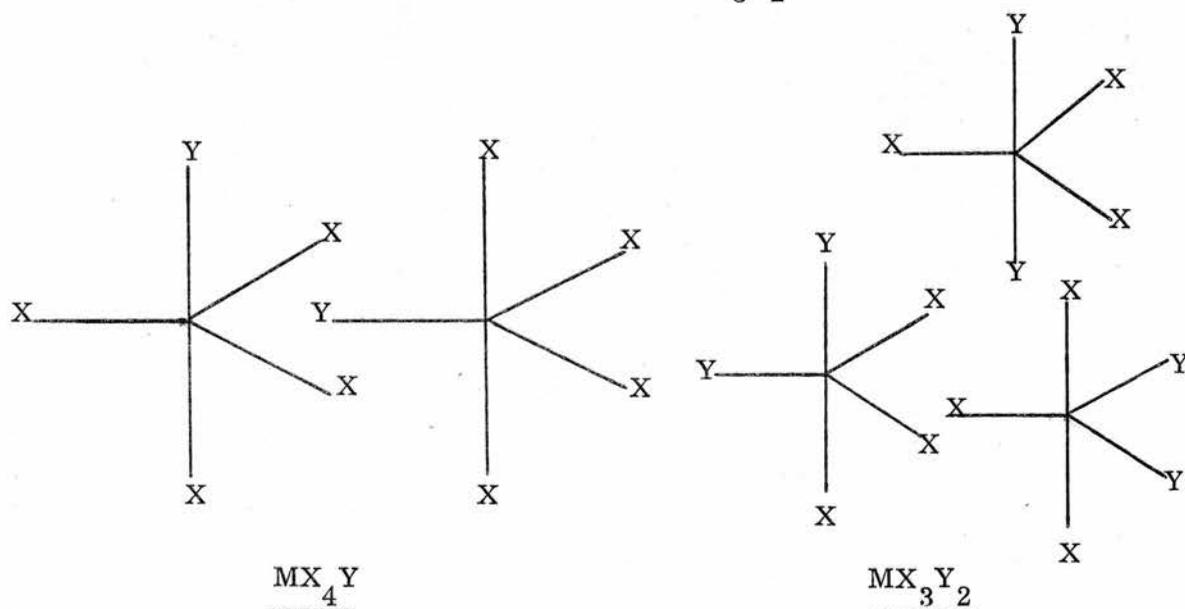
$\text{SbF}_5 - \text{SbCl}_5$, carried out in 1909 by Ruff et al.⁹⁷ have shown the existence of : $(\text{SbF}_3)_3 \cdot (\text{SbCl}_5)$, $(\text{SbF}_5)_2 \cdot (\text{SbCl}_5)$, $(\text{SbF}_5) \cdot (\text{SbCl}_5)$, $(\text{SbF}_5)_2 \cdot (\text{SbCl}_5)_3$, $(\text{SbF}_5) \cdot (\text{SbCl}_5)_2$, and $(\text{SbF}_5) \cdot (\text{SbCl}_5)_3$. Since none of these compounds have been isolated or structurally identified, their existence seems rather dubious.

Structure and Stereochemistry in Five-co-ordinated Compounds of Group VB Elements

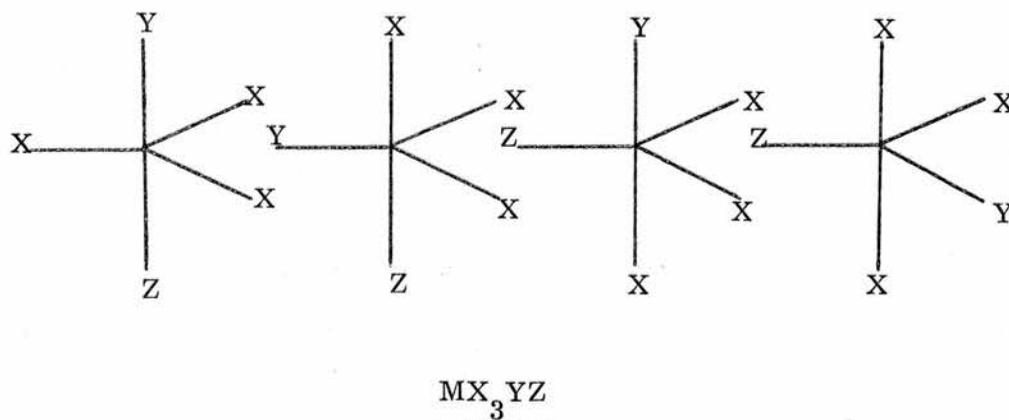
Recent synthetic advances which have made available a number of compounds of the type $\text{MX}_n\text{Y}_{5-n}$ (M = Group VB element ; X = alkyl, aryl, or halogen ; Y = halogen), in particular phosphorus, prompted many researchers to undertake extensive structural and stereochemical studies on this class of compound (mostly chlorofluorides). Techniques such as nuclear magnetic resonance (^{19}F , ^{31}P , and to certain extent ^1H), infra-red and Raman spectroscopy, chlorine or bromine nuclear quadrupole resonance spectroscopy, dipole moment measurements, X-ray and electron diffraction, were employed to elucidate the structures. From the data observed it seems certain that, as in the case of simple pentahalides, the mixed pentahalides and their related organo substituted molecules (with few exceptions, see elsewhere) possess the basic trigonal bipyramidal skeleton with two different bond lengths for the axial and equatorial bonds. In this geometry the axial bonds were invariably found to be longer than the equatorial ones¹⁰⁸. In this respect the many published articles on the geometry of this type of molecule demonstrate a continuing active interest in the location of substituents in the five-co-ordinated phosphorus framework^{109, 110}.

In halophosphoranes containing two different halogens there exists

the possibility of stereoisomerism and this subject has been extensively reviewed by Schmutzler^{106, 111}. Although there are various possible configurations for each of the $\text{MX}_n\text{Y}_{5-n}$ compounds (see below), the application of separation techniques has never detected the existence of more than one isomer of each. The stability of one form is obviously much greater than the other possibilities. In general, for molecules of the type MX_4Y , there are two possible arrangements based on trigonal bipyramid, and three for those of the type MX_3Y_2 .



Also, there are four stereoisomeric forms for molecules of the general formula MX_3YZ .



It should be noted that the number of possible isomers will be increased if we consider forms based on a square pyramidal structure also. In order to discuss the structure and stereoisomerism of these compounds, they are divided into two classes, the mixed pentahalides and the organo substituted halophosphoranes.

A. The Mixed Pentahalides

The most extensively studied compounds in this class are the phosphorus (V) chloride fluorides. Some of the known compounds in this series are now considered in turn :

PFCl₄

The three possible structures, with symmetries C_{2v} , C_{3v} , C_{4v} , which PFCl₄ may adopt are displayed in Figure 4. C_{3v} symmetry was the only one suggested by the ¹⁹F and ³¹P n.m.r. spectra of the compound PFCl₄¹¹². That the skeleton (Figure 4-a) is trigonal bipyramidal, has been further supported by chlorine quadrupole investigation¹¹³, vibrational spectra study¹¹², and dipole moment measurements¹⁰⁶.

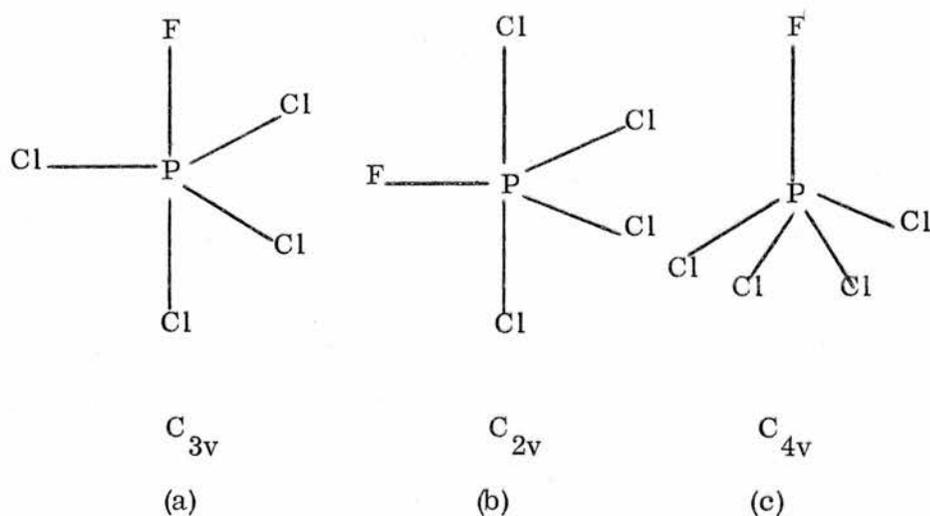


Figure 4. $PFCl_4$ Structure

Structure (c) in Figure 4, the square pyramid, can be regarded as arising from an angular distortion of the trigonal bipyramidal framework (b) - Figure 4. Although, however, the square pyramidal structure have not been observed in phosphorus chemistry, the compound Ph_5Sb ⁸⁷ and the SbF_5^{2-} ion in $(NH_4)_2SbF_5$ ¹¹⁴ are known to adopt it. Fluorotetrachloroantimony, $SbFCl_4$, in non-polar solvents such as chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4), is reported to have structure analogous to that of $PFCl_4$; that is, the fluorine atom occupies the axial position of the trigonal bipyramidal structure¹⁰⁶.

PF_2Cl_3

The trigonal bipyramidal configuration with equatorial fluorine atoms was suggested for the PF_2Cl_3 molecule by Holmes and Gallagher⁹² (Figure 5-a). In contrast, infra-red and Raman spectroscopy¹¹², ¹⁹F n.m.r. and ³⁵Cl nuclear quadrupole resonance¹¹³ studies indicate the same framework but with fluorine atoms occupying the axial sites as shown in Figure 5-b. This latter assignment is in accord with the

fact that the axial positions of the assumed trigonal bipyramidal structure ~~are~~ preferentially occupied by the most electronegative groups¹¹⁵.

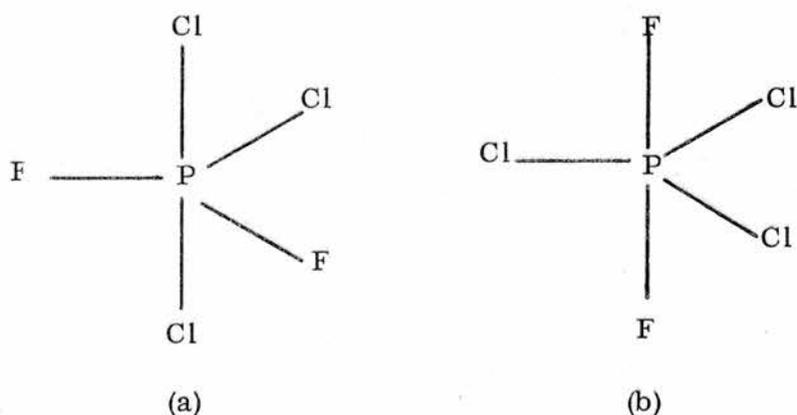


Figure 5. PF_2Cl_3 Structure

PF_3Cl_2

Early electron diffraction work by Brockway and Beach⁷¹ showed that PF_3Cl_2 had the trigonal bipyramidal structure of D_{3h} symmetry (Figure 6-I). This structure was apparently supported by ^{19}F n.m.r.⁹², dipole moment, and chlorine nuclear quadrupole resonance¹¹³ results. However, other studies using infra-red and low temperature Raman spectroscopy¹¹², chlorine nuclear quadrupole resonance¹¹³, and low temperature (below 80°C) ^{19}F n.m.r.^{113,115} indicated the same configuration but with C_{2v} symmetry (i. e. fluorine atoms in the axial positions) as shown in Figure 6-II. This finding was further supported by the infra-red spectrum results for PF_3Cl_2 obtained recently by Salthouse and Waddington¹¹⁶. They proposed that the axial fluorine atoms are bent slightly towards the equatorial one by electron pair repulsions ($\text{F}_{\text{axial}} - \hat{\text{P}} - \text{F}_{\text{axial}} = 177.8^\circ$ ¹¹⁷), and it has been suggested that this might account for the equivalence of the fluorine atoms found in

the room temperature nuclear magnetic resonance studies.

Muetterties et al.¹¹⁸ have reported that the spectroscopic non-equivalence of fluorine atoms at temperature below -115°C is due to intermolecular fluorine exchange and that the repulsion between chlorine atoms may provide the activation for this process¹¹⁵.

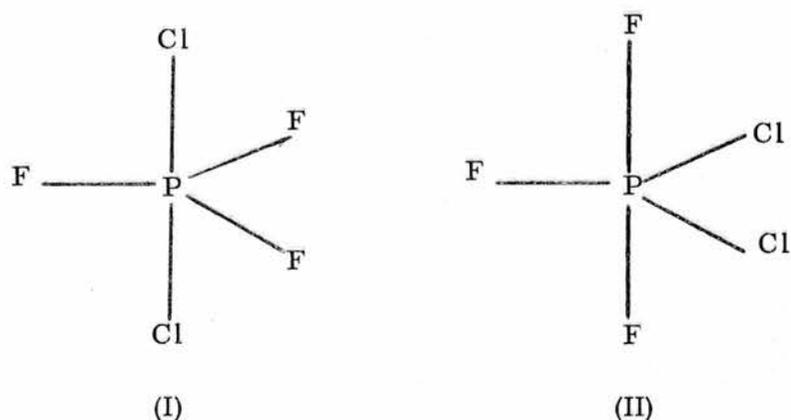
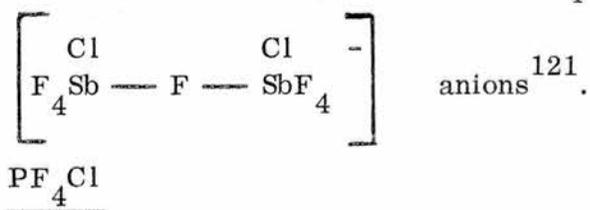


Figure 6. PF_3Cl_2 Structure

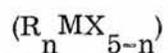
The corresponding bromofluorophosphorane PF_3Br_2 , has been investigated and has been found to be isostructural with PF_3Cl_2 ^{116, 118, 119}. The barrier to intermolecular fluorine exchange in PF_3Br_2 is reported to be lower than in PF_3Cl_2 ¹¹⁸. It has been shown, by infra-red and Raman spectra studies carried out by Dehnicke and Weidlein¹²⁰, that solid and liquid SbF_3Cl_2 has covalent trigonal bipyramidal structure possessing axial chlorine atoms. This type of axial location of the substituent of lower electronegativity is in contrast to that known in the analogous PF_3Cl_2 and other phosphorane derivative. However on the basis of low temperature ^{19}F n.m.r. data, Muetterties et al.¹¹⁸ showed that SbF_3Cl_2 in solution and molten phases has a more complicated structure involving association. Hexa-co-ordinated antimony atoms and bridging chlorine or fluorine atoms are present (cf. the structure

of SbF_5)⁸⁵. Recent X-ray structure analysis of solid SbF_3Cl_2 has shown it to be ionic, composed of SbCl_4^+ cations and



The structure of PF_4Cl has been determined by a study of its vibrational¹²² and ^{19}F , ^{31}P n.m.r. spectra¹²³. The observed results indicate, as in previously discussed compounds, that the fluorine atoms occupy the axial positions of a trigonal bipyramidal structure. Recently, Eisenhut et al.¹²⁴ have examined the temperature - dependent ^{31}P n.m.r. spectrum of this compound. They have shown that the interchange of axial and equatorial fluorine atoms follows the permutational scheme expected for Berry pseudorotation (to be discussed later); that is, both axial and equatorial fluorine atoms interchange at the same time.

B - The Organo- Substituted Pentahalides of Group VB Elements



The most extensively studied compounds in this series are the fluorophosphoranes. These compounds have been the subject of numerous studies, which have thrown considerable light on the actual distribution of halogen atoms among the axial and equatorial sites of the common trigonal bipyramidal configuration.

As in the case of mixed halides, similar structural problems are posed by the substituted PX_5 compounds, $(\text{R})_n \text{PX}_{5-n}$, and these have been subject to the same kinds of investigation. Some of the work done on elucidating the structures in the above series is collected in Table 5.

Table 5. The Fluorophosphoranes (R_nPF_{5-n})

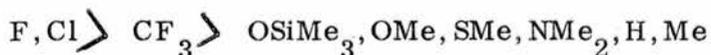
Year	Compound	Technique	Structure Proposed	Ref.
1963	a) RPF_4 b) R_2PF_3 c) R_3PF_2 $R=CH_3, C_2H_5,$ $n.C_4H_9, C_6H_5.$	I. R. ; ^{19}F n. m. r.		115
1964	a) R_2NPF_4 $R=C_2H_5$ b) $(R_2N)_2PF_3$ $R=C_2H_5, C_6H_5$	^{19}F n. m. r.		118
1965	$MePF_4$	I. R. , Raman		125
1965	a) $MePF_4$ b) Me_2PF_3	Electron - diffraction		117
1967	a) Me_2PF_3 b) Me_3PF_2	I. R. ; Raman; 1H n. m. r. ; ^{31}P n. m. r. ; ^{19}F n. m. r.		126

As can be seen from the Table, the basic trigonal bipyramidal framework is unambiguously established in these five-co-ordinated phosphorus compounds. The location of substituent ligands within this geometry is much less certain in cases where two or more different ligands are present. Early studies by Muetterties and coworkers¹¹⁵ suggested that, for a limited range of substituents, the axial position was preferentially occupied by the most electronegative group, perhaps as the result of greater ionic character of bonding in this direction or possibly as a consequence of enhanced π -bonding in the equatorial plane¹²⁷.

Cavell et al.¹²⁷ have demonstrated the capability of low temperature nuclear magnetic resonance spectroscopy in distinguishing axial and equatorial substituents in trigonal bipyramidal trifluoromethyl substituted phosphoranes. Thus, from a study of the low temperature ³¹P n. m. r., of a variety of halophosphoranes containing CF₃ groups, it was shown conclusively that CF₃ ligands occupy the equatorial positions in these structures^{127, 128}. These results are in keeping with the vibrational spectroscopy¹²⁹ and n. m. r.¹¹⁵ assignments for CF₃PF₄ (C_{2v}, equatorials CF₃).

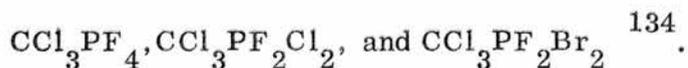
It has been reported that the back-bonding into the d-orbitals of the phosphorus atom being more effective from equatorial than from axial sites, will favour the occupation of the axial positions by groups of high "apicophilic" character and the equatorial sites by groups of less apicophilicity^{110, 130}. Each group therefore has a specific "apicophilic" character¹³⁰. Thus the observed nuclear magnetic resonance data, by Cavell et al.¹²⁷, were rationalised on the basis

of the following apicophilicity series:



The spectroscopic studies of the compounds CF_3PF_4 ^{115, 128, 129}, $(CF_3)_2PF_3$ ¹²⁸, and $(CF_3)_3PF_2$ ¹²⁸ indicate the CF_3 groups to be located in the equatorial sites of the trigonal bipyramidal structure. In contrast, ^{19}F n. m. r.¹¹⁵ and microwave¹³¹ investigations of $(CF_3)_2PF_3$ suggested a structure with axial CF_3 groups. Also, the compounds CF_3PCl_4 ¹³² and $(CF_3)_2PCl_3$ ¹³³ are reported to have axial CF_3 groups. Although, however, the reason for these conflicting results, concerning the location of CF_3 groups is not known, it has been suggested¹²⁸ that the inconsistency may arise from the fact that the studies have not been carried out on the same physical state of the compound (i. e. gaseous, solution). Thus further investigation into this problem is warranted.

Some other known halophosphoranes in which the fluorine atoms occupy the axial position of a trigonal bipyramidal structure, are:



The compounds of type R_3MF_2 ($M = As, Sb, Bi$) have also been studied. Their nuclear magnetic resonance spectra showed equivalence of fluorine atoms. Cryoscopic studies of these difluorides in benzene suggested that they are all monomers. The data obtained were consistent with the trigonal bipyramidal structure with axial fluorine atoms. However, this structure has not been established conclusively¹¹⁸.

Pseudorotation in Penta-co-ordinated Phosphorus

Trigonal bipyramidal structures are undoubtedly indicated for the

molecules: PF_5 , PF_3Cl_2 , and PF_4Cl by various physical methods. Because of the geometry of a trigonal bipyramid, the equatorial and axial sites are non-equivalent and it has been found that there are differences in the axial and equatorial phosphorus-halogen bond lengths. This has been reflected in their vibrational spectra. For example, the vibrational spectrum of PClF_4 ¹²² indicates the presence of two types of P-F bonds. In contrast, the ^{19}F nuclear magnetic resonance study at room temperature (or above) showed equivalent fluorine atoms in the compounds PF_5 ¹³⁵, PF_3Cl_2 ¹¹⁵, and PF_4Cl ⁸⁸. Berry⁶⁴ has explained this discrepancy in PF_5 by postulating a model in which intramolecular exchange of ligands is responsible for the observed equivalence of fluorine atoms in its ^{19}F nuclear magnetic resonance spectrum. This mechanism, presented schematically in Figure 7, has come to be known as "Berry Pseudorotation". In this process the positional exchange, in trigonal bipyramidal penta-coordinated compounds, occurs by pairwise exchange of axial and equatorial ligands.

Another mechanism, "Turnstile Rotation", is also reported in the literature to explain the interchange process^{136, 137}. This model which is illustrated in Figure 8 also involves angle compression and rotations of a pair of ligands against a trio. But, in contrast to "Berry Pseudorotation", "Turnstile Rotation" requires the rearrangement of penta-co-ordinated molecule by internal rotation.

Eisenhut et al.¹²⁴ in a recent paper, have studied the temperature-dependent ^{31}P n.m.r. spectra of the compounds PF_4Cl , CH_3PF_4 , and $(\text{CH}_3)_2\text{NPF}_4$ and have suggested that interchange of ligands in these

compounds occurs by the "Berry Pseudorotation" and not by "Turnstile Rotation". This is in line with the conclusion made by Strich and Veillard¹³⁸ concerning the compounds of general formula R_nPF_{5-n} .

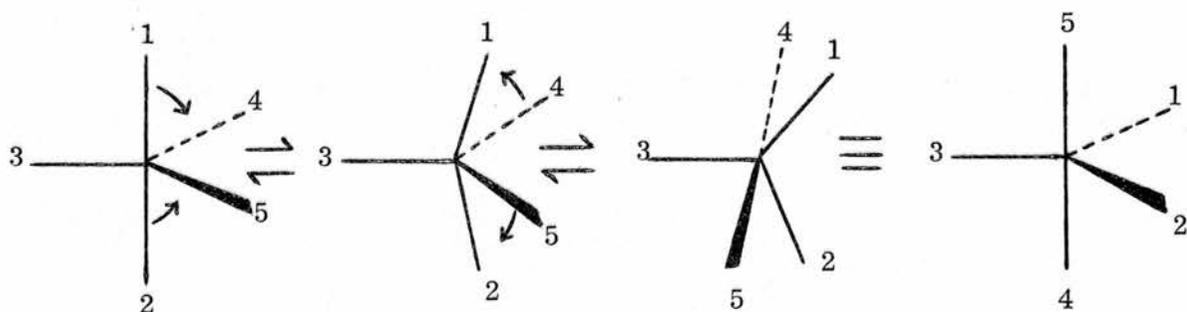


Figure 7. Berry Pseudorotation

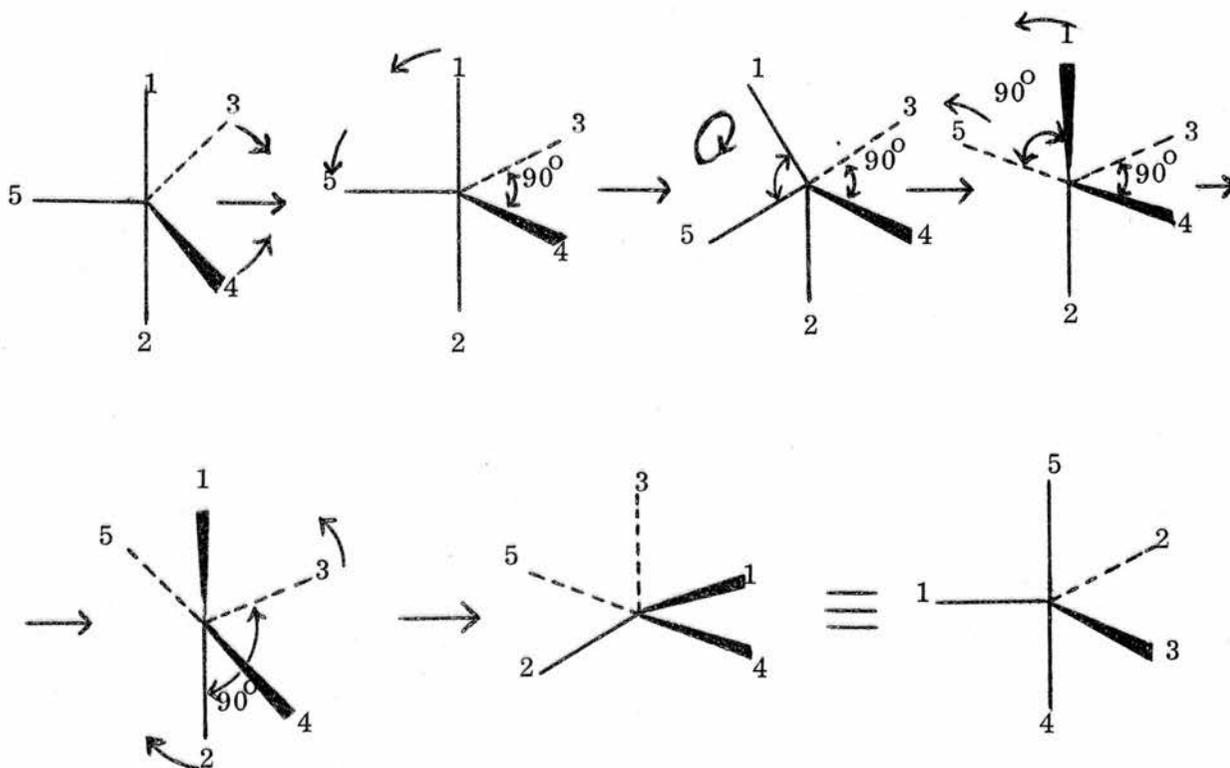


Figure 8. Turnstile Rotation

Bonding in Penta-co-ordinated Structure, MX_5

The covalent forms of phosphorus pentahalides in which phosphorus, the central atom, (ground state $1s^2; 2s^2, 2p^6; 3s^2, 3p^3$) is surrounded by five ligand atoms are examples of five-co-ordinated compounds. In these compounds, structural analyses, by ^{19}F and ^{31}P n.m.r., Raman and i.r. spectroscopy, electron diffraction, X-ray, etc., have revealed the trigonal bipyramidal configuration to be the one generally adopted and in the structures so far studied different bond lengths are found for the axial and equatorial P - Halogen bonds. This variation in bond length prompted many chemists to develop theories to explain the nature of bonding in penta-co-ordinated compounds, and to understand its influence on the type of the geometry adopted.

Of these theories, the Valence Bond approach describes the bonding in five-co-ordinated molecules in terms of σ -bonds involving a set of five sp^3d hybrid orbitals on the central atom. This description requires the promotion of an s electron into an empty d-orbital, mixing of the orbitals, and pairing up of the valence shell electrons with those of the ligands. A slight variation of this has been proposed by Muettterties and coworkers¹¹⁵ who suggested that in the trigonal bipyramidal structure the equatorial groups are bonded by sp^2 hybrids and the axial ligands by pd hybrids, and that the difference in energy levels between these two sets should reflect the s electron promotion energy. As the electronegativity of the ligands (i. e. halogens) increases the differences in energy of these hybrid orbitals become less and this is reflected in the relative bond distances:

$$\begin{aligned} \text{e.g. } P-Cl_{ax.} &= 2.19A^{\circ}, P-Cl_{eq.} = 2.04A^{\circ} & \Delta &= 0.15A^{\circ} \text{ and} \\ P-F_{ax.} &= 1.577A^{\circ}, P-F_{eq.} = 1.534A^{\circ} & \Delta &= 0.043A^{\circ} \quad 139. \end{aligned}$$

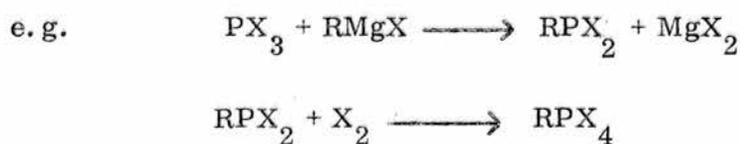
It has generally been thought that the high energy and diffuse nature of d - orbitals would not lead to effective hybridisation with s - and p - orbitals and that their diffuse nature would lead to poor overlap with neighbouring atoms and hence would contribute only very slightly towards effective bonding. In this connection it has been suggested that when electronegative groups are attached to the central atom contraction of the d - orbitals occurs thus allowing more effective overlap and stronger bonding¹⁴⁰. For this reason attempts have been made to explain the bonding in compounds such as pentahalides of phosphorus without recourse to d - orbitals. One such attempt is that of Rundle^{141, 142}. In this approach the X-P-X axial part of the molecule is regarded as being held together by a four electron three centre bond. The three centre bonding system arises from one atomic p - orbital from each atom giving rise to a bonding, a non-bonding, and an antibonding molecular orbitals, the former two of which each contain a pair of electrons. The equatorial bonds are normal electron pair bonds and involve sp^2 hybrid orbitals of the central atom.

Advantages of this scheme are (a) d - orbitals not involved (it is very much a controversial matter whether d - orbitals are involved in this sort of molecule) and (b) the longer axial bonds follow as a natural consequence of the three-centre bond system.

ORGANO - SUBSTITUTED PENTAHALIDES OF GROUP VB ELEMENTS

The tri-alkyl and tri-aryl derivatives of the Group VB elements were among the first organometallic compounds to be prepared and partially characterised^{143, 144, 145}. It was recognised, in the past, that many of these compounds reacted with halogens to produce adducts of the type R_3MX_2 (M = Group VB element; X = halogen)^{3,4}. This group of compounds, members of which are now well known, can be considered as members of the more general series R_nMX_{5-n} , where n = 1-5. The nature of these compounds has been discussed from time to time, and they are known to exhibit a considerable variety of structures, depending on the physical state and nature of the substituent groups.

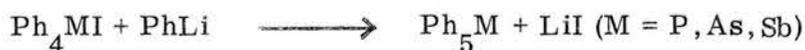
In the synthesis of these compounds it is usual for the organic group to be introduced at first to a phosphorus (III) compound, which can react further with halogen to give the phosphorus (V) derivative :



Thus the members of the series R_nMX_{5-n} can be readily obtained. The pattern of structures and properties of this series are briefly outlined in the following paragraphs :

(a) R_5M Compounds

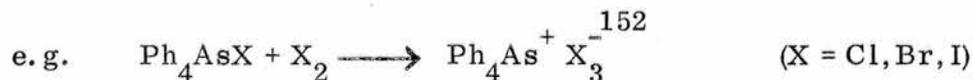
Fully substituted pentahalides of the phosphorus group elements are rare by comparison with the number of known partially substituted compounds, and are restricted to the pentaphenyls (Ph_5M)^{146, 147, 148}, and some penta-alkenyls¹⁴⁹. Wittig and Clauss^{147, 148} have prepared the pentaphenyls of the Group VB elements by the following two reactions :



Pentaphenylphosphorus is molecular and adopts the trigonal bipyramidal structure in which the axial bonds (1.987Å) are slightly longer than the equatorial ones (1.850Å)¹⁵⁰. Arsenic pentaphenyl (Ph₅As) is reported to be isomorphous with phosphorus pentaphenyl⁶², unlike antimony pentaphenyl which, anomalously, adopts tetragonal pyramidal geometry^{62, 87}. This is of considerable interest as it seems to be the only well established example of this stereochemistry in five-co-ordinated compounds of Group VB elements.

(b) R₄MX Compounds

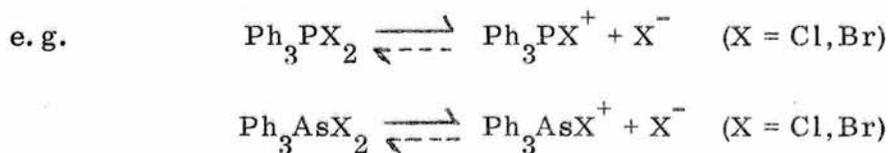
In this series, the chlorides, bromides, as well as iodides of phosphorus¹⁵¹ and arsenic¹⁵² are reported. The analogous chlorides and bromides of antimony are also known¹⁵¹. These compounds, which are high-melting crystalline solids, dissolve in polar solvents to give highly conducting solutions, suggesting that they are ionic in the solid phase and in solution. Further evidence for their electrolytic behaviour is the fact that Ph₄MX compounds can readily add a mole of halogen to form the adducts Ph₄MX₃ which contain the trihalide ion.



In addition, it has been shown conclusively by X-ray crystal structure analysis that Ph₄PI is ionic composed of tetrahedral Ph₄P⁺ ions and I⁻ ions¹⁵³.

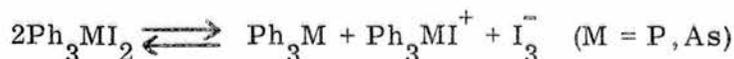
(c) R₃MX₂ Compounds

Compounds of this type are formed by each Group VB element except nitrogen. These compounds have been studied more extensively than any others in the series R_nPX_{5-n}; however, conflicting reports about their nature have appeared in the literature from time to time. Harris and co-workers^{154,155,156}, in particular, have investigated the Ph₃M-X₂ systems (M = P, As, Sb, Bi; X₂ = Cl₂, Br₂, I₂, ICl, IBr) in solvents of high dielectric constant, such as methyl cyanide, using conductometric-titrations, conductance measurements, and ion migration experiments. Their results, have shown that the dihalides of triphenylphosphine and triphenylarsine are electrolytes in methyl cyanide,



This mode of ionisation for the dihalides was independently supported by ³¹P n.m.r. spectrum studies¹⁵⁷ and by examination of the reaction of Ph₃PCl₂ with a strong chloride ion donor (Et₄N⁺Cl⁻)¹⁵⁸.

It is evident from the ultra-violet spectrum of methyl cyanide solutions of Ph₃PI₂ and Ph₃AsI₂, that triiodide ions are produced. Thus the following disproportionation equilibrium was suggested¹⁵⁶.



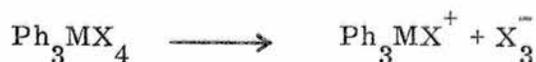
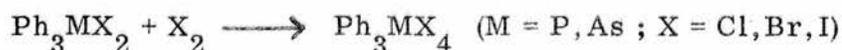
In contrast to the corresponding phosphorus and arsenic compounds, triphenylstibine dihalides and triphenylbismuthine dihalides were shown by conductance measurements to be non-electrolytes in methyl cyanide^{156,159}.

On the basis of their conductance experiments, Harris and co-workers

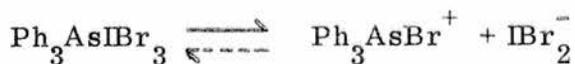
have suggested that the dihalides of triphenylphosphine may be ionic in the solid state (c.f. $\text{Me}_3\text{PX}_2 \equiv \text{Me}_3\text{PX}^+ \text{X}^-$ —see below), whilst the analogous dihalides of triphenylarsine and triphenylstibine are covalent.

Spectroscopic investigations of trimethylphosphine dihalides, Me_3PX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), have demonstrated that in the solid phase, an ionic structure of the type $\text{Me}_3\text{PX}^+ \text{X}^-$ is adopted¹⁶⁰, whereas trimethyl-, triethyl-, and triphenylstibine¹⁶¹ dihalide molecules have the basic trigonal bipyramidal configuration^{162, 163}. A similar structure was assigned, from infra-red and Raman spectral studies, for trimethyl-, and triphenylarsine dichloride¹⁶⁴.

The tetrahalides Ph_3PX_4 and Ph_3AsX_4 , which are formed by the addition of a mole of halogen to the corresponding dihalide, are strong electrolytes in polar solvents, producing trihalide ions^{154, 155, 156}.



Mixed tetrahalides of triphenylarsine and triphenylphosphine of the general formula $\text{Ph}_3\text{MI}_n\text{Br}_{4-n}$ ($n = 1-4$) are also known¹⁵⁵. Their methyl cyanide solutions are good conductors and their modes of ionisation, suggested by ultra-violet spectrum studies, are found to be¹⁵⁵:



Compared with phosphorus, arsenic, and antimony, very few compounds have been observed which contain a penta-co-ordinated bismuth atom,

although triphenylbismuthine dichloride and dibromide were reported by Wittig and Clauss¹⁴⁸. Some other examples of known pentavalent bismuth compounds are triphenylbismuthine difluoride¹⁶⁵ and triphenylbismuthine diiodide¹⁶⁶. Harris and co-workers¹⁵⁶ thought that under the influence of ionising solvents triphenylbismuthine might react with halogens to give ionic bismuthonium type compounds, a situation which avoids pentacoordination, thus :



However, a conductometric titration study of the $\text{Ph}_3\text{Bi}-\text{Br}_2$ system in methyl cyanide¹⁵⁶ showed no sign of an increase in conductance as bromine was added to triphenylbismuthine and hence the above reaction was not taking place. It was suggested that the reaction in methyl cyanide was :

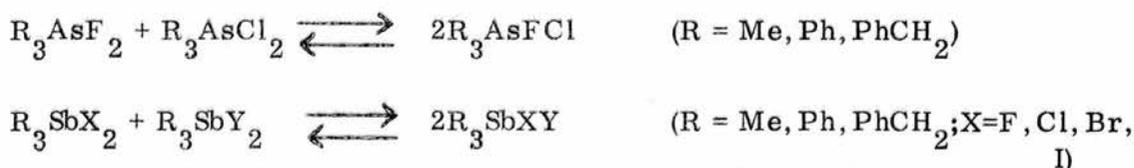


The compound Ph_3BiCl_2 has been reported by Jensen¹⁶⁷ to possess the trigonal bipyramidal structure, from its zero dipole moment in benzene solution. This framework has been recently confirmed by X-ray diffraction analysis¹⁶⁸. This compound, Ph_3BiCl_2 , has also been shown to be covalent in the polar solvent methyl cyanide ($\Lambda_m < 1.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.01 \text{ mol l}^{-1}$)¹⁵⁶.

The nature of the group R attached to the central atom in the series R_3MX_2 , has been shown to influence the electrolytic properties of these compounds. Harris and co-workers^{156, 169, 170} have shown that when the groups are strongly electronegative, (e. g. $\text{R} = \text{C}_6\text{F}_5$) the compounds are non-electrolytes or very weak electrolytes whereas when the compounds contain electron releasing groups (e. g. $\text{R} = \text{Me}_2\text{N}$) they behave as strong electrolytes.

Conductance studies of the series¹⁷¹: $(\text{H}_3\text{C}-\text{C}_6\text{H}_4)_3\text{AsX}_2$, $(\text{C}_6\text{H}_5)_3\text{AsX}_2$, $(\text{Cl}-\text{C}_6\text{H}_4)_3\text{AsX}_2$, in which the electron attracting power of substituents increases from left to right, supported the idea that increased electronegativity of the group attached to the central atom reduces the tendency of these compounds to ionise.

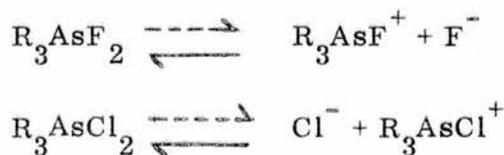
Halogen exchange reactions ("scrambling" reactions) are known to occur in organo-substituted pentahalides of group VB elements as well as in the phosphorus tri-, and pentahalides²⁵. Long et al.^{172,173} have shown, by means of room temperature nuclear magnetic resonance, that on mixing different pairs of the dihalides $(\text{R}_3\text{MX}_2 + \text{R}_3\text{MY}_2)$ in chloroform the mixed dihalide, R_3MXY , is formed in equilibrium with the starting dihalides. ^1H and ^{19}F n.m.r. spectroscopy¹⁷³ has been used recently in a more detailed study, at low temperatures, of the following two reactions



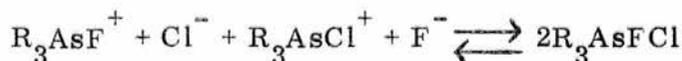
for which equilibrium constants have been determined.

It seems therefore reasonable to suggest that these redistribution reactions result from partial ionisation of the dihalides in the mixtures.

That is

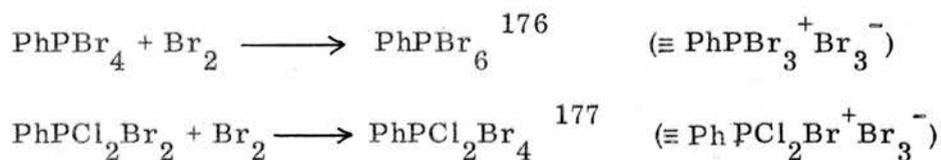


and then



(d) R₂MX₃ and RMX₄ Compounds

The nature of the R₂PX₃ and RPX₄ compounds, like the above mentioned R₃PX₂ compounds, is not clear cut and conflicting views concerning their structure have been put forward. Rochow et al.¹⁷⁴ have described R₂PX₃ and RPX₄ as covalent molecules, from their low melting points and ease of solubility in organic solvents. In contrast, Van Wazer²⁵ suggested that these adducts were ionic of type RPX₃⁺ X⁻ similar to phosphorus (V) halides. Kosolapoff¹⁷⁵ agreed with Van Wazer's views on the ionic nature of R₂PX₃ and RPX₄, on the basis of their ability to add a further mole of halogen to form polyhalides, for example :



In a similar way, R₂PX₃ (R = C₂H₅, C₃H₇) reacts with halogens to form R₂PX₅ compounds. Kuchen and Strolenberg¹⁷⁸ who have prepared these compounds, found that in ionising solvents R₂PX₅ has the dihalophosphonium salt type of structure (R₂PX₂⁺X₃⁻). However there now appears to be fairly firm evidence for both ionic and covalent forms in the R₂PX₃ and RPX₄ groups of compounds. Chloro-organo-phosphonium cations of the type expected for the ionic forms in R₂PX₃ and RPX₄ have been demonstrated, by ³¹P n.m.r. to be present in $\left[\text{Ph}_n \text{PCl}_{4-n} \right]^+ \left[\text{ClO}_4 \right]^-$ and $\left[\text{Ph}_n \text{PCl}_{4-n} \right]^+ \left[\text{SbCl}_6 \right]^-$ ¹⁷⁹.

The penta-co-ordinate organometallic - arsenic and (to a smaller extent) antimony derivatives of the type R₂MX₃ and RMX₄ are also known^{180, 181, 182}. The infra-red and Raman spectra of R₂AsCl₃ and RAsCl₄ (R = Me, Ph) indicate the trigonal bipyramidal framework for these

molecules and in this the R groups are equatorials ¹⁶⁴. A similar structure is reported from an X-ray analysis of Ph_2SbCl_3 ¹⁸²; in this compound the phenyl groups and one chlorine atom are in the equatorial plane ($\text{Sb} - \text{Cl}_{\text{ax.}} = 2.52 \text{ \AA}^{\circ}$ and $\text{Sb} - \text{Cl}_{\text{eq.}} = 2.431 \text{ \AA}^{\circ}$).

COMPOUNDS CONTAINING PHOSPHORUS WITH CO-ORDINATION NUMBER 6

As mentioned previously, the phosphorus atom exhibits various co-ordination numbers (3, 4, or 5) in its compounds. Compounds in which the phosphorus atom has a coordination number of 6 are relatively uncommon but recent publications have added to the number of compounds with this coordination number. The best known species are the PF_6^- ion (as in $\text{NH}_4^+ \text{PF}_6^-$ etc.) and the PCl_6^- ion (as in $\text{PCl}_4^+ \text{PCl}_6^-$ etc.).

Recently Dillon et al.¹⁸³ have confirmed, by ³¹P n.m.r. and ³⁵Cl n.q.r. spectroscopy, the presence of the hexachlorophosphate ions (PCl_6^-) as the only phosphorus - containing anion in the compounds: $\text{Ph}_3\text{PCl}^+\text{PCl}_6^-$, $[\text{C}_7\text{H}_7^+]_2 \text{PCl}_6^- \text{Cl}^-$, $\text{C}_7\text{H}_7^+ \text{PCl}_6^-$, $[\text{C}_8\text{H}_{12}\text{N}^+]_2 \text{PCl}_6^- \text{Cl}^-$, and $\text{Et}_4\text{N}^+ \text{PCl}_6^-$. Phosphorus pentafluoride¹⁸⁴ and fluorophosphoranes¹⁸⁵ are reported to form stable, non-ionic, six-co-ordinate complexes with organic donor molecules. From these reactions the compounds: $(\text{C}_5\text{H}_5\text{N})_2\text{PF}_5$ ¹⁸⁴ and $(\text{C}_{13}\text{H}_{18}\text{NO})_2\text{PRF}_4$ ¹⁸⁵ (R = F, Me, Et, or Ph), were isolated and fully characterised. It was shown by X-ray^{184, 185} analysis that in these molecules the phosphorus atom was surrounded octahedrally by six ligands. This skeleton (given in Figure 9) was further confirmed by ¹⁹F and ³¹P n.m.r. results which provided further evidence for the presence of an intramolecular N → P coordinate bond¹⁸⁵.

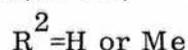
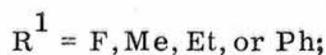
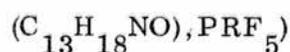
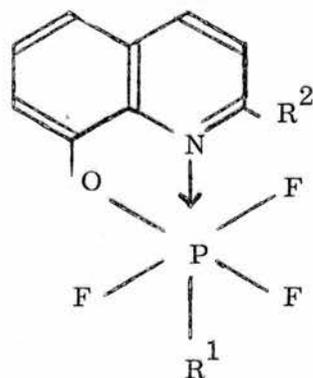
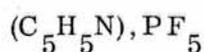
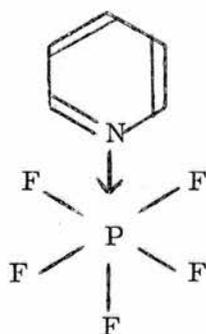
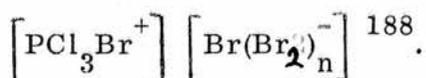


Figure 9 : Hexagonal Phosphorus Compounds

The Reaction of Phosphorus Trihalides With Halogens and Interhalogens

During the last twenty years many groups of workers have made a study of reactions of phosphorus trihalide with halogen or interhalogen. Many new compounds containing phosphorus and halogen have been obtained and a number of these have been found to possess unexpected and unusual stoichiometry composition. Efforts have been made, unsuccessfully in many cases, to elucidate the nature of these compounds.

Fialkov and Kuzmenko^{186, 187} studied the melting point diagram, the specific conductance, and the viscosity of the $\text{PCl}_3\text{-Br}_2$ system and from the results of these experiments, reported the existence of the compounds : PCl_3Br_4 , PCl_3Br_8 and $\text{PCl}_3\text{Br}_{18}$. By ionic migration methods it was shown that the structure of these compounds can be expressed by the formula



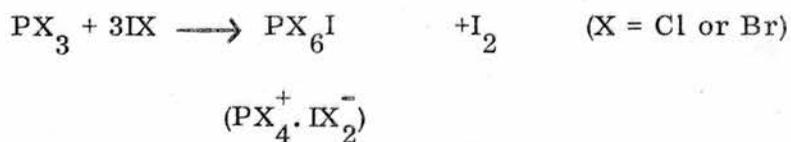
Although claims for the existence of PCl_3Br_2 have been made^{189, 190} no compounds of this stoichiometry has ever been isolated^{191, 192}. Popov

and his co-workers¹⁹³ have found that the $\text{PCl}_3\text{-Br}_2$ system does not yield stable solid phases corresponding to simple formulae. For example, direct reaction of phosphorus trichloride and bromine led to an unstable aggregate of composition $\text{PCl}_3\text{Br}_{5.7}$, which under reduced pressure yielded a stable mixed halide with the empirical formula $\text{PCl}_{4.67}\text{Br}_{0.33}$. The latter compound was shown by X-ray powder analysis to be built up of the ions PCl_4^+ , PCl_6^- , and Br^- present in proportions represented by the formula $[\text{PCl}_4^+]_8 [\text{PCl}_6^-]_4 [\text{Br}^-]_4$ ¹⁹³. The system $\text{PCl}_3\text{-Br}_2$ has also been investigated in different solvents by Harris and Payne¹⁹⁴.

In nitrobenzene, cryoscopic measurements indicated the existence of two equilibria one of which involved PX_5 species and the other PX_7 species. Isolation of solids was not attempted from this solvent but from carbon tetrachloride two compounds, of stoichiometry $\text{PCl}_3\text{Br}_7, \text{CCl}_4$ and $\text{PCl}_3\text{Br}_7, 2\text{CCl}_4$, were isolated. These adducts lost bromine on removal of the solvent. Equimolar amounts of the components of the above system on mixing in arsenic trichloride gave only one definite compound and this had the composition $\text{PCl}_{4.5}\text{Br}_{0.5}$: it is believed to contain the ions $[\text{PCl}_4^+] [\text{PCl}_5\text{Br}^-]$ ¹⁹⁵.

The reaction between phosphorus trichloride and bromine was further studied by Salthouse and Waddington¹⁹⁶. Conductometric titration of this system in liquid hydrogen chloride suggested the present of the bromotrichlorophosphonium ions PCl_3Br^+ . This was confirmed by examination of the infra-red spectrum of the tetrachloroborate salt of this cation $(\text{PCl}_3\text{Br}^+ \text{BCl}_4^-)$ ¹⁹⁶. The same authors have studied the interaction of phosphorus trichloride with chlorine and iodine monochloride in liquid hydrogen chloride using conductometric titration methods to follow the

reaction. The graph obtained in the former case, $\text{PCl}_3\text{-Cl}_2$, suggested the formation of a 1:1 ionic species. But in the latter case ($\text{PCl}_3\text{-ICl}$), iodine liberation was observed, on passing the 1:1 ratio of $\text{ICl} : \text{PCl}_3$. The adduct isolated from this system had the composition PCl_6I and was shown to be ionic, of the formula $\text{PCl}_4^+ \text{ICl}_2^-$ ¹⁹⁶. This adduct as well as PBr_6I were previously reported as ionic species by Fialkov and Kuzmenko¹⁹⁷.



Attempts have also been made by several workers to prepare various bromochlorophosphonium ions in the series $[\text{PCl}_n\text{Br}_{4-n}]^+$, ($0 \leq n \leq 4$) using PF_6^- , BCl_4^- and BBr_4^- as anions¹⁹⁸. The only pure adducts isolated were $[\text{PCl}_3\text{Br}]^+ [\text{PF}_6]^-$ and $[\text{PCl}_3\text{Br}]^+ [\text{BCl}_4]^-$. Dillon and Gates¹⁹⁹ in a recent publication, characterised the ions $\text{PCl}_n\text{Br}_{4-n}^+$ by means of solid state ^{31}P nuclear magnetic resonance spectroscopy. The ions $\text{PCl}_2\text{Br}_2^+$ and PClBr_3^+ are believed to be present in certain mixtures of phosphorus trichloride, bromine, and boron trichloride in liquid hydrogen chloride¹⁹⁸. Recently, Gabes et al.⁹⁵ succeeded in the preparation of PBr_4Cl from a mixture of phosphorus pentachloride and phosphorus pentabromide (4:3). This adduct was shown by X-ray analysis and Raman spectrum to be ionic having the structure $\text{PBr}_4^+ \text{Cl}^-$.

It is reported¹⁹⁶ that the 1:1 adduct PBr_3Cl_2 ($\text{PBr}_3\text{Cl}^+ \text{Cl}^-$) forms in solution when phosphorus tribromide reacts with chlorine in liquid hydrogen chloride. However the solid isolated at this ratio (i. e. 1:1 $\text{Cl}_2 : \text{PBr}_3$) is not PBr_3Cl_2 but is PCl_5 as is shown by its analysis and infra-red spectrum. Presumably in the course of crystallisation a halogen

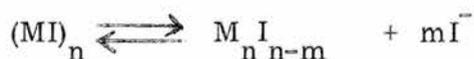
exchange reaction had occurred on account of bond energy differences between P-Cl and P-Br.

In the investigation of the $\text{PBr}_3\text{-Br}_2$ system in methyl cyanide conductometric titration gave a clear indication for the formation of phosphorus pentabromide⁸⁰, whereas in nitrobenzene PBr_7 as well as PBr_5 was shown to be present, from cryoscopic measurements. The absence of an inflection at the 2:1 ratio of Br_2 : PBr_3 (i. e. corresponding to PBr_7) in the conductometric - composition graph therefore suggests either that no new type of ions are being formed⁸⁰ or that any new ions formed have a similar mobility in methyl cyanide to those formed by phosphorus pentabromide. The melting point diagram of the P- Br_2 system shows four crystalline compounds : PBr_3 , PBr_5 , PBr_7 , and PBr_{17} ²⁵. A single - crystal X-ray diffraction study²⁰⁰ has shown conclusively that PBr_7 is composed of tetrahedral PBr_4^+ (P-Br distances all $\sim 2.17 \text{ \AA}$) and linear unsymmetric Br_3^- ions (Br-Br distances of 2.91 \AA and 2.39 \AA).

The phosphorus tribromide - iodine system has not been well investigated. A solution of iodine in phosphorus tribromide is known to be cherry red in colour, suggesting interaction between the compounds, but a solid phase has not been isolated. Phosphorus tribromide dissolves in molten iodine but as in the case of phosphorus trichloride the conductance of the solution is less than that of molten iodine²⁷.

Attempts to prepare a 1:1 adduct of phosphorus trichloride and iodine have been unsuccessful and the non-existence of PCl_3I_2 was explained by Colten²⁰¹ to be either due to the inherent instability of the compound, or else that the iodine molecule is too large to approach close enough to the phosphorus atom to react.

The behaviour of systems involving phosphorus triiodide and halogens or interhalogens is not well known. However the specific conductance of solutions of phosphorus triiodide in molten iodine increased with concentration and the maximum value of $1.24 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, was reached at 9.69 mole % PI_3 . After this point the specific conductance dropped. The conductivity of iodine in liquid phosphorus triiodide, in the range (4-20) mole % I_2 was somewhat less than that of pure liquid iodine, but of the same order (of magnitude $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$)²⁰². From these data Plotnikov et al.²⁰² have suggested that the conductivity of iodides in liquid iodine is due to electrolytic dissociation of associated iodide molecules, but not the formation of polyiodides. Thus, they have described the dissociation process in its simplest form as :



It appears from this brief survey that the reactions between phosphorus trihalides and halogens or interhalogens are rather complicated, and many types of behaviour are observed. This is probably attributable to a number of factors such as, size of the halogen atoms, solvent interactions and solubility as well as the tendency of phosphorus (V) compounds to undergo dissociation.

It was thought that it would be useful to carry out a further study of certain systems ($\text{PBr}_3 - \text{Hal}_2$) and ($\text{PI}_3 - \text{Hal}_2$) using methyl cyanide as solvent and following their behaviour by conductometric titration in order to throw light on the electrolytic behaviour of the adducts formed in these systems.

Related Systems Previously Studied

Systems involving triarylphosphine and halogens or interhalogens have been extensively studied, mainly by conductometric methods, in methyl cyanide by Harris and co-workers. On the basis of conductance measurements, they have demonstrated that in the series $(\text{Me}_2\text{N})_3\text{P-X}_2$, $(\text{C}_6\text{H}_5)_3\text{P-X}_2$ and $(\text{C}_6\text{F}_5)_3\text{P-X}_2$, the molar conductance of the dihalides decrease with the increase in electronegativity of the organic group attached to phosphorus. In order to investigate the effect of replacement of a phenyl group by halogen, MacPherson²⁰³ studied the behaviour of $\text{Ph}_2\text{PCl-Hal}_2$ and $\text{PhPCl}_2\text{-Hal}_2$ ($\text{Hal}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{ICl}, \text{IBr}, \text{and ICl}_3$) in methyl cyanide. Thus, it was thought worthwhile to study the analogous bromine and iodine systems in a similar way in methyl cyanide. The results from this investigation, which involved a study of the systems $\text{Ph}_n\text{PX}_{3-n}\text{-Hal}_2$ ($n = 0, 1, 2$; $\text{X} = \text{Br}, \text{I}$; $\text{Hal}_2 = \text{Br}_2, \text{I}_2, \text{IBr}$), are described in the first part of this thesis. The second part of the thesis is concerned with the reactions of triphenylphosphine and triphenylarsine with pseudohalogenhalides, CNX ($\text{X} = \text{Br}, \text{I}$). This was thought to be desirable, since much information is already known about the $\text{Ph}_3\text{M-X}_2$ systems ($\text{M} = \text{P}, \text{As}$), and hence a comparison in behaviour between these two different systems (or their adducts) would be of interest. Finally, the third part of the thesis deals with the reactions of the ditertiary arsines, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ with halogens ($\text{Br}_2, \text{I}_2, \text{IBr}$) in methyl cyanide.

RESULTS AND DISCUSSION

PART 1

THE REACTION OF HALOGENS WITH HALOGENOPHENYLPHOSPHINES

AND PHOSPHORUS TRIHALIDES, ($\text{Ph}_n\text{PX}_{3-n}$; X = Br, I and n = 2, 1, 0).

Results and Discussion

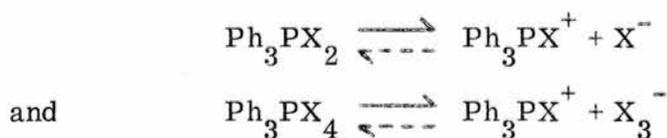
Part 1

The Reactions of Halogens with Halogenophenylphosphines and phosphorus Trihalides

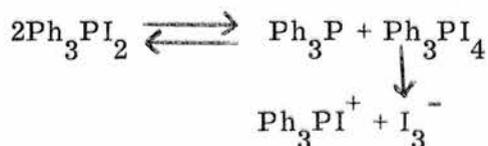
Introduction

The addition compounds of halogens with triphenylphosphine have been well characterised. Harris and co-workers have used conductometric titration studies extensively to investigate the reactions of halogens and interhalogens with compounds of the type R_nPX_{3-n} ($R = Ph, Me, C_6F_5$, etc. ; $X = \text{halogen}$; $n = 0, 1, 2$). In this technique (conductometric titration) conductance values are measured during the addition of halogen in a nonaqueous solvent of high dielectric constant such as methyl cyanide, to the phosphine in the same solvent. From the inflections in the titration graphs (specific conductance plotted against mole ratio of reactants) useful information about the course of the reaction is often obtained. Thus, the compounds which are members of the general series $Ph_3PX_nY_{4-n}$ ($n = 0, 1, 2, 3, 4$; $X = Cl, Br, I$) were predicted by this method and have subsequently been isolated.

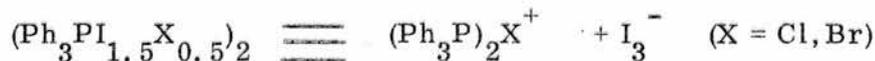
Reactions of halogens with halogenophosphines give rise to two types of compounds which we may call PX_5 compounds and PX_7 compounds. Both of these types are found to be good electrolytic conductors, in methyl cyanide. Ph_3PX_2 (a PX_5 compound) and Ph_3PX_4 (a PX_7 compound) for example ionise in methyl cyanide as follows



However, the situation can be more complicated than this. Such is the case with the diiodides which undergo disproportionation to produce triiodide ions in the solution.



Also, the mixed dihalides of tertiary phosphines are not straight forward. Adducts of formula $\text{Ph}_3\text{PI}_{1.5}\text{X}_{0.5}$ ($\text{X} = \text{Cl}, \text{Br}$), and not Ph_3PIX , were isolated during attempts to prepare the latter. From conductance and ultra-violet spectrum studies it has been suggested that the formula of these adducts should be doubled and that they should be formulated as follows ²⁰⁴

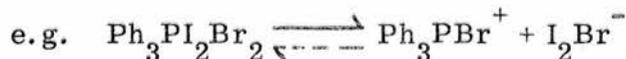


Although the structure of $(\text{Ph}_3\text{P})_2\text{X}^+$ ions has not been determined, it has been suggested that one of the two possibilities is likely :



It might be noted that a structure analogous to (a) is found in $[\text{IPy}_2^+] \text{I}_3^-$, which has been shown by X-ray analysis ²⁰⁵ to contain the planer ion, $[\text{Py} - \text{I} - \text{Py}^+]$.

A point of interest concerns the ionisation of mixed tetrahalides of type $\text{Ph}_3\text{PX}_n\text{Y}_{4-n}$ where it is found that ionisation follows a course in which the cation contains the halogen of lower atomic number ¹⁵⁵.



Compared with the work that has been done on the $\text{PCl}_3\text{-X}_2$ and $\text{PBr}_3\text{-X}_2$ systems, very little is known about the reactions of halogens with halogenophosphines of formula $\text{Ph}_n\text{PX}_{3-n}$ ($\text{X} = \text{Br}, \text{I}$; $n = 1, 2$), and with

phosphorus triiodide. Thus it was thought desirable to investigate the electrolytic properties of such systems in methyl cyanide using conductance techniques. As in previously studied systems, conductometric titration studies were conducted to indicate the type and the nature of the species present in solution. Attempts to isolate solid adducts, which are indicated by the conductance - composition graphs, were made in polar solvents, like methyl cyanide, and also in non-polar solvents, such as petroleum-ether (40-60°C), carbon tetrachloride and benzene. Since phosphine halogen systems are known to be extremely sensitive towards moist air, the conductometric titration studies were therefore performed within a nitrogen-field dry box using a special apparatus developed by Harris and co-workers^{156, 206} in which contact with moist air, tap grease, and rubber is avoided.

A. THE REACTION OF HALOGENS WITH $\text{Ph}_n\text{PBr}_{3-n}$ (n = 2, 1, 0)

(1) The Reaction of Dibromophenylphosphine with Halogens

(1.1) The $\text{PhPBr}_2 - \text{Br}_2$ System

The reaction between dibromophenylphosphine and bromine was studied in methyl cyanide solution by means of conductometric titration. The results are recorded in Table 6 and illustrated graphically in Figure 10, plot 1. The graph shows a definite break at the 1:1 mole ratio ($\text{Br}_2:\text{PhPBr}_2$), at which point during the titration the colourless solution turned pale yellow. The break at 1:1 ratio indicates the formation of a 1:1 adduct (PhPBr_4) in methyl cyanide solution. The molar conductance value at this mole ratio is: $\Lambda_m = 66.95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.016057 \text{ mol l}^{-1}$ indicating

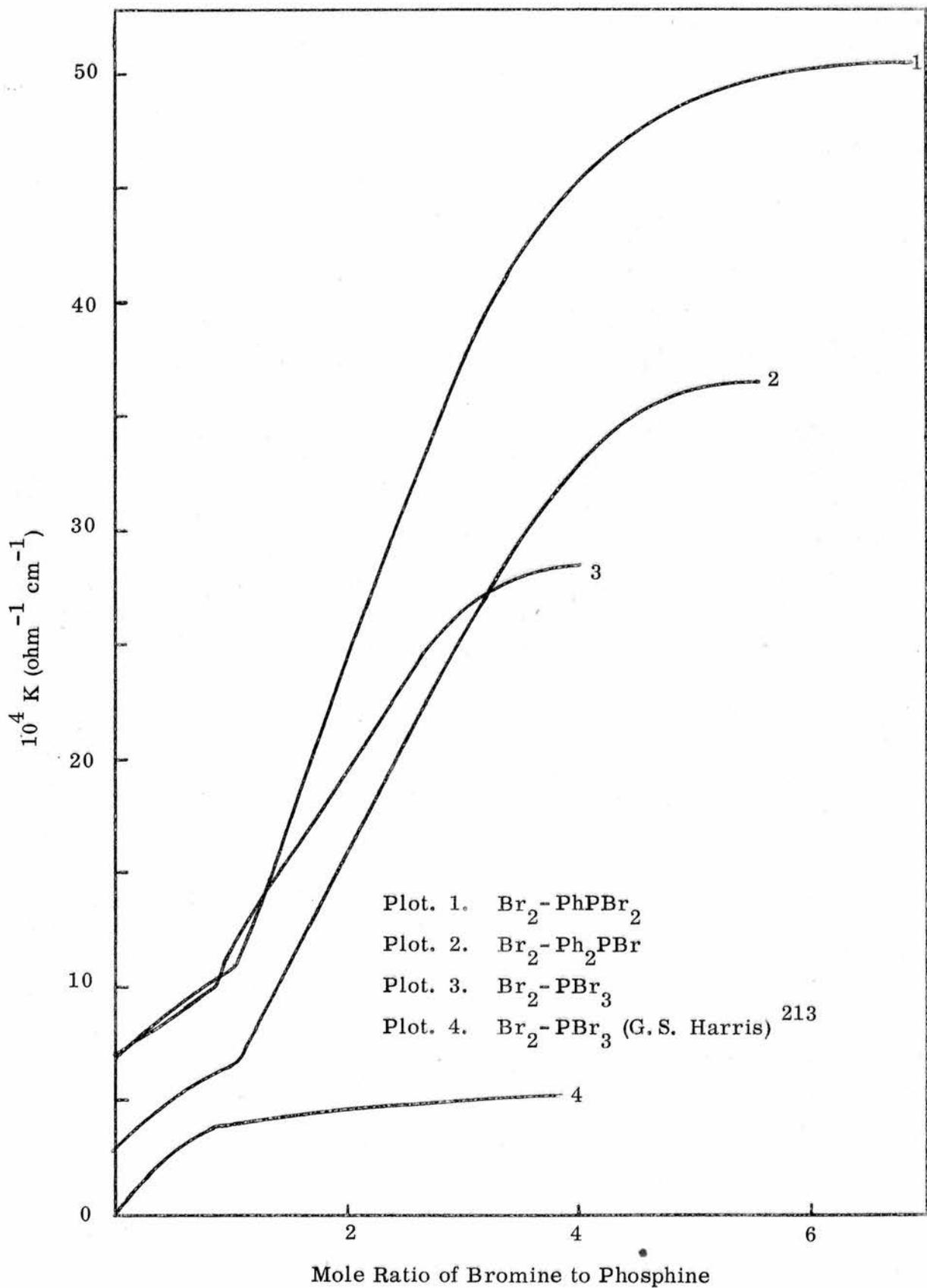
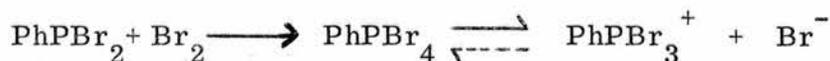
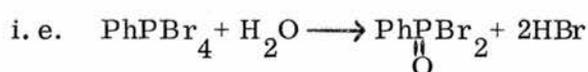


Figure 10. Conductometric Titration of the Systems $\text{Ph}_n\text{PBr}_{3-n}\text{-Br}_2$ ($n=2, 1, 0$)
in Methyl Cyanide

that PhPBr_4 is a fairly strong 1:1 electrolyte in the given solvent. It is of interest to note that the analogous chlorine compound (PhPCl_4) was found by MacPherson²⁰³ to be a weak electrolyte in methyl cyanide solution. $\Lambda_m = 16.88 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.02884 \text{ mol l}^{-1}$. The ultra-violet spectrum of a methyl cyanide solution of bromine and dibromophenylphosphine at the mole ratio $\sim 0.8:1$ indicates that there is no tribromide ion present. From these observations it is suggested that the reaction proceeds as follows :

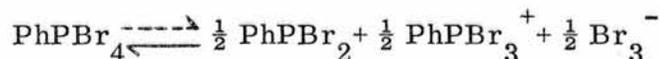


A yellow solid (m. p. $225-227^\circ\text{C}$) of stoichiometry PhPBr_4 was isolated from both methyl cyanide and petroleum ether ($40-60^\circ\text{C}$) solutions at the 1:1 ratio ($\text{Br}_2 : \text{PhPBr}_2$). The mass spectrum results for the compounds PhPBr_4 and PhPBr_2 are given in Table 7 ; they suggest that during transfer to the mass spectrometer some hydrolysis of the former had occurred,



This demonstrates the extreme sensitivity of PhPBr_4 towards moist air and shows that relative to dibromophenylphosphine it is much more labile, thus emphasizing the need for extensive precautions to exclude oxygen and water vapour during the investigation of phosphorus (V) halide derivatives of this type. Examination of the ultra-violet spectrum of a methyl cyanide solution of PhPBr_4 showed traces of tribromide ion to be present. This is in contrast to the behaviour of a methyl cyanide solution containing an equimolar mixture of bromine and dibromophenylphosphine. By analogy with the behaviour of Ph_3PI_2 ¹⁵⁶, the tribromide ion may be produced

from slight disproportionation of PhPBr_4 in methyl cyanide, thus,



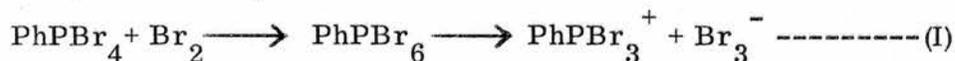
During the conductometric titration the solution remained colourless until just before the 1:1 ratio at which point it turned pale yellow. On further addition of bromine the solution progressively darkened. At the 2:1 ratio it had a strong yellow colour and after the 3:1 ratio it became orange. The colour change at the 1:1 ratio is indicative of Br_3^- ion formation and to confirm this a systematic study of the ultra-violet spectrum of methyl cyanide solutions containing bromine and dibromophenylphosphine in different mole ratios was carried out. Trihalide ions have characteristic absorption bands in the ultra-violet range and the maxima for these are given in Table 8.

Table 8.

Anion	Maximum λ (m μ)	Absorption Coefficient (ϵ)	Maximum λ (m μ)	Absorption Coefficient (ϵ)
(Br_3^-) 207	269	55,000		
(I_3^-) 208	362	31,090	292	57,680
(I_2Br^-) 208	351	9,670	280	44,550
(IBr_2^-) 207	370	606	256	54,000

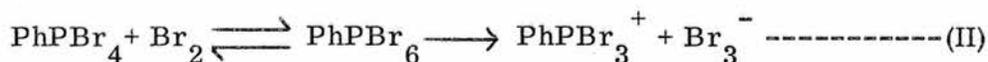
The results, set out in Table 9, confirm the presence of tribromide ions after the 1:1 ratio. Also, after this ratio the conductance of the solution increased sharply up to the 3:1 ratio and thereafter the increase gradually tailed-off giving a rather rounded appearance to the conductometric titration

graph with no sharp breaks. From the graph it is not possible to say with certainty what compounds are forming in solution after the 1:1 ratio, although it is clear that these are highly conducting. The formation of tribromide ions in solution after the 1:1 ratio falls in line with what is known of other phosphine-bromine systems [e.g. $\text{ph}_3\text{P}-\text{Br}_2$ ²⁰⁸, (cyclohexyl)₃P-Br₂²⁰⁶], and the expected reaction in this range is



This reaction could explain the increase in conductance after the 1:1 ratio (since PhPBr_4 is not completely ionised) but if it occurred to completion a sharp break in the conductometric titration graph at the 2:1 ratio would be expected.

The absence of a 2:1 break is probably due to the fact that the reaction (I) is not complete at the equivalence point and the adduct, PhPBr_6 , is in equilibrium with PhPBr_4 and bromine as well as its ions.



Complete production of the PhPBr_6 is not therefore achieved until excess bromine is present in the system. This behaviour would delay the achievement of maximum conductance of the solution to beyond the 2:1 ratio and give the graph rounded appearance as is observed.

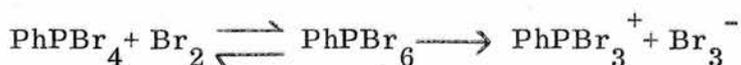
Table 9 : Solution Spectra of the System $\text{PhPBr}_2\text{-Hal}_2$

System	mole ratio (Hal_2 : PhPBr_2)	u. v. Maxima ($m\mu$)	u. v. Indicates
Br_2^- - PhPBr_2	0.8 : 1	--	no Br_3^-
	1.2 : 1	270	B_3^- ion present
	1.6 : 1	269	Br_3^- ion present
I_2^- - PhPBr_2	0.3 : 1	285, 356	traces of a mixture of I_2Br^- and I_3^-
	0.6 : 1	286, 356	traces of a mixture of I_2Br^- and I_3^-
	0.8 : 1	290, 361	I_3^- only
	1.0 : 1	290, 360	I_3^- only
	1.8 : 1	290, 360	I_3^- only
IBr-PhPBr_2	0.3 : 1	278, 352	traces of I_2Br^-
	0.6 : 1	278, 352	traces of I_2Br^-
	1.2 : 1	280, 352	I_2Br^- only
	1.8 : 1	273	mixture of I_2Br^- and IBr_2^-
	2.6 : 1	258	IBr_2^- ion present

If the equilibrium (II) does exist, it seemed reasonable to expect that it might be shown up in the value obtained for the extinction coefficient for the tribromide ion absorption in the ultra-violet spectrum of the system. The reported value for the extinction coefficient of the tribromide ion is $55,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$ ²⁰⁷. If however

the system at the 2:1 ratio is best represented by the scheme (II) then the value found for the extinction coefficient of the tribromide ion (based on the theoretical molar concentration of PhPBr_6) should be less than 55,000.

The ultra-violet spectrum of methyl cyanide containing $\text{Br}_2 + \text{PhPBr}_2$ (2:1 ratio) at a concentration in the range used in the conductometric titration studies, was measured in specially designed (see experimental section) short path length cells. The value obtained for the extinction coefficient (ϵ) was $25,800 \text{ l mol}^{-1} \text{ cm}^{-1}$ which is less than half of the reported value for the tribromide ion. This is taken as showing conclusively that at the 2:1 ratio in the conductometric titration the adduct PhPBr_6 (or more correctly, the products of ionisation of this adduct) is not formed quantitatively (degree of formation $\sim 47\%$) and is evidence for the postulated equilibrium (II), i. e. ,



Identical yellow-orange crystalline solids (m. p. $201-203^\circ\text{C}$) were isolated by mixing methyl cyanide solution of bromine and dibromophenylphosphine at mole ratios 2:1 and 3:1 respectively. These substances, rather unexpectedly, had the empirical formula, PhPBr_5 , and their mass spectra were identical to that of PhPBr_4 .

Although in 1876 Michaelis and Kohler¹⁷⁶ reported the compound PhPBr_6 , a number of attempts (see Table 10 overleaf) to prepare this compound resulted in the formation of a compound with the formula PhPBr_5 .

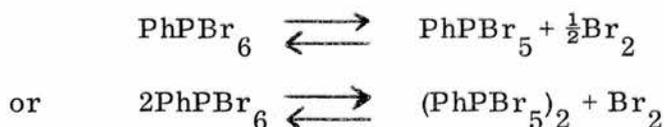
Table 10.

Mole Ratio Br ₂ : PhPBr ₂	Solvent	Method of Isolation of the Product	Analytical Results*		
			C %	H %	Br %
2:1	CH ₃ CN	The Solvent was re- moved by filtration and the solid dried under vacuum.	14.32	1.08	78.22
3:1	"	As above	13.96	1.01	
2:1	"	The solvent was re- moved by pumping the reaction mixture.	14.49	1.24	78.41
---	---	The 1:1 adduct (PhPBr ₄) was pumped for 16 hours.	14.74	1.20	

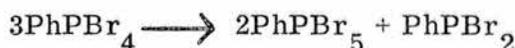
* PhPBr₅ requires C, 14.19; H, 0.99; Br, 78.71 %

PhPBr₆ requires C, 12.24; H, 0.85; Br, 81.63 %

MacPherson²⁰³ isolated what appears to be the same compound from the reaction between bromine (2 moles) and dibromophenylphosphine (1 mole) in methyl cyanide, (found C, 14.13; H, 1.02; Br, 80.2 %). However, he reported this as being the impure 2:1 adduct, PhPBr₆, the pure compound at first formed having lost some bromine. From the above results, it seems reasonable to suggest that although PhPBr₆ may exist in solution, the only higher bromine adduct which is stable in the solid state is PhPBr₅.



PhPBr_5 is clearly a very stable solid phase in the $\text{PhPBr}_2 - \text{Br}_2$ system and appears also to form on pumping PhPBr_4 for a prolonged period.



The ultra-violet spectrum of PhPBr_5 dissolved in methyl cyanide showed the presence of tribromide ion ($\lambda_{\text{max}} = 269 \text{ m}\mu$) and the molar conductance of the solution measured at 25°C was,

$$\Lambda_m = 89 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; c_m = 0.01 \text{ mol l}^{-1}$$

(c_m based on the formula PhPBr_5)

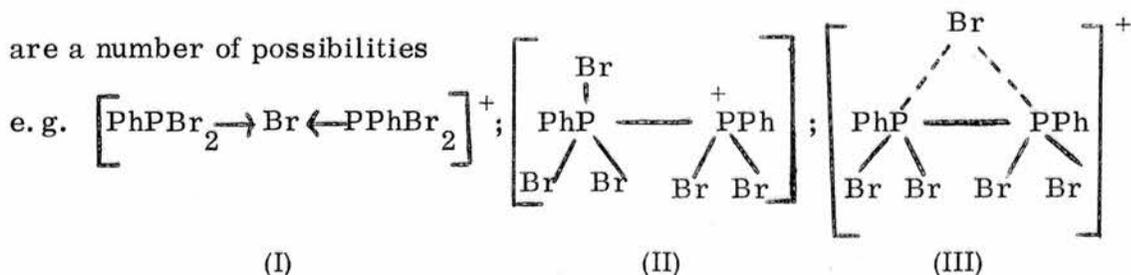
In view of its unusual stoichiometry (PX_6) for a phosphorus halide derivative and on the basis of the ultra-violet and conductance data it would seem best to regard this compound as the dimer $(\text{PhPBr}_5)_2$ since this enables reasonable suggestions to be made about its structure. Three possibilities are put forward :



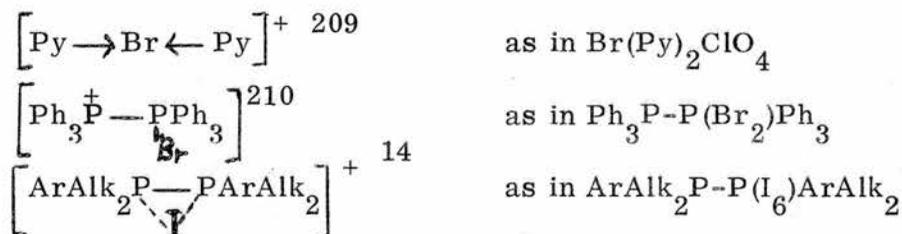
These three possibilities are now considered in turn :

Structure (a).

The cation $\left[(\text{PhPBr}_2)_2 \text{Br} \right]^+$ is analogous to $\left[(\text{Ph}_3\text{P})_2 \text{Br} \right]^+$ which was postulated by Ali and Harris²⁰⁴ as being present in the compounds $\text{Ph}_3\text{P} \cdot \text{HgBr}_4 \left[= (\text{Ph}_3\text{P})_2 \text{Br}^+ \text{HgBr}_3^- \right]$ and $\text{Ph}_3\text{PBr} \cdot 0.5 \text{I}_2 \left[= (\text{Ph}_3\text{P})_2 \text{Br}^+ \text{I}_3^- \right]$. Although the structure of this type of cation has not been established there



The structure I, II and III are analogous to cations already described or proposed in other systems, namely and respectively

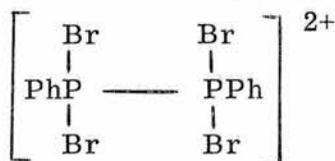


II and III are closely similar except that in II all of the halogen atoms are localised on one or other of the phosphorus atoms. Information at our disposal is insufficient to enable us to confirm one or other of these three structures although the fact that the infra-red spectrum did not show any shift in the P-Br stretching frequency may be taken as evidence against the bridged structures I and III.

The pentabromide ion, which has to be postulated as part of this structure, is a very uncommon polyhalide ion and for this reason the suggested structure is not perhaps a strongly favoured one.

Structure (b).

This contains the cation $(\text{PhPBr}_2)_2^{2+}$ which, if it exists, would most likely have a structure containing a p-p bond



However this structure implies the existence of adjacent phosphonium centres which for electrostatic reasons seems very unlikely.

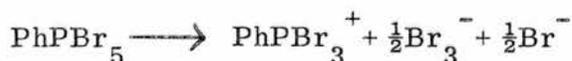
The infra-red spectrum of the compound PhPBr_5 was very similar to that of PhPBr_2 but, in addition there was a strong absorption band in the region 615 cm^{-1} . The P-P stretching frequency in ions of the type $(\text{Ph}_3\text{P})_2\text{Hal}^+$ lies in range $600\text{-}350 \text{ cm}^{-1}$. In the ion under discussion

however, the P-P vibration will not be infra-red active for symmetry reasons. The band observed at 615 cm^{-1} is therefore most likely to be due to P-C stretching.

Structure (c).

In this structure two different anions are present. This feature is not unknown, for example Harris and Inglis²¹¹ have isolated the compound $\text{Ph}_3\text{As}(\text{OH})\text{Br}_2$ which they showed to be $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^- \text{Br}^-$.

If $(\text{PhPBr}_5)_2$ has this structure then its solution in methyl cyanide is equivalent to an equimolar mixture of $\text{PhPBr}_4 \left[\rightleftharpoons \text{PhPBr}_3^+ + \text{Br}^- \right]$ and $\text{PhPBr}_6 \left[\rightleftharpoons \text{PhPBr}_3^+ + \text{Br}_3^- \right]$. It should therefore behave as a strong 1:1 electrolyte, producing effectively two singly charged ions per formula unit (PhPBr_5).



The observed molar conductance values are in keeping with this.

Again, if structure (c) is correct, then the molar extinction coefficient (ϵ) obtained for methyl cyanide solution of the compound should be half of the normal value (55,000)²⁰⁷. Quantitative analysis of the ultra-violet spectrum of $(\text{PhPBr}_5)_2$ gave the value of $23,550 \text{ l mol}^{-1} \text{ cm}^{-1}$ and this is regarded as good support for the idea that $(\text{PhPBr}_5)_2$ behaves as an equimolar mixture of PhPBr_4 and PhPBr_6 in methyl cyanide. To substantiate this further, the reaction between $(\text{PhPBr}_5)_2$ and bromine in methyl cyanide was studied by conductometric titration since the bromide ion present would be expected to react with bromine to give Br_3^- and this reaction might be expected to give a break (at the 1:1 ratio) in the conductometric titration graph. $(\text{PhPBr}_3^+)_2\text{Br}_3^- \text{Br}^- + \text{Br}_2 \longrightarrow 2\text{PhPBr}_3^+ \cdot \text{Br}_3^-$

The graph of the titration is shown in Figure 11 (Table 11). Addition of bromine causes the conductance to rise, but there is no sharp inflection at the 1:1 ratio. The conductance continues to rise after this ratio and tails off gradually giving a rather blunt break round about 3:1 and levelling off after 4:1. This is in good agreement with the complete conductometric titration graph for the $\text{PhPBr}_2 - \text{Br}_2$ system (with which it is equivalent, in terms of stoichiometry, from the 1.5:1 ratio onward). The absence of a sharp break at the 1:1 ratio and the gently curved appearance of the graph beyond this can be explained in terms of the equilibrium mentioned earlier.

NOTE ON THE RESULTS OF THE CONDUCTOMETRIC TITRATION OF CERTAIN PHOSPHINES AND ARSINES.

The conductometric titration of triphenylarsine with bromine has been reported by Beveridge and Harris¹⁵⁵ and a graph of this is shown in Figure 12. It is to be noted that as well as a break at the 1:1 ratio (indicating the formation of Ph_3AsBr_2) a break at the 2:1 ratio (indicating the formation of Ph_3AsBr_4) is present. The sharpness of this latter break and its occurrence very close to the 2:1 ratio is in contrast with the findings of this present work and of that of Beaumont²¹² in respect of titrations of certain phosphines with bromine. Using the halophosphines PhPBr_2 and Ph_2PBr and the methylphenylphosphines PhMe_2P and Ph_2MeP ²¹² it has been found that although the general shapes of conductometric titration graphs are similar, the second break lacks sharpness and certainly appears to occur at mole ratios near 3:1 or 4:1, even though it is possible to isolate 2:1 adducts from a solution containing the reactants at the 2:1 ratio.

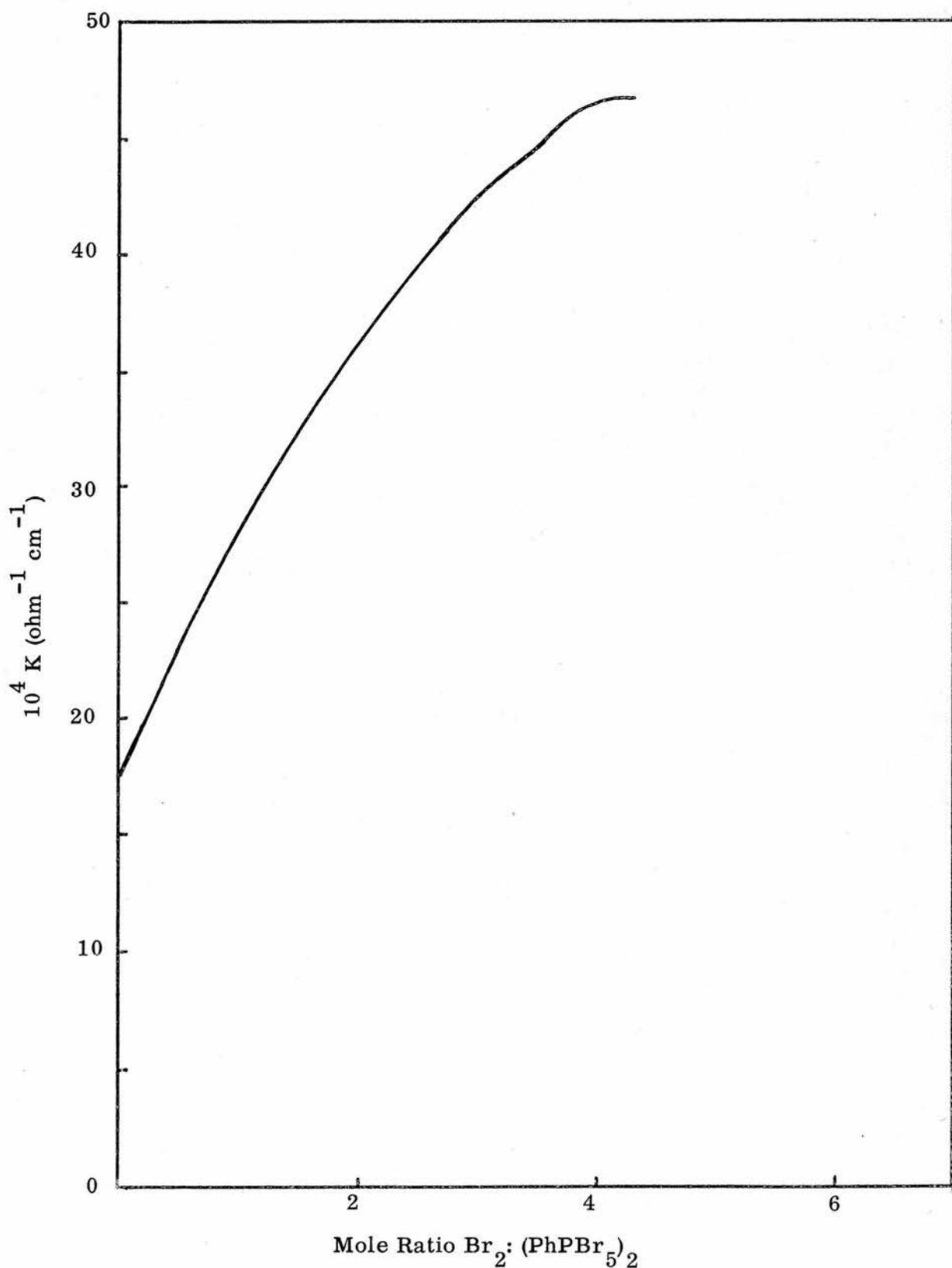


Figure 11. Conductometric Titration of the System $(\text{PhPBr}_5)_2 - \text{Br}_2$ in Methyl Cyanide

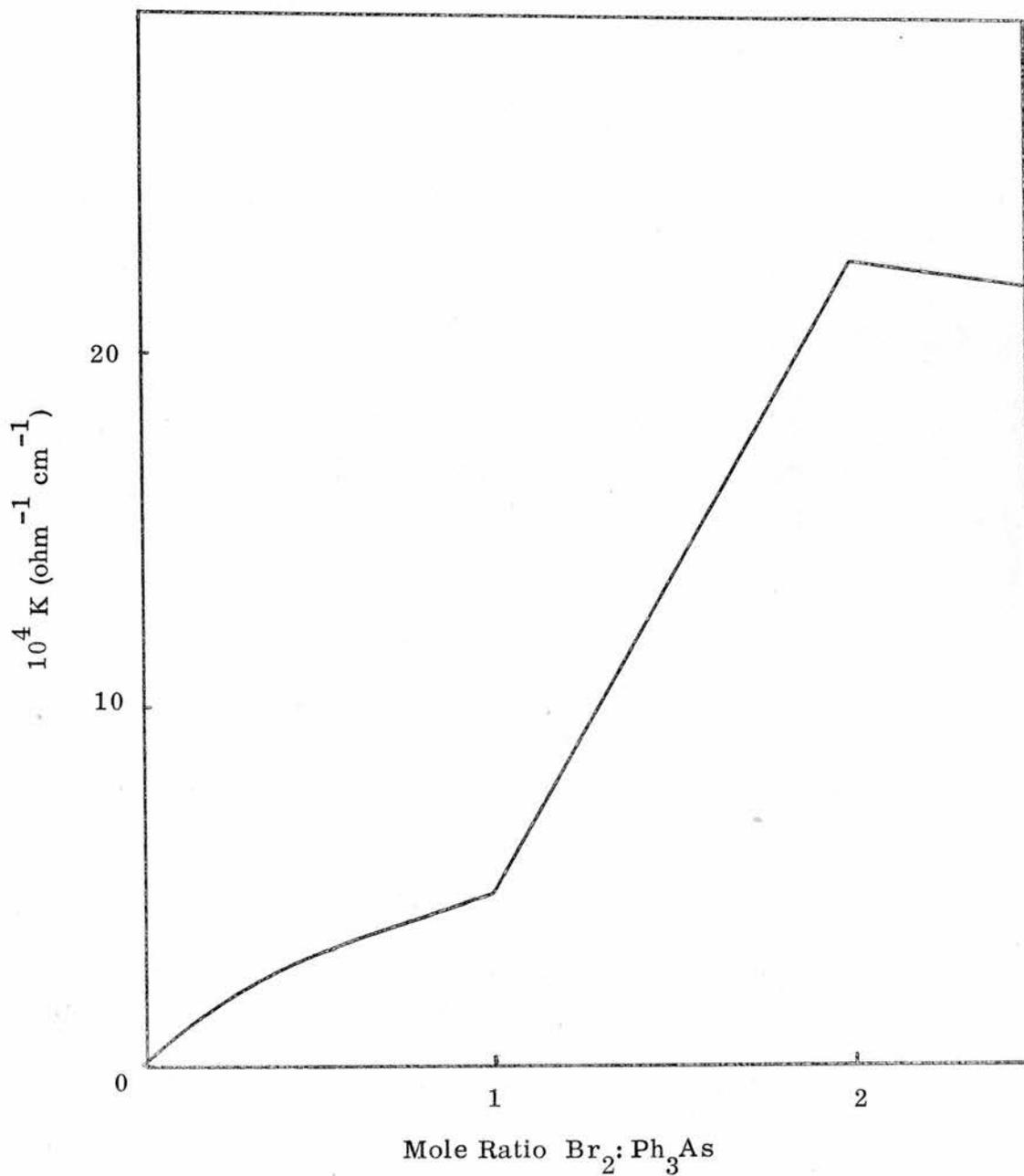
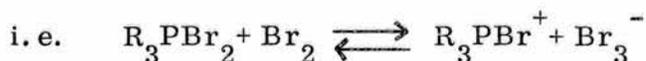


Figure 12. Conductometric Titration of the System
 Br_2 - Ph_3As in Methyl Cyanide. (A. D. Beveridge) 208

This is interpreted as indicating that in those reactions which give indistinct breaks in their conductometric titration graphs the reaction occurring after the 1:1 ratio has not yet gone to completion at the 2:1 ratio. That is we have an equilibrium situation, and only when a certain excess of bromine is present in the system can the reaction be regarded as complete



To verify this, ultra-violet measurements have been made of the amount of Br_3^- ion present in methyl cyanide at a 2:1 ratio ($Br_2 : R_3P$) of the components. The Table (12) below gives values of the molar extinction coefficient (Br_3^-) calculated on the assumption that the reaction $R_3PBr_2 + Br_2 \longrightarrow R_3PBr^+ + Br_3^-$ goes to completion.

Table 12

System	Mole Ratio (Br_2 : Phosphine)	c_m^{-1} ($mol\ l^{-1}$)	ϵ ($l\ mol^{-1}\ cm^{-1}$)
Ph_3As-Br_2	2:1	0.012681	56,700 ²⁰⁸
$PhPBr_2-Br_2$	2:1	0.012681	25,800
	4:1	0.006543	58,745
$Ph_2PBr-Br_2$	2:1	0.012681	30,000
	4:1	0.004598	55,731
$PhMe_2P-Br_2$	2:1	0.001909	42,150
	3:1	0.005205	54,485
$Ph_2MeP-Br_2$	2:1	0.001489	46,172
	3:1	0.004031	58,915

It should be noted that the molar extinction coefficient value for the $\text{Ph}_3\text{As}-\text{Br}_2$ system is 56,700 which is close to the reported value (55,000 $\text{l mol}^{-1} \text{cm}^{-1}$)²⁰⁷. In contrast, the molar extinction coefficient values for the $\text{PhPBr}_2-\text{Br}_2$, $\text{Ph}_2\text{PBr}-\text{Br}_2$, $\text{PhMe}_2\text{P}-\text{Br}_2$ and $\text{Ph}_2\text{MeP}-\text{Br}_2$ systems fall short of this indicating that the theoretical amount of Br_3^- , is not present at the 2:1 ratio. Also, it is seen from figures that a value close to the theoretical value of $\epsilon(\text{Br}_3^-)$ is attained at mole ratios between 3:1 and 4:1.

Therefore, it is clear that this feature in conductometric titration graphs of the $\text{R}_3\text{P}-\text{Br}_2$ system can be attributed to the equilibrium nature of the second stage of the reaction.

(1.2) The $\text{PhPBr}_2-\text{I}_2$ System

The results of the conductometric titration of dibromophenylphosphine with iodine in methyl cyanide are assembled in Table 13 and depicted graphically in Figure 13, plot 1. Addition of iodine solution to the dibromophenylphosphine solution causes an increase in the specific conductance of the latter. The conductance rises smoothly with increasing mole ratio and as shown by the graph there is no significant discontinuity present which might indicate the stoichiometry of the reaction occurring in solution. To ensure that dilution effects were not obscuring any breaks in the conductometric titration graph, the titration was repeated using solid iodine as titrant. The results of this titration are contained in Table 14 and plotted in Figure 13, curve 2. This graph is rather similar to the previous one (curve 1) and shows no clear cut breaks. Thus no compounds are positively indicated by these experiments. The continuous rise in

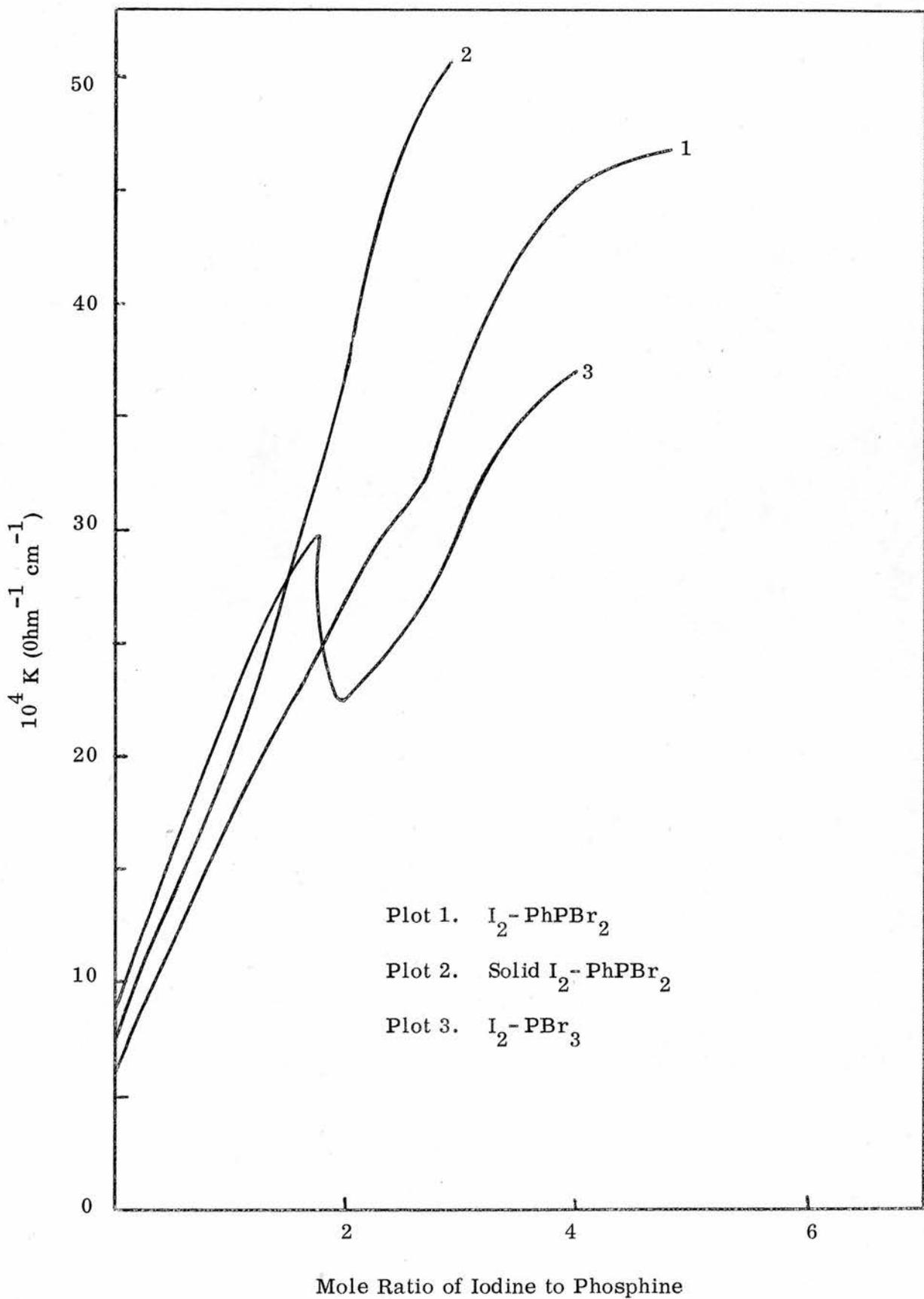
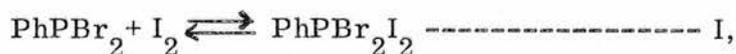


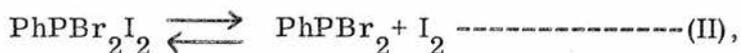
Figure 13. Conductometric Titration of the Systems $I_2 - PhPBr_2$ and $I_2 - PBr_3$
in Methyl Cyanide

conductance as iodine added to dibromophenylphosphine does point to the presence of an ion-forming reaction which does not go to completion at the expected stoichiometric end points. Thus we are dealing with a system which consists of an equilibrium reaction or two or more overlapping equilibria.

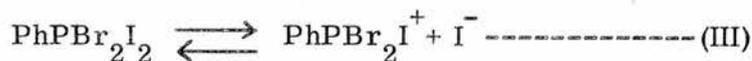
Since mixed phosphorus (V) bromide chlorides are known to be labile species, it can be inferred that the 1:1 reaction will not yield a product quantitatively and should be represented as an equilibrium,



which in effect implies that the phosphorus (V) compound undergoes molecular dissociation.



This compound would be expected also to undergo ionisation to a greater or lesser degree, thus,



the iodide ion from which would unite with the iodine from equilibrium (II) to yield triiodide ions.



Therefore to describe the reaction that occurs between iodine and dibromophenylphosphine a second equilibrium has to be taken into account namely

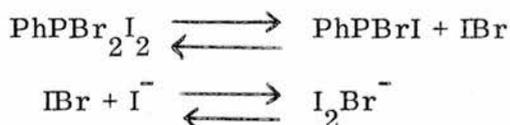
$$\text{PhPBr}_2\text{I}_2 + \text{I}_2 \rightleftharpoons \text{PhPBr}_2\text{I}^+ + \text{I}_3^- \text{----- (IV)}$$

In support of this second equilibrium is the fact that trihalide ions are produced from the first addition of titrant onwards (see footnote*).

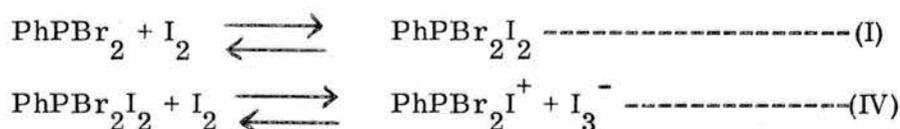
*At mole ratios near and at 1:1 (I_2 : PhPBr_2) only I_3^- is present in solution (Table 9), but near the beginning of the titration both I_3^- and I_2Br^- are present. This latter fact implies that at low mole ratios the system is

*Footnote continued.

*rather more complex and that two further equilibria must be present :



It is suggested therefore that the $\text{PhPBr}_2\text{-I}_2$ system is best described in terms of the two equations (I) and (IV), i. e. ,



Determination of the apparent extinction coefficient for the I_3^- ion [based on 2 x molar concentration of PhPBr_2 , (see footnote**)] at the 1:1 mole ratio of reactants gave the value, $41,400 \text{ l mol}^{-1} \text{ cm}^{-1}$ which is less than the theoretical value ($\epsilon_{\text{I}_3^-} = 57,680$ for peak at $290 \text{ m}\mu$)²⁰⁸ and this lends strong support for these incomplete reactions.

The absence of a break in the conductometric titration graphs at the 2:1 ratio (I_2 : PhPBr_2) and the continued rise in conductance after this ratio is passed indicates that complete production of $\text{PhPBr}_2\text{I}^+\text{I}_3^-$ is not achieved until iodine, well in excess of that indicated in equilibrium (IV), has been added to the solution.

**At mole ratio 1:1, if the reaction (I) and (IV) were completely to right hand side then the overall stoichiometry at this stage can be re-presented:

$$\text{PhPBr}_2 + \text{I}_2 \longrightarrow \frac{1}{2}\text{PhPBr}_2 + \frac{1}{2}\text{PhPBr}_2\text{I}^+ + \frac{1}{2}\text{I}_3^-$$

(unreacted)

i. e. 0.5 mole of I_3^- ion is formed per mole of dibromophenylphosphine in the system and therefore the molar extinction coefficient for I_3^- must be calculated on the basis of 2 x the molar concentration of dibromophenylphosphine.

Attempts to isolate the 1:1 and 2:1 adducts, PhPBr_2I_2 and PhPBr_2I_4 , by addition of iodine to a methyl cyanide solution of PhPBr_2 resulted in the separation of dark red oils. Analysis showed that these oils had the compositions $\text{PhPBr}_2\text{I}_2 \cdot 0.5 \text{CH}_3\text{CN}$ and $\text{PhPBr}_2\text{I}_4 \cdot \text{CH}_3\text{CN}$ respectively. Trituration of these oils with ether and addition of ether to the methyl cyanide solution of the reactants, failed to give solids. Also, it was not possible to remove completely traces of the solvent (CH_3CN) even on pumping for a prolonged period. Many attempts to isolate solids using other solvents (petroleum ether 40-60°C, carbon tetrachloride) were also unsuccessful.

Failure to isolate these adducts as crystalline solid is presumably tied up with the strong tendency of phosphorus bromide chlorides to undergo dissociation (and it is this same tendency which is reflected in the form of the conductometric titration graphs for the reaction in methyl cyanides). Parallel behaviour is found in the $\text{PCl}_3\text{-Br}_2$ system where adducts are found to be solvated low melting solids or oils¹⁹⁴.

The mass spectrum data shown in Table 15 demonstrates the existence of the compound PhPBr_2I_2 . Although the spectrum did not show any significant fragment with an m/e ratio higher than 524, 522 and 520 ($\text{PhPBr}_2\text{I}_2^+$), the existence of PhPBr_2I_4 cannot be ruled out.

(1.3) The $\text{PhPBr}_2\text{-IBr}$ System

Table 16 and Figure 14 contain the relevant conductometric titration data for the $\text{PhPBr}_2\text{-IBr}$ system. The graph is rather similar to that found in the $\text{PhPBr}_2\text{-Br}_2$ system. The conductance increased gradually to a point beyond the 1:1 mole ratio of $\text{IBr}:\text{PhPBr}_2$ (ca. 1.5:1) and thereafter it increased

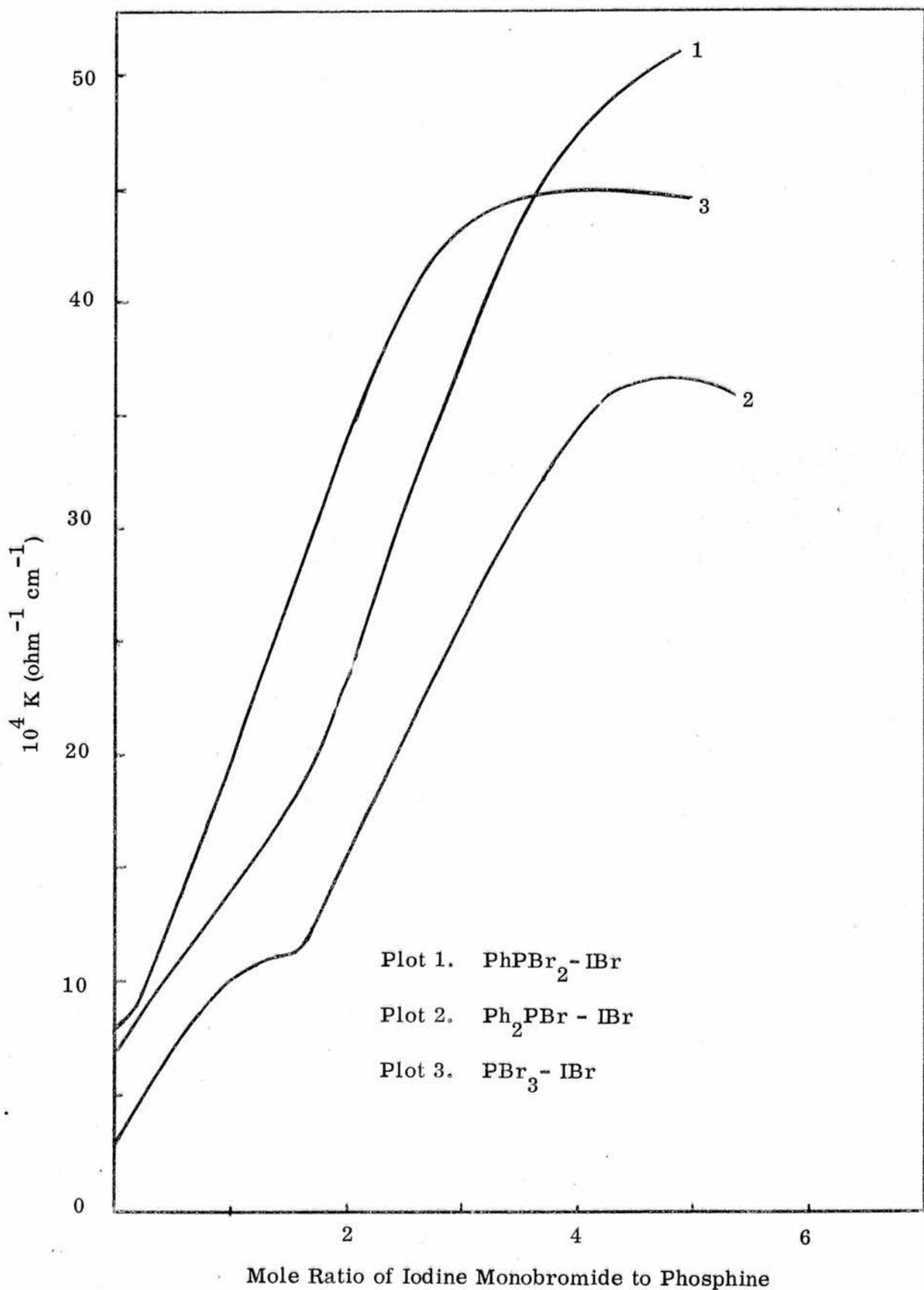


Figure 14. Conductometric Titration of the Systems $\text{Ph}_n\text{PBr}_{3-n} - \text{IBr} (n=2, 1, 0)$
in Methyl Cyanide

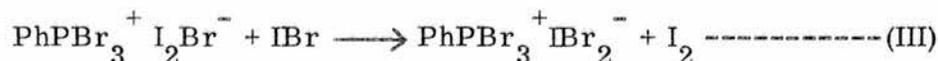
slightly more steeply until the region of the 3:1 ratio after which the increase slowly tailed-off. In this titration the originally colourless dibromophenylphosphine solution turned orange on the first addition of iodine monobromide solution and it progressively darkened on further additions of titrant.

The production of colour in the solution indicates the formation of polyhalide ions and this was confirmed by the ultra-violet spectrum of the solution (see later).

Although the conductometric titration graph possesses a change of slope **giving** a rather indistinct 'break' in the region of the 1.5:1 mole ratio it was believed that no deduction could be made from this regarding the stoichiometry of the reaction(s) occurring in solution. In fact it would seem that the system should be interpreted in the same way as the $\text{PhPBr}_2 - \text{I}_2$ system by assuming the presence of overlapping equilibria as follows :



This interpretation is supported by the absence of any well defined breaks in the titration curve and from the ultra-violet spectrum of the solution (Table 9) during titration which clearly indicates that I_2Br^- ions are present from the start. At higher mole ratio of $\text{IBr} : \text{PhPBr}_2$ (ca. 1.8:1) the presence of a mixture of I_2Br^- and IBr_2^- is shown and at still higher ratios (ca 2.8:1) only IBr_2^- is present. This suggests that a third equilibrium has to be considered in describing this system, namely



Preparation of Adducts

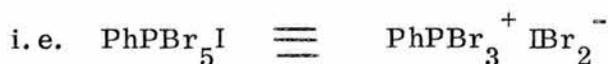
Three red oils were formed on mixing methyl cyanide solutions of iodine monobromide and dibromophenylphosphine in the 1:1, 1.5:1 and 2:1 mole ratios respectively. Addition of ether and carbon tetrachloride failed to give any solids. It was shown by analysis that these substances were similar, of the same stoichiometry PhPBr_3I with some solvation (methyl cyanide). It was not possible to remove traces of the solvent even on prolonged pumping. The ultra-violet spectrum of the adduct, PhPBr_3I , in methyl cyanide solution showed an absorption maximum corresponding to that of the I_2Br^- ion ($\lambda_{\text{max}} = 280 \text{ m}\mu, 350 \text{ m}\mu$). Thus on dissolving the adduct it is evident that equilibria (I) and (II) are set up in solution. The value obtained for the extinction coefficient of I_2Br^- ion was $36,200 \text{ l mol}^{-1} \text{ cm}^{-1}$ which is considerably less than the theoretical value $44,550^{208}$, thus again pointing to the fact that reactions represented by equilibria (I) and (II) are by no means complete.

The mass spectrum results listed in Table 18 confirm the existence of an adduct of composition PhPBr_3I . The highest peaks observed in the spectrum at m/e 478, 476, 474 and 472 were assigned to the PhPBr_3I^+ fragment.

Attempts were made to prepare solid adducts in this system using a variety of different solvents but these were unsuccessful with two exceptions, namely PhPBr_5I and PhPBr_4I .

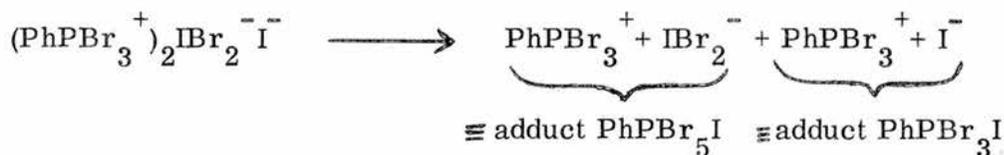
The compound PhPBr_5I was isolated as a brown solid (m.p. $87-89^\circ\text{C}$) from petroleum ether ($40-60^\circ\text{C}$) solution containing iodine monobromide and dibromophenylphosphine in the 2:1 mole ratio. It is interesting to note

that the stoichiometry of this adduct is that of the adduct represented on the right-hand side of one of the equilibria (III) occurring in methyl cyanide. The compound behaves as a strong electrolyte in methyl cyanide and the ultra-violet spectrum of the solution suggests ^{the} presence of ^{the} IBr_2^- ion ($\lambda_{\text{max}} = 257 \text{ m}\mu$) in keeping with the proposed structure.



A red-brown solid (m. p. $93-94^\circ\text{C}$) was precipitated when equimolar solutions of iodine monobromide and dibromophenylphosphine in petroleum ether ($40-60^\circ\text{C}$) were mixed. Analysis showed that the compound had the composition PhPBr_4I and its mass spectrum (Table 18) was found to be similar to that of ~~the~~ PhPBr_5I (see later). By analogy with the proposed structure for the compound PhPBr_5 (discussed earlier), and the known compound $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$ ²¹⁷, the solid PhPBr_4I may **adopt** the structure $(\text{PhPBr}_3^+)_2\text{IBr}_2^-\text{I}^-$. In support of this, the ultra-violet spectrum of the solid dissolved in methyl cyanide was measured. The spectrum showed a maximum at $260 \text{ m}\mu$.

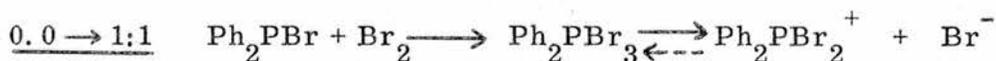
This indicated that the predominant trihalide ion present was in fact the IBr_2^- (peak at $257 \text{ m}\mu$) but that another (e. g. I_2Br^- max. at $280 \text{ m}\mu$) may be present in ^{solution} λ to some extent. This would be so, if the following scheme represented the behaviour of the adduct in methyl cyanide as seems very likely.



2. The Reaction of Bromodiphenylphosphine with Halogens

(2.1) The $\text{Ph}_2\text{PBr} - \text{Br}_2$ System

This reaction was carried out by stepwise addition of bromine to bromodiphenylphosphine in methyl cyanide solution, and followed conductometrically. A plot of the findings listed in Table 19 is shown in Figure 10, plot 2. The graph indicated a clear inflexion at the 1:1 mole ratio ($\text{Br}_2 : \text{Ph}_2\text{PBr}$) at which point the colourless solution became pale yellow. The ultra-violet spectrum, of methyl cyanide solutions containing bromine and bromodiphenylphosphine in different mole ratios (Table 20), demonstrates the absence of tribromide ion up to the \sim 1:1 ratio. The break at the 1:1 ratio shows the formation of a fairly strong 1:1 electrolyte ($\Lambda_m = 61.35 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.010596 \text{ mol l}^{-1}$) of the stoichiometry Ph_2PBr_3 , in methyl cyanide. Thus, a reasonable explanation for the reaction occurring in this region is :



As can be seen from the graph, this system seems to be very similar to ^{the} $\text{PhPBr}_2 - \text{Br}_2$ system, studied previously. The conductance rose sharply after the 1:1 and up to ^{the} $\sim 3:1$ halogen to phosphine mole ratio, after which the slope became less steep giving a rather rounded appearance to the conductometric titration graph with no sharp breaks. The solution which was yellow at the 2:1 ratio darkened progressively when further bromine solution was added. Although the colour change by itself is indicative of tribromide ion formation, the ultra-violet spectrum, of methyl cyanide solutions containing bromine and bromodiphenylphosphine at various mole ratios ~~was~~ studied. The results are contained in Table 20.

Table 20 Solution spectra of the $\text{Ph}_2\text{PBr} - \text{Hal}_2$ System

System	Mole Ratio $\text{Hal}_2 : \text{Ph}_2\text{PBr}$	u. v. maxima ($m\mu$)	u. v. Indicates
$\text{Br}_2 - \text{Ph}_2\text{PBr}$	0.42 : 1	---	No Br_3^-
	0.84 : 1	---	No Br_3^-
	1.25 : 1	269	Br_3^- present
	1.65 : 1	269	Br_3^- present
$\text{I}_2 - \text{Ph}_2\text{PBr}$	0.25 : 1	291, 362	I_3^- present
	0.73 : 1	291, 362	I_3^- present
	1.22 : 1	291, 362	I_3^- present
	1.71 : 1	291, 362	I_3^- present
$\text{IBr} - \text{Ph}_2\text{PBr}$	0.30 : 1	---	No polyhalide
	0.51 : 1	280, 350	I_2Br^- present (traces)
	0.84 : 1	279, 350	I_2Br^- present
	1.32 : 1	278, 350	I_2Br^- present with traces of IBr_2^-
	1.80 : 1	274, 352	I_2Br^- with traces of IBr_2^-
	2.74 : 1	256	IBr_2^- present *

* also iodine was shown in the visible region (462 $m\mu$)

It is obvious from the Table, that the tribromide ion was formed just after the 1:1 mole ratio ($\text{Br}_2 : \text{Ph}_2\text{PBr}$), and beyond.

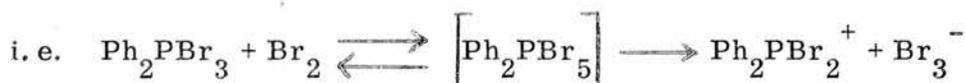
The molar conductance at the 2:1 ratio ($\text{Br}_2 : \text{Ph}_2\text{PBr}$) calculated from the conductometric titration graph indicates that a very strong electrolyte is present.

$$2.00 : 1, \quad \Lambda_m = 157.88 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; \quad c_m = 0.009818 \text{ mol l}^{-1}$$

A reasonable explanation for the increase in conductance, just after the 1:1 ratio, and the existence of tribromide ion is the formation of the adduct Ph_2PBr_5 according to the reaction:



The absence of the 2:1 break suggests that the above reaction has not gone to completion. In this respect the behaviour of this system parallels that of the $\text{PhPBr}_2 - \text{Br}_2$ system, implying the presence of an equilibrium.



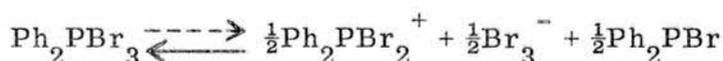
To confirm the existence of this equilibrium which results in incomplete formation of Ph_2PBr_5 (or more correctly, the ionisation products of this adduct), the ultra-violet spectrum of methyl cyanide solution containing the starting materials in the ratio 2:1 of $\text{Br}_2 : \text{Ph}_2\text{PBr}$ was analysed quantitatively. A value of $30,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the extinction coefficient for the tribromide ion absorption was obtained. This value is just over half of the reported extinction coefficient for the tribromide ion ($55,000$)²⁰⁷. Therefore the presence of the aforementioned equilibrium is substantiated. Hence excess bromine, well beyond the 2:1 ratio, is required for complete production of the compound Ph_2PBr_5 in methyl cyanide. This in fact was found as the conductance did not level-off until the 4:1 mole ratio of $\text{Br}_2 : \text{Ph}_2\text{PBr}$ had been reached.

An off-white crystalline solid (m. p. $227-229^\circ\text{C}$) of composition close

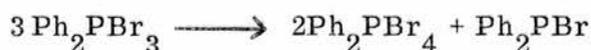
to Ph_2PBr_3 was precipitated from a solution containing equimolar amounts of bromine and bromodiphenylphosphine in methyl cyanide. This solid was found to be very unstable even in the dry box; it became yellow on standing thus analysis was carried out immediately after its preparation. Its instability was clearly shown by the mass spectrum (see Table 21). This contained peaks at m/e 282 and 280 which were attributed to the Ph_2PBrO^+ fragments (^{81}Br and ^{79}Br) formed as a result of hydrolysis.



In contrast to the behaviour of methyl cyanide solutions containing a 1:1 mole ratio of Br_2 : Ph_2PBr , the ultra-violet spectrum of a solution of the adduct Ph_2PBr_3 in the same solvent showed that traces of tribromide ion were present. A possible explanation for this, is that in these solutions which are more concentrated than those of the conductometric titration, the adduct Ph_2PBr_3 disproportionates slightly in methyl cyanide according to :

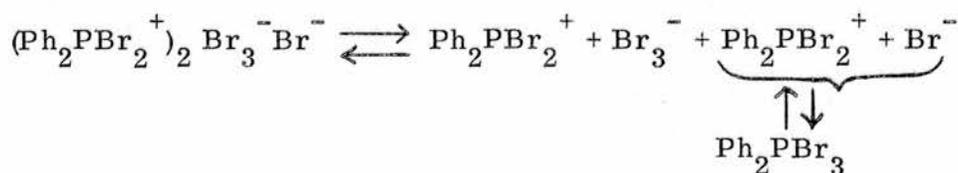


A second bromine adduct was isolated from this system. It was obtained when solutions of bromine and bromodiphenylphosphine were mixed in 2:1 mole ratio either in methyl cyanide or petroleum ether (40-60°C). This compound was a yellow solid (m. p. 95-97°C) of composition Ph_2PBr_4 . This adduct (i. e. Ph_2PBr_4) was also formed when Ph_2PBr_3 was pumped for several hours. Presumably the compound Ph_2PBr_3 had decomposed to the more stable Ph_2PBr_4 according to the following reaction:



The ultra-violet spectrum of a methyl cyanide solution of Ph_2PBr_4

showed that it contained the tribromide ion ($\lambda_{\max} = 269 \text{ m}\mu$). Methyl cyanide solutions of the adduct were found also to be very highly conducting ($\Lambda_m = 190.00 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.01 \text{ mol l}^{-1}$). From these observations and by analogy with the compounds $(\text{PhPBr}_5)_2$, $(\text{PhPBr}_4\text{I})_2$ of similar stoichiometry, obtained from the Br_2 , IBr-PhPBr_2 systems, as well as the known $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$ ²¹¹, the dimeric formula $(\text{Ph}_2\text{PBr}_4)_2$ with the ionic structure $(\text{Ph}_2\text{PBr}_2^+)_2\text{Br}_3^-\text{Br}^-$ is suggested for this adduct. Therefore, a reasonable scheme for the behaviour of this compound in methyl cyanide is :



If this is the case, the extinction coefficient of the tribromide ion (peak at $269 \text{ m}\mu$) calculated on the basis of the ionic formula $(\text{Ph}_2\text{PBr}_2^+)_2\text{Br}_3^-\text{Br}^-$ should be close to the reported value of $55,000$ ²⁰⁷ $\text{l mol}^{-1} \text{ cm}^{-1}$, and indeed the value of $54,000$ was obtained.

(2.2) The $\text{Ph}_2\text{PBr} - \text{I}_2$ System

The shape of the conductometric-composition graph obtained here was similar to that of the $\text{PhPBr}_2 - \text{I}_2$ system previously studied. The titration results are to be found in Table 22, and the conductance composition graph is reproduced in Figure 15, plot 1. The graph shows no definite breaks, but the conductance attains a maximum value near the 4:1 iodine to phosphine mole ratio, and thereafter the conductance levels-off. To eliminate the dilution effect, which sometimes obscures the breaks in a conductometric titration graph, a second titration was carried out

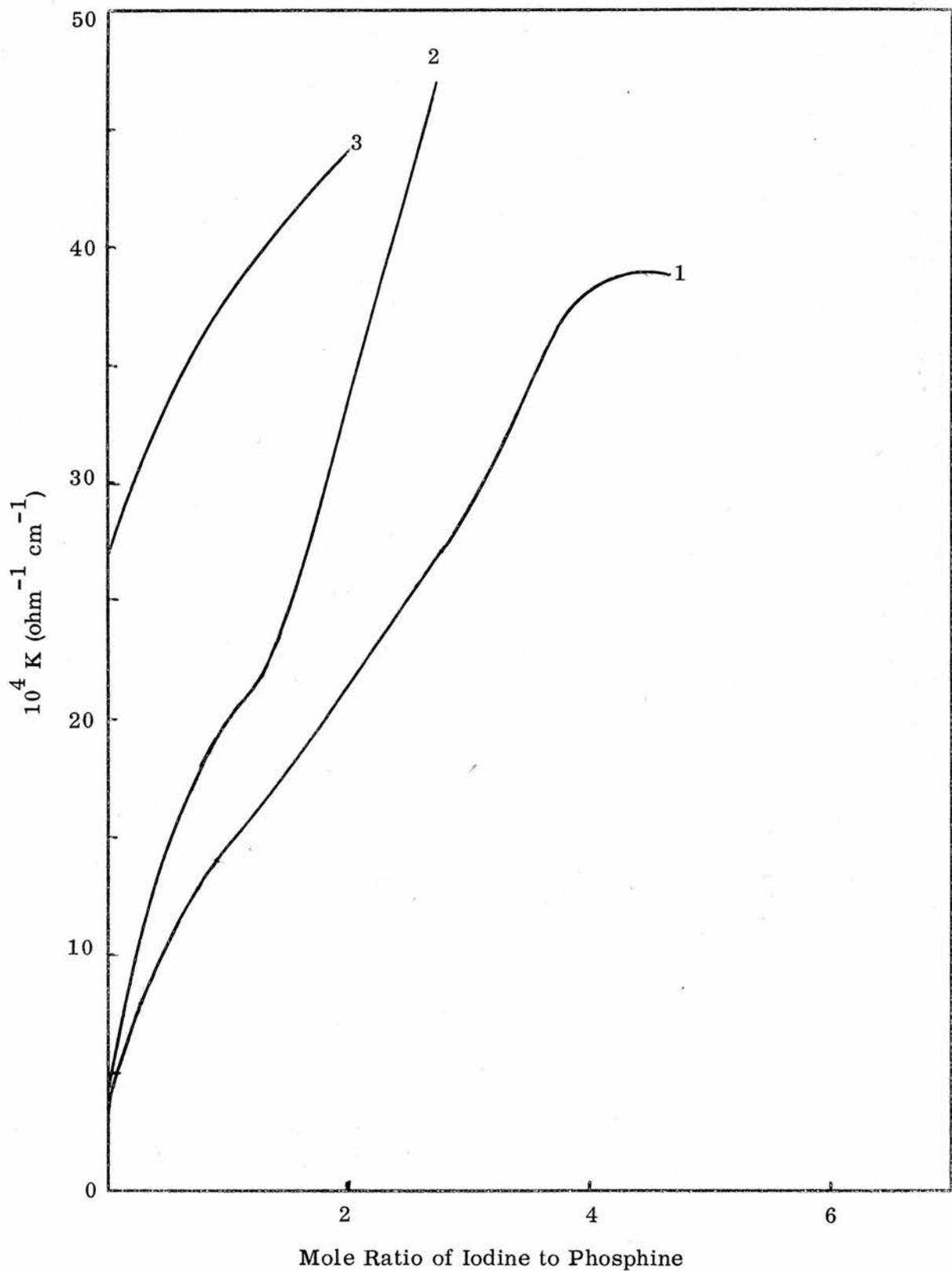


Figure 15. Conductometric Titration of the Systems:

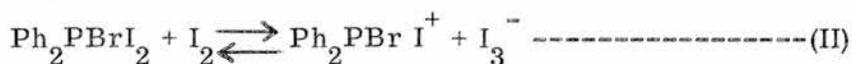
I₂-Ph₂PBr ----- plot 1

Solid I₂-Ph₂PBr -----plot 2

I₂-(PBr₃+ IBr) -----plot 3

using solid iodine (solvent free) as titrant. The graph in Figure 15, plot 2 obtained from the results, of this titration, listed in Table 23, is similar to the previous one (curve 1) and shows no clear cut breaks.

The conductometric titration graphs point to the presence of an ion forming reaction which does not go to completion at the expected stoichiometric end points. The ultra-violet spectrum, of solutions containing iodine and bromodiphenylphosphine in different mole ratios, demonstrates the existence of triiodide ion (Table 20). These observations suggest an equilibrium reaction which may consist of two or more overlapping equilibria. It seems therefore, that this system behaves in a similar fashion to the $\text{PhPBr}_2\text{-I}_2$ system described earlier. Thus by analogy, it seems reasonable to suggest that the $\text{Ph}_2\text{PBr-I}_2$ system is best represented by the following equilibria :



The immediate formation of triiodide ion in the titration is accounted for by the presence of equilibrium (II).

It was not possible to prepare an adduct of stoichiometry Ph_2PBrI_2 from mixtures of iodine and bromodiphenylphosphine (1:1 and 0.5 : 1 mole ratios) in various solvents (methyl cyanide, petroleum ether or carbon tetrachloride). The isolated compound was in each case identical to that precipitated at the 2:1 mole ratio, and had the composition Ph_2PBrI_4 . This dark red solid (m.p. 108-109°C) was shown by mass spectrum (Table 24) to undergo hydrolysis readily (see later).

The ultra-violet spectrum of the substance Ph_2PBrI_4 when it was dissolved in methyl cyanide showed the characteristic absorptions of

triiodide ion ($\lambda_{\text{max}} = 291,361 \text{ m}\mu$)²⁰⁸. This observation however, is in line with the proposed scheme for the reactions occurring during the conductometric titration in methyl cyanide.

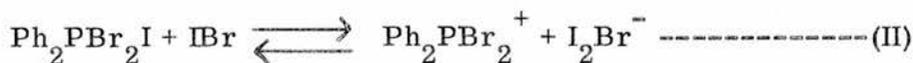
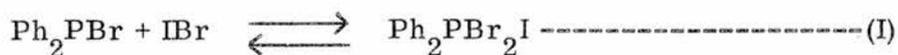


(2.3) The Ph₂PBr - IBr System

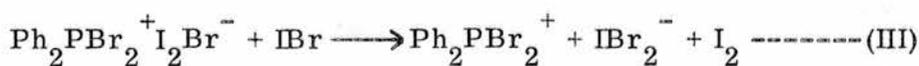
The bromodiphenylphosphine - iodine monobromide system shows a behaviour which is rather like that of the PhPBr₂ - IBr system. The results of the conductometric titration are displayed in Figure 14 and recorded in Table 25. The graph shows a break between the 1:1 and 1.5:1 mole ratio of IBr: Ph₂PBr. After the 0.5:1 ratio the previously colourless solution turned pale orange whereafter it progressively darkened until the 1.5:1 ratio (IBr: Ph₂PBr). Further additions of iodine monobromide solution beyond this ratio caused a sharp increase in conductance along with intensification in the colour up to the 4:1 ratio, after which it immediately tailed-off. The colour of the solution by itself is indicative of polyhalide ion formation in methyl cyanide. To verify this, the ultra-violet spectrum of methyl cyanide solutions containing the reactants at various mole ratios, was studied. The results recorded in Table 20 demonstrate the presence of I₂Br⁻ up to the 1.5:1 ratio and IBr₂⁻ ion (in addition to iodine) beyond this ratio.

The absence of any well defined breaks in the conductometric titration graph and the formation of polyhalide ions from the 0.51:1 ratio (IBr: Ph₂PBr), are in line with the behaviour shown by the Ph_nPBr_{3-n}⁻ Hal₂ (where n = 1, 2 and Hal₂ = I₂, IBr) systems, studied previously. This parallel behaviour therefore, implies the presence of overlapping

equilibria in this system. Thus, the shape of the graph could be interpreted as follows :



The detection of iodine in the visible region at higher mole ratios of IBr: Ph₂PBr (ca. 2.7 :1) suggests the presence of a third equilibrium, namely



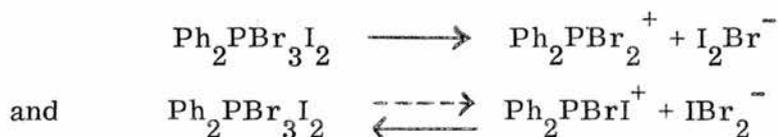
The formation of I₂Br⁻ and IBr₂⁻ ions beyond the 1.3 :1 mole ratio of IBr: Ph₂PBr lends support to this. Thus the system is best described by these three equilibria (I, II and III) present in methyl cyanide.

Equilibrium I, from ultra-violet spectrum clearly predominates at low mole ratios (IBr: Ph₂PBr) but as the ratio is increased, equilibrium II comes into play and at high mole ratios equilibrium III is important.

It is believed that the break at ca. 1.4:1 arises from interplay of the equilibria and is of no special significance; also, that the rounded break at ca. 4:1 simply represents final pushing of equilibrium III to right-hand side by excess iodine monobromide present.

Attempts to prepare the 1:1 adduct using mole ratio of 0.5:1, 1:1, and 1.5:1 of IBr: Ph₂PBr in petroleum ether (40-60°C) or carbon tetrachloride, resulted in the separation of three red-brown solids (m.p. 99-101°C). The three compounds were shown, by analysis, to be identical and of 2:1 adduct stoichiometry with the formula Ph₂PBr₃I₂. Examination of the ultra-violet spectrum of methyl cyanide solutions of the red-brown solid demonstrates the presence of I₂Br⁻ ion ($\lambda_{\text{max}} = 278 \text{ and } 350 \text{ m}\mu$)

with slight traces of IBr_2^- . The mode of ionisation of this solid in methyl cyanide could be therefore represented by the reaction :

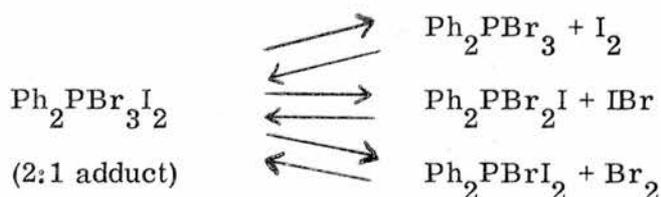


The isolation of a solid 2:1 adduct from solutions of mole ratio lower than 2:1 is in keeping with the interpretation of this system as involving several overlapping equilibria. The 2:1 adduct is represented by the right-hand side of equilibrium II.

A second compound of 2:1 stoichiometry, $\text{Ph}_2\text{PBr}_2\text{I}_3$, was precipitated as a sticky dark red solid, when petroleum ether (40-60°C) solutions of iodine monobromide and bromodiphenylphosphine in a ratio of 2:1, were mixed. This adduct was shown by ultra-violet spectrum to produce only triiodide ions in methyl cyanide. Thus its ionisation scheme in this solvent is

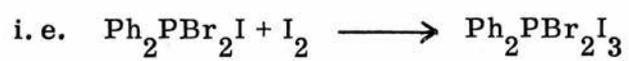


The isolation of this adduct at 2:1 mole ratio of $\text{IBr}:\text{Ph}_2\text{PBr}$ is rather peculiar. Presumably in a non polar solvent of low dielectric constant like petroleum ether, any adduct formed in solution will tend to undergo molecular dissociation (cf. PBr_5)⁷⁷ so that we may have the following



With a mixture of molecular species as is indicated on right-hand side of this scheme it is clear that a large number of adducts becomes possible and the one which crystallises from particular solvent will be dictated by

solubility factors. In this case it is the adduct $\text{Ph}_2\text{PBr}_2\text{I}_3$ (formed from the products of dissociation of $\text{Ph}_2\text{PBr}_3\text{I}_2$) which comes out of solution.



3. The Reaction of Phosphorus Tribromide with Halogens

In order to complete the conductometric investigations of the systems involving halogens and compounds of the general formula $\text{Ph}_n\text{PBr}_{3-n}$ in methyl cyanide, it was desirable to study the reaction between halogens ($\text{Br}_2, \text{I}_2, \text{IBr}$) and $\text{Ph}_n\text{PBr}_{3-n}$ where $n = 0$, (i. e. phosphorus tribromide).

Although many mixed phosphorus pentahalides are known, the $\text{PBr}_3\text{-I}_2$ and $\text{PBr}_3\text{-IBr}$ systems, have not been studied in methyl cyanide previously. To gain some information about the behaviour of these systems, the reactions were carried out by stepwise addition of the halogen to phosphorus tribromide, and this was followed conductometrically.

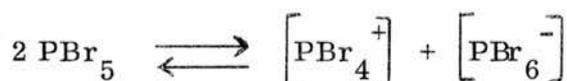
This technique has been found convenient in the study of such reactions, since it indicates when compound formation occurs by a 'break' or change in gradient of the graph as more halogen is added to the phosphine.

(3.1) The $\text{PBr}_3\text{-Br}_2$ System

80, 213

This particular system was previously examined by Harris et al. and the conductometric - composition graph (Figure 10 plot 4) obtained from the reaction between bromine and phosphorus tribromide in methyl cyanide, indicates a reaction corresponding to a 1:1 mole ratio ($\text{Br}_2 : \text{PBr}_3$), forming an adduct of the stoichiometry PBr_5 , i. e. phosphorus pentabromide.

From ion migration experiments, it is reported by the same authors that phosphorus pentabromide undergoes ionisation in methyl cyanide according to the scheme :

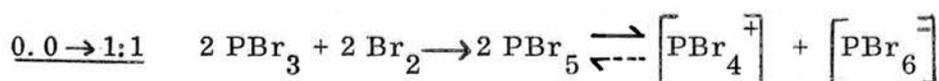


It is of interest to note that on repeating the conductometric titration

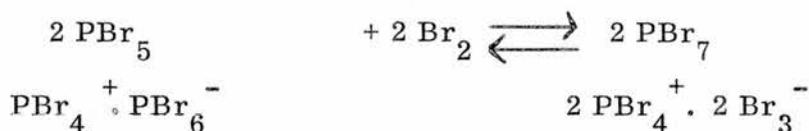
study of this system, a slightly different conductometric titration graph was obtained. The graph in Figure 10 - plot 3 (relevant data in Table 26), shows a break at the 1:1 mole ratio of $\text{Br}_2 : \text{PBr}_3$, similar to that observed by Harris (his graph is plot in Figure 10 - plot 4). The molar conductance calculated at this ratio is

$$\Lambda_m = 71.48 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; c_m = 0.015740 \text{ mol l}^{-1}$$

demonstrating the formation of phosphorus pentabromide as a fairly strong 1:1 electrolyte in methyl cyanide. Thus, by analogy with the above equilibrium, the following scheme of ionisation is suggested:



In contrast to what was found previously, further additions of bromine solution beyond the 1:1 ratio caused a sharp increase in conductance until the 3:1 mole ratio ($\text{Br}_2 : \text{PBr}_3$) after which it slowly tailed-off. The increase in specific conductance after the 1:1 ratio and the absence of a 2:1 break show clearly that there is a parallel in the behaviour of this system with the $\text{Br}_2 - \text{PhPBr}_2$ and $\text{Br}_2 - \text{Ph}_2\text{PBr}$ systems. This implies the presence of an equilibrium, thus



and the position as well as the round form of the break shows that this reaction is not complete at the 2:1 ratio.

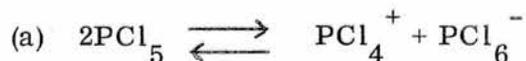
Although the present findings are in accord with that outlined for the systems $\text{Br}_2 - \text{PhPBr}_2$ and $\text{Br}_2 - \text{Ph}_2\text{PBr}$, it is at variance with the previously reported conductometric titration study of $\text{Br}_2 - \text{PBr}_3$ system and it is very difficult to suggest a reason for this.

In comparing the two studies we can consider three features of

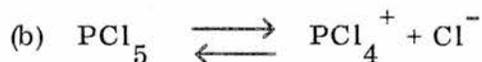
differences

- (a) the concentration of the solution in the titration flask
- (b) the apparatus used.
- (c) the time lag between successive additions of titrant.

(a). The influence of concentration on the mode of ionisation of phosphorus pentabromide could be important. It has been found that this is the case for phosphorus pentachloride (PCl_5) from a study of its behaviour in various ionising solvents. Shore et al.⁷⁸ have shown by Raman spectroscopy and freezing point depression methods that two competing equilibria occurred in the solvents CH_3CN , CH_3NO_2 and $\text{C}_6\text{H}_5\text{NO}_2$, namely,



and



It was found that (a) predominates in solutions of concentration $> 0.03\text{M}$ and (b) predominates at lower concentrations.

However, in the $\text{Br}_2 - \text{PBr}_3$ system the concentration used by Harris et al.^{80,213} was 0.0133M and in the present work the concentration was 0.0157M . It is thought unlikely that this difference would have any significant effect on the mode of ionisation predominating and in any case by analogy with phosphorus pentachloride it would favour the ions $\text{PBr}_4^+ \text{PBr}_6^-$ as being present in the solution used in the present study, (i. e. the same ions as were assumed by Harris to be present in this titration).

(b). In the present work the experiment was carried out on a semi-micro scale within a nitrogen - filled dry box whereas the previous experiment carried out on a large scale outwith dry box in an apparatus specially

designed to exclude moisture. It is difficult to make an assessment of this but if the earlier apparatus were less efficient at excluding moisture then a difference in results would be expected.

(c). In the conductometric titration carried out by Harris the time between each addition of titrant was less than in present titration*. Thus it may be that in his titration sufficient time was not allowed for reaction of phosphorus pentabromide with bromine to yield new ions. This reaction essentially involves break down of PBr_6^- ion and this may not be a fast process.



(3.2) The $\text{PBr}_3 - \text{I}_2$ System

A variety of experimental approaches which had been employed on the system $\text{PBr}_3 - \text{I}_2$ by Fialkov and Kuz'menko²⁷, showed no indication of compound formation. Size contribution have been invoked to explain this lack of reactivity²⁰¹, just as in explaining the nonexistence of phosphorus pentaiodide. As the system $\text{PhPBr}_2 - \text{I}_2$ and $\text{Ph}_2\text{PBr} - \text{I}_2$, were studied conductometrically, it was thought worthwhile to investigate the $\text{PBr}_3 - \text{I}_2$ system in the same way to throw some light on its behaviour in methyl cyanide.

The conductometric titration data are recorded in Table 27 and illustrated graphically in Figure 13, plot 3. Conductance rises steadily without inflexion until ca. 1.9:1 mole ratio ($\text{I}_2 : \text{PBr}_3$) where there is a sudden drop in specific conductance over a 0.1:1 mole ratio interval after which the conductance goes on rising without inflexion, but the increase

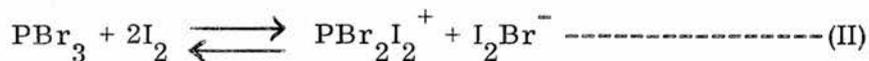
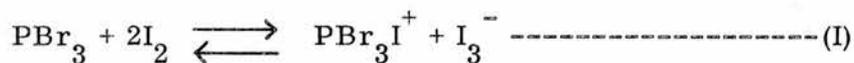
*G. S. Harris, Personal communication.

tails-off at higher mole ratios. This feature in a conductometric titration graph is characteristic of precipitation in the solution being titrated.

(In the present case this could not be confirmed owing to the difficulty of observing the presence of dark solids in the dark coloured solutions).

It is assumed that a small quantity of solid ($\text{PBr}_3\text{I}^+ \cdot \text{I}_3^-$?, see below) adduct precipitated momentarily but redissolved as the equilibria involved were shifted in addition of further amounts of iodine solution.

Again it is obvious that this system is one involving equilibria and that clear cut reactions do not occur in solution. The following equilibria would seem to describe the system adequately :



The ultra-violet spectrum results (Table 28 overleaf) indicate that equilibrium (II) predominates above the 1:1 mole ratio of iodine to phosphorus tribromide.

Table 28 The Solution Spectra of the PBr_3 - Hal_2 System

System	Mole ratio $\text{Hal}_2 : \text{PBr}_3$	u. v. maxima ($\text{m}\mu$)	u. v. Indicates
$\text{I}_2 - \text{PBr}_3$	0.8 : 1	286,358	I_2Br^- and I_3^-
	1.8 : 1	281,350	I_2Br^-
	3.1 : 1	280,350	I_2Br^-
$\text{IBr} - \text{PBr}_3$	0.3 : 1	263	mostly IBr_2^-
	1.0 : 1	258	IBr_2^-
	2.0 : 1	256	IBr_2^- only
	3.0 : 1	256	IBr_2^- only
$\text{I}_2 - (\text{PBr}_3 + \text{IBr})$	1.0 : 1	288,358	I_3^- *
	2.1 : 1	288,359	I_3^-

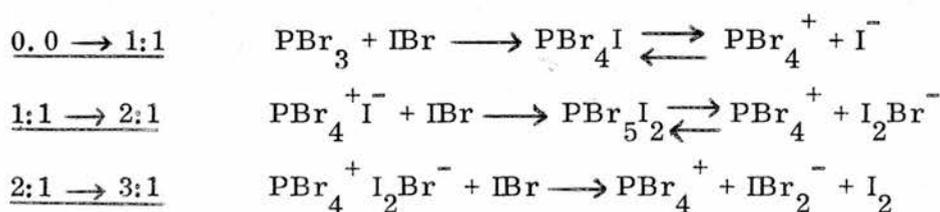
(* Probably traces of I_2Br^- is present).

The molar conductance value calculated at the 2:1 ratio is :

$\Lambda_m = 179.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.012556 \text{ mol l}^{-1}$ indicating the presence of a very strong 1:1 electrolyte in methyl cyanide.

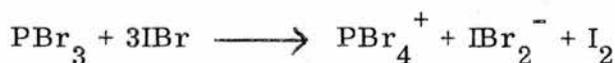
(3.3) The PBr_3 - IBr System

The reaction between phosphorus tribromide and iodine monobromide in methyl cyanide is thought to be straight forward. It was thought that this reaction would take place in the three stages given by the following scheme :



If this were the case, three breaks in the conductometric titration graph would therefore be expected. The conductance results assembled in Table 29 and depicted in Figure 14 plot 3, show that the above postulation is incorrect - the reaction does not proceed in three clear cut stages. The graph shows only one break and this occurs at the 3:1 mole ratio (IBr : PBr₃). The colourless solution became yellow from the first addition of iodine monobromide and gradually darkened on further additions of the titrant. Although the colour change by itself is indicative of polyhalide ion formation, the ultra-violet spectrum, of methyl cyanide solutions containing the starting materials at different mole ratios was examined. The results are summarised in Table 28. They indicate the existence of IBr₂⁻ ions ($\lambda_{\text{max}} = 256 \text{ m}\mu$)²⁰⁷ at all stages of the titration.

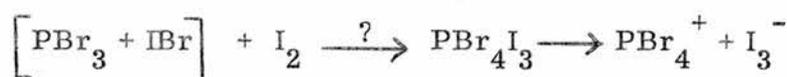
It appears therefore, from the conductometric - composition graph and the spectrophotometric analysis, that a 3:1 (IBr : PBr₃) reaction took place from the beginning, thus



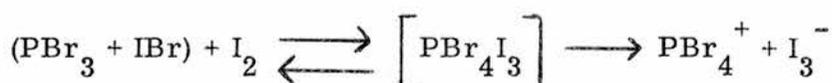
The molar conductance calculated from the graph at this ratio was,
 $\underline{3:1} \quad \Lambda_m = 376.97 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, c_m = 0.011473 \text{ mol l}^{-1}$
 indicating a strong 1:1 electrolyte formation. The compound PBr₄⁺IBr₂⁻ has been reported else where^{27,77} as a ruby-red solid.

(3.4) The (PBr₃ + IBr) - I₂ System

The adduct PBr₆I which was shown in the previous section to exist in methyl cyanide as PBr₄⁺·IBr₂⁻ is also known as a solid containing the same ions⁷⁷. Although the PBr₄⁺ ion is not of widespread occurrence (it exists in PBr₄⁺Br⁻ and PBr₄⁺Br₃⁻), the IBr₂⁻ ion exists in conjunction with a fairly wide variety of cations (Cs⁺IBr₂⁻, Ph₄P⁺IBr₂⁻, Ph₄As⁺IBr₂⁻, etc) and is one of the more stable trihalide ions known. Another stable trihalide ion is the triiodide ion and it was thought probable that it might be able to form with the PBr₄⁺ ion, the compound PBr₄⁺I₃⁻. Attempts were therefore made to demonstrate the existence of this compound by titration of [PBr₃ + IBr] (1:1 mixture) with iodine which is stoichiometrically "correct" for the adduct in question



A sharp break in the conductometric titration graph at 1:1 ratio would indicate that the above reaction proceeds well to the right. The results obtained are listed in Table 30 and illustrated graphically in Figure 15 plot 3. As can be seen from the graph the conductance rises steadily from the beginning of the titration without any distinct breaks appearing. The ultra-violet spectrum of the solution (Table 28) at the 1:1 ratio whilst showing that the triiodide ion predominates suggests also the presence of traces of another trihalide ion (most likely IBr₂⁻). It is clear then that the expected reaction is probably occurring but does not proceed to completion when the theoretical amounts of the reagents have been mixed.



(3.5) Preparation of Some Mixed Phosphorus Polyhalides

As a follow-up to the conductometric titration of the $\text{PBr}_3 - \text{Hal}_2$ ($\text{Hal}_2 = \text{Br}_2, \text{I}_2, \text{IBr}$) and $\text{I}_2 - (\text{PBr}_3 - \text{IBr})$ systems, attempts were made to prepare adducts suggested from the titration and ultra-violet studies, namely PBr_6I (already known), PBr_3I_4 and PBr_4I_3 .

It was possible to isolate only three adducts, PBr_4I_3 , PBr_5I_2 , and PBr_6I from reactions between the constituents as is shown in Table 31 below. The Table also contains the results of the ultra-violet spectra of these adducts dissolved in methyl cyanide.

Table 31*

Reaction Mixture	Solvent used	u. v. maxima	Trihalide ion indicated by u. v.	Probable Structure
$(\text{PBr}_3 + \text{IBr}) + \text{I}_2$	Petroleum ether (40-60°C) and CH_3CN	289, 359	I_3^-	$\text{PBr}_4^+ \text{I}_3^-$
$(\text{PBr}_3 + \text{Br}_2) + \text{I}_2$	Methyl cyanide (CH_3CN)	278, 350	I_2Br^-	$\text{PBr}_4^+ \text{I}_2\text{Br}^-$
$\text{PBr}_3 + \text{IBr}$	Methyl cyanide	258	IBr_2^-	$\text{PBr}_4^+ \text{IBr}_2^-$
$\text{PBr}_3 + 2\text{IBr}$	Methyl cyanide	257	IBr_2^-	$\text{PBr}_4^+ \text{IBr}_2^-$

* All the adducts were isolated as dark red oils.

As can be seen from the Table, the isolation of one and the same product using either a 1:1 or a 2:1 mole ratios of $\text{IBr} : \text{PBr}_3$ in methyl cyanide supports the suggestion that the reaction between iodine monobromide

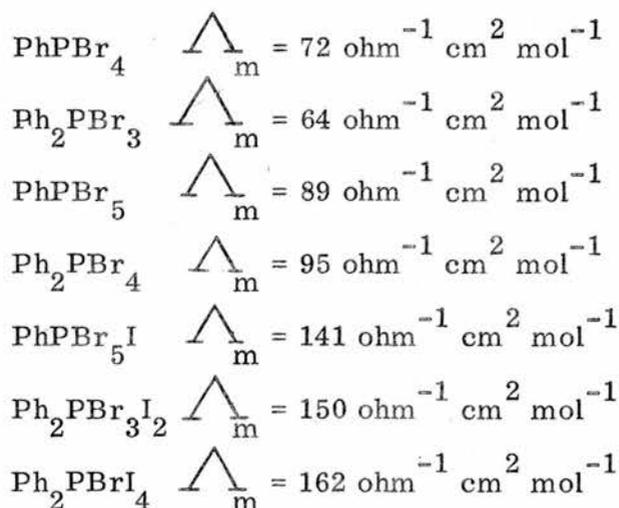
and phosphorus tribromide proceeds as a 3:1 reaction (see page 84).

It was not possible to isolate any compound from the reaction between iodine and phosphorus tribromide. Presumably, the mixed cation PBr_2I_2^+ suggested by the conductometric titration and ultra-violet studies, does not exist in the solid state. This seems to be in line with the fact that this type of compounds are not known so far.

(4) The Electrolytic Conductance of Some Dibromophenylphosphine and Bromodiphenylphosphine Halides in Methyl Cyanide

The specific conductance of the solid halogen adducts of dibromophenylphosphine and bromodiphenylphosphine was measured in methyl cyanide under strictly anhydrous conditions at 25°C. The solutions were prepared in a dry-box and the molar concentration (c_m) was calculated on the basis of the molecular formulae given in Table 32. The values of molar conductance are displayed in Figure 16.

As can be seen from Figure 16, these values when plotted against the square root of the molar concentration ($\sqrt{c_m}$) fall in a straight line of negative slope. For comparison the values for the molar conductance at 0.01M obtained by extrapolation of the graphs are found to be :



Since the compounds of the empirical formula PhPBr_5 and Ph_2PBr_4 were shown, by quantitative analysis of their ultra-violet spectra in methyl cyanide, to adopt the structure $[\text{PhPBr}_3]^+ \text{Br}_3^- \text{Br}^-$ and $[\text{Ph}_2\text{PBr}_2]^+ \text{Br}_3^- \text{Br}^-$ respectively, their molar conductances therefore, must be doubled.

This then gives a value which indicates strong 1:1 electrolyte behaviour for these adducts.

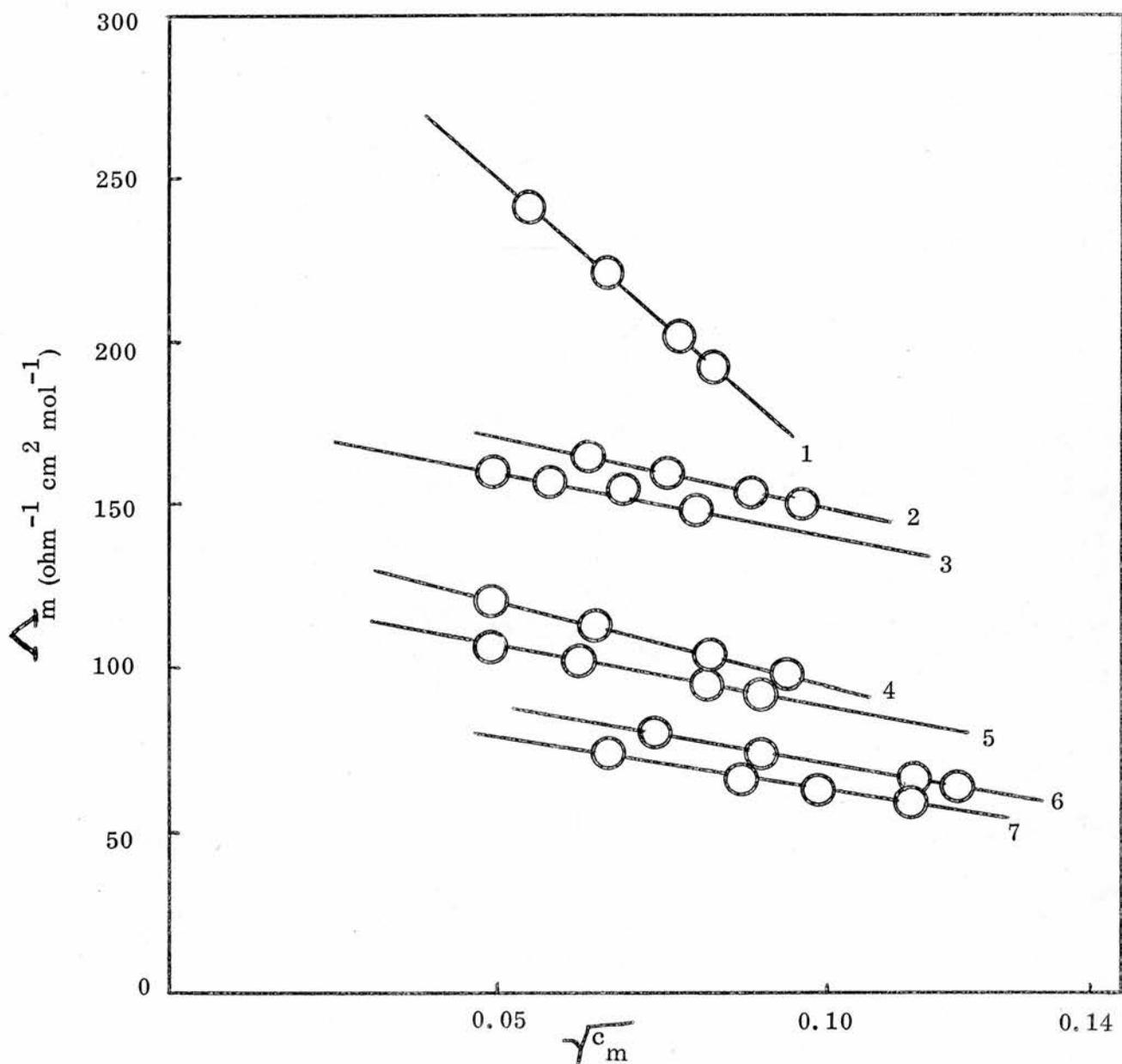


Figure 16. Electrolytic Conductance of Dibromophenylphosphine and Bromodiphenylphosphine Halides in Methyl Cyanide at 25°C

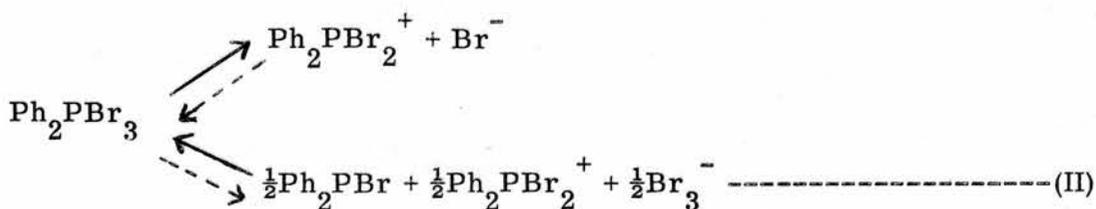
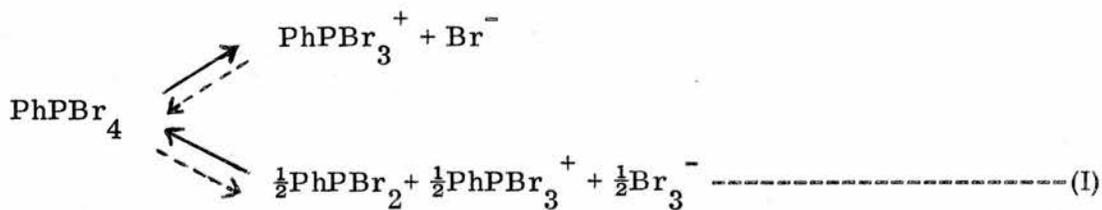
- | | |
|---|-------------------------------|
| 1 - Ph_2PBrI_4 | 4 - Ph_2PBr_4 |
| 2 - $\text{Ph}_2\text{PBr}_3\text{I}_2$ | 5 - PhPBr_5 |
| 3 - PhPBr_5I | 6 - PhPBr_4 |
| 7 - Ph_2PBr_3 | |

The observed molar conductance values for the PhPBr_4 and Ph_2PBr_3 ($72 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $64 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively), demonstrate that they are fairly strong 1:1 electrolytes (strong electrolyte has an average value for Λ_m of $100\text{-}150 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at 0.01M solution), but have not completely ionised in methyl cyanide.

Table 32. Electrolytic Conductance of $\text{Ph}_n\text{PBr}_{3-n}$ ($n = 1, 2$) Halides in Methyl Cyanide at 25°C

Compound	c_m mol l^{-1}	$\sqrt{c_m}$	$10^4 K$ $\text{ohm}^{-1} \text{ cm}^{-1}$	Λ_m $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
PhPBr_4	0.005410	0.0736	4.39	81.17
	0.008101	0.0903	6.16	75.48
	0.013022	0.1141	8.67	66.62
	0.014281	0.1195	9.17	64.18
PhPBr_5	0.002419	0.0492	2.60	107.52
	0.003891	0.0624	4.05	104.05
	0.006689	0.0818	6.42	95.97
	0.008012	0.0895	7.39	92.28
Ph_2PBr_3	0.004422	0.0665	3.35	75.76
	0.007483	0.0865	5.00	66.82
	0.009702	0.0985	6.22	64.11
	0.012801	0.1131	7.77	60.70
Ph_2PBr_4	0.002371	0.0487	2.90	122.36
	0.004219	0.0648	4.78	113.75
	0.006692	0.0818	7.01	104.78
	0.008839	0.0940	8.73	98.75
PhPBr_5I	0.002429	0.0493	3.91	160.86
	0.003338	0.0578	5.28	158.18
	0.004720	0.0687	7.36	155.86
	0.006448	0.0803	9.62	149.20
$\text{Ph}_2\text{PBr}_3\text{I}_2$	0.004016	0.0641	6.79	165.46
	0.005741	0.0758	9.27	161.43
	0.007846	0.0886	12.23	155.92
	0.009242	0.0961	13.97	151.18
Ph_2PBrI_4	0.003051	0.0550	7.35	240.98
	0.004460	0.0670	9.89	221.75
	0.006129	0.0781	12.42	202.58
	0.006942	0.0831	13.41	193.23

Thus, their modes of ionisation, in methyl cyanide are :



The lower limbs of ionisation schemes, (I) and (II), explain the ultra-violet results which showed the present of traces of tribromide ions. In contrast, the PX_7 type compounds PhPBr_5I and $\text{Ph}_2\text{PBr}_3\text{I}_2$ are very strong 1:1 electrolytes and the species present in solution are $\text{PhPBr}_3^+ \text{I}_2\text{Br}_2^-$ and $\text{Ph}_2\text{PBr}_2^+ \text{I}_2\text{Br}^-$.

(5) The Mass Spectra of the Halogen Adducts of Dibromophenylphosphine and Bromodiphenylphosphine

The mass spectra of the adducts isolated in the $\text{PhPBr}_2 - \text{Hal}_2$ and $\text{Ph}_2\text{PBr} - \text{Hal}_2$ ($\text{Hal}_2 = \text{Br}_2, \text{I}_2$, and IBr) systems have been recorded. The ratio of mass to charge (m/e) of most of the peaks shown in the spectra are assigned to different ions according to their elemental composition. The relative abundance of each ion is expressed as a percentage, the most abundant fragment being set equal to 100 per cent. Bromine having two isotopes, ^{79}Br and ^{81}Br , of nearly the same abundance, will produce an 'isotopic cluster'. Thus its presence in an ion is often easily recognised in the spectrum and the number of bromine atoms present can also be determined from the appearance of the cluster. The mass spectrum of bromine shows prominent molecular ions at masses 162, 160 and 158 of relative intensities 1:2:1 due to the ions $^{81}\text{Br}_2$, $^{81}\text{Br}^{79}\text{Br}$ and $^{79}\text{Br}^{81}\text{Br}$ and $^{79}\text{Br}_2$ respectively. Any ion containing two bromine atoms will show a similar 1:2:1 pattern. Likewise, any ion structure containing three bromine atoms will exhibit four peaks (of intensity pattern 1:3:3:1) at intervals of two mass units.

The mass spectra of the title compounds are now considered in turn :

PhPBr_4 , $(\text{PhPBr}_5)_2$ and PhPBr_3I .

The mass spectrum results of these compounds which are listed in Table 7 and 17 are found to be identical (excluding the fragments of m/e 254 and 127 due to the presence of iodine in PhPBr_3I). The highest mass peaks at 286, 284, and 282 are assigned to the $\text{PhP}^{81}\text{Br}_2^+$,

$\text{PhP}^{81}\text{Br}^{79}\text{BrO}^+$, and $\text{PhP}^{79}\text{Br}_2\text{O}^+$ fragments respectively. Other peaks present in the spectrum are assigned on the basis of their elemental composition.

The absence of peaks corresponding to either bromine (m/e 162, 160, 158) or iodine monobromide (208, 206) molecules lends support for an ionic structure for these compounds. The presence of oxygenated species is accounted for by some hydrolysis occurring during measurement. Thus it would be expected that partial hydrolysis of the PhPBr_3^+ would give PhPBr_2O and HBr and the species are present in the spectrum. The high lability of these adducts under such conditions is thus demonstrated.

PhPBr_4I , PhPBr_5I , PhPBr_2I_2 and PhPBr_2I_4 .

Tables 18, 33 and 15 contain the mass spectrum results of the compounds PhPBr_4I , PhPBr_5I and PhPBr_2I_2 respectively. The mass spectrum of PhPBr_2I_4 is very similar to that of PhPBr_2I_2 . The highest mass peaks in the spectra of PhPBr_4I and PhPBr_5I are assigned to the PhPBrI_3^+ fragment, whereas the highest ones in the spectra of PhPBr_2I_2 and PhPBr_2I_4 are assigned to $\text{PhPBr}_2\text{I}_2^+$. As can be seen from the Tables (18, 33 and 15), the compounds on the whole give rather similar fragments.

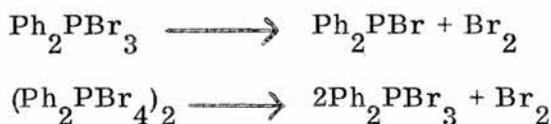
From the presence of the ions PhPBrI_3^+ , $\text{PhPBr}_2\text{I}_2^+$ and PhPBr_3I^+ in the spectra it is suggested that the adducts, under the influence of heat, have undergone thermal dissociation in the mass spectrometer. The mass spectrum results demonstrate the instability and ease of oxidation of these compounds also. Therefore it is very difficult to gain from these results any detailed information regarding the structure of the adducts.

Ph₂PBr₃ and (Ph₂PBr₄)₂.

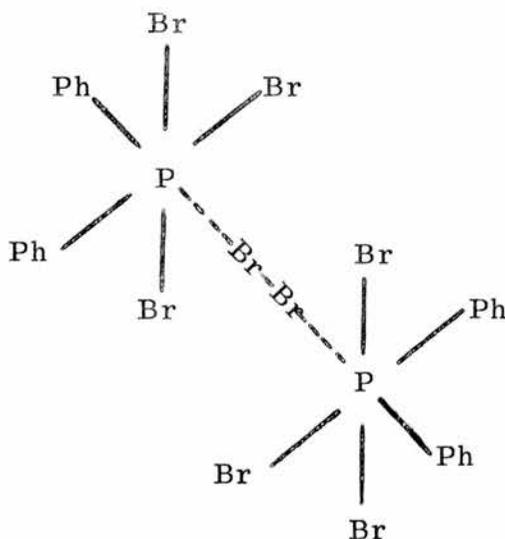
The highest peaks in the spectrum of (Ph₂PBr₄)₂ is a cluster at m/e 428, 426, 424 and 422 whereas the highest ones in Ph₂PBr₃ is at 282 and 280. These m/e values are attributed to PhPBr₃⁺ (⁸¹Br₃, ⁸¹Br₂⁷⁹Br, ⁸¹Br⁷⁹Br₂, ⁷⁹Br₃) and Ph₂PBrO⁺ (⁸¹Br, ⁷⁹Br) respectively.

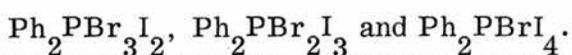
As can be seen from Table 21 the spectra are similar, below m/e 280.

The spectra show peaks at m/e 162 (⁸¹Br₂), 160 (⁸¹Br⁷⁹Br), and 158 (⁷⁹Br₂), suggesting that the compounds lose bromine. It seems not unlikely that compounds of this type would lose a mole of bromine through molecular dissociation, thus



It is suggested that (Ph₂PBr₄)₂, (which was postulated as having the ionic structure [Ph₂PBr₂⁺]₂ Br₃⁻ Br⁻ in methyl cyanide), in the solid state may have a structure in which two pentaco-ordinated phosphorus atoms are linked (loosely) by a bromine molecule, thus raising the coordination number of the phosphorus atom to six as follows :





The mass spectrum of the adduct $\text{Ph}_2\text{PBr}_3\text{I}_2$ (Table 34), showing highest mass peaks at 474 ($\text{Ph}_2\text{P}^{81}\text{Br}_2\text{I}^+$), 472 ($\text{Ph}_2\text{P}^{81}\text{Br}^{79}\text{BrI}^+$) and 470 ($\text{Ph}_2\text{P}^{79}\text{Br}_2\text{I}^+$) in addition to the fragments I^{81}Br and I^{79}Br of m/e 208 and 206, suggests that this compound is thermally unstable, undergoing molecular dissociation.



The results for $\text{Ph}_2\text{PBr}_2\text{I}_3$ are recorded in Table 35. The peaks at m/e 520, 518, 208 and 206 are assigned to $\text{Ph}_2\text{P}^{81}\text{BrI}_2^+$, $\text{PhP}^{79}\text{BrI}_2^+$, I^{81}Br , and I^{79}Br respectively, they indicate molecular dissociation of this adduct also.

In contrast to this, the mass spectrum of Ph_2PBrI_4 (Table 24) did not give an indication of molecular dissociation. The highest mass peaks (at 393 and 391) are assigned to the Ph_2PBrI^+ fragments. The spectrum of this compound (Ph_2PBrI_4) may be considered as an evidence for its formation with an ionic structure, $\text{Ph}_2\text{PBrI}^+\text{I}_3^-$. In addition to the assigned fragments contained in Tables 7, 15, 17, 18, 21, 24, 33, 34 and 35, there were other peaks of m/e values between 77 and 31 which could be related to fragments formed from the break down of the aromatic ring (C_6H_6).

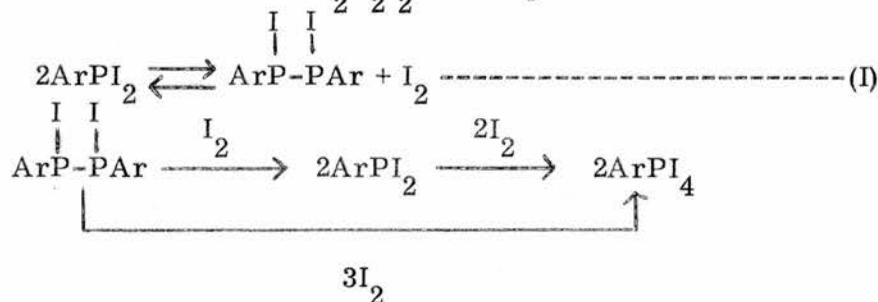
B. THE REACTION OF HALOGENS WITH $\text{Ph}_n\text{PI}_{3-n}$ ($n = 2, 1, 0$)

(1) The Reaction of Diiodophenylphosphine with Halogens

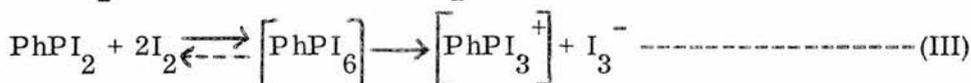
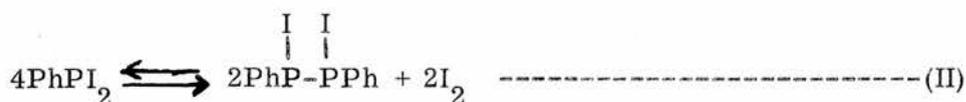
(1.1) Preparation and Stability of Diiodophenylphosphine in Methyl Cyanide

Many attempts to prepare diiodophenylphosphine by the method outlined by Feshchenko et al.^{14, 214}, either in benzene or carbon tetrachloride, resulted in the separation of a yellow solid (m. p. 171°C) of the composition $\text{Ph}_2\text{P}_2\text{I}_2$. However, the preparation of diiodophenylphosphine was successful and reproducible when the reaction between dichlorophenylphosphine (1 mole) and anhydrous lithium iodide (2 moles) was carried out in absence of a solvent (see experimental section). The dark brown-red diiodophenylphosphine (b. p. $(0.7 \text{ mm}) = 136^\circ\text{C}$) was confirmed by analysis, mass spectrum (Table 55), and its infra-red spectrum showed the absence of any oxidation product. In addition, its solution in methyl cyanide was shown (from its ultra-violet spectrum) to contain small amount of triiodide ion ($\lambda_{\text{max}} = 291 \text{ and } 360 \text{ m}\mu$).

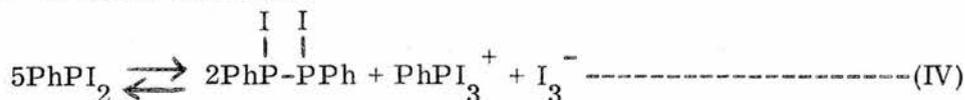
Feshchenko and co-workers^{14, 214} found that under the action of ether diiodophenylphosphine and other aryldiiodophosphines were converted to 1,2-diiododiphenyldiphosphine ($\text{Ph}_2\text{P}_2\text{I}_2$) and 1,2-diaryldiiodophosphine ($\text{Ar}_2\text{P}_2\text{I}_2$). These authors also reported the formation of ArPI_4 from the reaction of iodine with $\text{Ar}_2\text{P}_2\text{I}_2$ in non-polar solvents.



Moreover, they have shown that reaction (I) has an equilibrium character. By analogy with this therefore, the formation of triiodide ion in methyl cyanide solution of diiododiphenylphosphine could be explained by the following equilibria :



the sum of II and III being :



For the purpose of working out the extinction coefficient of the triiodide ion (peak at 292 m μ) in this solution if it is assumed that reaction (IV) is complete then c_m , the molar concentration of triiodide ion, equals one fifth of the molar concentration of the starting material (PhPI_2).

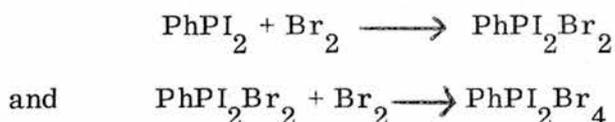
Calculation of the molar extinction coefficient on this basis gives the value 19,900 l mol⁻¹ cm⁻¹ which is considerably less than the reported value (57,680 for $\lambda_{\text{max}} = 292$)²⁰⁸. Obviously therefore reaction (IV) is not complete but is in fact an equilibrium which lies to the left hand side.

Further evidence for the above equilibrium (IV) comes from the isolation of a yellow solid of composition $\text{Ph}_2\text{P}_2\text{I}_2$ obtained on standing from a concentrated solution of diiododiphenylphosphine in methyl cyanide. Its melting point, analysis, and mass spectrum were identical to those of 1,2-diiododiphenyldiphosphine prepared by literature method^{14, 214}.

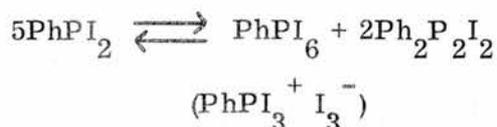
(1.2) The PhPI_2 - Br_2 System

The results of the conductometric titration of bromine versus diiododiphenylphosphine in methyl cyanide are given in Table 37, and

illustrated graphically in Figure 17, plot 1. The graph obtained from this titration shows two sharp breaks at approximately 1:1 and 2:1 mole ratios of Br_2 : PhPI_2 . This suggests that the system is simple and that the reaction of bromine with diiodophenylphosphine occurs in two distinct stages; these are :



Further support for this straight forward interpretation comes from the isolation of two adducts of stoichiometry PhPI_2Br_2 and PhPI_2Br_4 at 1:1 and 2:1 ratios of Br_2 : PhPI_2 respectively. However examination of ultraviolet spectra of solutions at different stages during titration (Table 38) showed that this system behaves in a way much more complicated than that outlined above. It is worthwhile noting that before addition of bromine triiodide ion was present in the red solution of diiodophenylphosphine in methyl cyanide. As was found in the previous section, (from quantitative u. v. spectrum of PhPI_2 solution), the presence of this trihalide ion, I_3^- , is accounted for by the equilibrium :



From the data in Table 38, it is clear that the triiodide ion is the predominant trihalide ion present till near the 1:1 mole ratio (Br_2 : PhPI_2) at which point the trihalide ion in solution was IBr_2^- . It is therefore suggested that bromine had reacted with the dissociation products of diiodophenylphosphine, and that four equilibria are present between the 0:1 and ca. 1:1 mol ratios.

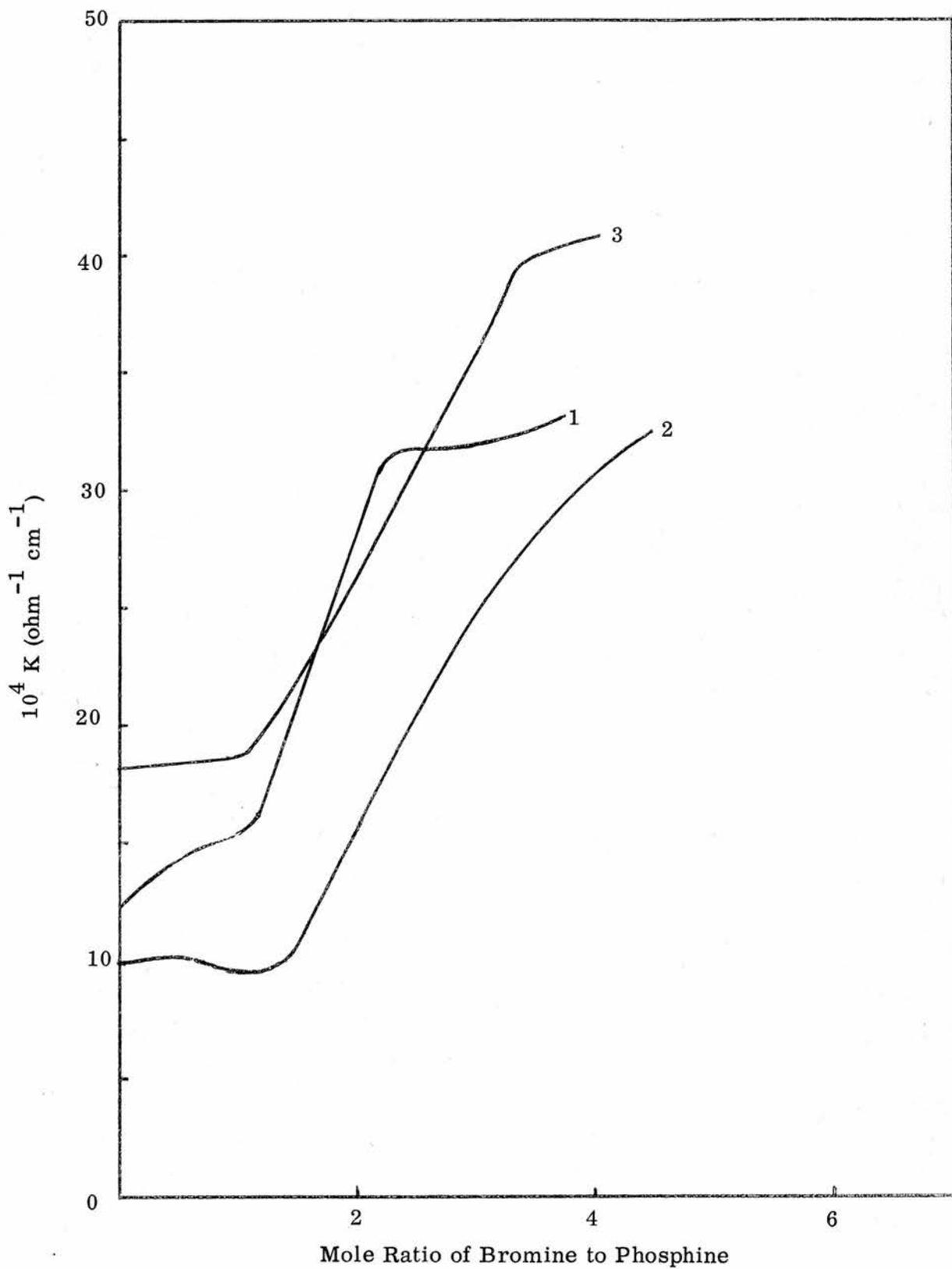
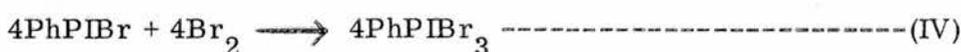
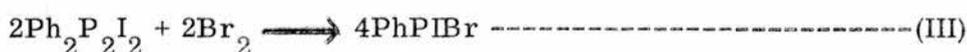
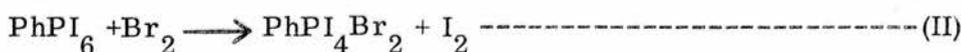
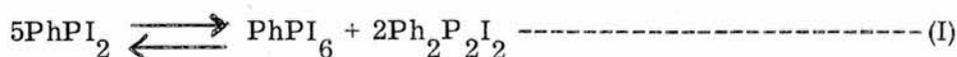


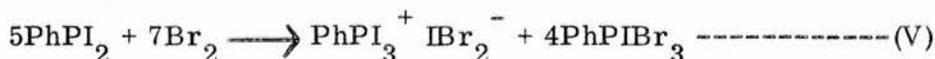
Figure 17. Conductometric Titration of the Systems $\text{Ph}_n\text{PI}_{3-n} - \text{Br}_2$ ($n = 2, 1, 0$)
in Methyl Cyanide

Plot 1. $\text{Br}_2 - \text{PhPI}_2$ Plot 2. $\text{Br}_2 - \text{Ph}_2\text{PI}$

Plot 3. $\text{Br}_2 - \text{PI}_3$



The sum of reactions : I, II, III, and IV being



Thus, a break in conductometric - composition graph is expected just after the 1:1 ratio (ca. 1.4:1). At this stage, it is clear from reaction (V) that the amount of highly conducting $\text{PX}_7(\text{PX}_4^+ \text{X}_3^-)$ - type compound is small, hence a relatively small increase in specific conductance between 0:1 and 1:1 ratios would be expected, and this is what is observed.

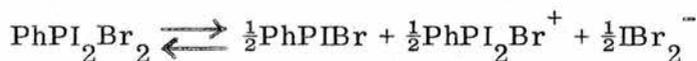
Beyond the 1:1 mole ratio (Br_2 : PhPI_2) the conductance increased sharply until the region ca. 2:1 after which it tailed-off (nearly at 2.3:1). The colour of the solution at this point was orange and the ions present in methyl cyanide solution was IBr_2^- , (see Table 38). It seems therefore reasonable to suggest that the increase in conductance arises from the reaction of bromine with the PX_5^- type compound PhPIBr_3 to give a highly conducting $\text{PX}_7(\text{PX}_4^+ \text{X}_3^-)$ - type compound.



This brings the mole ratio of the reaction up to 2.2:1 (i. e. at the 2.2:1 ratio: 4 moles of $\text{PhPBr}_3^+ \text{IBr}_2^-$ and one mole of $\text{PhPI}_3^+ \text{IBr}_2^-$ are formed from the interaction of 11 moles of Br_2 with 5 moles of PhPI_2). These equilibria fit ultra-violet spectrum and conductometric titration results reasonably well. However although solids of the PX_5

and PX_7 types (1:1 and 2:1) were isolated, the proportion of bromine and iodine in them differs from that postulated for reactions occurring in solution.

Examination of the ultra-violet spectrum of the methyl cyanide solution of $PhPI_2Br_2$ and $PhPI_2Br_4$ showed the present of IBr_2^- only in both cases ($\lambda_{max} = 257 \text{ m}\mu$). Thus, the existence of the following modes of ionisation in solution are indicated,



The adducts therefore did not reflect the stoichiometries suggested by the conductometric titration study. This is not unexpected, since the system under discussion is obviously a very complex one involving many equilibria and extensive reorganisations of halogens attached to the phosphorus atom. Parallel behaviour in other systems is not unknown, for example, although PBr_3-Cl_2 system gave a 1:1 break in liquid hydrogen chloride, the adduct isolated at this ratio was PCl_5 and not PBr_3Cl_2 ¹⁹⁶.

It is clear that in such a complicated system as the $PhPI_2-Br_2$ one a study of the variation of a physical property (e.g. conductometric titration) with mole ratio of the constituents can not give much detailed information about the system.

(1.3) The $PhPI_2-I_2$ System

In contrast to the Br_2-PhPI_2 system, the conductometric titration of iodine against diiodophenylphosphine gave no clear break at the 1:1 mole ratio of $I_2: PhPI_2$. The graph depicted in Figure 18, plot 1, was obtained from the results tabulated in Table 39. To verify this result and confirm

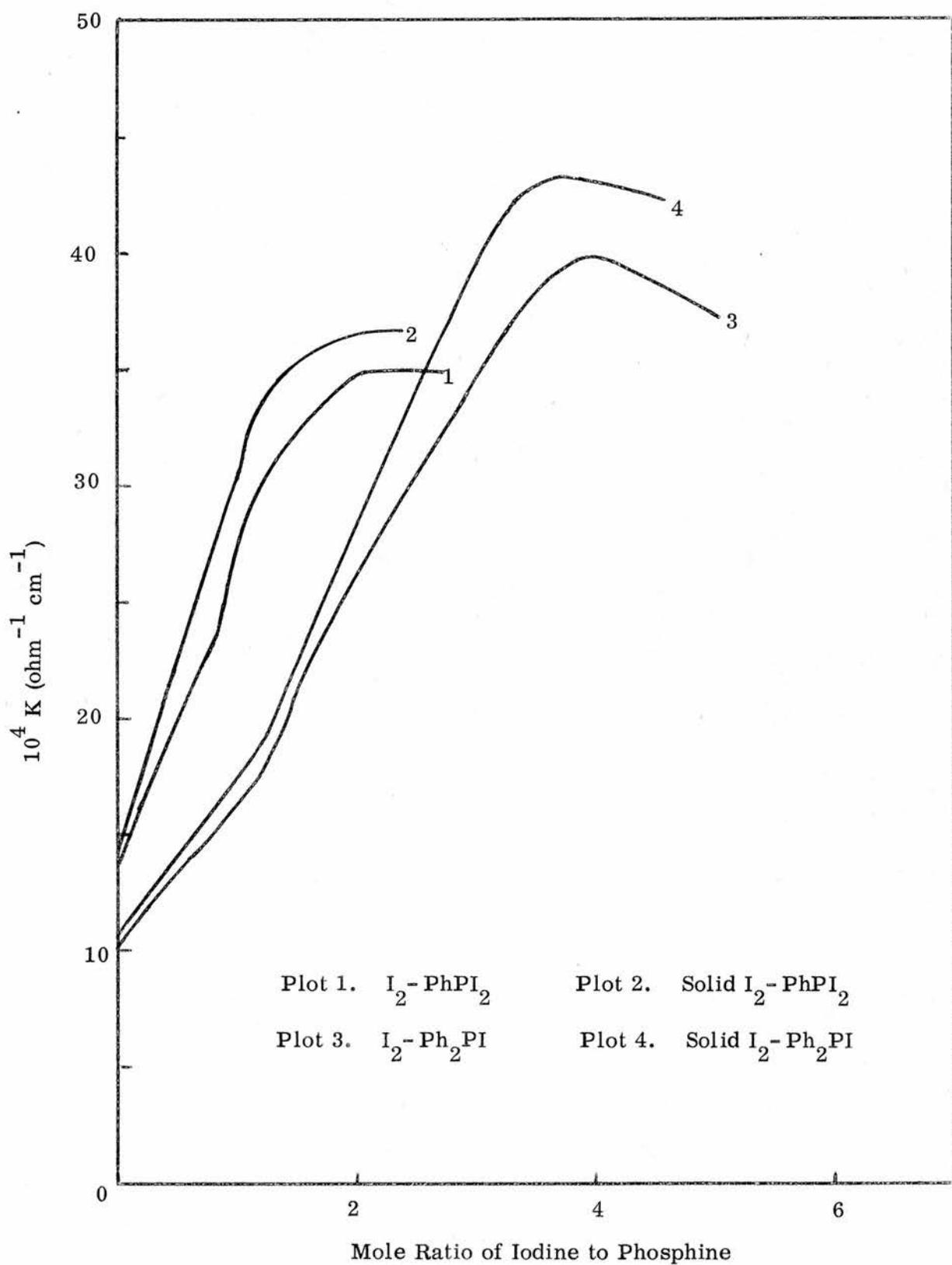


Figure 18. Conductometric Titration of the Systems $I_2 - Ph_n PI_{3-n}$ ($n = 2, 1$) in Methyl Cyanide

the position of the breaks in the graph, another titration was carried out using direct (solvent free) addition of solid iodine to the phosphine solution in methyl cyanide. The graph of this titration is also displayed in Figure 18, plot 2, and the results set out in Table 40.

As can be seen from the graph, good reproducibility was obtained. The conductance increased steeply at first, but in the later stages of this titration rose less rapidly giving a rounded appearance to the graph with levelling-off at the 2:1 ratio. The originally yellow solution changed to red from the start of titration and progressively darkened on further additions of iodine. This change in colour is characteristic of triiodide ion formation, and indeed ultra-violet spectrum of solution prepared at different mole ratios of I_2 : $PhPI_2$ confirmed this fact after the ca. 0.5:1 mole ratio (see Table 38).

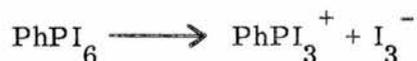
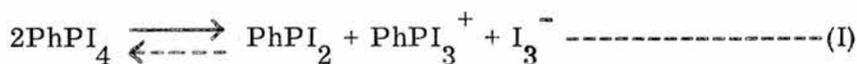
Table 38: Solution Spectra of the System $\text{PhPI}_2 - \text{Hal}_2$

System	Mole Ratio ($\text{Hal}_2 : \text{PhPI}_2$)	u. v. maxima ($m\mu$)	u. v. Indicates
$\text{Br}_2 - \text{PhPI}_2$	0.40:1	291, 361	I_3^- is present
	0.95:1	260	IBr_2^-
	1.60:1	258	IBr_2^-
	1.99:1	257	IBr_2^-
$\text{I}_2 - \text{PhPI}_2$	0.50:1	292, 362	I_3^-
	0.99:1	291, 361	I_3^-
	1.99:1	291, 361	I_3^-
$\text{IBr} - \text{PhPI}_2$	0.44:1	292, 362	I_3^-
	0.88:1	291, 360	I_3^-
	1.10:1	290, 360	I_3^-
	1.95:1	286, 355	I_2Br^- and I_3^-
	2.95:1	281, 352	I_2Br^- only
	4.40:1	260	IBr_2^- with traces of I_2Br^-

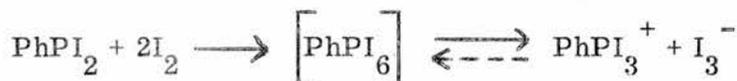
Two solid compounds of stoichiometry PhPI_4 and PhPI_6 were isolated from both petroleum ether (40-60°C) and benzene solutions containing the phosphine and iodine in the appropriate mole ratios. The adduct PhPI_4 has been reported previously by Feshchenko and his co-workers^{14, 214}.

Ultra-violet examination of these adducts in methyl cyanide indicated the presence of triiodide ion ($\lambda_m = 291$ and $361 m\mu$). From this and the high molar conductance values of PhPI_4 and PhPI_6 at 0.01M

(see later) the following modes of ionisation in methyl cyanide are suggested.



Thus, on account of the disproportionation of the 1:1 adduct, PhPI_4 , in methyl cyanide the absence of a 1:1 break in the conductometric titration graph is not unexpected. Disproportionation of 1:1 iodine adducts of phosphines and arsines in dilute methyl cyanide solution has been found in other systems. This means that the same ions are formed in solution from the start of the reaction through the 1:1 ratio and right up to the 2:1 ratio. A break at the 1:1 ratio would not then be expected. Therefore a reasonable explanation for the reaction took place during conductometric titration is



The respective molar conductance values for both titrations at this ratio were :

(a) Iodine added in methyl cyanide solution

$$\Lambda_m = 260.18 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, c_m = 0.013260 \text{ mol l}^{-1}$$

(b) Iodine added as solid

$$\Lambda_m = 191.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, c_m = 0.018975 \text{ mol l}^{-1}$$

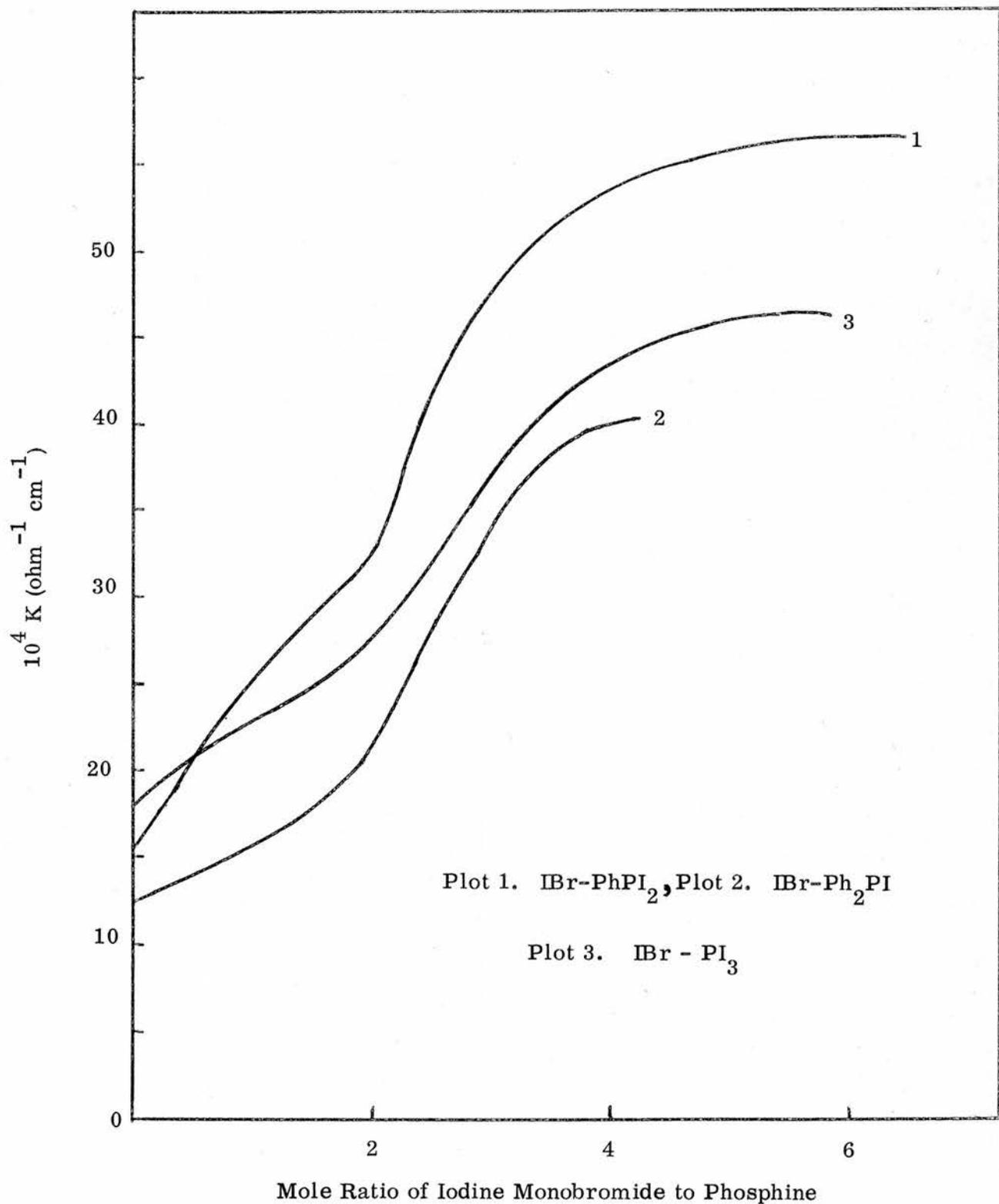
These values indicate that the 2:1 adduct is a very strong electrolyte in methyl cyanide.

(1.4) The PhPI_2 - IBr System

The conductometric titration of diiodophenylphosphine with iodine monobromide in methyl cyanide differs from that of the bromine and iodine (discussed previously). The graph in Figure 19, plot 1, which is obtained

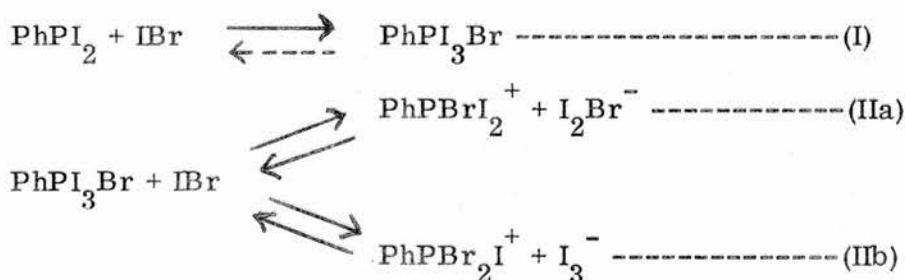
Figure 19. Conductometric Titration of the Systems $\text{Ph}_n\text{PI}_{3-n} - \text{IBr}(n=2,1,0)$

in Methyl Cyanide



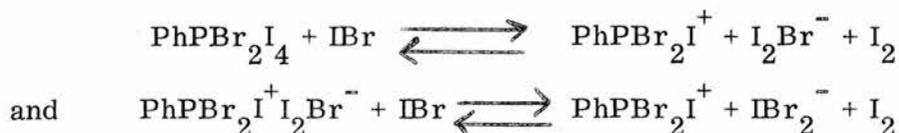
from the results assembled in Table 41, is rather similar to those of the $\text{PhPBr}_2 - \text{IBr}$ and $\text{Ph}_2\text{PBr} - \text{IBr}$ systems. The conductance which increased sharply up to the region of the 2:1 mole ratio ($\text{IBr}:\text{PhPI}_2$) increased even more steeply until the 3:1 ratio whereafter it gradually tailed-off giving a rather obtuse break. The pale yellow solution turned orange on the first addition of IBr , and it progressively darkened on further additions of titrant. As was expected from the colour change, the ultra-violet spectrum of methyl cyanide solutions of the reactants in different mole ratios, showed the present of polyhalide ions. The results laid out in Table 38 demonstrate the domination of triiodide ion up to the 1.1:1 ratio ($\text{IBr} : \text{PhPI}_2$), the presence of a mixture of I_2Br^- and I_3^- at ca. 2:1, and the IBr_2^- ion at higher mole ratios.

From this and the form of the graph (c. f. $\text{PhPBr}_2 - \text{IBr}$ and $\text{Ph}_2\text{PBr} - \text{IBr}$ systems) seems reasonable to suggest that in this system, the following overlapping equilibria are present.



The formation of triiodide ion in the titration from the start could be accounted for by the presence of equilibrium (IIb).

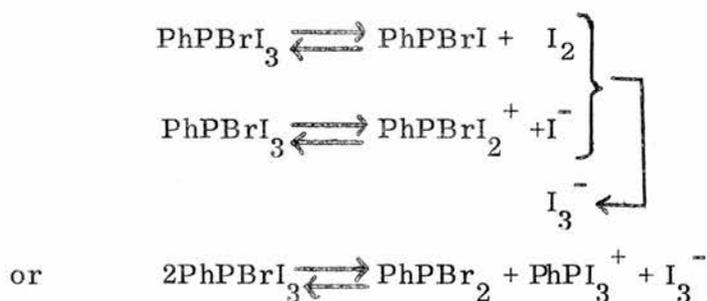
The ultra-violet spectrum, showing I_2Br^- after the 2:1 ratio (ca. 2.95 : 1) and a mixture of I_2Br^- and IBr_2^- (I_2Br^- in traces) at higher mole ratio (ca. 4.4:1), suggests the existence of further two equilibria :



With the presence of these overlapping equilibria in this system, sharp breaks in the conductometric titration graph would not be expected and in fact none were observed. The blunt breaks near the 2:1 and 4:1 ratios are not meaningful guides to the stoichiometry of the reaction(s).

Two dark-red semi-solids of the formula PhPBrI_3 and PhPBr_2I_4 were isolated from solutions containing 1:1 and 2:1 mole ratios of $\text{IBr} : \text{PhPI}_2$ respectively. In the former case the solvent was methyl cyanide and in the latter case petroleum-ether (40-60°C). The ultra-violet spectra of these two substances in methyl cyanide, were similar and indicated the presence of the triiodide ion. The 2:1 adduct, PhPBr_2I_4 , is represented by the right-hand side of equilibrium (IIb), i. e.

$\text{PhPBr}_2\text{I}_4 \longrightarrow \text{PhPBr}_2\text{I}^+ + \text{I}_3^-$. The fact that the compound PhPBrI_3 (which is also produced in $\text{PhPI}_2 - \text{Br}_2$ system) produces the triiodide ion in methyl cyanide is in accord with the solution spectra carried out during titration (c.f. 0.88:1 and 1.1:1 in Table 38). This behaviour could be explained by the following equations :



The molar extinction coefficient value of $27,230 \text{ l mol}^{-1} \text{ cm}^{-1}$ (c_m used = c_m of PhPBrI_3) obtained from quantitative analysis of the ultra-violet spectrum of PhPBrI_3 (which is nearly half of the reported value 57,680)²⁰⁸ in methyl cyanide, lend support to this postulation.

(2) The Reaction of Diphenylidophosphine with Halogens(2.1) The $\text{Ph}_2\text{PI} - \text{Br}_2$ System

The general form of the conductance - composition graph for this system is rather similar to those obtained from the systems $\text{PhPBr}_2 - \text{Br}_2$ and $\text{Ph}_2\text{PBr} - \text{Br}_2$. The graph is displayed in Figure 17, plot 2 from data listed in Table 42. The conductance decreased very slightly until the 1:1 ratio and after this point it increased very steeply up to the 3:1 ratio after which the conductance gradually tailed-off. The colour changes in solution (pale yellow \rightarrow red \rightarrow orange) were shown by ultra-violet spectroscopy to be due to variation in the type of polyhalide ion present. The results of this investigation are assembled in Table 43, below.

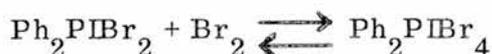
Table 43. Solution Spectra of the System $\text{Ph}_2\text{PI} - \text{Br}_2$

Mole ratio $\text{Br}_2 : \text{Ph}_2\text{PI}$	Colour of the Solution	u. v. maxima ($m\mu$)	u. v. Indicates
1.13:1	red	278, 352	I_2Br^- with slight traces of I_3^- and IBr_2
1.51:1	pale-red	262	IBr_2^- with traces of I_2Br^-
1.70:1	orange	257	IBr_2^- ion only
1.89:1	pale orange	257	IBr_2^- ion only
2.27:1	very pale orange	257	IBr_2^- ion only

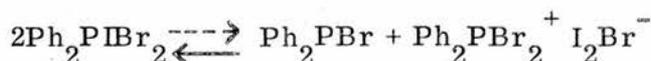
From the graph, the break at the 1:1 ratio ($\text{Br}_2 : \text{Ph}_2\text{PI}$) indicates the formation of the 1:1 adduct in methyl cyanide, thus :



Conductance behaviour after the 1:1 ratio is in keeping with the formation of PX_7^- type compound in an equilibrium reaction, thus



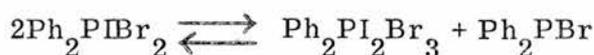
Present of polyhalide ion (I_2Br^-) in solution at the 1:1 ratio suggests the disproportionation of the 1:1 adduct



Also, the ultra-violet spectrum of solution at 2:1 ratio indicates IBr_2^- which arise from the expected mode of ionisation of the 2:1 adduct.

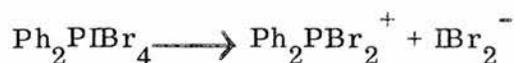


Attempts were made to isolate the 1:1 and 2:1 adducts from methyl cyanide and other solvents. These attempts failed in the case of the 1:1 adduct. A solid was obtained from equimolar mixture of diphenyl-iodophosphine and bromine in petroleum-ether (40-60°C) but this had the composition of a 2:1 adduct, namely $Ph_2PI_2Br_3$. It should be noted that an adduct of this composition has been isolated in other systems ($Ph_2PBr - IBr$ and $Ph_2PI - IBr$), thus it must be regarded as a compound whose formation as a solid is favoured in these mixed halogen systems. By analogy with the systems $Ph_2PBr - IBr$ and $Ph_2PI - IBr$ (in which identical unexpected adducts were isolated), $Ph_2PI_2Br_3$ could arise from the presence of various types of molecular dissociations in the non-polar solvents, a process which may be summarised as :



The adduct Ph_2PIBr_4 was isolated as an orange solid (m. p. 83-85 °C) from the interaction of bromine (2 moles) with diphenyl-iodophosphine (1 mole) in petroleum-ether (40-60°C). Its ultra-violet spectrum in methyl cyanide which showed the presence of IBr_2^- ion

($\lambda_{\text{max}} = 257 \text{ m}\mu$), demonstrates that the ionisation mode of PhPIBr_4 in methyl cyanide is :



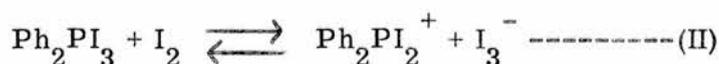
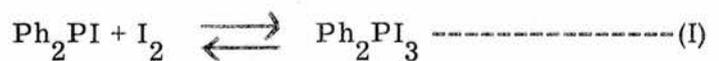
(2.2) The $\text{Ph}_2\text{PI} - \text{I}_2$ System

The conductometric titration of this system in methyl cyanide gave the results recorded in Table 44 and graph illustrated in Figure 18 plot 3. The conductance which rises smoothly with increasing mole ratio attains a maximum value near the 4:1 ratio of I_2 : Ph_2PI and thereafter it decreases (presumably due to lack of further ion formation in the solution of increasing volume). The graph shows no clear cut breaks (at 1:1 and 2:1 mole ratio) which might indicate the stoichiometry of the reaction occurring in methyl cyanide solution. As in previous systems, the colour of the solution was shown by ultra-violet spectroscopy to be caused by polyhalide ion formation ; triiodide ions were present from the start (see Table 45). The conductometric titration of this system was repeated using solid iodine as titrant to ensure that the breaks were not obscured by dilution effect. The graph obtained in Figure 18 plot 4 (relevant data in Table 46), was very similar to the previous one (curve 3), and once again showed no well defined breaks.

Table 45. Solution Spectra of the $\text{Ph}_2\text{PI} - \text{Hal}_2$ System

System	Mole Ratio $\text{Hal}_2 : \text{Ph}_2\text{PI}$	u. v. maxima $m\mu$	u. v. Indicates
$\text{I}_2 - \text{Ph}_2\text{PI}$	0.24:1	292, 362	I_3^- present
	0.73:1	292, 360	I_3^- present
	1.21:1	291, 360	I_3^- present
	2.18:1	291, 360	I_3^- present
$\text{IBr} - \text{Ph}_2\text{PI}$	0.52:1	290, 360	I_3^- only
	1.03:1	288, 357	I_3^- + traces of I_2Br^-
	1.55:1	286, 356	mixture of I_3^- and I_2Br^-
	2.06:1	284, 354	I_2Br^- + traces of I_3^-
	2.86:1	281, 351	I_2Br^- only

From the above observations, it seems that this system shows a parallel behaviour to the $\text{PhPBr}_2 - \text{I}_2$ and $\text{Ph}_2\text{PBr} - \text{I}_2$ systems. This similarity therefore, implies the presence of the following equilibria in the $\text{Ph}_2\text{PI} - \text{I}_2$ system.



The formation of triiodide ion from the start of titration is accounted for by the presence of equilibrium (II), and the equilibria do not lie well to the right-hand side until excess of iodine is added to the solution.

Attempts to prepare Ph_2PI_3 from equimolar mixtures of iodine

and diphenyliodophosphine (Ph_2PI) resulted in the separation of an impure Ph_2PI_5 . Surprisingly however a red solid of composition Ph_2PI_3 was isolated from the systems $\text{Br}_2 - \text{Ph}_2\text{PI}$ and $\text{ICN} - \text{Ph}_2\text{PI}$ (see experimental section).

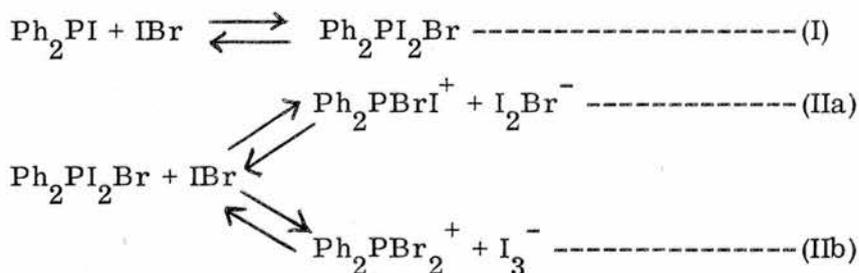
Two solids both crimson-red and of melting point $130-132^\circ\text{C}$ were precipitated from the reaction between iodine and diphenyliodophosphine when the mole ratios were 2:1 and 3:1. The two solids were shown, by analysis, to be identical and to have the formula Ph_2PI_5 . The mass spectrum of this compound was very similar to that of Ph_2PI_3 (see later).

(2.3) The $\text{Ph}_2\text{PI} - \text{IBr}$ System

As can be seen from Figure 19, plot 2, the conductance composition graph for the system $\text{Ph}_2\text{PI} - \text{IBr}$ is very similar in shape to that of the $\text{PhPI}_2 - \text{IBr}$ system. The relevant data are listed in Table 47. The conductance increased gradually up to the ca. 2:1 mole ratio ($\text{IBr} : \text{Ph}_2\text{PI}$) at which point the slope becomes slightly more steep until near the region of the 3:1 ratio after which it slowly tailed-off. The solution which was pale red from the start of titration darkened progressively on further additions of iodine monobromide. Examination of the ultra-violet spectrum of the solution at different stages during the conductometric titration gave maxima which showed that the nature of the trihalide ion present varied as the titration proceeded. The results demonstrate the presence of triiodide ion at first followed by a mixture of triiodide and I_2Br^- , then I_2Br^- ions at the final stages (see Table 45).

From this and the shape of the graph (which in fact does not show clear cut breaks), the way in which this system behaves falls in line with

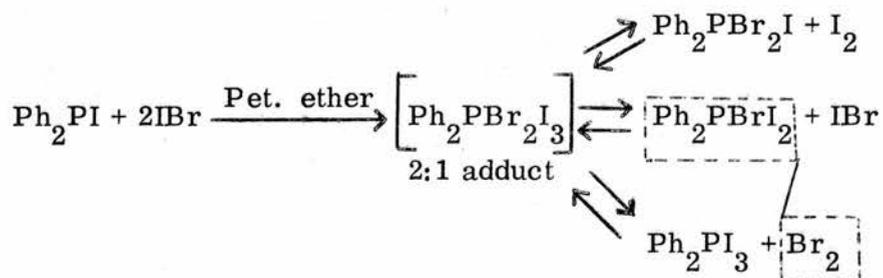
several other systems studied (namely, the $\text{PhPBr}_2 - \text{IBr}$, $\text{Ph}_2\text{PBr} - \text{IBr}$ and $\text{PhPI}_2 - \text{IBr}$ systems). This parallel behaviour implies the existence of overlapping equilibria in this system also. The reaction occurring can therefore be represented by the following equilibria :



The presence of triiodide ion at 0.52:1 mole ratio of $\text{IBr} : \text{Ph}_2\text{PI}$ is accounted for by the equilibrium (IIb), and the detection of a mixture of I_2Br^- and triiodide ions at higher mole ratios (see Table 45) by the presence of both IIa and IIb. That an equilibrium as represented by IIa or IIb is present in this system from the beginning of the titration is substantiated by the isolation of the adduct, $\text{Ph}_2\text{PBr}_2\text{I}_3$. This 2:1 adduct was isolated as a dark-red coloured oil from methyl cyanide solutions which contained either a 1:1 or 2:1 mixture of $\text{IBr} : \text{Ph}_2\text{PI}$. The ultra-violet spectrum of the adduct in methyl cyanide showed (λ_{max} 292 and 361 μ), the characteristic absorption maxima of triiodide ion. That is, the right-hand side of equation IIb represents the ions produced by $\text{Ph}_2\text{PBr}_2\text{I}_3$.

As was found in the $\text{Ph}_2\text{PBr} - \text{IBr}$ system, an adduct of the unexpected composition was isolated. This compound which had the formula $\text{Ph}_2\text{PBr}_3\text{I}_2$ separated as a red-brown solid (m. p. $98-99^\circ\text{C}$), when iodine monobromide and diphenyliodophosphine (2:1 ratio) were mixed in petroleum-ether ($40-60^\circ\text{C}$). By analogy with the $\text{Ph}_2\text{PBr} - \text{IBr}$ system, therefore, the 2:1 adduct, $\text{Ph}_2\text{PBr}_2\text{I}_3$, which is presumably formed first, may undergo various forms of molecular dissociation in the non-polar

solvent as follows



The solid obtained, $\text{Ph}_2\text{PBr}_3\text{I}_2$, can be regarded as having formed according to the equation :



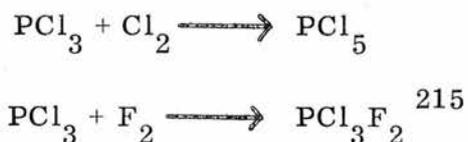
from molecular dissociation products of the original 2:1 adduct. On dissolving the adduct $\text{Ph}_2\text{PBr}_3\text{I}_2$ in methyl cyanide it produces I_2Br^- ions, thus



It should be noted that these two adducts, $\text{Ph}_2\text{PBr}_3\text{I}_2$ and $\text{Ph}_2\text{PBr}_2\text{I}_3$, were also isolated as solids from the $\text{Ph}_2\text{PBr} - \text{IBr}$ system.

(3) The Reaction of Phosphorus Triiodide with Halogens

It is well known that when a mole of halogen is added to phosphorus trihalides, pentahalide derivatives of phosphorus are formed. In this way the simple and mixed pentahalides of phosphorus are readily obtained -



A notable exception to this rule is the addition of halogens to phosphorus triiodide which does not add a mole of iodine to give phosphorus penta-iodide. So far this compound, PI_5 , has not been prepared.

The other simple pentahalides being well known, the absence of the penta-iodide, PI_5 , was thought to be due to steric factors preventing formation of a stable molecule. However, models of this hypothetical adduct, based on the trigonal bipyramidal structure, showed that overcrowding round the phosphorus atom is unlikely to affect its formation¹¹. Therefore, it has been suggested that incompatibility of the 3d orbitals of phosphorus with the 7s, 7p and 7d orbitals of iodine is responsible for the non-existence of the phosphorus penta-iodide molecule. It is conceivable, however, that phosphorus penta-iodide might exist in the ionic form $\text{PI}_4^+ \text{I}^-$ since this would result in less crowding around phosphorus atom. By analogy with reported tetra-iodide compounds, for example SI_4 , which is isoelectronic with PI_4^+ and is relatively stable, the existence of the tetra-iodophosphonium ion might be expected in certain compounds. In this respect, Payne^{11a} stated that "Although the lack of knowledge of phosphorus (V) iodide suggests that its 'stability' is low, it may be that in suitable solvents a solvated form either of PI_5

or more likely of PI_4^+ , might occur". To examine this comment, it was of interest to carry out a conductance study of the $\text{PI}_3\text{-I}_2$ system in methyl cyanide. Methyl cyanide being a polar solvent of high dielectric constant, and also a good donor, it was thought that the PI_4^+ ion if it can exist might be stabilised under these circumstances. Thus if the species $\text{PI}_4^+ \text{I}^-$ is possible it should be detectable by carrying out a conductometric titration of phosphorus triiodide with iodine



(3.1) The Stability of Phosphorus Triiodide in Methyl Cyanide

Phosphorus triiodide was prepared by a method described in the literature²¹⁶. The compound is a dark red crystalline solid (m.p. 61 °C). A solution of phosphorus triiodide in methyl cyanide was shown by ultra-violet spectroscopy to contain triiodide ions, and on standing, yellow-orange crystals (m.p. 125-126 °C) were deposited. This latter solid was shown by analysis to be diphosphorus tetraiodide. This presumably arises from the presence of the equilibrium :



The same conversion is reported to occur in ether¹³, and diiodophenylphosphine in ether behaves in an analogous way yielding the diphosphine derivative, $\text{Ph}_2\text{P}_2\text{I}_2$ ^{14, 214}.

The presence of triiodide ions in the methyl cyanide solutions of phosphorus triiodide would seem to demand the presence of a second equilibrium,



The phosphorus pentaiodide appearing on the right-hand side of this equilibrium will react with the iodine from the first equilibrium giving triiodide ions



Solutions of phosphorus triiodide in methyl cyanide therefore are not simple.

(3.2) The $\text{PI}_3 - \text{I}_2$ System

The reaction between iodine and phosphorus triiodide was studied by conductometric titration in methyl cyanide. Two titrations were carried out. In one of these, portions of solid iodine were added directly to phosphorus triiodide in methyl cyanide whereas in the other the phosphorus triiodide was titrated with a methyl cyanide solution of iodine. The results of the two titrations are recorded in Table 48 and 49 and depicted graphically in Figures 20 and 21 respectively. It can be seen that the graphs of these titrations are closely similar. At the start of titration the phosphorus triiodide solution was cloudy because of the relative insolubility of the compound in methyl cyanide. As the titration proceeded the cloudiness disappeared and around the 1:1 ratio the solution was perfectly clear and was coloured dark red. On further addition of the titrant the solution darkened progressively. The colour of the solution was shown by ultra-violet study (Table 50) to be caused by the formation of triiodide ions in methyl cyanide.

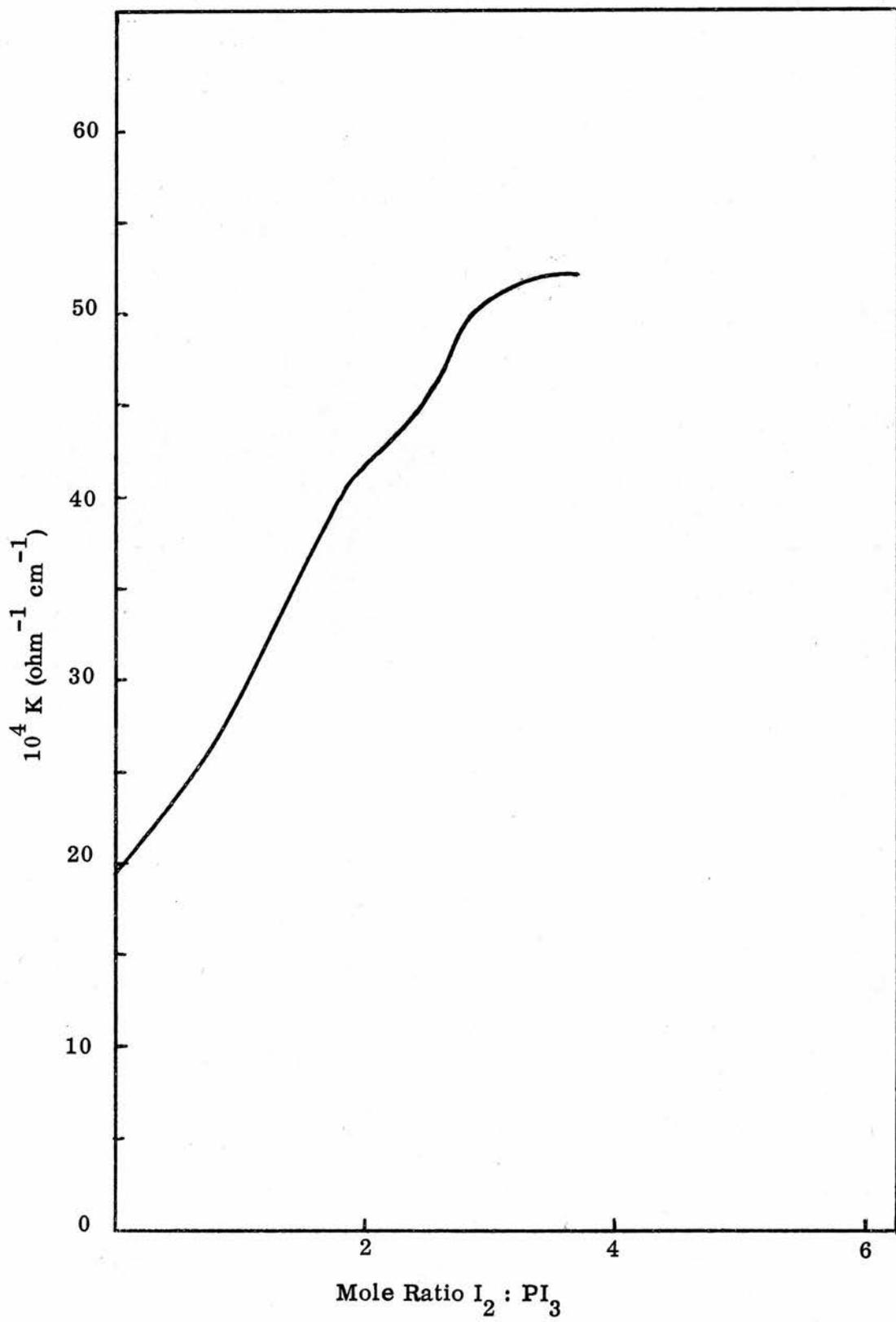


Figure 20. Conductometric Titration of the System solid $\text{I}_2 - \text{PI}_3$ in Methyl Cyanide

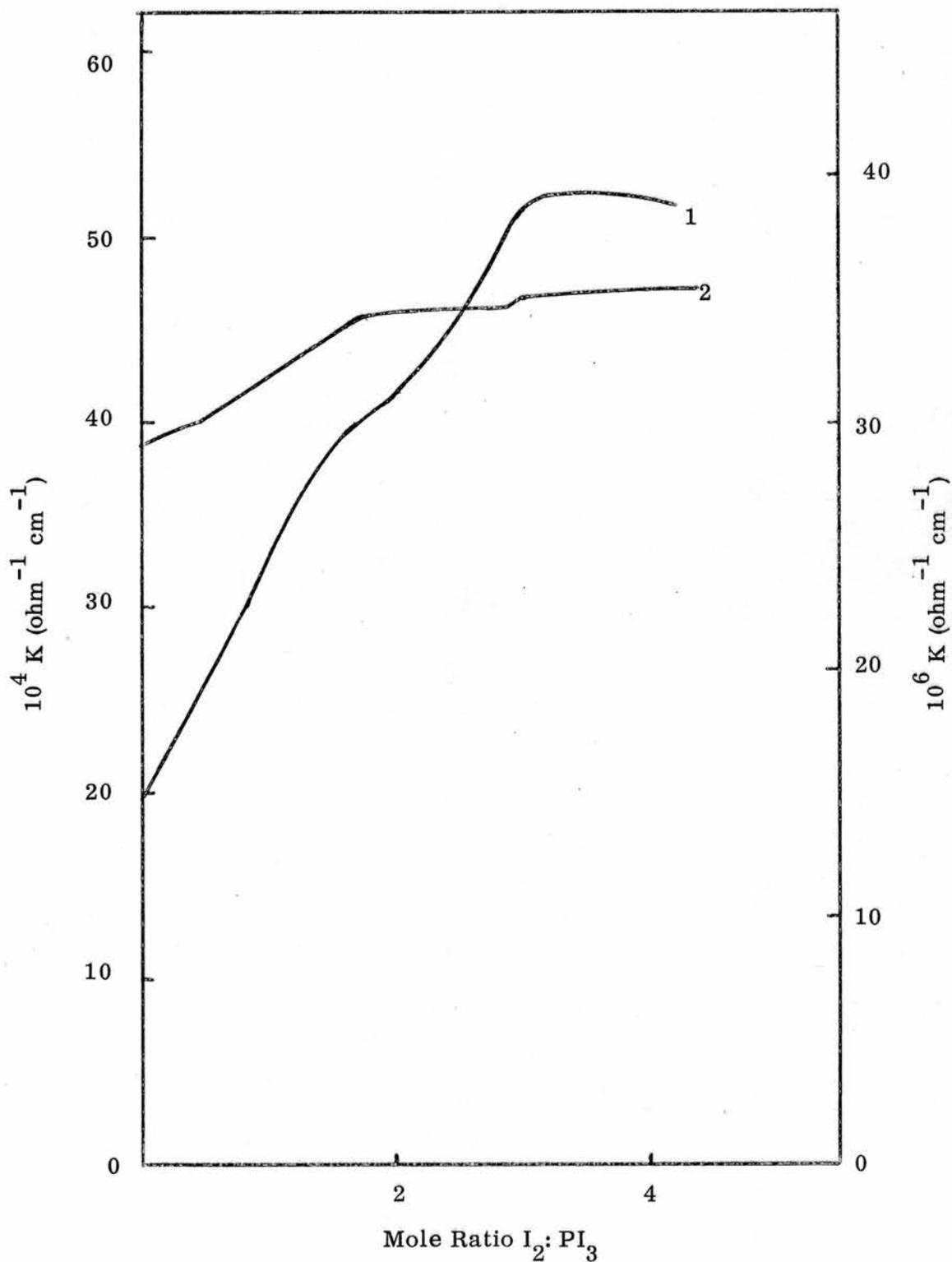


Figure 21. Conductometric Titration of the System I₂-PI₃.

Plot 1. I₂-PI₃ in methyl cyanide

Plot 2. I₂-PI₃ in nitrobenzene,

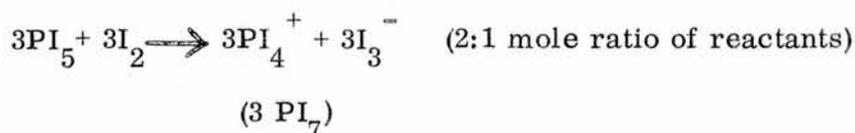
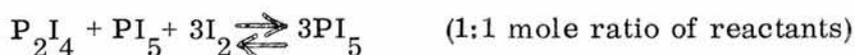
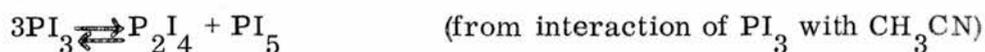
(conductance scale on the right-hand side).

Table 50. Solution Spectra of the PI_3 - Hal_2 System

System	Mole Ratio $\text{Hal}_2 : \text{PI}_3$	u. v. maxima $m\mu$	u. v. Indicates
I_2 - PI_3	0.00:1	290,360	I_3^-
	0.57:1	290,360	I_3^-
	1.52:1	290,360	I_3^-
IBr - PI_3	0.56:1	272	mixture of I_2Br^- (mainly), IBr_2^- and I_3^- (traces)
	1.12:1	257	IBr_2^- only
	1.68:1	256	IBr_2^- only
	2.24:1	256	IBr_2^- only
Br_2 - PI_3	0.53:1	257	IBr_2^-
	1.06:1	257	IBr_2^-
	1.59:1	257	IBr_2^-
	2.12:1	257	IBr_2^-

The form of the graph (a steep rise in conductance up to the region 3:1 and thereafter tailing off), suggests that the interaction of phosphorus triiodide with iodine is an ion-forming reaction of a type involving one or more equilibria. The absence of any well defined break and the production of triiodide ions, even before the start, therefore suggest the presence of several equilibria in methyl cyanide from the beginning of the titration.

It is suggested that these may be the following :



To obtain further support for the existence of the ionic PI_4^+ containing species in solution a further conductometric titration of the system $\text{PI}_3\text{-I}_2$ was carried out, this time using nitrobenzene as solvent. The graph of this titration is illustrated in Figure 21 (relevant data in Table 51). It shows a break at the 2:1 mole ratio of $\text{I}_2:\text{PI}_3$ indicating the formation of the species of the stoichiometry PI_7 (i. e. $\text{PI}_4^+\text{I}_3^-$) in solution. It should be noted that in contrast to the behaviour of the $\text{PI}_3\text{-I}_2$ system in methyl cyanide the 2:1 adduct has a rather low molar conductance in nitrobenzene ($\Lambda_m = 3.39 \text{ ohm}^{-1} \text{ cm}^2 \text{ l}^{-1}$; $c_m = 0.0010031 \text{ mol l}^{-1}$). This is presumably due to the greater viscosity of the solvent.

These experiments point to the existence of ionic addition compounds formed from the reaction between iodine and phosphorus triiodide in solvents of high dielectric constant. It would seem likely, from the evidence, that the favoured adduct is the 2:1 compound $\text{PI}_4^+\text{I}_3^-$ although one cannot exclude the possibility of a 1:1 adduct PI_4^+I^- (i. e. pentaiodide) being present in small amounts in solution.

Attempts to prepare the 1:1 and 2:1 iodine adducts of phosphorus triiodide were made in a variety of solvents (methyl cyanide, carbon tetrachloride, petroleum-ether, benzene and carbon disulphide). With

the exception of carbon disulphide, it was not possible to isolate any solid or liquid adducts from these solvents. This failure, could be attributed either to the interaction of phosphorus triiodide with the solvents resulting the equilibrium :



or, to molecular dissociation of the adducts if they form



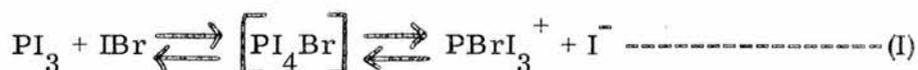
Another factor preventing formation of solids from these solutions could be the presence of excess iodine. Similar difficulties in adduct isolation from the system $\text{PCl}_3 - \text{I}_2$ in liquid hydrogen chloride have been encountered by Salthouse and Waddington¹⁹⁶ who attribute them to the presence of free iodine in the solution.

When carbon disulphide was used as solvent two dark, sticky solids of the same melting point ($37-40^\circ\text{C}$) and analytical composition were isolated. These were obtained at the mole ratios 1:1 and 2:1 (iodine to phosphorus triiodide) respectively. Although the analysis results did suggest that these two substances were phosphorus pentaiodide the compound is clearly very unstable, breaking down, presumably to iodine and phosphorus triiodide. When dissolved in methyl cyanide, the triiodide ion is present which proves that in this solvent decomposition has occurred.

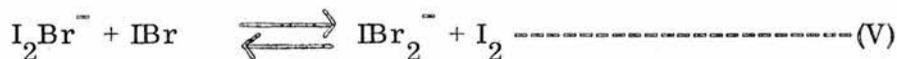
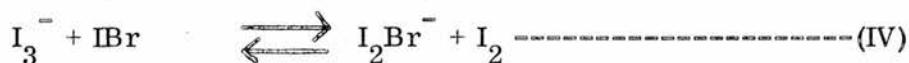
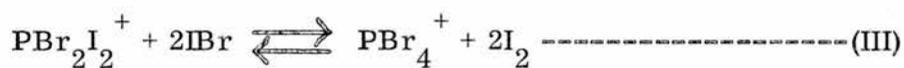


(3.3) The Reaction of Iodine Monobromide with Phosphorus Triiodide

The data and the graph of the conductometric titration of the PI_3 -IBr system are contained in Table 52 and Figure 19 respectively. The graph is obviously of similar form to that obtained from the systems PhPI_2 -IBr and Ph_2PI -IBr and so, the reaction can be expected to be analogous. The conductance increased steadily up to the 2:1 ratio (IBr : PI_3) and then the slope became more steep until the point 3:1 after which it tailed-off gradually giving a rather blunt break round about the 4:1 ratio. The solution which was originally cloudy became clear and red in colour when the 1:1 mole ratio of IBr : PI_3 was attained. The strong colour suggested the presence of polyhalide ion in the solution. This was confirmed by an ultra-violet spectrum study of solutions containing different mole ratios of halogen to phosphorus triiodide. The results of this investigation are contained in Table 50, and these indicate the formation of a mixture of the trihalides, I_3^- , I_2Br^- and IBr_2^- near the beginning of the titration, and only one type of trihalide ion, IBr_2^- , after the 0.56:1 mole ratio (IBr : PI_3). By analogy with the PhPI_2 -IBr and Ph_2PI -IBr systems, the presence of several overlapping equilibria is assumed, thus,



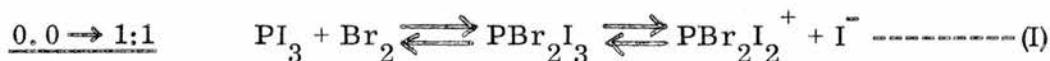
Further addition of iodine monobromide may replace the iodine in the PBr_2I_2^+ ion by bromine and convert the triiodide ion first to I_2Br^- and then to IBr_2^- ,



The presence of the equilibria II, IV and V explains the existence of I_3^- , I_2Br^- and IBr_2^- ions from the start of the titration ($\text{IBr} - \text{PI}_3$ system) in methyl cyanide.

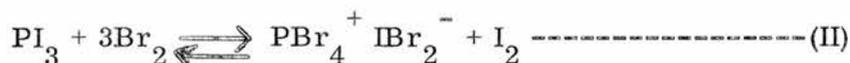
(3.4) The Reaction of Bromine with Phosphorus Triiodide

The conductance - composition graph of the $\text{PI}_3 - \text{Br}_2$ system in methyl cyanide is similar to that of the $\text{PhPBr}_2 - \text{Br}_2$ and $\text{Ph}_2\text{PBr} - \text{Br}_2$ systems. The graph in Figure 17 plot 3 (relevant data in Table 53) showing a discontinuity at the 1:1 ratio ($\text{Br}_2 : \text{PI}_3$) indicates the formation of PI_3Br_2 in solution. During the titration the conductance increased slightly up to the 1:1 ratio and thereafter it rose up sharply until the region of the 3:1 ratio, after which the conductance tailed-off gradually with no clear break. The solution which was originally cloudy and red in colour became clear near the ratio 0.7:1 ($\text{Br}_2 : \text{PI}_3$) and on further additions of bromine the solution became orange in colour presumably due to the formation of IBr_2^- ions. Indeed, this ion was confirmed from the ultra-violet spectrum of the solution (see Table 50). The 1:1 break shown by the conductometric titration graph may indicate the presence of the equilibrium :



However, the ultra-violet spectrum demonstrates the presence of IBr_2^- from the beginning of the titration, thus conflicting with the above postulated scheme (i. e. equilibrium I). From this and the form of

conductance - composition graph (i. e. levelling-off just after the 3:1 ratio) it is believed that the reaction between bromine and phosphorus triiodide in methyl cyanide proceeds via formation of PBr_6I , that is,



The inflexion at the 1:1 ratio does not therefore appear to have any significance concerning the stoichiometry of the reaction occurring, it may be due to the fact that phosphorus triiodide is not completely soluble in methyl cyanide but dissolves gradually in addition of halogen and solution is complete just before the 1:1 ratio ($\text{Br}_2:\text{PI}_3$).

In support of the equilibrium (II) is the fact that the phosphorus bromide iodide, PBr_6I , is known to exist and is reported to have the ionic structure $\text{PBr}_4^+ \text{IBr}_2^-$ in polar solvents, like methyl cyanide (cf. $\text{PCl}_4^+ \text{ICl}_2^-$)⁷⁷.

(3.5) Preparation of Adducts in the $\text{PI}_3\text{-Br}_2$ and $\text{PI}_3\text{-IBr}$ Systems

As in the previous investigations, attempts were made to prepare the adducts whose existence is suggested from the results of the conductometric titration. Once again using the same range of solvents as used in the $\text{PI}_3\text{-I}_2$ system, all efforts to prepare the expected solid halogen addition compounds of phosphorus triiodide failed. However, in some cases the yellow-orange solid, P_2I_4 , was isolated and on other occasions, the isolated substances, always dark oils, gave analytical figures which did not fit the requirements of any single feasible product. For example, the following are the analytical results of some of the isolated products

$(\text{PI}_3 + 3\text{IBr})$, found : C, 1.39; H, 0.52; N, 0.76; I, 82.79% .

$(\text{PI}_3 + \text{Br}_2)$, found : C, 10.11; H, 2.69; N, 0.98; I, 60.70% .

$(\text{PI}_3 + 3\text{Br}_2)$, found : C, 5.81; H, 1.66; N, 2.94; I, 75.35% .

The theoretical percentage of iodine in phosphorus triiodide is 92.47% and in diphosphorus tetraiodide, is 89.12% . It was thought therefore, that the interaction of phosphorus triiodide with the solvent which follows the equilibrium : $2\text{PI}_3 \rightleftharpoons \text{P}_2\text{I}_4 + \text{I}_2$ may interfere with isolation of adducts. Also, since the products contain a measurable percentage of nitrogen, reaction with the solvent has occurred. This could be due to the fact that the concentration used in preparative experiments was much greater than in the conductometric titration.

(4) Electrolytic Conductance of $\text{Ph}_n\text{PI}_{3-n}$ ($n = 1, 2$) Halides in Methyl Cyanide

The molar conductances of various halides and poly halides of diiodophenylphosphine and diphenyliodophosphine were measured at different concentrations in methyl cyanide at 25°C . Solutions of each solid contained in conductance cell were prepared in a dry-box and then immersed in a thermostat at 25°C . Readings were taken after about thirty minutes when steady values were obtained. Methyl cyanide was used as a solvent due to its high dielectric constant (36.7 at 25°C). The molar concentrations (c_m) of these solutions were calculated on the basis of the formulae $\text{Ph}_n\text{PX}_{5-n}$ and $\text{Ph}_n\text{PX}_{7-n}$ ($n = 1, 2$). The square root of these values ($\sqrt{c_m}$), assembled in Table 54, when plotted against the molar conductance gave straight lines (figure 22 and 23) from which it was possible for comparative purposes to obtain by extrapolation values of conductance at the concentration 0.01 M.

Values of molar conductance at $c_m = 0.01 \text{ mol l}^{-1}$ are :-

$$\text{PhPI}_4 \quad \Lambda_m = 183.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Ph}_2\text{PI}_3 \quad \Lambda_m = 57.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{PhPI}_6 \quad \Lambda_m = 256.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Ph}_2\text{PI}_5 \quad \Lambda_m = 206.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{PhPI}_3\text{Br} \quad \Lambda_m = 149.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{PhPI}_2\text{Br}_4 \quad \Lambda_m = 155.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Ph}_2\text{PIBr}_4 \quad \Lambda_m = 139.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Ph}_2\text{PI}_2\text{Br}_3 \quad \Lambda_m = 143.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Ph}_2\text{PI}_3\text{Br}_2 \quad \Lambda_m = 132.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

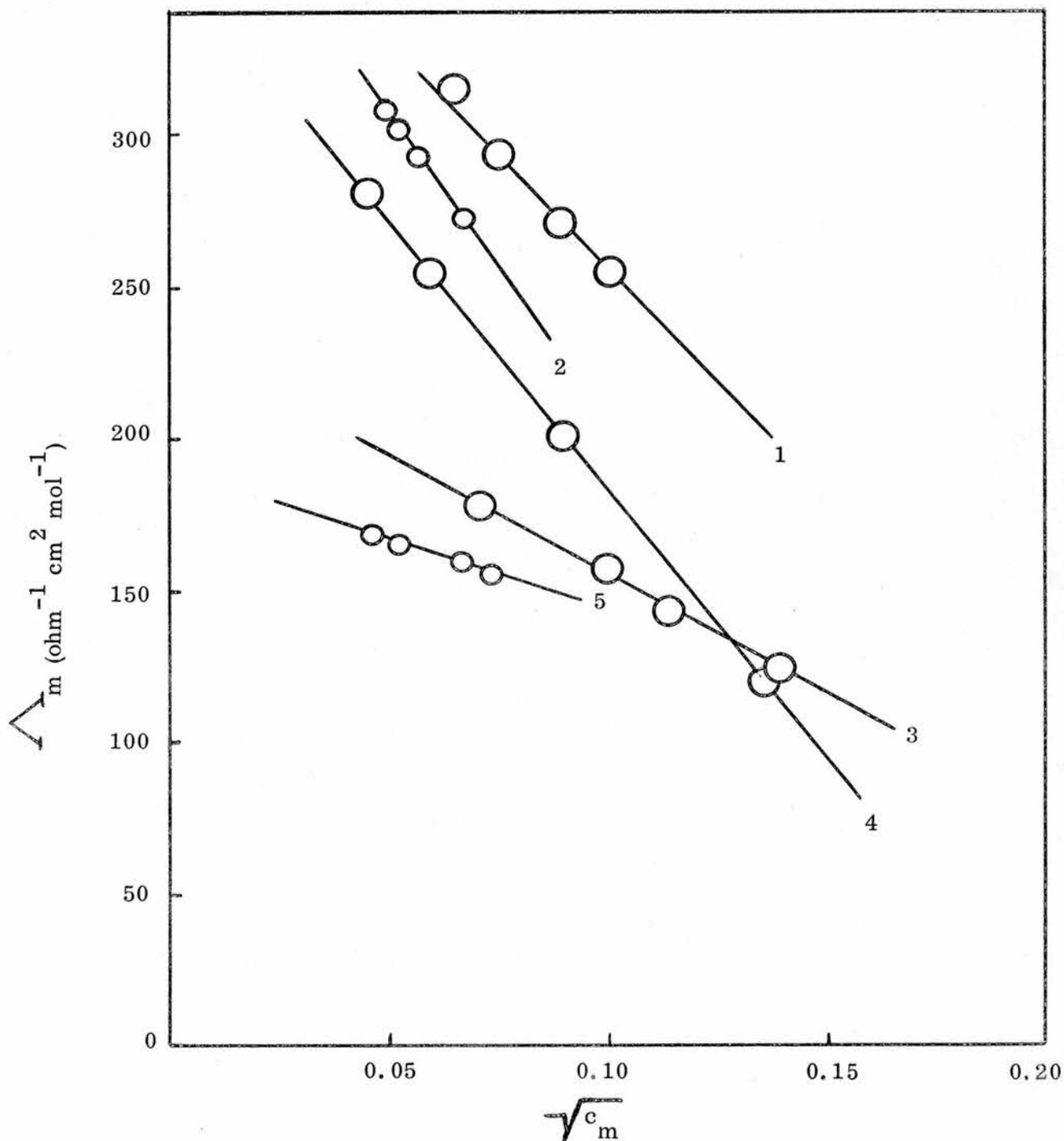


Figure 22. Electrolytic Conductance of Diiodophenylphosphine and Diphenyliodophosphine Halides in Methyl Cyanide at 25°C

1 - PhPI_6

3 - PhPI_2Br_4

2 - Ph_2PI_5

4 - PhPI_4

5 - $\text{Ph}_2\text{PI}_2\text{Br}_3$

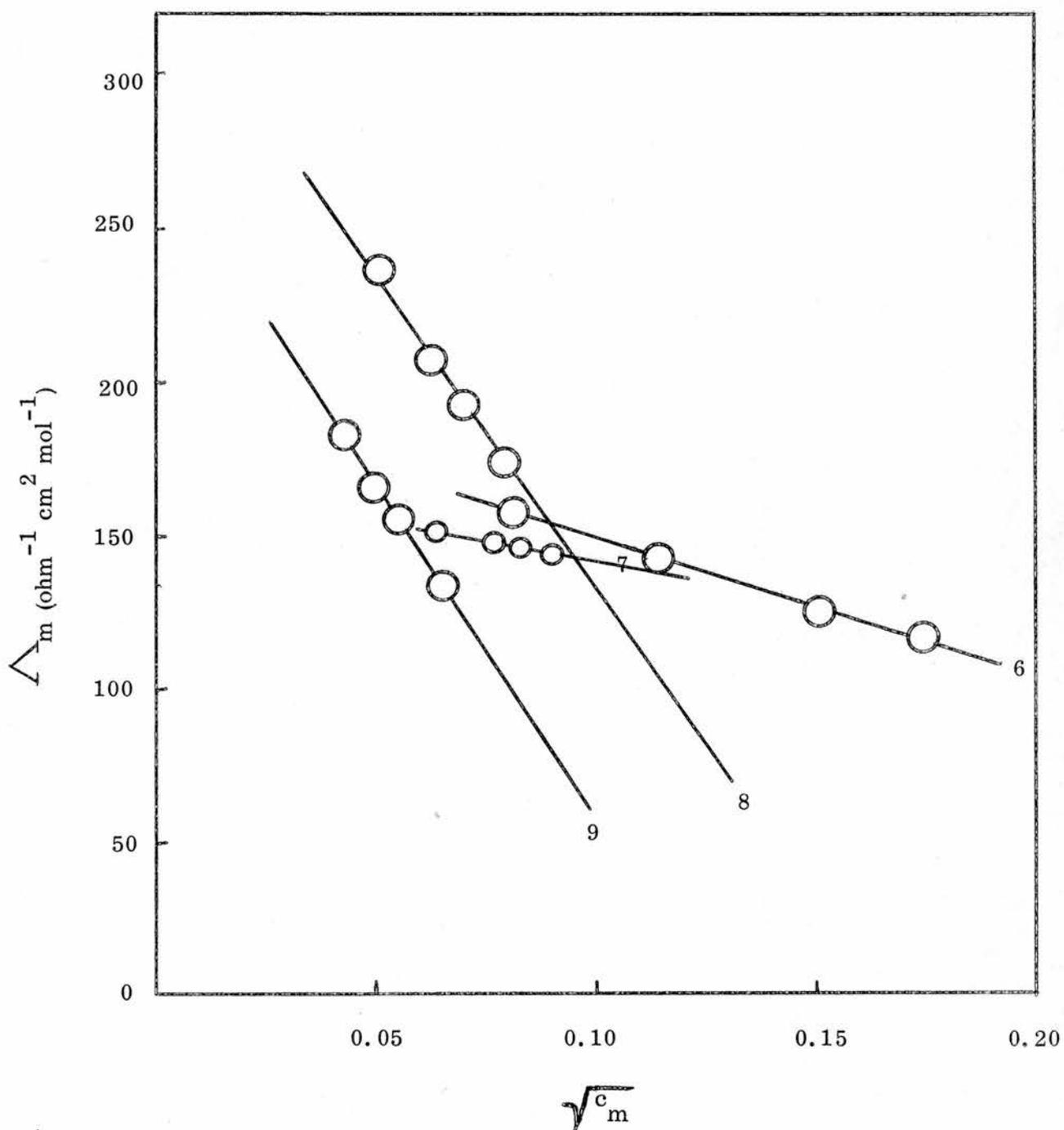
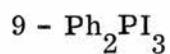
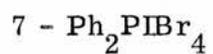
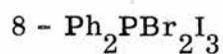
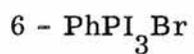


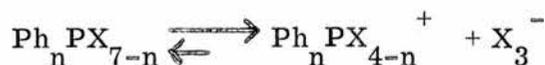
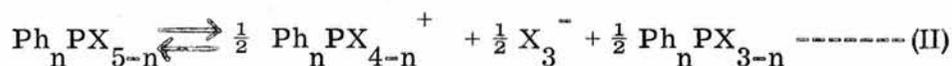
Figure 23. Electrolytic Conductance of Diiodophenylphosphine and Diphenyliodophosphine Halides in Methyl Cyanide at 25C



These values indicate that all these compounds are strong 1:1 electrolytes in methyl cyanide. The modes of ionisation are



or



[ionisation mode (II) is proposed to explain the formation of trihalide ion in the case of certain PX_5 compounds.]

Table 54. Electrolytic Conductance of $\text{Ph}_n \text{PI}_{3-n}$ ($n=1, 2$) Halides in

Methyl Cyanide at 25°C

Compound	c_m mol l ⁻¹	$\sqrt{c_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
PhPI ₄	0.002139	0.0462	5.99	280.51
	0.003612	0.0601	9.21	254.92
	0.008190	0.0905	16.36	199.76
	0.018741	0.1369	22.51	120.10
PhPI ₆	0.004296	0.0655	13.55	315.44
	0.005799	0.0761	17.02	293.51
	0.008715	0.0934	23.62	271.03
	0.01033	0.1016	26.32	254.78
PhPI ₃ Br	0.001407	0.0375	2.52	179.10
	0.006682	0.0817	10.52	157.51
	0.02311	0.1520	28.77	124.48
	0.030395	0.1743	34.62	113.91
PhPI ₂ Br ₄	0.005128	0.0716	9.12	177.78
	0.010009	0.1000	15.70	156.86
	0.013157	0.1147	18.80	142.60
	0.019593	0.1400	24.50	124.86

To be continued overleaf.

Table 54 continued.

Compound	c_m mol l ⁻¹	$\sqrt{c_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
Ph ₂ PI ₃	0.001804	0.0424	3.29	182.82
	0.002469	0.0500	4.12	164.74
	0.003070	0.0557	4.83	155.71
	0.004423	0.0663	5.90	134.21
Ph ₂ PI ₅	0.002531	0.0500	7.71	308.55
	0.002763	0.0529	8.47	302.45
	0.003434	0.0583	10.07	293.29
	0.004586	0.0678	12.58	273.50
Ph ₂ PI ₃ Br ₂	0.002658	0.0516	6.30	236.84
	0.003926	0.0627	8.17	207.80
	0.005011	0.0708	9.64	192.43
	0.006447	0.0803	11.26	174.64
Ph ₂ PI ₂ Br ₃	0.002205	0.0469	3.72	168.95
	0.003027	0.0548	5.00	164.93
	0.004602	0.0678	7.35	159.74
	0.005600	0.0748	8.71	155.61
Ph ₂ PIBr ₄	0.004032	0.0635	6.11	151.58
	0.006037	0.0777	8.90	147.36
	0.006806	0.0825	9.94	145.91
	0.008213	0.0906	11.83	144.02

(5) The Mass Spectra of (a) the Products from the Interaction of
 $\text{Ph}_n\text{PI}_{3-n}$ ($n = 0, 1$) with Methyl Cyanide and (b) the Halogen Adducts
of $\text{Ph}_n\text{PI}_{3-n}$ ($n = 1, 2$).

The mass spectra of the compounds listed in the title have been recorded. The major fragments for each compound are tabulated together with probable ion assignments. The relative intensities of each ion are expressed by setting the most abundant m/e peak (base peak) at a value of 100%, and relative to this the other abundances are proportionally determined.

The mass spectrum results of the starting materials PhPI_2 , Ph_2PI , and PI_3 are given in Tables 55, 56 and 57 respectively. In each compound the m/e attributed to the molecular ion was observed. Other peaks of different m/e were assigned to different ions resulting from fragmentation of the original species.

The mass spectra of $\text{Ph}_2\text{P}_2\text{I}_2$ and P_2I_4 prepared by literature methods are also recorded. The observed peaks at m/e 470 (Table 58) and 570 (Table 59) are assigned to the fragments $\text{Ph}_2\text{P}_2\text{I}_2^+$ and P_2I_4^+ respectively. The solid products of the interaction of phosphorus triiodide and diiodophenylphosphine with methyl cyanide (i. e. P_2I_4 and $\text{Ph}_2\text{P}_2\text{I}_2$ respectively), showed individually identical fragments to the above mentioned ones (Tables 59 and 58). Thus the existence of the mentioned earlier equilibria, in methyl cyanide solutions of PhPI_2 and PI_3 , is further substantiated.

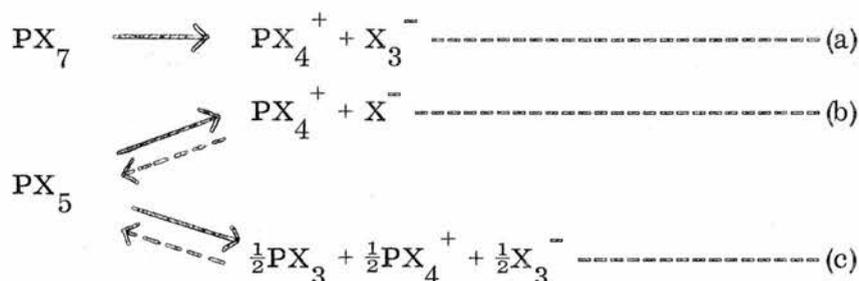
The compound PhPI_6 showed a very similar spectrum to that of PhPI_4 (Table 60) : the mass spectra of the adducts Ph_2PI_5 and Ph_2PI_3

(Table 61) were identical. As can be seen from these Tables, the iodine adducts did not show fragments related to the molecular ions, thus illustrating their instability.

The bromine adducts isolated in these systems gave mass spectra very similar to those observed in the related Br_2 , $\text{IBr} - \text{PhPBr}_2$ and Br_2 , $\text{IBr} - \text{Ph}_2\text{PBr}$ systems (see Tables 24, 33, 34, 35 and 62).

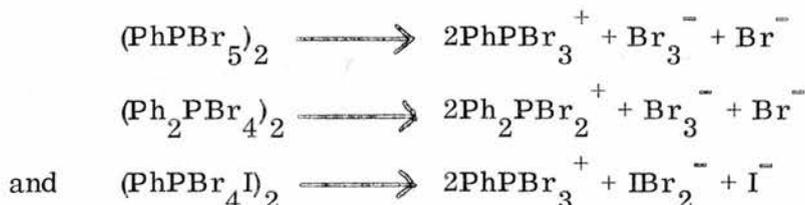
General Conclusion

Dibromophenylphosphine, bromodiphenylphosphine, diiodophenylphosphine and diphenyliodophosphine have been shown to react with the halogens and interhalogens, bromine, iodine and iodine monobromide to give 1:1 and 1:2 adducts which are members of the series of the general formula $\text{PhPBr}_n\text{I}_{4-n}$ ($n = 0, 1, 2, 3, 4$), $\text{Ph}_2\text{PBr}_n\text{I}_{3-n}$ ($n = 0, 3$), $\text{PhPBr}_n\text{I}_{6-n}$ ($n = 0, 2, 4, 5$) and $\text{Ph}_2\text{PBr}_n\text{I}_{5-n}$ ($n = 0, 1, 2, 3, 4$). The individual members of these series which were isolated are: PhPI_4 , PhPBrI_3 , PhPBr_2I_2 , PhPBr_3I , PhPBr_4 , Ph_2PI_3 , Ph_2PBr_3 , PhPI_6 , PhPBr_2I_4 , PhPBr_4I_2 , PhPBr_5I , Ph_2PI_5 , Ph_2PBrI_4 , $\text{Ph}_2\text{PBr}_2\text{I}_3$, $\text{Ph}_2\text{PBr}_3\text{I}_2$ and $\text{Ph}_2\text{PBr}_4\text{I}$. Measurement of molar conductances has shown that the PX_5^- -type compound (1:1 adducts) are fairly strong electrolytes whereas the PX_7^- -type (2:1 adducts) are strong electrolytes in methyl cyanide. The ultra-violet spectrum studies indicate that PX_7^- and to a lesser extent PX_5^- -type compounds produce the trihalide ions in methyl cyanide; trihalide ion is present in the solution of the latter compounds (PX_5^-) from a disproportionation reaction [(c) below],



In the systems $\text{PhPBr}_2-\text{Br}_2$, $\text{Ph}_2\text{PBr}-\text{Br}_2$ and $\text{PhPBr}_2-\text{IBr}$, the adducts isolated at the 2:1 mole ratio of halogen to phosphine were PhPBr_5 , Ph_2PBr_4 and PhPBr_4I respectively. These compounds which are

of unexpected stoichiometry suggesting hexa-coordinated phosphorus, are strong electrolytes and have the following ionisation modes in methyl cyanide.



In the case of the $\text{PBr}_3\text{-Hal}_2$ systems, three members of the series $\text{PBr}_n\text{I}_{7-n}$ ($n = 4, 5, 6$) were isolated, namely PBr_4I_3 , PBr_5I_2 , PBr_6I and these had the ionic structure $\text{PBr}_4^+\text{I}_3^-$, $\text{PBr}_4^+\text{I}_2\text{Br}^-$ and $\text{PBr}_4^+\text{IBr}_2^-$ in methyl cyanide respectively.

Conductometric titration studies of the systems $\text{Br}_2\text{-Ph}_n\text{PBr}_{3-n}$ ($n = 0, 1, 2$) and $\text{Br}_2\text{-Ph}_n\text{PI}_{3-n}$ ($n = 0, 1, 2$) in dilute methyl cyanide solution resulted in conductance - composition graphs which exhibited well defined breaks at the 1:1 ratio (and at the 2:1 ratio in the case of $\text{Br}_2\text{-PhPI}_2$ system) of halogen to phosphine. In contrast, the conductometric titration graph of the systems $\text{Ph}_n\text{PBr}_{3-n}\text{-Hal}_2$ ($n = 0, 1, 2$; $\text{Hal}_2 = \text{I}_2, \text{IBr}$), $\text{Ph}_n\text{PI}_{3-n}\text{-Hal}_2$ ($n = 0, 2$; $\text{Hal}_2 = \text{I}_2, \text{IBr}$) and $\text{PhPI}_2\text{-IBr}$ showed no distinct breaks which might indicate the stoichiometry of the reactions occurring in solution. The absence of the 2:1 breaks in the former systems and of any significant discontinuities in the latter case, was confirmed by ultra-violet spectrum analysis to be caused by the presence of two or more equilibria resulting in incomplete formation of the adducts at the expected mole ratios. However, the only system which is excluded from the above ones is the $\text{I}_2\text{-PhPI}_2$ systems which showed a well defined 2:1 break in its conductometric titration graph.

In the system $\text{PI}_3 - \text{I}_2$, the conductometric titration study suggests the existence of the tetraiodophosponium ion (PI_4^+) in methyl cyanide. The ultra-violet spectrum of methyl cyanide solutions of phosphorus triiodide and diiodophenylphosphine demonstrates that these compounds rearrange under the influence of the solvent. This results in the formation of P_2I_4 and $\text{Ph}_2\text{P}_2\text{I}_2$ respectively from the above systems.

Mass spectral studies of most of the aforementioned compounds were also conducted but the results were not very helpful in elucidating their molecular structure. This failure was thought to arise from the following difficulties :

1. The occurrence of hydrolysis during the process of measuring the mass spectra.
2. The lability of the compounds which lose halogen very easily.
3. The occurrence of rearrangement in the mass spectrometer.

However, results fit formulae determined by elemental analysis and postulated to interpret data.

PART 2

THE REACTION OF PSEUDOHALOGEN HALIDES
WITH TRIPHENYLPHOSPHINE AND TRIPHENYLARSINE

IntroductionI - Cyanogen Halides

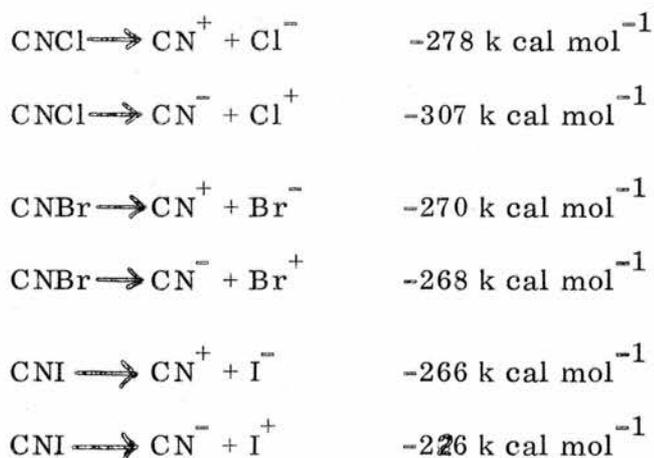
Pseudohalogen halides are of great value industrially, as their trimers, tetramers, and polymers serve as starting points for the synthesis of dyestuffs and drugs. They have also been used in the organic field as reagents for alkaloid degradation, cyanation of aromatic derivatives, and for N - dealkylations. The dual behaviour of cyanogen halides giving either the cyanide anion or the halide anion depending upon the relative electronegativities of the functions or some times on the mode of attack by the substrate, led to contradictory results. In addition to all these interesting features and others, like forming charge - transfer complexes with some solvents, (for example 1:1 charge transfer complexes between cyanogen iodide and five different sulphoxides have been identified by infra-red and ultra-violet absorption spectra²¹⁷) the cyanogen halides being one of the simplest triatomic molecules with three different atoms and with a linear configuration have excited the curiosity of physical chemists and chemical physicists with regard to their physical properties such as their ultra-violet, microwave, infra-red and nuclear magnetic resonance spectra.

A chain structure has been postulated²¹⁸ for cyanogen bromide from X-ray data which shows the bromine atom of one molecule to be bonded weakly to the nitrogen of the next molecule in the chain. Quadrupole coupling measurements²¹⁸ of the bromine and nitrogen nuclei in cyanogen bromide support the above chain structure. X-ray studies of cyanogen chloride²¹⁹ and cyanogen iodide²²⁰ revealed that these molecules are

isostructural with cyanogen bromide. From crystal structure analysis, quadrupole coupling^{218, 221} and dipole moment measurements²²² of cyanogen bromide and cyanogen iodide the following mesomeric forms were suggested to explain the shortening of the carbon-halogen bonds in these molecules.



Concerning the behaviour of the cyanogen halides as halides on the one hand or as cyanides on the other, Fairbrother²²³ has studied their reactions in different solvents like carbon tetrachloride, benzene, di-isobutylene and dioxan. He has shown that in solution, cyanogen halides are explicable by a solvolytic ionisation, and that their dual behaviour is due, not to any structural difference in the free molecules but to the differences in solvent-solute interaction. Lord and Woolf²²⁴ have calculated the values of the heat of reaction for the dissociation of cyanogen halides into ions in alkaline solutions, these are :



Thus they have shown that for cyanogen iodide, the formation of CN^+ is more endothermic than CN^- , whereas for cyanogen bromide, the two

processes are nearly of the same energy.

The solvent effect in reactions in which cyanogen bromide takes part was noticed by Thyagarajan and Rajagopalan²²⁵. They identified the formation of two different compounds from the action of cyanogen bromide on sodium salicylate in two different solvents. In contrast with Fairbrother's conclusion²²³ Woolf²²⁶ from conductance measurements of liquid cyanogen halides and from their reactions with metals and organic compounds in the absence of a solvent, showed that the different behaviours of the cyanogen halides are governed partly by their dissociation to free halogens and partly by their self-ionisation. It was also shown from conductance measurements of liquid cyanogen halides²²⁶, that cyanogen bromide undergoes slow dissociation into CN^+ and Br^- whereas cyanogen iodide forms iodine which causes the increase in conductivity.

Furthermore, concerning the reactivity of the individual cyanogen halides, Foster and Cohn²²⁷ have shown recently that it decreases as the carbon-halogen bond strength increases, hence in terms of reactivity the cyanogen halides can be arranged in the order



II - The Cyanogen Halide Derivatives of Group VB Elements

Harris and co-workers have previously studied a number of organophosphine-halogen systems in polar solvents such as methyl cyanide. They have shown that the reaction between halogens and phosphines produce two distinct sets of compounds, the dihalides R_3PX_3 and the tetrahalides R_3PX_4 . However, although one would expect a rather

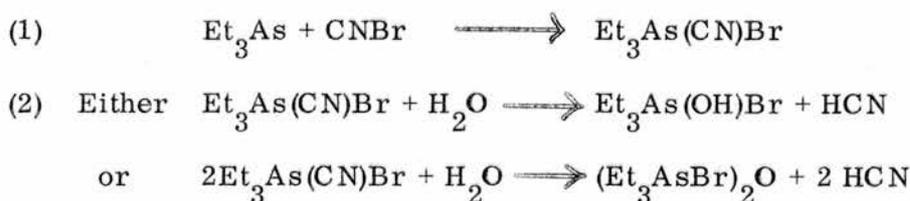
similar behaviour in the case of the cyanogen halides, the work carried out on the reactions between phosphines or arsines and cyanogen halides have demonstrated that these systems are much more complicated than the halogen - phosphine systems.

The isolation of the 1:1 adducts, $R_3M(CN)X$ ($R = \text{alkyl or aryl}$; $M = P, As, Bi$; $X = Br, I$) have been reported by several authors. These claims were based either on the determination of the cyanogen group or on the results of the analysis of the hydrolysis products of these compounds, $R_3M(CN)X$. The difficulties involved in the preparation of such compounds due to their extreme instability and to the limited facilities at the chemists' disposal at the beginning of this century, is responsible for the present lack of information on the properties of cyanogen halide derivatives of phosphorus group elements. Most of the work done so far has been concerned primarily with the synthesis of the cyanogen halide adducts, but more recently some work has been carried out to elucidate their properties.

The interaction of cyanogen iodide and cyanogen bromide with triphenylbismuthine has been studied in boiling benzene and ether by Challenger and Allpress¹⁶⁵. They have shown that with cyanogen iodide the products were cyanodiphenylbismuthine and iodobenzene, whereas with cyanogen bromide there was no reaction in ether. In contrast to this, cyanogen bromide and cyanogen chloride are reported to react with triphenylbismuthine on direct heat in sealed tubes¹⁶⁶, the products being bromodiphenylbismuthine and chlorodiphenylbismuthine respectively. The reaction between cyanogen iodide and triphenylphosphine,

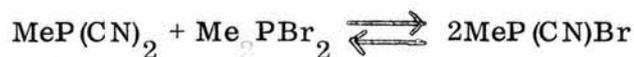
triphenylarsine and triphenylbismuthine have also been attempted in ether¹⁶⁶. The products of these reactions contained nitrogen and iodine and were very unstable being readily converted by hydrolysis to the oxyhalides or hydroxyhalides²²⁸.

The action of cyanogen bromide on other organosubstituted arsine or phosphine has been studied by various authors²²⁹⁻²³¹ and the formation of very unstable 1:1 addition products are reported. In some cases where the cyanogen bromide adducts could not be isolated, their existence was inferred from the fact that their hydrolysis products (i. e. hydroxybromides) were isolated²³². Steinkopf and Muller²²⁹ have claimed the isolation of the addition compound $\text{Et}_3\text{As}(\text{CN})\text{Br}$ from petroleum-ether in a Wolfram²³⁰ apparatus, under very dry conditions. They have also reported that on standing in air this compound is converted to the hydroxybromide or oxybromide. This latter compound was obtained directly when the reaction was carried out in ether. The authors²²⁹ have suggested that the oxyhalide or hydroxyhalide had resulted from the $\text{Et}_3\text{As}(\text{CN})\text{Br}$ according to the following reaction.



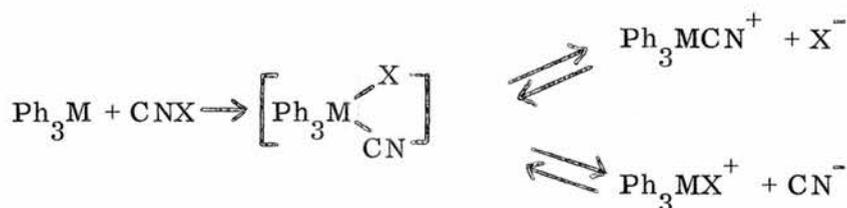
The formation of $\text{Ph}_3\text{P}(\text{CN})\text{Br}$ has been reported²³³, and its hydrolytic and thermal decomposition identified²³⁴. This may be represented in a similar way as follows :

bromide by means of ^1H , ^{31}P n. m. r. and mass spectroscopy, and have shown that the products include dibromomethylphosphine, dicyanophenylphosphine and bromocyanomethylphosphine²²⁷. The first two compounds, MePBr_2 and $\text{MeP}(\text{CN})_2$, were isolated and characterised individually whereas the separation of $\text{MeP}(\text{CN})\text{Br}$ could not be achieved. The presence of $\text{MeP}(\text{CN})\text{Br}$ was also confirmed (by ^1H , ^{31}P n. m. r.) when a mixture of dicyanomethylphosphine and dibromomethylphosphine were allowed to stand for 48 hours at 24°C , and it is suggested that this results from a ligand exchange reactions of the type found with other phosphorus (III) halides systems^{236, 237}.



The Reaction of Cyanogen Halides with Triphenylphosphine and Triphenylarsine

Although the preparation of few phosphorus and arsenic compounds of the type $R_3As(CN)X$ and $R_3P(CN)X$ ($R = \text{alkyl or aryl}$; $X = \text{Br or I}$) have been reported²²⁹⁻²³⁴, the reactions of cyanogen halides with Group VB elements has not been thoroughly investigated. By analogy with the reactions of halogens with phosphines and arsines it was thought that the analogous type of reaction using cyanogen halides would be the best method of preparing the compounds. Since the ionic nature of the triphenylphosphine (and triphenylarsine) - halogen adducts in methyl cyanide solution has been established by the extensive work carried out by Harris and co-workers¹⁵⁴⁻¹⁵⁶, it was thought likely that the compounds $R_3M(CN)X$ ($M = P, As$; $X = Br, I$) would behave as electrolytes in this solvent and ionise according to one of the following ionisation schemes :



In view of the success achieved in the previous work from studying the systems by conductometric titrations it was thought that this technique would throw light on the behaviour of the $Ph_3M - CNX$ systems and on the adducts likely to be obtained from them. The following paragraphs deal with various reactions of cyanogen bromide and cyanogen iodide with triphenylphosphine and triphenylarsine in methyl cyanide. Attempts to prepare the adducts which are indicated by the titration graphs are also described.

1. The Reaction of Triphenylphosphine with Cyanogen Halides

(1.1) The Triphenylphosphine-Cyanogen Iodide System

The interaction of triphenylphosphine with cyanogen iodide in methyl cyanide was studied by conductometric titration and the results of this are assembled in Table 63 and depicted graphically in Figure 24, plot 1.

Since triphenylphosphine and cyanogen iodide are effectively non-conductors in methyl cyanide,

$$\begin{aligned} \text{Ph}_3\text{P} : \quad \Lambda_m &= 0.25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} ; c_m = 0.015 \text{ mol l}^{-1} \\ \text{CNI} : \quad \Lambda_m &= 0.144 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} ; c_m = 0.01 \text{ mol l}^{-1} \end{aligned}$$

it is quite evident from the results that the above reaction is accompanied by the formation of ions. However, the conductance increased smoothly up to the point $\sim 0.8:1$ (CNI : Ph_3P), and then it decreased gradually until the $\sim 1.3:1$ mole ratio and thereafter the conductance decreased more rapidly until the region $\sim 1.75:1$ at which point it began to level off. The solution, which was colourless initially, became pale orange at the mole ratio $\sim 0.8:1$ and on further additions of the titrant became red and darker. The appearance of the red colour in solution after the 1:1 ratio (CNI : Ph_3P) was shown from its ultra-violet spectrum to be due to the presence of triiodide ion (see Table 64). The ultra-violet spectrum results also indicate the formation of iodine in the solution at higher mole ratios of CNI : Ph_3P (i. e. $\sim 1:1$).

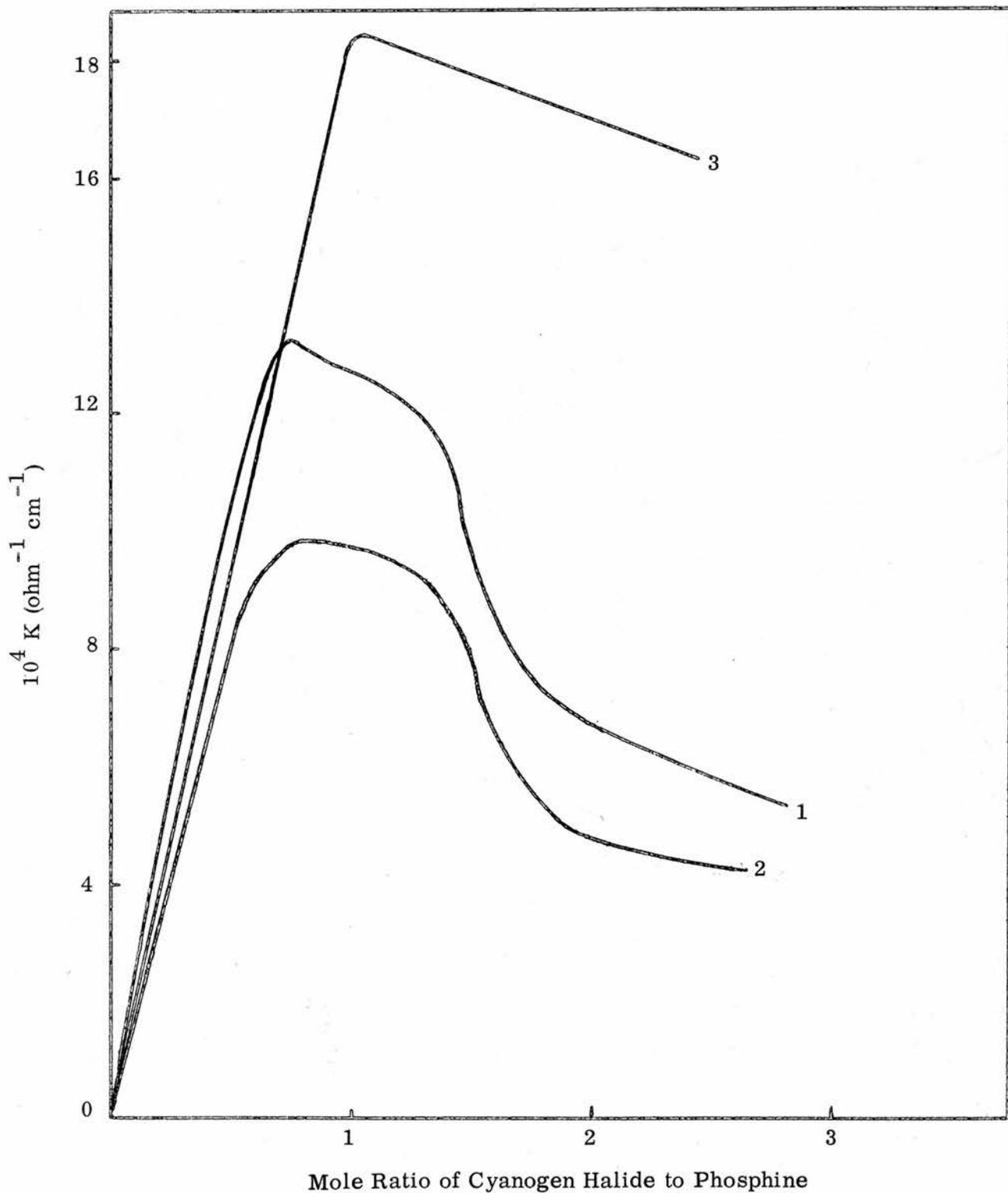


Figure 24. Conductometric Titration of the Systems:

- CNI - Ph₃P ----- plot 1
- Solid CNI - Ph₃P ----- plot 2
- CNBr - Ph₃P ----- plot 3

Table 64. Ultra-Violet Spectrum of the System $\text{Ph}_3\text{P} - \text{CNI}$ in Methyl Cyanide.

Mole Ratio $\text{CNI} : \text{Ph}_3\text{P}$	u. v. maxima (m, μ)	u. v. Indicates	Visible maxima	Visible Indicates
0.32 : 1	-	-	-	-
1.10 : 1	291, 360	I_3^-	-	-
1.71 : 1	292, 362	I_3^-	462	I_2

The form of the graph showing two inflexions at approximately the 1:1 and 2:1 mole ratios, and the molar conductance values, calculated at these ratios, indicate the presence of a fairly strong 1:1 electrolyte of stoichiometry Ph_3PCNI and a weak 2:1 electrolyte (its formula to be described later) in methyl cyanide.

$$\underline{1:1}, \quad \Lambda_m = 67.19 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; c_m = 0.0192 \text{ mol l}^{-1}$$

$$\underline{2:1}, \quad \Lambda_m = 37.57 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; c_m = 0.0173 \text{ mol l}^{-1}$$

As in the previous studies this titration was repeated using solid cyanogen iodide (i. e. the cyanogen halide was not added in solution) as a titrant. The graph obtained (Figure 24, plot 2 ; relevant data in Table 65) was identical to the one observed using a methyl cyanide solution of cyanogen iodide as titrant.

To explain the reaction occurring during the conductometric titration of the $\text{Ph}_3\text{P} - \text{CNI}$ system, it was thought useful to attempt the preparation of adducts. Methyl cyanide was the first solvent to be used in these preparations. From this solvent, it was not possible to isolate the expected 1:1 adduct, $\text{Ph}_3\text{P}(\text{CN})\text{I}$. At the 1:1 ratio of the reactants

Ph_3PI_2 (yellow crystalline solid m.p. 190-191 °C) was isolated as well as a yellow solid (m.p. 111-113 °C) which appeared to be a hydrolysis product. Analytical results for this latter substance suggested a formulation $(\text{Ph}_3\text{PO})_2\text{HI}_3$ and this was supported by infra-red spectrum (see later). This compound is a likely hydrolysis product of $\text{Ph}_3\text{P}(\text{CN})\text{I}$ which is expected to be extremely moisture sensitive. The adduct $(\text{Ph}_3\text{PO})_2\text{HI}_3$ was also isolated from the reaction between triphenylphosphine and cyanogen iodide in petroleum-ether (40-60 °C). The formula allocated to this substance was indicated by analysis and confirmed by infra-red spectrum. The observed broad peak at (840-940) cm^{-1} is indicative of the presence of the cation $(\text{Ph}_3\text{PO})_2\text{H}^+$ which contains a very strong O-----H-----O hydrogen bond²³⁸. Also, the ultra-violet spectrum of the substance in methyl cyanide demonstrates the presence of triiodide ions, hence the ionic structure $(\text{Ph}_3\text{PO})_2\text{H}^+ \text{I}_3^-$ is suggested. The analogous arsine compound $(\text{Ph}_3\text{AsO})_2\text{H}^+ \text{I}_3^-$ was prepared by Inglis¹⁷¹.

Further attempts to isolate $\text{Ph}_3\text{P}(\text{CN})\text{I}$, from the interaction of triphenylphosphine with cyanogen iodide were carried out using petroleum-ether (40-60 °C) and benzene as solvents but these were also unsuccessful. The results of these unsuccessful preparative experiments are summarised in Table 66 overleaf.

Table 66*

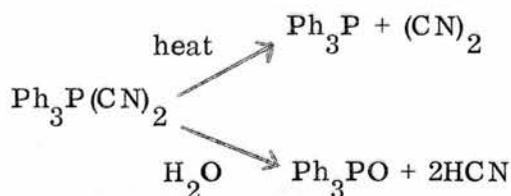
Compound Number	Mole Ratio CNI : Ph ₃ P	Colour and State of the Compound	Solvent	% C	% H	% N
I	1 : 1	brown-red solid	Petroleum-ether(40-60)	41.99	2.65	3.41
II	1 : 1	dark red solid	"	40.03	2.70	2.52
III	1 : 1	yellow solid	"	46.90	3.23	2.25
IV	1 : 1	brown solid	"	47.25	3.07	3.22
V	2 : 1	brown solid	"	43.19	2.93	2.02
VI	1 : 1	brown-yellow solid	Benzene	51.30	3.41	2.27
VII	1 : 1	yellow solid	"	50.97	3.72	0.91
VIII	2 : 1	yellow-brown solid	"	41.18	2.81	-

*Required for Ph₃PI₂ C, 41.89; H, 2.93%

Ph₃P(CN)I C, 54.57; H, 3.61; N, 3.35%

Ph₃P(CN)₂ C, 76.42; H, 4.81; N, 8.91%

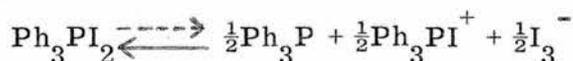
Although the preparation of pure $\text{Ph}_3\text{P}(\text{CN})\text{I}$ was unsuccessful, a white crystalline solid (m.p. 117-118°C) of the composition $\text{Ph}_3\text{P}(\text{CN})_2$ was isolated along with an impure product (number VI in Table 66) from an equimolar mixture of triphenylphosphine and cyanogen iodide in benzene. Preparation of the new adduct $\text{Ph}_3\text{P}(\text{CN})_2$ was reproducible. Support for the formulating $\text{Ph}_3\text{P}(\text{CN})_2$ comes from examination of the infra-red and mass spectra. The infra-red spectrum exhibits a sharp strong absorption at ca. 2175 cm^{-1} which, by analogy with the spectrum of $\text{P}(\text{CN})_3$ ($\nu_{\text{C}\equiv\text{N}} = 2204\text{ cm}^{-1}$)²³⁹ and PF_2CN ($\nu_{\text{C}\equiv\text{N}} = 2194\text{ cm}^{-1}$)⁹, is assigned for the $\text{C}\equiv\text{N}$ stretching mode in $\text{Ph}_3\text{P}(\text{CN})_2$. The molar conductance of $\text{Ph}_3\text{P}(\text{CN})_2$ demonstrates that this adduct is a very weak electrolyte in methyl cyanide ($\Lambda_m = 1.39\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$; $c_m = 0.005001\text{ mol l}^{-1}$). It appears from the mass spectrum that $\text{Ph}_3\text{P}(\text{CN})_2$ (Table 67) is a very unstable compound, decomposing and undergoing hydrolysis due to the presence of some moist air in the mass spectrometer chamber.



The impure reaction products (Table 66) obtained in attempts to prepare adducts seem to be made up of a mixture of Ph_3PI_2 , $\text{Ph}_3\text{P}(\text{CN})\text{I}$ and $\text{Ph}_3\text{P}(\text{CN})_2$. This is deduced from the following :

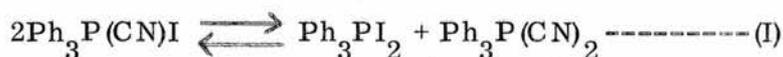
- a. The analytical figures did not fit the requirements of any single feasible product. However, the figures for the sample (VI) fit reasonably the requirements of the mixture : Ph_3PI_2 (33%), $\text{Ph}_3\text{P}(\text{CN})_2$ (4%) and $\text{Ph}_3\text{P}(\text{CN})\text{I}$ (62%).

- b. The products did not have sharp melting points.
- c. The mass spectra of these samples were similar and showed fragments indicative of the presence of iodine, cyanogen, phosphorus and phenyl groups (see Table 68).
- d. The ultra-violet spectrum of these substances in methyl cyanide indicates the presence of some triiodide ion which could arise from the known decomposition of Ph_3PI_2 in methyl cyanide.



- e. The infra-red spectra clearly indicate the presence of the cyanide group in these products (Figure 25). The observed spectra show, in addition to the peaks for Ph_3PI_2 , absorptions at 2175 cm^{-1} and 2215 cm^{-1} . These bands can be assigned to the $\text{C}\equiv\text{N}$ stretching modes in $\text{Ph}_3\text{P}(\text{CN})_2$ and $\text{Ph}_3(\text{CN})\text{I}$ respectively.

From all of the above facts and from the well known lability of the cyanogen halide adducts of triphenylphosphine²²⁹⁻²³³ we suggest that the existence of the following equilibrium in solution causes difficulties in the isolation of pure $\text{Ph}_3\text{P}(\text{CN})\text{I}$.



Foester and Cohn²²⁷ have found similar difficulties in isolating the compound $\text{MeP}(\text{CN})\text{Br}$ and thus they put down to the existence of a rearrangement equilibrium in the solvent i. e. $2\text{MeP}(\text{CN})\text{Br} \rightleftharpoons \text{MePBr}_2 + \text{MeP}(\text{CN})_2$

Interpretation of the conductometric titration graph

The breaks occurring near, but not precisely, at the 1:1 and 2:1 ratios ($\text{CNI} : \text{Ph}_3\text{P}$) being not sharp tend to support the presence of

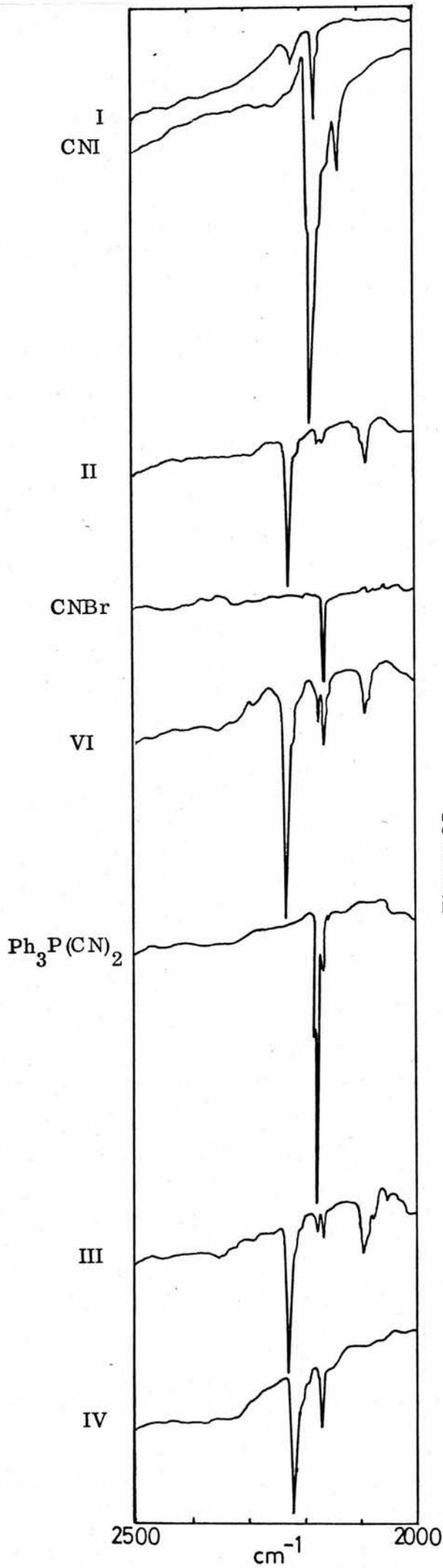


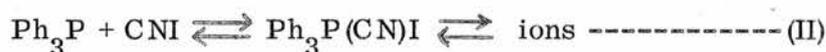
Figure 25

The infra-red spectra of Cyanogen bromide, cyanogen iodide and some of the products of the reactions between Cyanogen iodide and triphenylphosphine, in the region (2500-2000) cm^{-1} .

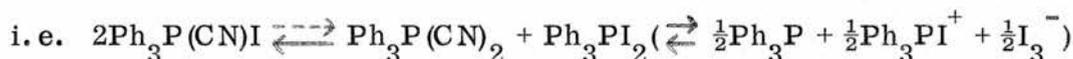
equilibrium reactions in methyl cyanide. These reactions are now considered in turn :

0:1 → 1:1

The increase in the specific conductance up to the 1:1 ratio indicates the formation of an ionic adduct which can be best described by the equilibrium :

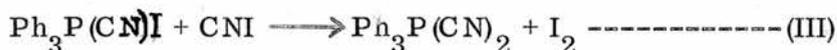


However, the solution at this ratio contained some triiodide ions (shown by the ultra-violet spectrum), and the amount increased beyond this ratio during titration. It is suggested that the rearrangement equilibrium mentioned earlier is responsible for the triiodide ions formation in solution.



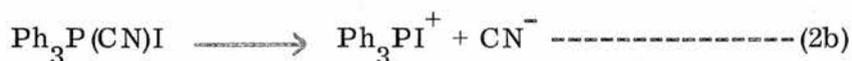
1:1 → 2:1

The decrease in conductance between the 1:1 and 2:1 ratio would support an overall reaction believed to be

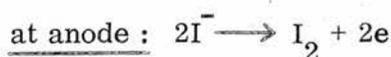


The fact that both $\text{Ph}_3\text{P}(\text{CN})_2$ and iodine are low conductors in methyl cyanide support this interpretation. Moreover, in this range the solution was very dark and its ultra-violet spectrum indicated the presence of molecular iodine in solution as is required by equation III.

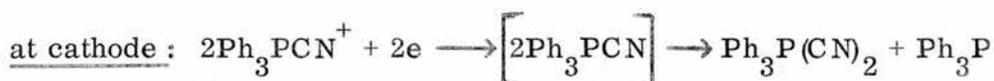
In the 1:1 reaction (i. e. II) suggested above the ions produced by $\text{Ph}_3\text{P}(\text{CN})\text{I}$ were not specified. In fact there are two plausible modes of ionisation,



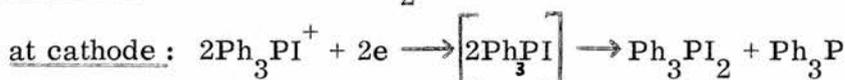
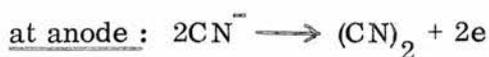
To determine the correct one, electrolysis of a solution containing $\text{Ph}_3\text{P}^+\text{CNI}$ in the 1:1 mole ratio was carried out in a small H-type cell and colour changes noted (the original solution is pale yellow). For ionisation mode 2a one would expect the following electrode processes to occur :



Pale red in MeCN

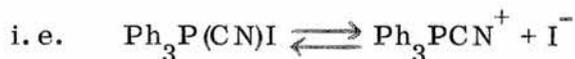


On the other hand for ionisation mode 2b the expected processes are :



(colourless mixture in
MeCN)

The equimolar solution of triphenylphosphine and cyanogen iodide in methyl cyanide on electrolysis produced a red coloured solution in the anode compartment of the cell and a colourless one in the cathode compartment, thus $\text{Ph}_3\text{P}(\text{CN})\text{I}$ ionises according to mode 2a in methyl cyanide



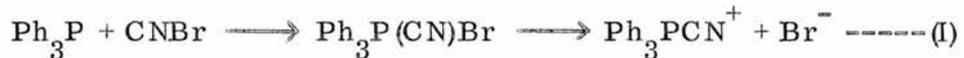
(1.2) The $\text{Ph}_3\text{P} - \text{CNBr}$ System

The conductance composition graph of the triphenylphosphine-cyanogen bromide system in methyl cyanide differs in form (after the 1:1 ratio of cyanogen bromide to phosphine) from that obtained from the $\text{Ph}_3\text{P} - \text{CNI}$ system. The graph in Figure 24-plot 3, obtained from the results recorded in Table 69, shows a steep rise in conductance up to the

1:1 mole ratio (CNBr:Ph₃P) after which the specific conductance began to drop slightly and uniformly giving a sharp 1:1 break. The solution which was initially colourless turned to pale-yellow at the 1:1 ratio and in contrast to the previous Ph₃P - CNI system the addition of excess titrant (well beyond the 2:1 ratio) did not cause any intensification in the colour. The 1:1 break and the molar conductance, calculated from the graph at this ratio, indicate the formation of a strong 1:1 electrolyte of the composition Ph₃P(CN)Br in methyl cyanide.

$$\Lambda_m = 108.24 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; c_m = 0.017003 \text{ mol l}^{-1}$$

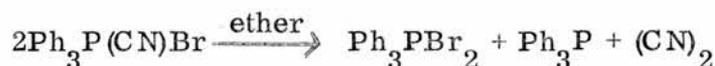
The form of the graph (showing no steep drop in the conductance after 1:1 as found in the Ph₃P - CNI system) suggests that only one reaction is occurring during the conductometric titration. This results in the formation of Ph₃P(CN)Br in methyl cyanide, thus



Attempts to prepare the adduct Ph₃P(CN)₂ from this system were not successful, and this along with the ultra-violet spectrum results which gave no indication of trihalide ion supports the above interpretation. The ionisation mode of Ph₃P(CN)Br in methyl cyanide given in reaction (I) was confirmed by an electrolysis experiment in which it was shown that there was an accumulation of bromine at the ~~anode~~ anode of the cell.

The 1:1 adduct indicated by the conductometric titration was isolated by freeze drying of a solution containing equimolar amounts of triphenylphosphine and cyanogen bromide in methyl cyanide. It is an off-white solid, of m.p. 242-244 °C. Addition of excess dry ether to an equimolar mixture of triphenylphosphine and cyanogen bromide was

found to yield triphenylphosphine dibromide, Ph_3PBr_2 . This suggests that addition of ether to the methyl cyanide solution containing $\text{Ph}_3\text{P}(\text{CN})\text{Br}$ caused rearrangement, thus



$\text{Ph}_3\text{P}(\text{CN})\text{Br}$ was found to be extremely sensitive to moisture (even more so than Ph_3PBr_2). Due to this, attempts to obtain its infra-red spectrum were unsuccessful even although the usual strict precautions to prevent contact with moist air were taken. It was thus not possible to observe the position of the $\text{C} \equiv \text{N}$ stretching mode in this compound.

2. The Reaction of Triphenylarsine with Cyanogen Halides

(2.1) The $\text{Ph}_3\text{As} - \text{CNI}$ System

The graph in Figure 26-plot 1, (relevant data in Table 70) obtained from the conductance study of the $\text{Ph}_3\text{As} - \text{CNI}$ system indicates the presence of an ion-forming reaction in methyl cyanide. Addition of the cyanogen iodide to triphenylarsine (both dissolved in methyl cyanide) caused an increase in the specific conductance up to the 1.5:1 mole ratio of $\text{CNI} : \text{Ph}_3\text{As}$ after which it gradually drops giving a sharp break at the 1.5:1 ratio. The titration was repeated (for similar reasons to those discussed previously for the $\text{CNI} - \text{Ph}_3\text{P}$ system) using solid cyanogen iodide as a titrant. The graph (Figure 26-plot 2 and Table 71) obtained from this titration again shows a break at the 1.5:1 ratio ($\text{CNI} : \text{Ph}_3\text{As}$). In both cases the initially colourless solution became yellow after the first addition of cyanogen iodide solution and when the 1:1 mole ratio was attained the solution consumed a red colour which did not darken

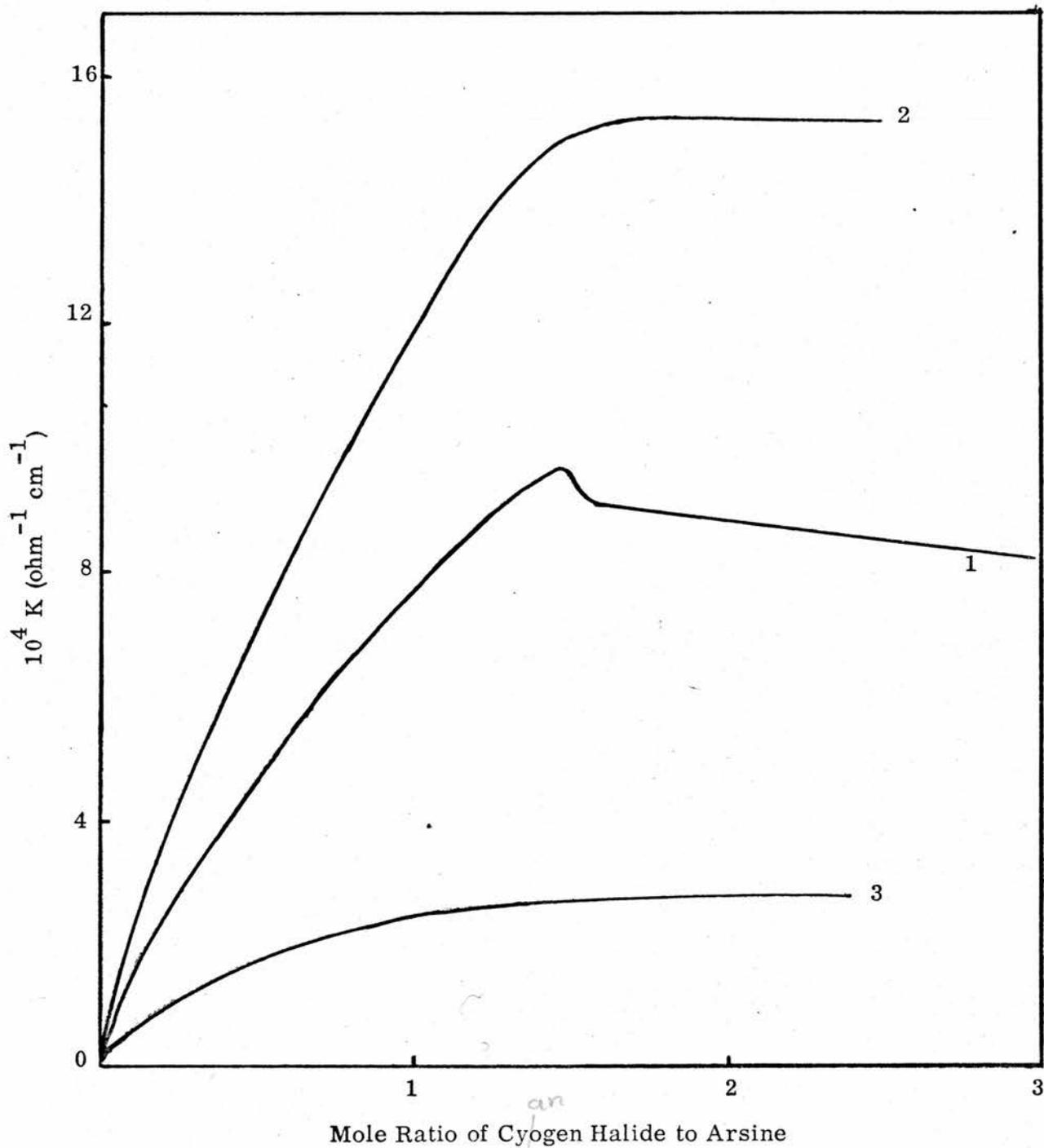


Figure 26. Conductometric Titration of the Systems:

CNI - Ph_3As ----- plot 1

Solid CNI - Ph_3As -----plot 2

CNBr - Ph_3As ----- plot 3

on further addition of cyanogen iodide up to the 3:1 ratio. The initial yellow coloration was shown from its ultra-violet spectrum to be due to the presence of triiodide ion (see Table 72).

Table 72. Solution Spectra of the $\text{Ph}_3\text{As} - \text{CNI}$ System

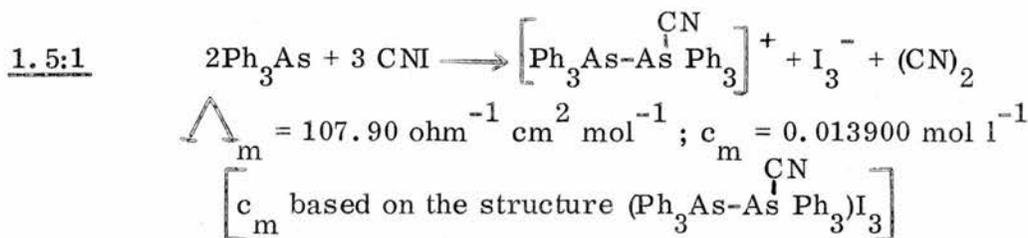
Mole Ratio of $\text{CNI} : \text{Ph}_3\text{As}$	u. v. Maxima	u. v. Indicates
0.32 : 1	292, 362	traces of I_3^-
0.74 : 1	292, 362	" " "
1.63 : 1	292, 362	I_3^-

The lack of intensification of the colour of the solution after the 1:1 ratio suggested that molecular iodine was not being formed and this was confirmed from the spectra of the solution in the visible region. This is in contrast with the behaviour of the $\text{CNI} - \text{Ph}_3\text{P}$ system and may be taken as indicating that $\text{Ph}_3\text{As}(\text{CN})_2$ is not being formed in solution in the present system. In fact $\text{Ph}_3\text{As}(\text{CN})_2$ was not isolated from this system.

The molar conductance of the solution at the 1.5:1 ratio calculated from the graph $\left[c_m \text{ based on } \text{Ph}_3\text{As}(\text{CNI})_{1.5} \right]$ demonstrates the formation of a fairly strong electrolyte in methyl cyanide

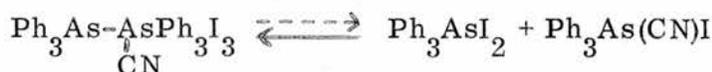
$$\underline{1.5:1} \quad \Lambda_m = 53.95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; \quad c_m = 0.027800 \text{ mol l}^{-1}$$

From this, and the form of the graph, and the ultra-violet spectrum results, it is suggested that the reaction occurring in solution is the following



A dark violet crystalline solid (m. p. 174-176 °C) was isolated on reacting triphenylarsine with cyanogen iodide (either at the 1:1 or 2:1 mole ratio of CNI : Ph₃As) in methyl cyanide and petroleum-ether (40-60 °C). This solid was shown by analysis to have the composition (Ph₃As)₂CNI₃. In addition to this adduct, an orange crystalline solid of the stoichiometry Ph₃AsI₂ (m. p. 135-136 °C) was isolated from the same reaction. The mass (Table 73), and infra-red, and ultra-violet spectra of these products have been recorded. The infra-red spectrum of (Ph₃As)₂CNI₃ shows a sharp peak at 2164 cm⁻¹ which is assigned to the C≡N stretching mode. The ultra-violet spectrum of a methyl cyanide solution of this compound indicates the presence of triiodide ion (extinction coefficient 41,440 l cm⁻¹ mol⁻¹ for $\lambda_{\text{max}} = 292 \text{ m}\mu$). On the basis of the results the ionic formulation $(\text{Ph}_3\text{As}-\overset{+}{\underset{\text{CN}}{|}{\text{As}}}\text{Ph}_3)\text{I}_3^-$ is suggested.

A structure similar to this has been proposed for chloriodide of elemental composition Ph₃PCl_{0.5}I_{1.5} isolated by Ali and Harris²⁰⁴ and believed to have an ionic structure $(\text{Ph}_3\text{P}-\overset{+}{\underset{\text{Cl}}{|}{\text{P}}}\text{Ph}_3)\text{I}_3^-$. The isolation of Ph₃AsI₂ in addition to (Ph₃As)₂CNI₃ from the same reaction can only be accounted for by assuming the presence of the equilibrium:



Attempts to prepare the above solids from benzene resulted in the formation of the hydrolysis product, (Ph₃AsO)₂HI₃. This product which has been reported by Harris and Inglis²¹¹ must have formed

because of the presence of minute traces of moisture during the preparation, thus demonstrating the extreme lability of $(\text{Ph}_3\text{As})_2\text{CNI}_3$.

(2.2) The Triphenylarsine-Cyanogen Bromide System

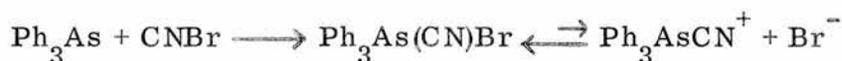
The results of the titration of cyanogen bromide with triphenylarsine in methyl cyanide are given in Table 74 and illustrated graphically in Figure 26-plot 3. Addition of cyanogen bromide solution to triphenylarsine resulted in a small increase only in conductance and solution remained colourless throughout titration. From the graph it would seem that this system behaves like the corresponding triphenylphosphine-cyanogen bromide system, giving only one break (a rather indefinite one) at the 1:1 mole ratio of $\text{CNBr}:\text{Ph}_3\text{As}$. However, it is worth noting that the conductance at the 1:1 break is much less than that of the $\text{Ph}_3\text{P}-\text{CNBr}$ system.

1:1 ($\text{CNBr}:\text{Ph}_3\text{As}$) :- $\Lambda_m = 15.32 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.016011 \text{ mol l}^{-1}$

1:1 ($\text{CNBr}:\text{Ph}_3\text{P}$) :- $\Lambda_m = 108.24 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.017003 \text{ mol l}^{-1}$

Thus the adduct $\text{Ph}_3\text{As}(\text{CN})\text{Br}$ indicated by the graph must be regarded as a weak electrolyte in methyl cyanide.

The reaction occurring may be represented



Electrolysis of an equimolar solution of cyanogen bromide and triphenylarsine in methyl cyanide confirmed that the ionisation occurred as indicated above.

In contrast to the behaviour of the $\text{Ph}_3\text{As}-\text{CNI}$ system it was possible to isolate a 1:1 adduct. $\text{Ph}_3\text{As}(\text{CN})\text{Br}$ was isolated as a cream coloured solid (m.p. $> 300^\circ$) from methyl cyanide or benzene containing the reactants in the 1:1 mole ratio. The infra-red spectrum had a sharp

absorption band at $\sim 2183 \text{ cm}^{-1}$ which is assigned to the stretching mode of the $\text{C} \equiv \text{N}$ group.

General Conclusion

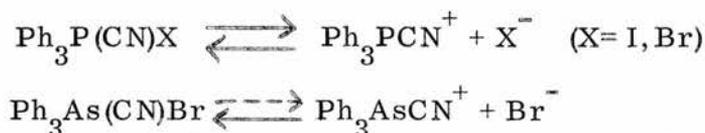
Triphenylphosphine and triphenylarsine have been shown to react in concentrated solutions with cyanogen bromide and cyanogen iodide to give the compounds, $\text{Ph}_3\text{P}(\text{CN})_2$, Ph_3PI_2 , $\text{Ph}_3\text{P}(\text{CN})\text{Br}$, $(\text{Ph}_3\text{As})_2\text{CNI}_3$ and Ph_3AsI_2 . The cyanogen halide adducts are very unstable compounds undergoing immediate hydrolysis on contact with moist air or damp solvents.

The 1:1 adduct, $\text{Ph}_3\text{P}(\text{CN})\text{I}$, indicated by conductometric titration of the $\text{Ph}_3\text{P} - \text{CNI}$ system, was not isolated. Attempts to prepare it yielded a mixture whose analysis and infra-red spectrum suggested the presence of $\text{Ph}_3\text{P}(\text{CN})\text{I}$, Ph_3PI_2 , and $\text{Ph}_3\text{P}(\text{CN})_2$. From these observations it is suggested that in solution the following equilibrium occurs.



Conductometric titration studies of the $\text{Ph}_3\text{P} - \text{CNBr}$ and $\text{Ph}_3\text{As} - \text{CNBr}$ systems in dilute methyl cyanide gave titration graphs with sharp 1:1 breaks. The $\text{Ph}_3\text{P} - \text{CNI}$ and $\text{Ph}_3\text{As} - \text{CNI}$ systems behave differently, the former giving two breaks (1:1 and 2:1 ratio of $\text{CNI} : \text{Ph}_3\text{P}$) and the latter only one (1.5:1 ratio of $\text{CNBr} : \text{Ph}_3\text{As}$).

The mode of ionisation of the adducts present at the 1:1 breaks in the case of the $\text{Ph}_3\text{P} - \text{CNI}$, $\text{Ph}_3\text{P} - \text{CNBr}$, and $\text{Ph}_3\text{As} - \text{CNBr}$ systems was shown by electrolysis experiments to be the following:



PART 3

THE REACTION OF HALOGENS WITH SOME
TERTIARY BIARSINES

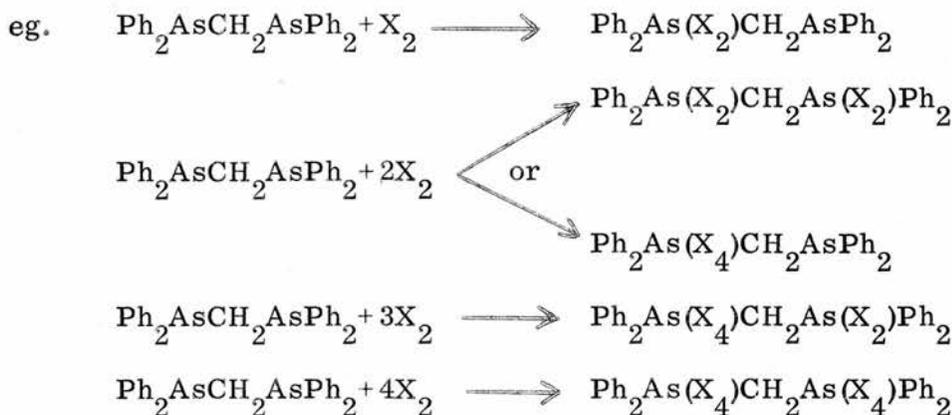
Part 3The Reaction of Halogens with some Tertiary BiarsinesIntroduction

Substituted biarsines and biphosphines of type $R_2M(CH_2)_nMR_2$ ($M=As$ or P) are well known²⁴⁰⁻²⁴⁵, and are relatively easy to prepare from the reaction of dihaloalkanes and alkali metal derivatives of the phosphine or arsine,

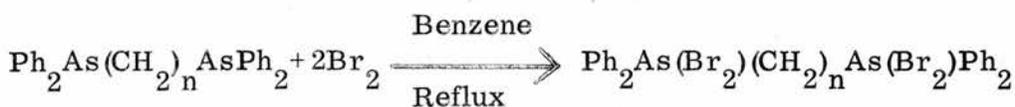
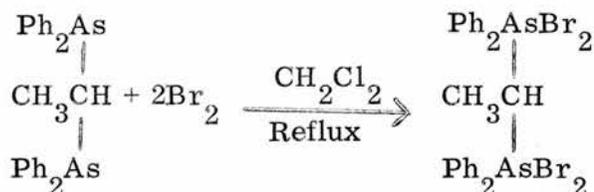


These tertiary biarsines and biphosphines are of interest because of their ability to form very stable complexes with transition metal and other metal halides. Many examples of these have been reported, eg. $M(\text{CO})_2L_2X_2$ ²⁴⁶, $M(\text{NO})_2LX_2$ ²⁴⁷, $M(\text{NO})_2L_2X_2$ ²⁴⁷, $\text{Re}(\text{CO})_nLX$ ²⁴⁸ ($M=Mo, W; L=\text{Ph}_2\text{PCH}_2\text{PPh}_2$ or $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$; $X=\text{Cl, Br, I}$; $n=3, 4$), $\text{Pd}(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)_nX_2$ ($n=1, 2; X=\text{Cl, ClO}_4$)²⁴⁹. In these complexes, $\text{Ph}_2M(\text{CH}_2)_nM\text{Ph}_2$ behaves either as a monodentate ligand (donating one pair of electrons to the metal atom) or as a bidentate ligand (donating two pairs of electrons to the metal atom). Apart from this, little is known about their chemistry.

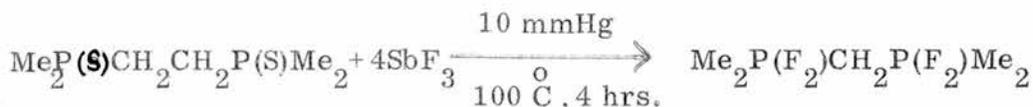
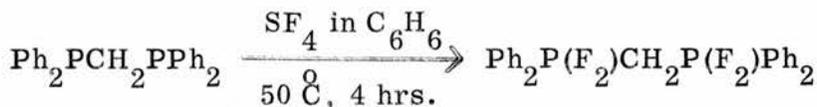
By analogy with the known reactions of monophosphines and monoarsines with halogens, the reactions of tertiary biarsines (or biphosphines) should, in principle, lead to a greater variety of types of halogen adduct.



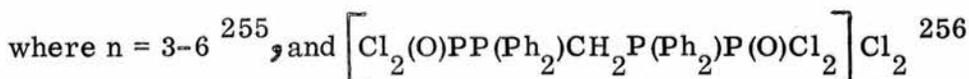
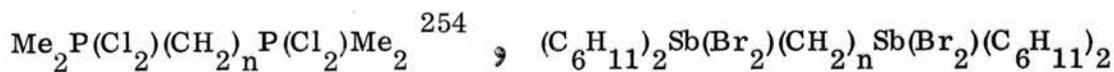
References to a few such compounds can be found in the literature, but only those with one halogen molecule per arsenic (or phosphorus) atom have been reported²⁵⁰⁻²⁵³. 1,1-Bis(dibromodiphenylarsino) ethan²⁵¹ and $\text{Ph}_2\text{As}(\text{Br}_2)(\text{CH}_2)_n\text{As}(\text{Br}_2)\text{Ph}_2$ ²⁵⁰ have been produced by the following reactions:



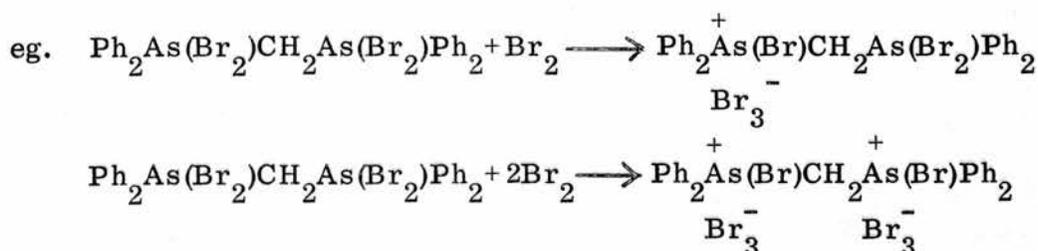
Halogen adducts of some tertiary biphosphines have also been prepared. For example fluorine adducts have been obtained indirectly by fluorination of bis(diphenylphosphino) methane (using sulphur tetrafluoride)²⁵² and 1,2-bis(dimethylthiophosphino) ethane (using antimony trifluoride)²⁵³.



Other compounds of this type which have been isolated are:



By analogy with the formation of tetrahalides (eg. Ph_3AsBr_4) by mono arsines, it was thought that similar higher adducts might be formed by the biarsines.



To obtain direct information on the nature of the products resulting from such reactions, it was thought that a systematic study of the ultra-violet spectra and the conductance properties of these systems (biarsine- Hal_2) should be carried out. This section of the thesis is devoted to the reactions of biarsines with halogens and interhalogens in methyl cyanide.

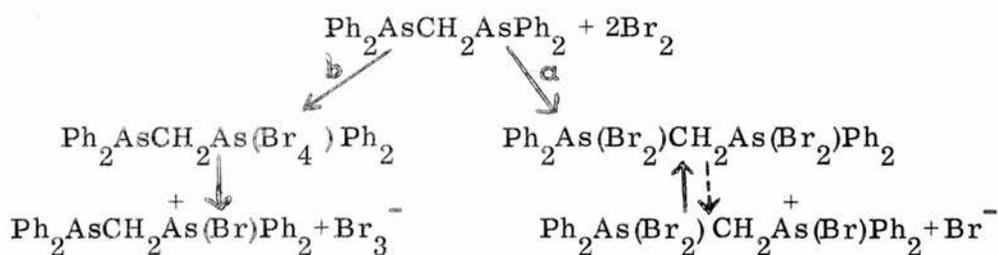
RESULTS AND DISCUSSION

A. The Reaction of Bis(diphenylarsino) methane with Bromine, Iodine, and Iodine Monobromide.

The results of the conductometric titration of the $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{-Br}_2$, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{-I}_2$, and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{-IBr}$ systems in methyl cyanide are given in Figures 27-plot 1 (Table 75), 27-plot 2 (Table 76), and 28-plot 1 (Table 77) respectively.

The first of these systems showed a slight increase in conductance up to the region 2:1 (Br_2 :biarsine) and the methyl cyanide solution remained colourless. After this ratio, the solution became yellow and the conductance rose sharply, eventually attaining a steady value at about the ratio 6:1. The sharp 2:1 break clearly indicates the formation of a 2:1 adduct which, from the low value of conductance at this point ($\Lambda_m = 32.26 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.013858 \text{ mol l}^{-1}$), is a weak electrolyte. There are two possible schemes for the formation of a 2:1 adduct:

0.0 \rightarrow 2:1



Since (b) leads to a strong 1:1 electrolyte it can be concluded that the reaction follows course (a). Furthermore since the solution is colourless up to this stage the absence of tribromide ions is indicated and this was confirmed from the ultra-violet spectrum (results in Table 78).

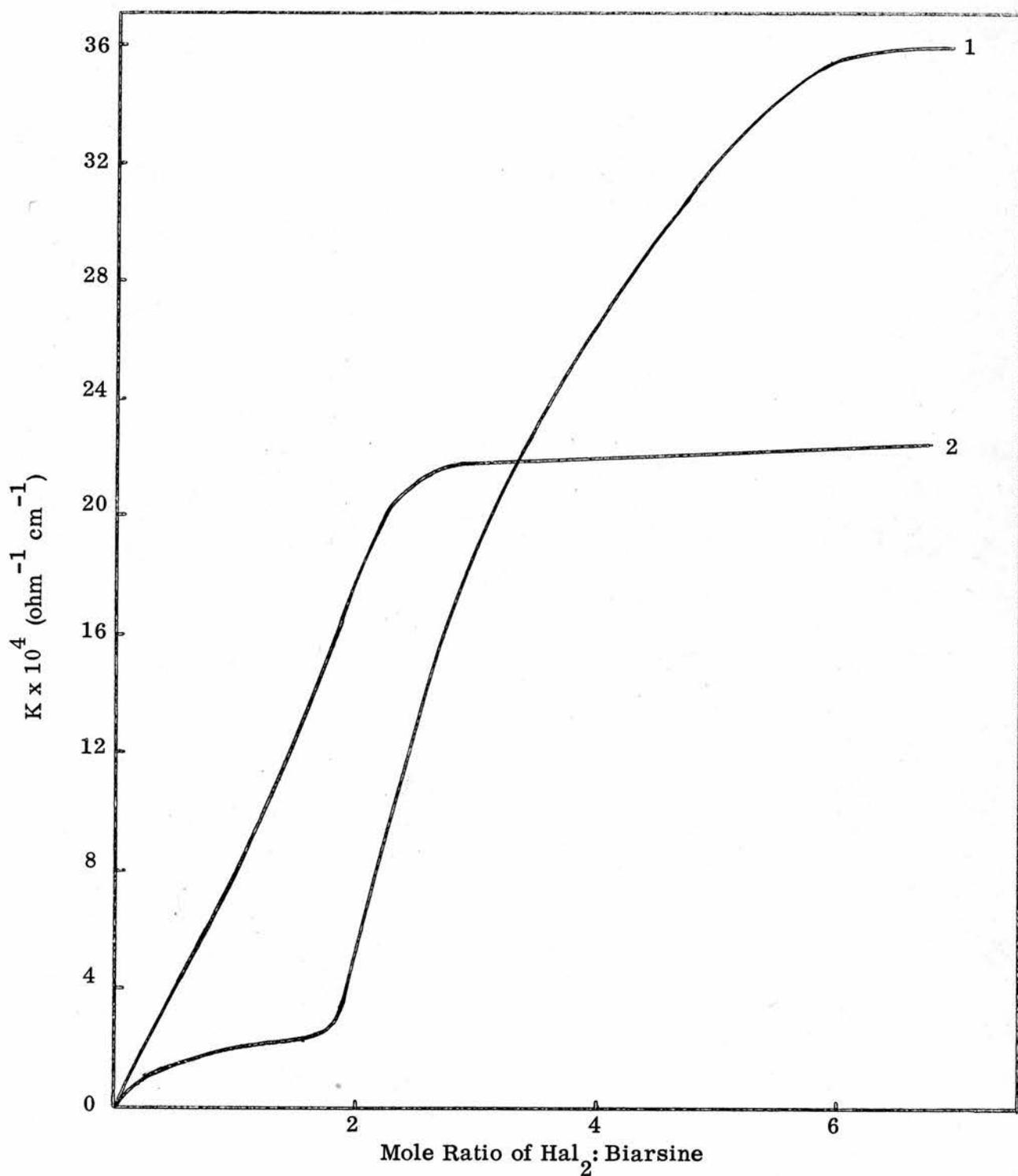


Figure 27. Conductometric Titration of the Systems:

$\text{Br}_2 - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ----- plot 1

$\text{I}_2 - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ----- plot 2

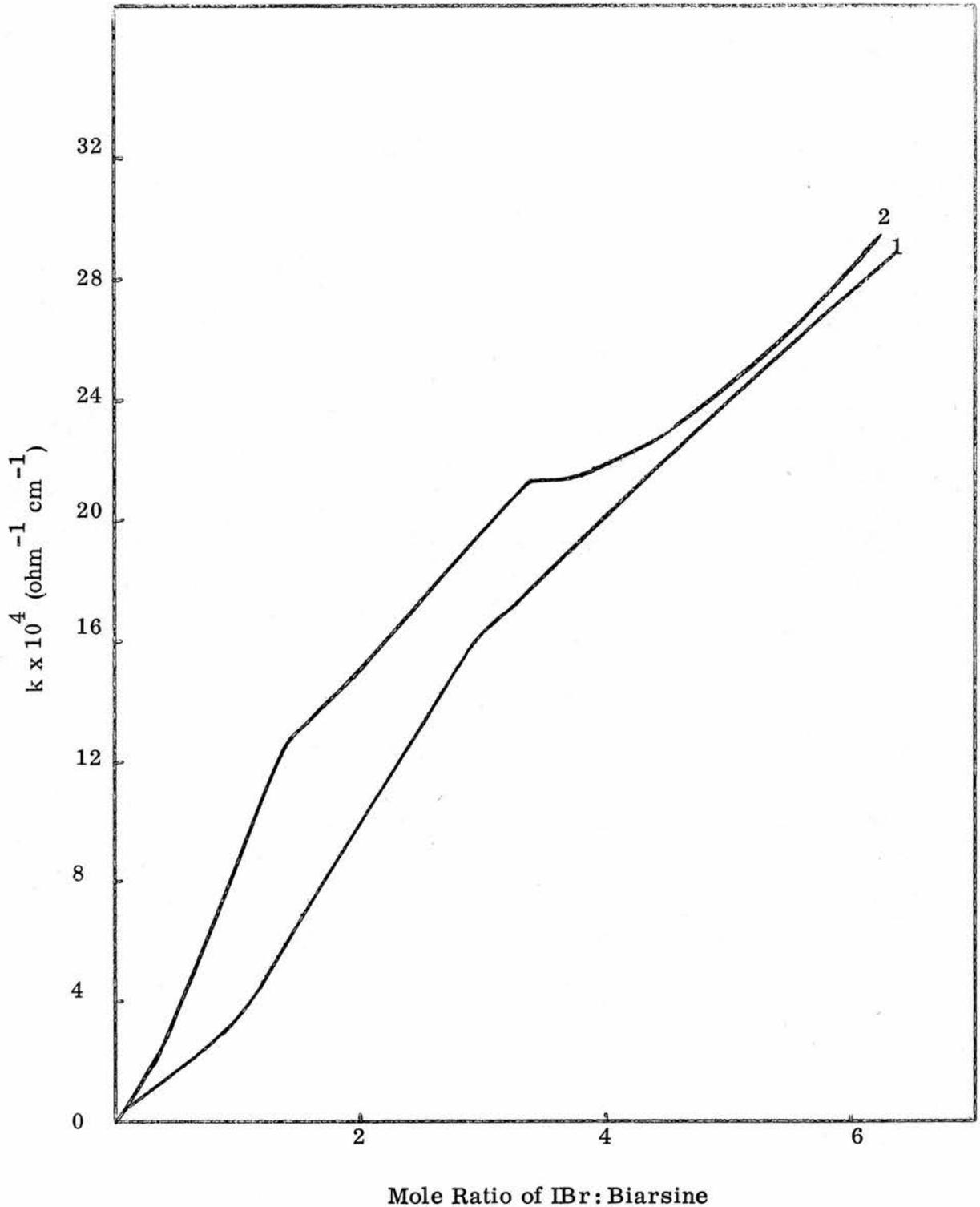


Figure 28. Conductometric Titration of the Systems:

IBr - $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ----- plot 1

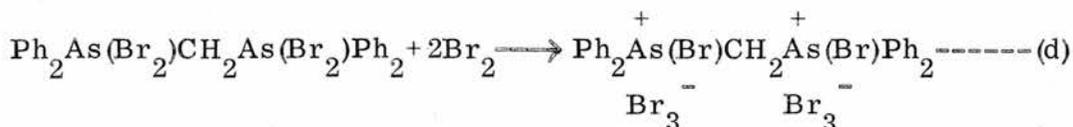
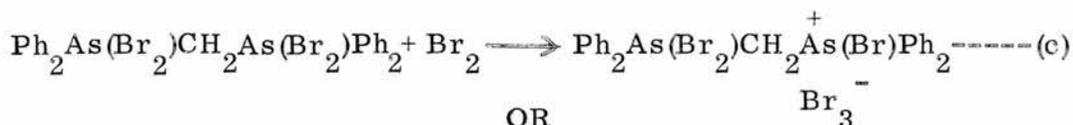
IBr - Substance A -----plot 2

Table 78. Solution Spectra of the Systems $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{Hal}_2$ in Methyl Cyanide

System	Mole ratio of $\text{Hal}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$	u. v. maxima	u. v. Indicates
$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{Br}_2$	1.79:1	-	no Br_3^-
	1.99:1	-	no Br_3^-
	2.39:1	269 w	Br_3^- present (traces)
$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{I}_2$	0.13:1	-	no I_3^-
	0.27:1	292, 362	traces of I_3^-
	0.53:1	292, 362	traces of I_3^-
	1.05:1	291, 361	I_3^-
$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{IBr}$	0.12:1	-	no trihalide present
	0.49:1	-	" "
	1.01:1	274, 353	Traces of I_3^- , I_2Br^- and IBr_2^- in mixture
	2.04:1	273, 353	mixture of I_3^- , I_2Br^- and IBr_2^-
	2.53:1	273, 353	" "
	3.57:1	265	" "
	6.2:1	256	IBr_2^- only

There are two probable reactions after the 2:1 ratio which would account for the observed sharp increase in conductivity. These are

reactions of 3:1 and 4:1 stoichiometry respectively



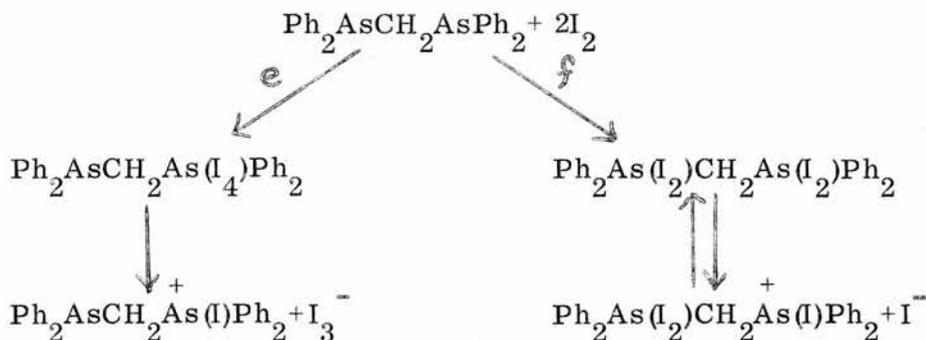
However, breaks do not occur either at the 3:1 or the 4:1 ratio, suggesting that whichever reaction occurs, it does not go to completion at the required stoichiometry. Conductometric titration thus does not elucidate completely the behaviour of this system after the 2:1 ratio except to indicate an increase in the conducting species. It is clear, however, that one or both of these reactions is occurring (the ultra-violet spectrum shows tribromide ions), and it is also evident that the reaction(s) does not go to completion at the required stoichiometric point. Assuming that the reaction does go to completion at nearly 6:1 ratio of Br_2 :biarsine (i. e. where the conductance reaches a maximum value), the molar conductance calculated at this stage (Λ_m at 6:1 = $289.39 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.012205 \text{ mol l}^{-1}$) is rather high for that of a 1:1 electrolyte suggesting that a 2:1 electrolyte may be present. Reaction (d) would thus seem to be favoured even though it contains two positive centres close together in the same structure.

The other two systems, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2-\text{I}_2$ and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2-\text{IBr}$, apparently, from their conductance-composition graphs, behave differently. In both, the conductance increased sharply from the start, but when the titrant was iodine the conductance levelled off near the 2:1 ratio (I_2 : $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$), whereas in the case of iodine monobromide

the conductance continued rising up with no sign of levelling off even at 6:1 ratio ($\text{IBr}:\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$). It should be noted that in these two systems, colour developed in the solution from the beginning of the titration and progressively darkened.

The 2:1 break in the $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2-\text{I}_2$ system coupled with the molar conductance value of the solution at this point ($\Delta_m = 147.42 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $c_m = 0.013858 \text{ mol l}^{-1}$) indicates that the adduct $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot 2\text{I}_2$ is behaving as an ionic compound. There are two probable formulations for such a 2:1 adduct namely, $\text{Ph}_2\text{AsCH}_2\text{As}(\text{I}_4)\text{Ph}_2$ or $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}(\text{I}_2)\text{Ph}_2$,

i. e.

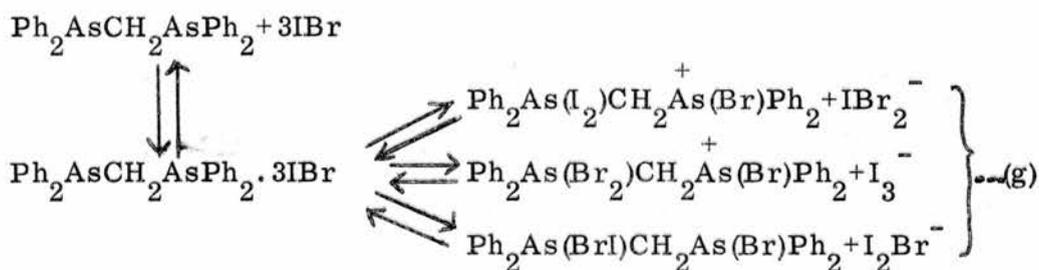


The ultra-violet spectrum of the solution at the 1:1 ratio and at points leading up to this (Table 78) shows the presence of triiodide ion thus pointing conclusively to the presence of reaction (e) in this system. The fact that the conductometric titration graph shows no appreciable increase in conductance after 2:1 ratio would seem to suggest that the second arsenic atom does not quaternise since this would lead to a 2:1 electrolyte which would cause the conductance to rise.

The form of the conductometric titration graph of the $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2-\text{IBr}$ system is rather similar to those obtained from the $\text{Ph}_n\text{PBr}_{3-n}-\text{I}_2$ and $\text{Ph}_n\text{PBr}_{3-n}-\text{IBr}$ systems, in that no well defined

breaks are present. This parallel behaviour implies that several overlapping equilibria are also present in the biarsine system. Ultra-violet spectrum results (summarised in Table 78) clearly show that the ions I_2Br^- , IBr_2^- and I_3^- are present up to about the ratio 3.5:1 and from there on only IBr_2^- ions. From these facts, it would seem that this system should be interpreted as involving the following overlapping equilibria.

0.0 → 3:1



Beyond this ratio, further addition of iodine monobromide would be expected to result in (1) bromination of I_2Br^- and I_3^- ions to IBr_2^- and (2) replacement of As-I bonds by As-Br. Both of these processes release iodine which is responsible for the very dark colour of the solution.



Adduct Preparation

Attempts to prepare halogen adducts of bis(diphenylarsino)-methane were made using methyl cyanide as solvent and using different mole ratios of halogen to biarsine. The compounds isolated along with their melting points and colour are listed in Table 79. The solids were highly conducting when dissolved in methyl cyanide. e.g.

$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_4$ and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_6$ gave molar conductance

Table 79*. The Isolated Halogen Adducts of Bis(diphenylarsino)methane

System	Mole Ratio (Reactants)	Compounds Isolated	Colour	m. p. °C
Br ₂ -Ph ₂ AsCH ₂ -AsPh ₂	3:1	Ph ₂ AsCH ₂ AsPh ₂ Br ₇	pale-yellow	122-124
	4:1	Ph ₂ AsCH ₂ AsPh ₂ Br ₈	yellow	111-113
	6:1	Ph ₂ AsCH ₂ AsPh ₂ Br ₁₀	orange	103-105
I ₂ -Ph ₂ AsCH ₂ -AsPh ₂	2:1	Ph ₂ AsCH ₂ AsPh ₂ I ₄	brown	113-115
	3:1	Ph ₂ AsCH ₂ AsPh ₂ I ₆	very dark	90-92
	4:1	Ph ₂ AsCH ₂ AsPh ₂ I ₆	very dark	90-92
	6.7:1	Ph ₂ AsCH ₂ AsPh ₂ I ₁₀	black	67
IBr-Ph ₂ AsCH ₂ -AsPh ₂	1:1			
	2:1	Ph ₂ AsCH ₂ AsPh ₂ I ₃ Br ₃	brown-yellow	156-158
	3:1			
	6.2:1	Ph ₂ AsCH ₂ AsPh ₂ I ₆ Br ₂	dark red	(oil)

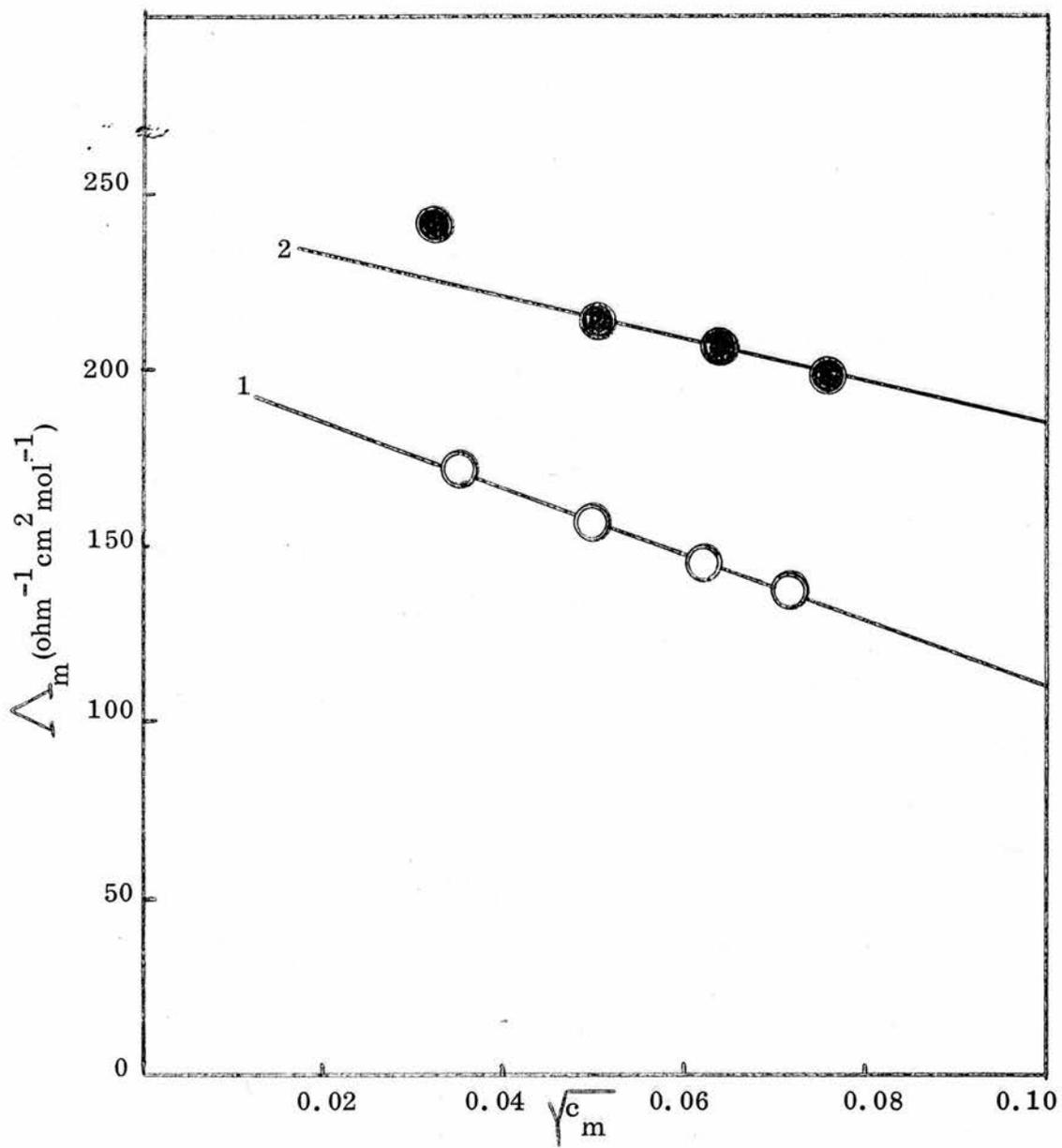
* The formulae are based on the results of analysis.

values of 110.0 and 184.0 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in 0.01M solutions respectively (see Figure 29). Unfortunately the bromine and iodine monobromide adducts were almost insoluble in methyl cyanide. It was therefore not possible to obtain molar conductance values which could be compared with those of the iodides. The ultra-violet spectra of the iodine adducts $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot \text{I}_4$ and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot \text{I}_6$ indicate the presence of triiodide ions in solution and the following ionic structures are suggested: $\text{Ph}_2\text{AsCH}_2\text{As}^+(\text{I})\text{Ph}_2 \cdot \text{I}_3^-$ and $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}^+(\text{I})\text{Ph}_2 \cdot \text{I}_3^-$ and $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}^+(\text{I})\text{Ph}_2 \cdot \text{I}_3^-$.

It is noted that a 4:1 adduct, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot \text{I}_8$, was not isolated. There are two possible structures for such a 4:1 adduct, namely $\text{Ph}_2\text{As}^+(\text{I})\text{CH}_2\text{As}^+(\text{I})\text{Ph}_2 \cdot 2\text{I}_3^-$ and $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}^+(\text{I})\text{Ph}_2 \cdot \text{I}_5^-$. The absence of this adduct is presumably due either to the inherent instability of the bipoisitive cation or the inability of the $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}^+(\text{I})\text{Ph}_2$ and I_5^- ions to build a stable crystal lattice. The 5:1 adduct, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot \text{I}_{10}$, which was obtained, presumably contains the heptaiodide ion thus, $\text{Ph}_2\text{As}(\text{I}_2)\text{CH}_2\text{As}^+(\text{I}) \cdot \text{I}_7^-$. Compounds containing I_7^- ion have been reported in literature²⁵⁷.

In the system $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{IBr}$, the only adduct isolated was $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot (\text{IBr})_3$ (Table 79). This adduct was isolated from solutions containing the reactants in the 1:1, 2:1 and 3:1 ratios. This solid produced a mixture of I_2Br^- , IBr_2^- and I_3^- in methyl cyanide. Such behaviour is in line with the interpretation of the conductometric titration graph of this system which is summarised in reaction scheme(g). On freeze drying a mixture containing iodine monobromide and the

Figure 29. Electrolytic Conductance of the iodine adducts of Bis(diphenylarsino) methane in Methyl Cyanide 25 °C

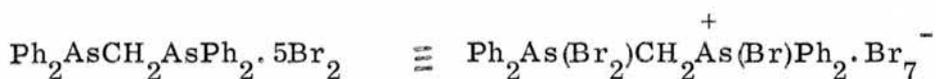
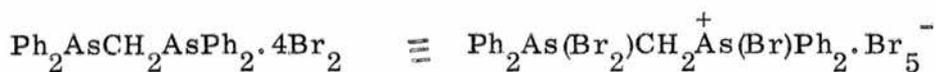
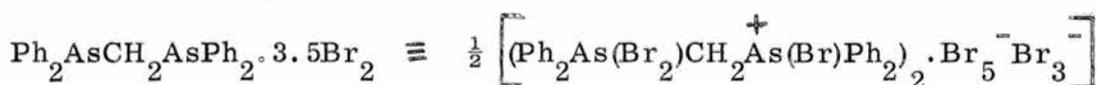


Plot 1: $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{AsI}_4$

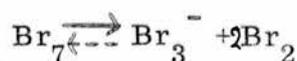
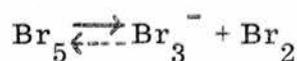
Plot 2: $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_6$

biarsine in mole ratio just over 6:1 in methyl cyanide, instead of the expected product $\left[\text{Ph}_2\text{As}(\text{Br}_2)\text{CH}_2\overset{+}{\text{As}}(\text{Br})\text{Ph}_2 \cdot \text{IBr}_2^- \right]$ (cf. equation h), a dark red oil of stoichiometry $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot \text{I}_6\text{Br}_2$ was obtained. Its ultra-violet spectrum when redissolved in methyl cyanide showed triiodide ions as the only absorbing species thus suggesting the ionic formulation $\text{Ph}_2\overset{+}{\text{As}}(\text{Br})\text{CH}_2\overset{+}{\text{As}}(\text{Br})\text{Ph}_2 \cdot 2\text{I}_3^-$.

The compounds, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot 3.5\text{Br}_2$, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot 4\text{Br}_2$, and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \cdot 5\text{Br}_2$, isolated from the Br_2 -biarsine system are described in Table 79. All these solids produced tribromide ions in methyl cyanide. The following ionic structures are therefore suggested for these adducts,



The fact that only tribromide ions are found in the ultra-violet spectrum of solutions of these compounds is accounted for by the following equilibria,



Although the graph of the conductometric titration of the $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 - \text{Br}_2$ system showed a break at the 2:1 ratio, attempts to prepare the 2:1 adduct were not successful. When the reactants were mixed in this ratio a cream coloured solid was obtained and it was clear from its infra-red and mass (Table 80) spectrum that this solid is a hydrolysis product.

The infra-red spectra of the halogen adducts (Table 79) were recorded taking all possible precautions to avoid contact with moist air. The spectra, in general, were similar to one another and to that of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$. They showed absorption bands corresponding to both the phenyl and methylene protons. The proton nuclear magnetic resonance spectra of solutions of the compounds listed in Table 79 were studied. The ^1H n.m.r. spectrum of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ in CCl_4 , CDCl_3 and d_6 dimethylsulphoxide showed peaks at ~ 2.56 and 2.76τ (phenyl protons) and 7.41τ (methylene protons) with the expected integration ratio of $\sim 10:1$ for phenyl protons: methylene protons. In contrast, the ^1H n.m.r. spectra of the halogen adducts in d_6 dimethylsulphoxide showed peaks corresponding to the protons of phenyl groups only. This would seem to indicate that complete replacement of methylene protons by halogen (Br_2, I_2) had taken place. These surprising results are in conflict with the infra-red spectra which showed absorption at a wave number expected for methylene protons. In spite of the n.m.r. results, it was thought that substitution is unlikely since the adducts were prepared under very mild conditions. Also, it has been reported that the fluorine adduct of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{F}_2)\text{CH}_2\text{P}(\text{F}_2)\text{Ph}_2$ ²⁵², exists with undisturbed methylene protons (shown by ^1H n.m.r. spectra) even though the conditions used in the preparation of this compound are quite severe. It was also thought that even if substitution did occur replacement of both hydrogens in the methylene group would be sterically unlikely. It is suggested (taking into account the infra-red results) that the absence of methylene proton signals in the ^1H n.m.r. spectra could be related

to a quadrupole effect.

Arsenic and halogen (Br_2 and I_2) nuclei possess quadrupole moments and when a molecule contains both of these nuclei it is possible that broadening of the signals of the methylene protons will occur to such an extent that they are not observed.

B. Preparation of 1,2-Bis(diphenylarsino) ethane and its Reaction with Halogens

Attempts to prepare the title compound were made using the method described by Hewertson and Watson^{241b}. The white crystalline product melted at $85\text{--}87^\circ\text{C}$ which is considerably lower than the reported value of the melting point ($100\text{--}101^\circ\text{C}$)^{241b}. However, the analytical figures were very close to the empirical formula $\text{C}_{26}\text{H}_{24}\text{As}_2$. Therefore, further attempts were made to prepare the compound varying slightly the conditions each time and on every occasion the product melted at $85\text{--}87^\circ\text{C}$. The analytical and ^1H n. m. r. data for the product (henceforth referred to as A) of these preparations are summarised in Table 81. The mass spectrum of this substance (Table 82) clearly shows the presence of the molecular ion $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2^+$ (highest peak at m/e 486) and the results are very similar to those reported by Colton and Porter²⁴². Also, the analytical and infra-red data are in keeping with the formula $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ for the reaction product. The ^1H n. m. r. spectrum of a compound of formula $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ should exhibit two multiplets (due to the ortho and meta/para protons) and a singlet (due to the ethylene protons) of integration ratio 5:1. The n. m. r. spectrum of the product was however not in keeping with this. The results are to be

Table 81. The Analytical and Proton Nuclear Magnetic Resonance Results
of The Substance A *

Preparation number	m. p. °C	Analytical results			Proton nuclear magnetic resonance results		
		% C	%H	%As	Peak Position	Type	Integral **
I	87	64.67	4.36		2.40 2.74 7.89	Multiplet Multiplet Singlet	1 10 1
II	86-87	64.39	4.50		2.40 2.74 7.89	Multiplet Multiplet Singlet	3 11 1
III	85-87	64.87	4.37				
IV	85-86	64.61	4.71	30.54 30.69	2.40 2.78 7.89	Multiplet Multiplet Singlet	2 8 1
V	86-87	64.70	4.39		2.40 2.74 7.90	Multiplet Multiplet Singlet	2 9 1
VI	86-87	64.32	4.39		2.43 2.80 2.94	Multiplet Multiplet Singlet	2 10 1
VII	85-87	64.77	4.25		2.42 2.74 7.90	Multiplet Multiplet Singlet	2 8 1
VIII	85-87	64.64	4.37		2.43 2.76 2.92	Multiplet Multiplet Singlet	1 9 1

* $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ requires: C, 64.22% ; H, 4.94% ; As, 30.81%

** Calculated integral for $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ is 5:1 (phenyl protons:
ethylene protons)

found in Table 81 where it is apparent that the ratio of the integrals is not only inconsistent with the suggested formula, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$, but also varies from one sample to another (even though the samples had the same analytical figures). It was thought that the n. m. r. spectrum of the product indicated the presence of an impurity. However Thin Layer Chromatography did not indicate an impurity and recrystallisation, sublimation and column chromatography (using a column filled either with silica or alumina and using various eluting solvents such as benzene, petroleum-ether, ether, toluene, acetone and chloroform) yielded a product of unchanged melting point and analysis. It should be noted that two different melting points, all higher than the one found in the present work, for $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ have been mentioned in the literature: $114-115^\circ\text{C}$ ^{240a} and $99-103^\circ\text{C}$ ^{241a}.

A commercial sample of $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (supplied by Aldrich Chemical Co. INC) was examined and it was found that after recrystallisation using the recommended method^{241b}, the melting point was $84-85^\circ\text{C}$, and it gave similar analytical results (C, 64.68; H, 4.53%), ¹H n. m. r. spectrum (two multiplets centred at 2.41 and 2.67 τ plus a singlet at 7.86 τ of integration ratio 2:11:1) and infra-red spectrum to the reaction product of the present work.

In spite of the discrepant n. m. r. spectrum found for the reaction product and the consequent doubt cast on its nature it was decided on the basis of its analytical results to go ahead and study its reaction with halogens. The conductometric titration and ultra-violet spectrum findings of the A-Br₂, A-I₂ and A-IBr systems are assembled in Table 83.

Table 83. Conductometric Titration and Solution Spectra of the A-Hal₂ Systems*

System	Ratio of conductometric titration break	Solution colour during titration	u. v. Indicates	Graph Number	Table Number
A-Br ₂	2:1 (levelling off after 6:1)	Colourless until the 2:1 ratio & orange beyond it	Br ₃ ⁻ ions after the 2:1 ratio	30-plot 1	84
A-I ₂	2:1	Pale orange from the start & darkening thereafter	I ₃ ⁻ ions from the start of the titration	30-plot 2	85
A-IBr	No breaks	Pale yellow from the beginning & progressively darkening on further addition of the titrant	A mixture of I ₂ Br ⁻ , IBr ₂ ⁻ and I ₃ ⁻ from the 0.5:1 ratio and up to the 6:1 ratio	28-plot 2	86

* The conductometric titration graphs of these systems are similar to those obtained from the Ph₂AsCH₂AsPh₂-Hal₂ systems.

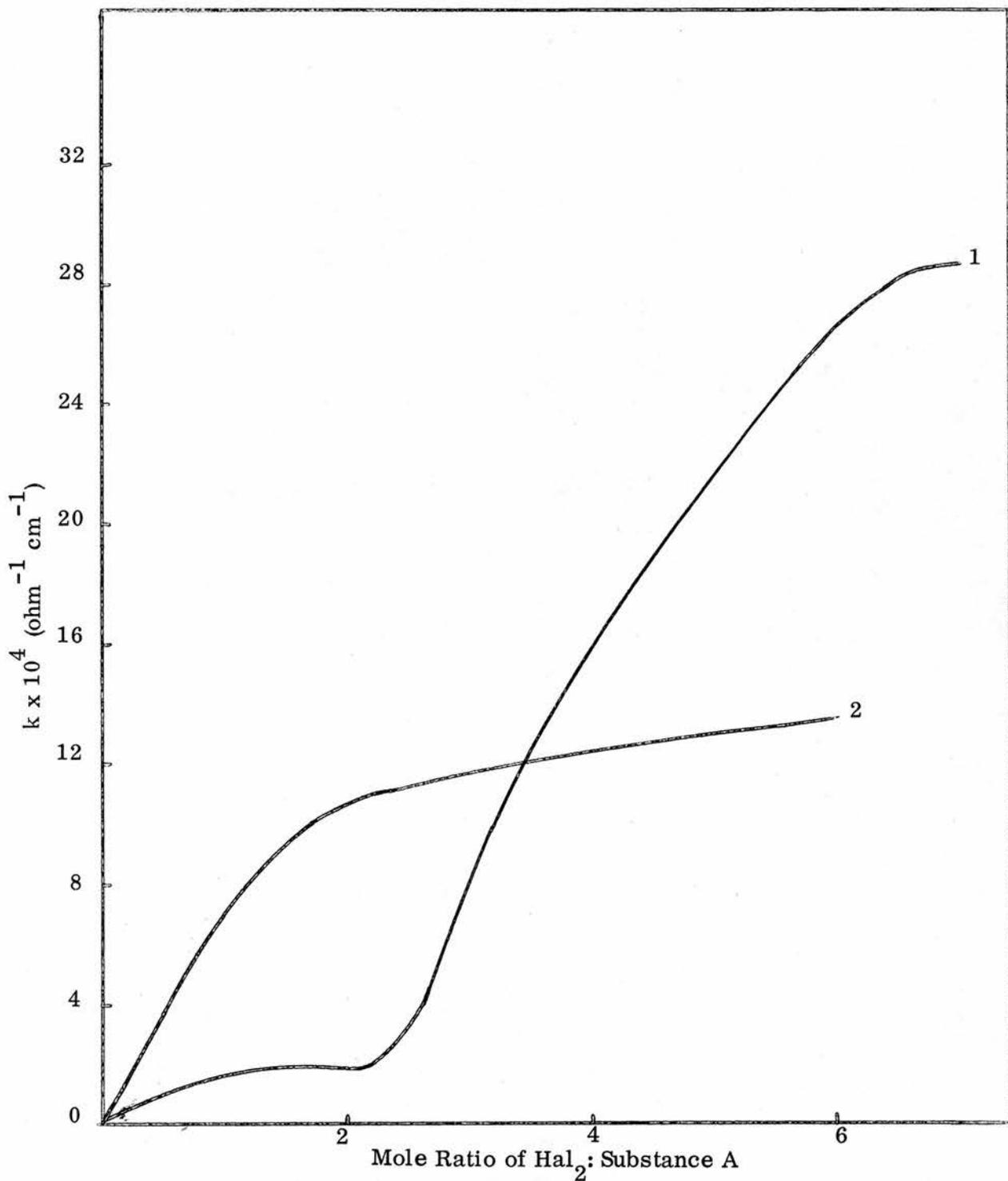


Figure 30. Conductometric Titration of the Systems:

Br₂ - Substance A ----- plot 1

I₂ - Substance A ----- plot 2

A large number of halogen adducts were isolated and these are listed in Table 87 together with the results of their analysis and the ultra-violet spectra of their methyl cyanide solutions. Possible structures of these are not discussed in view of the uncertainty about substance A.

Once again, as in the case of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{-Hal}_2$ systems, the ^1H n. m. r. spectra of the halogen adducts of A showed no signals corresponding to the protons of the ethylene group. But an interesting feature of the spectra is that in each case, it contained only one complex multiplet centred at 2.24 - 2.26 τ .

In conclusion it is worth noting that the analytical results of these adducts fit in with the assumption that the starting material is in fact $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$. However the results of the study of the reactions of A with halogens did not throw any light on the problem of the anomalous n. m. r. spectra of the reaction product, A.

Table 87. Observations from the isolated halides of the compound (A)

Mole Ratio of Reactants	Isolated Halide	Colour	m.p. °C	u. v. Indicates	Analytical Results of the Isolated Halides			Calculated Results based on $A = Ph_2AsCH_2CH_2AsPh_2$		
					% C	% H	%Hal	% C	% H	%Hal
1:1	A_2I_2	yellow	106-108	Traces of I_3^-	49.94	3.10	21.82	50.91	3.94	20.96
2:1	A_4I_4	brown	93-94	I_3^-	30.48	2.10	50.37	31.42	2.43	51.07
3:1	A_6I_6	violet	111-112	I_3^-	26.91	2.06	60.65	25.03	1.94	61.02
4:1	A_8I_8	dark violet	99-101	I_3^-	20.90	1.53	67.79	20.80	1.61	67.61
5:1	$A_{10}I_{10}$	black	79-81	I_3^-	17.30	1.21	73.21	17.79	1.38	72.30
6:1	$A_{12}I_{12}$	black	83	I_3^-	15.22	1.05	76.45	15.54	1.20	75.80
1:1	A_2Br_2	white	95-98	-	50.74	3.85	22.23	48.33	3.74	24.73
2:1	$(A_3Br_3)_2$	cream	144-146	-	44.31	3.47	33.51	43.03	3.34	33.02
3:1	A_6Br_6	pale yellow	103-104	Br_3^-	32.91	2.11	49.20	32.34	2.51	49.64
4:1	A_8Br_8	yellow	119-121	Br_3^-	28.21	2.04	56.38	27.74	2.15	56.79
6:1	$A_{10}Br_{10}$ $2CH_3CN$	orange	79-81	Br_3^-	26.43	2.07	57.75	26.35	2.21	58.34
2:1	$A_2I_2Br_2$	Red-brown	106-110	mix. of I_2Br^- , IBr_2^- , I_3^-	32.86	2.26		34.70	2.69	
3:1	$A_3I_3Br_3$	orange	92-93	only IBr_2^-	27.30	2.30		28.22	2.19	
4:1	$A_4I_4Br_4$	brown	101-103	mix. of I_2Br^- , IBr_2^- , I_3^-	30.51	2.26		29.48	2.28	

E X P E R I M E N T A L

EXPERIMENTAL

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EXPERIMENTAL

1. General Techniques

(a) Handling of Materials

Because of the hydrolytic instability of the compounds studied in this work, strict precautions were required to ensure the absence of moisture and air at all times. This was achieved by the extensive use of a nitrogen-filled dry-box kept dry by traps of phosphorus pentoxide. The nitrogen was commercial oxygen-free nitrogen dried by passage through a column of molecular sieve (AEI - Birlec, Ltd., adsorber type AB 12.5). Certain manipulations, chiefly removal of solvents, were carried out in a simple vacuum line, thus avoiding exposure of the sensitive halides to both atmospheric moisture and elevated temperatures. Compounds so handled were stored in sample tubes sealed with plastic stoppers and kept either in the dry-box or in a partially evacuated desiccator over silica gel.

(b) Vacuum System

The vacuum system was made up of a pumping unit connected via protective sludge traps to a main line from which branched various sub-sections designed for special operations, e.g. vapour pressure measurement and freeze-drying.

(c) Conductance Measurements

A standard pair of smooth platinum dipping electrodes was used in a sealed cell. The cell constant was determined by using a standard potassium chloride solution. A weighed amount of dry solvent was placed in the cell, and successive additions of the solid from small sample tubes

were always made inside the dry-box. After each addition the cell was placed in a thermostat bath at 25°C and complete solution allowed to take place. The conductance of these solutions was measured using a Wayne Kerr B641 Autobalance Bridge ; therefore molar conductances could be calculated and plotted against $\sqrt{c_m}$.

(d) Conductometric Titrations

A convenient technique for studying the reactions of phosphines (or arsines) with halogens (or interhalogens, or pseudohalogen halides) has been shown to be the conductometric titration^{155, 156}. Information may be obtained not only on the stoichiometry of the reaction products but also on their electrolytic nature.

Methyl cyanide was usually employed as a solvent as its high dielectric constant (36.7 at 25°C) results in high conductances of electrolytes and consequent easy distinction between non-electrolytes and weak electrolytes. Strong 1:1 electrolytes have Λ_m ca. $100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, and weak electrolytes have Λ_m ca. $10\text{-}20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in methyl cyanide.

In some previously studied phosphine - Halogen systems the type of the apparatus used was designed to prevent the solutions coming into contact with atmospheric moisture or tap grease. A description of the apparatus and its operation has been published¹⁶⁹. However, because of its size this apparatus could only be used in the open laboratory; in order to reduce the chance of interference by oxygen and atmospheric moisture, another apparatus was developed by McKechnie²⁰⁶ to enable the entire titration to be performed within the confines of the nitrogen

filled dry-box. The conductometric titrations of all the phosphine (or arsine) - halogen (or interhalogen or pseudohalogen halide) systems reported in this thesis were performed using this apparatus which is displayed in Figure 31 below.

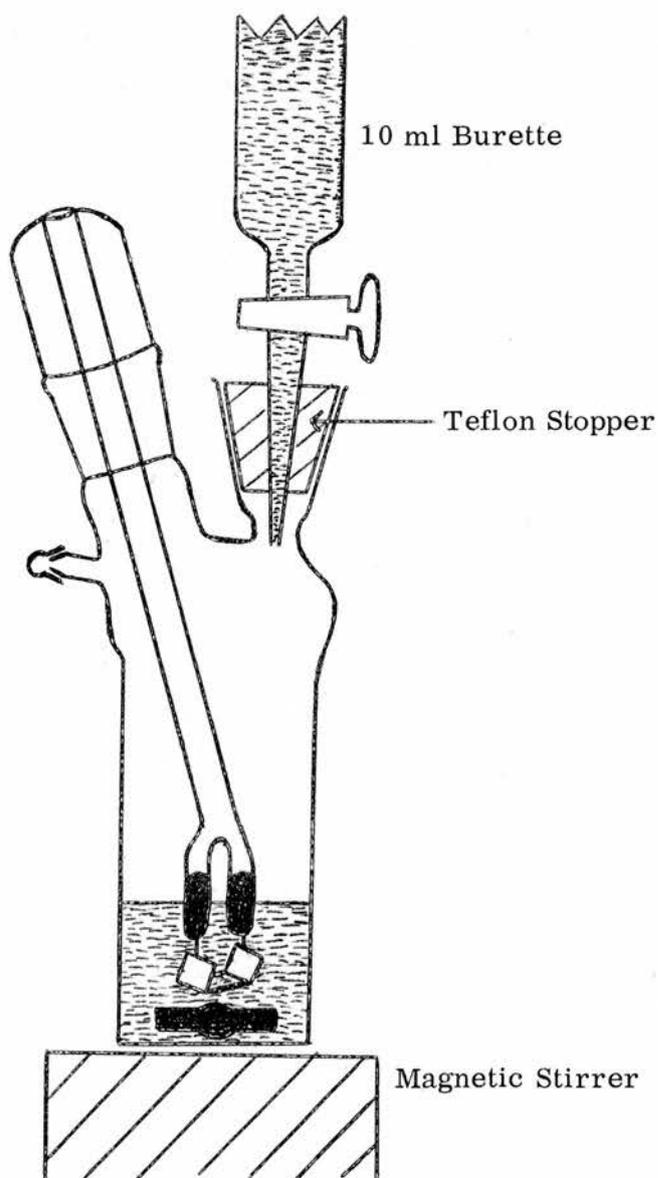


Figure 31. Dry-box Conductometric Titration Apparatus

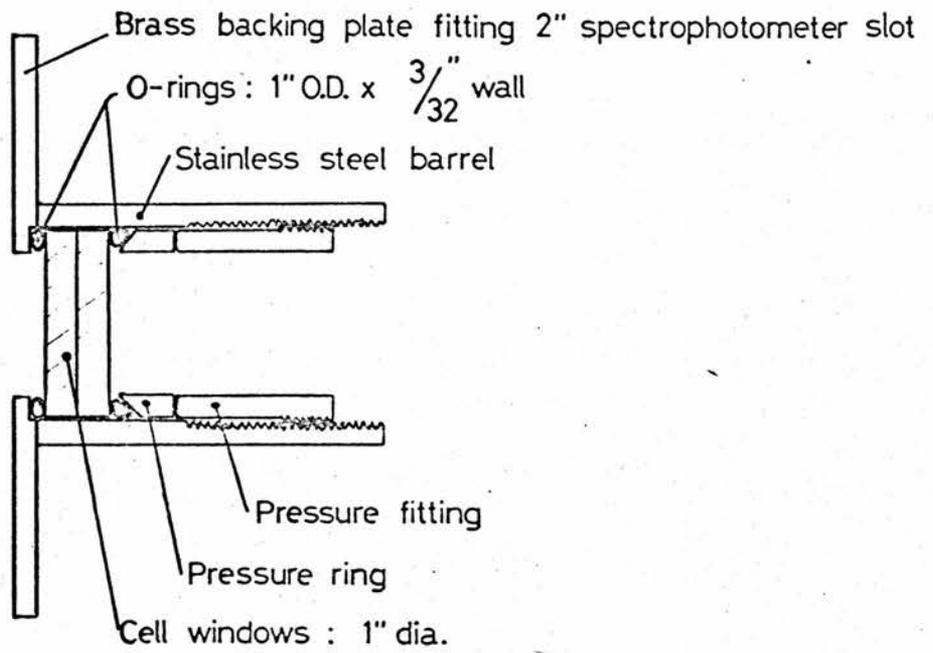
The dipping electrodes and the conductance bridge used were the same ones previously mentioned for conductance measurements. The conductance was measured when equilibrium had been attained after each addition of halogen solution.

(e) Infra-red Spectra

Infra-red spectra were recorded on a Perkin - Elmer model 621 (and in some cases model 257) Grating Infra-red Spectrophotometer over the range $4000-200\text{ cm}^{-1}$ (and $4000-625\text{ cm}^{-1}$ in the case of the latter). The samples were prepared in the dry-box as mulls in nujol or Kel - F oil or Hexachlorobutadiene, and placed between plates of potassium bromide or caesium iodide. Previously, these alkali halide windows were sealed around the circumference with "Sellotape" to prevent attack by moisture. This technique was found to be difficult and the possibility of moisture attack could never be completely eliminated.

A new sample holder was constructed as shown in Figure 32 which held the sample in the infra-red spectrophotometer with no possibility of attack on the mull by either air or moisture.

A mull was prepared and placed between a pair of one inch (1") alkali halide windows in the dry-box as usual and inserted in the barrel of the cell between O - rings. The pressure ring and pressure fitting were fitted and then tightened so that the circumference of the windows was sealed before removal from the dry-box by the O - rings and the barrel of the cell. This assembled cell could then be inserted into the standard 2" sample slot of any infra-red spectrophotometer.



Demountable Cell for Air Sensitive Samples

Figure 32.

(f) Ultra-violet Spectra

Ultra-violet spectra were recorded on a Unicam SP800B UV/visible recording spectrophotometer. Stoppered quartz cells of 1 cm or 0.1 cm path length were used, measurements being made at room temperature (ca. 20 °C).

In order to study the ultra-violet spectra of solutions with concentrations similar to those used in the conductometric titration, it was necessary to construct an ultra-violet cell of very short path length.

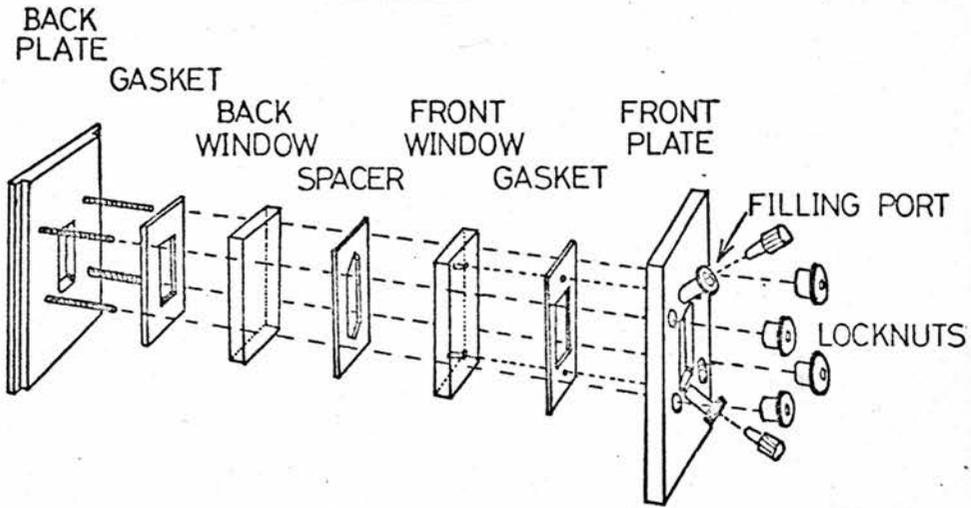
Initially a cell was assembled using a standard infra-red type solution cell fitted with silica windows (Optro), but this cell was found to be unsuitable because an efficient seal could not be maintained in the region of the filling ports, and because the corrosive halogen - containing solutions attack the steel front plate and ports of the cell.

To remedy this situation the front gasket and front plate of the cell were modified as shown in Figure 33.

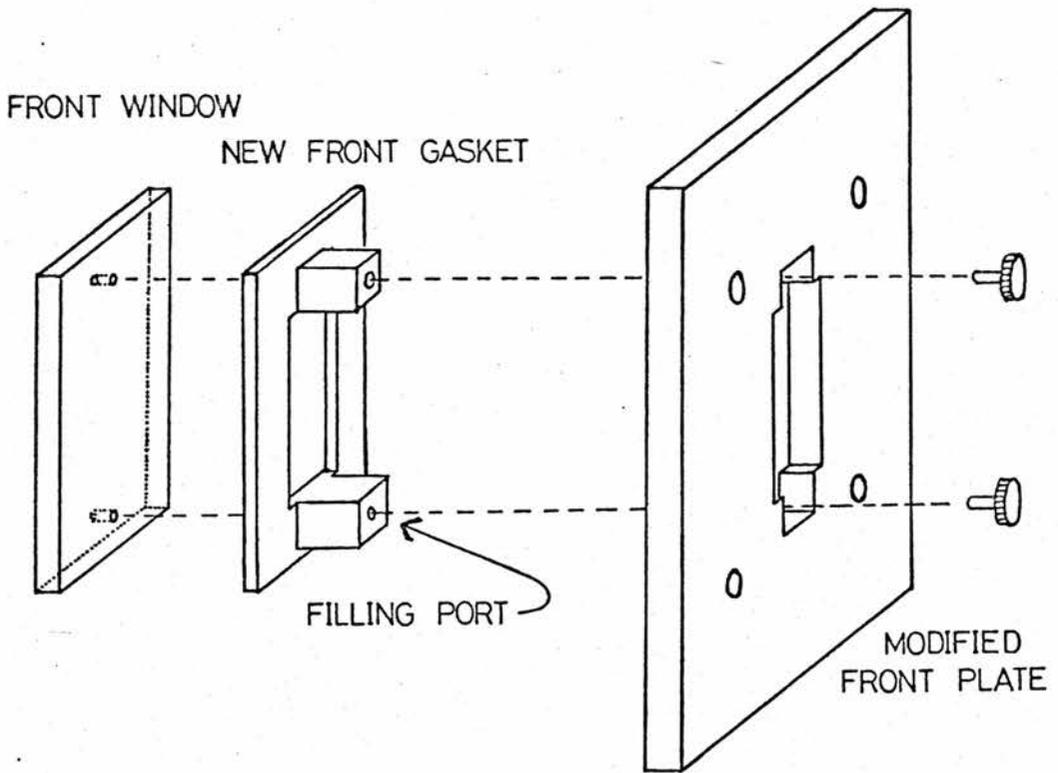
A new front gasket was manufactured from a solid piece of PTFE so that the filling ports were an integral part of the gasket. The front plate was then modified so that these filling ports could pass through it. (Assembly of the cell is carried out as usual, but is easier because there is no necessity to line up separate holes in the filling ports and front gasket).

This cell was found to be leak proof and there is no danger of corrosion as the sample only comes in contact with the silica windows and the PTFE spacer, front gasket and stoppers. A further advantage of the cell is that the smaller PTFE filling ports enable the use of normal

Figure 33.



(a) STANDARD LIQUID CELL



(b) FRONT OF LIQUID CELL FOR CORROSIVE SAMPLES

dropping pipettes rather than expensive syringes.

The path length of this cell was determined by the interference method :

$$l = \frac{n}{2(\bar{\nu}_1 - \bar{\nu}_2)} \quad \text{cm}$$

n = number of fringes (= 9)

$\bar{\nu}_1, \bar{\nu}_2$ = frequencies between which fringes are contained (= 3910 cm^{-1} and 2520 cm^{-1} respectively).

The value found for the path length of this ultra-violet cell was 0.0032 cm.

(g) Nuclear Magnetic Resonance (n. m. r.) Spectra

Nuclear magnetic resonance spectra were recorded on a Varian Associates HA100 spectrometer. The compounds were dissolved in either d_6 dimethylsulphoxide or deuterio-chloroform for proton nuclear magnetic resonance. All ^1H n. m. r. chemical shifts were based on tetramethylsilane.

(h) Mass Spectra

Mass spectra were recorded on an AEI MS902 mass spectrometer. Samples were submitted in sealed tubes, however, contact with atmospheric moisture was unavoidable during injection into the spectrophotometer, and therefore many of the spectra of bromine, iodine and iodine monobromide adducts showed hydrolysis products.

(i) Column and Thin Layer Chromatography

The compound was dissolved in benzene and applied to an alumina or silica column prepared with petroleum-ether (40-60 $^{\circ}\text{C}$). It was eluted

in turn with the following solvents : Benzene, Petroleum-ether (40-60 °C), diethyl ether, Toluene, acetone and chloroform.

The Thin layer chromatography (TLC) was carried out on silica (M. N. Kieselgel G) coated plates.

(j) Analyses

Microanalyses for carbon, hydrogen and nitrogen were performed in the Chemistry Department of St. Andrews University on a Perkin - Elmer Model 240 Elemental Analyzer by Mr. James Bews.

Analysis for arsenic was performed by Alfred Bernhardt of West Germany.

Halogen analyses were carried out potentiometrically using an adaptation of the method described by Lingane²⁵⁸. Approximately 50 mg of sample was accurately weighed into a stoppered 50 ml quickfit conical flask, the addition of sample being made in the dry-box. The sample was then hydrolysed with 20 ml of 2M sodium hydroxide, the hydrolysis being performed in a closed system to prevent the possible escape of hydrogen halide. The resultant solution or suspension was left to stand for one hour before boiling for a minimum of fifteen minutes to ensure complete hydrolysis. It was then cooled and made just acidic with concentrated sulphuric acid before immediately bubbling sulphur dioxide gas, through the solution, for two minutes to reduce any hypohalite ion present. Further boiling served both to drive off excess sulphur dioxide and reduce the bulk of the solution. After cooling, the solution was neutralised with concentrated ammonia. It was then thoroughly washed with distilled water into a 100 ml beaker, 2.5 g A. R. barium nitrate added, followed by 10 ml

A. R. acetone and 3-5 drops of boiled out 6M nitric acid, before titrating against 0.1M silver nitrate. The solution was stirred throughout the titration by the use of a magnetic stirrer. A silver wire was used as an indicator electrode and a saturated calomel electrode as the reference electrode with a salt bridge containing 3M ammonium nitrate solution.

The electrode potential (mV) of the initial halide solution was determined, and corresponding measurements taken at intervals of 0.1 ml addition of silver nitrate from the burette. A more rapid increase in the change in potential signified that the end - point was being approached, and the potential reading were taken at more frequent intervals. A graph was plotted of mV readings against ml of silver nitrate added, the points of inflection being regarded as the end - point of the titration

NOTE :- Good analytical data were not obtained for some of the compounds reported in this thesis, partly because of the inherent instability of these compounds at room temperature, and partly because of experimental difficulties.

(k) Electrolysis

The electrolysis cell was of the H-type as shown in Figure 34 the electrodes consisting of smooth platinum foil. The apparatus was thoroughly washed with acetone and then oven dried. The cell was transferred to the dry-box, rinsed with the solution to be electrolysed and after it was filled, the solution was electrolysed for 1-2 hours by the passage of direct current (12v).

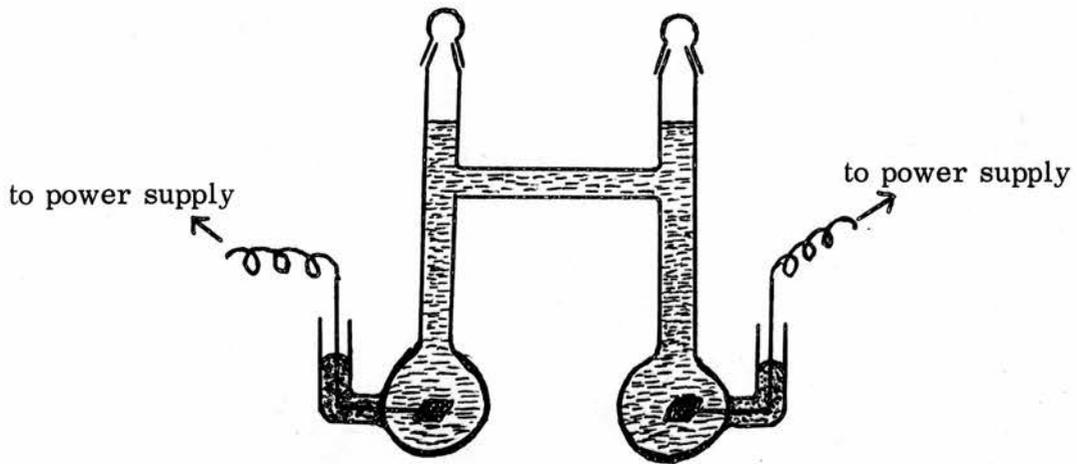


Figure 34 Electrolysis Cell

2. SOURCE AND PURIFICATION OF MATERIALS

(a) Solvents

(I) Methyl Cyanide

Pure anhydrous methyl cyanide suitable for conductance studies was prepared by a modification of the method described by Smith and Witten²⁵⁹. The commercial material (Hopkins and Williams) was stirred, using a large magnetic stirrer, over potassium hydroxide pellets for twenty-four hours. It was then filtered and distilled into a flask containing calcium chloride (14-20 mesh) before stirring for a further twenty-four hours. It was again filtered and then distilled onto phosphorus pentoxide; the distillate was refluxed and distilled onto fresh phosphorus pentoxide. Finally, after adding some fresh phosphorus pentoxide, the methyl cyanide was refluxed and distilled into a flat bottomed flask, which contained oven dried Type 4A Molecular Sieve, using a nine inch column of glass helices which had also been oven dried. The fraction boiling between 81-82 °C was collected and after tightly stoppering the flask, using a PTFE (Teflon) sleeve, it was stored in a large desiccator over silica gel. The dry solvent was distilled on the vacuum line as required, to remove any traces of sieve powder or drying agent. The specific conductance of methyl cyanide purified by this method was always ca. $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25 °C.

A spectroscopic grade methyl cyanide for ultra-violet spectral studies was obtained by using the method of purification reported recently by Walter and Ramaley²⁶⁰. The commercial material (Hopkins and Williams) was refluxed over anhydrous aluminum chloride (15 grams per liter of methyl cyanide) for one hour followed by rapid distillation. The

distillate was then refluxed over lithium carbonate (10 grams per liter of methyl cyanide) for one hour followed by rapid distillation. This was refluxed again over calcium hydride (2 grams per liter of methyl cyanide) for one hour and then followed by a careful fractionation from a helice packed column at high reflux ratio.

(II) Nitrobenzene

A. R. grade nitrobenzene was distilled twice, once at atmospheric pressure, when the fraction boiling at 207-208 °C was collected and the other at reduced pressure (ca. 2 mm) incorporating a nitrogen leak and a Vigreux column. The fraction boiling at 67 °C was collected. The specific conductance of this nitrobenzene was less than $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25 °C.

(III) Carbon Tetrachloride

The method used to obtain pure carbon tetrachloride was a variation of that described by Popov and Schmorrr⁷⁷. The crude solvent (500 ml) was refluxed for ten hours with a saturated solution of potassium permanganate in 2M sodium hydroxide solution (100 ml). The carbon tetrachloride was then separated and washed several times with water. After a preliminary drying with anhydrous magnesium sulphate, the carbon tetrachloride was filtered and distilled onto phosphorus pentoxide, and then distilled several times onto fresh phosphorus pentoxide. The fraction boiling between 75.5-76.0 °C, at atmospheric pressure, was collected.

(IV) Diethyl Ether

Diethyl ether was preliminary dried over calcium chloride and then sodium wire was added. The ether was allowed to stand over the sodium

wire for several days before use.

(V) Benzene

Benzene (commercial grade) was preliminary dried over anhydrous calcium chloride for 24 hours, filtered and then sodium wire added. After a further two days, it was refluxed over fresh sodium wire for three hours, followed by rapid distillation. This process was repeated three times and finally the distillate was stored over sodium wire. Before use it was redistilled under nitrogen.

(VI) Petroleum - ether (40-60 °C)

The commercial grade solvent was well-shaken twice with concentrated sulphuric acid (10% of the volume). Vigorous shaking was continued with successive portions of a concentrated solution of potassium permanganate in 10% sulphuric acid until the colour of permanganate remained unchanged. The mixture was then transferred to a separating funnel and the extracted petroleum-ether was washed thoroughly with a large volume of water and dried over anhydrous calcium chloride. After twenty four hours it was filtered. The filtrate was twice distilled over sodium wire and the fraction boiling between 40-60 °C was collected. It was stored in a tightly stoppered flask in a desiccator containing phosphorus pentoxide. Before use, petroleum-ether was redistilled under nitrogen.

(VII) Carbon Disulphide

Pure carbon disulphide was obtained by using the method described by Malone and Ferguson²⁶¹. A.R. grade carbon disulphide was agitated in a glass-stoppered bottle with successive portions of pure mercury until

all of the free sulfur was removed. This required prolonged agitation with several portions of mercury. The treatment was continued in every case until no tarnish appeared on the bright surface of the mercury after several minutes of contact with the carbon disulphide. The solvent was filtered and fractionated, the middle fraction was collected and then refluxed over phosphorus pentoxide. This process was repeated twice and the solvent was then used immediately.

(b) Reagents

(I) Bromine

A. R. bromine was first stored over calcium bromide. It was filtered into a small flask under a nitrogen hood, then attached to the vacuum system and pumped to remove the more volatile impurities. The bromine was then cooled to ca. -3°C and distilled in vacuo into small ampoules cooled to liquid nitrogen temperature. Thus, known weights of bromine were stored in sealed ampoules. Solutions were made by breaking a given ampoule under a known weight of solvent.

(II) Iodine

A. R. grade iodine was resublimed and stored in a desiccator over phosphorus pentoxide.

(III) Iodine Monobromide

Iodine monobromide was always freshly prepared before use by breaking a bromine ampoule alongside its molar equivalent of finely powdered iodine, under a known weight of solvent.

(c) Starting Materials(I) Dibromophenylphosphine

Dibromophenylphosphine was prepared by the method of Nannelli et al.²⁶² Fifty grams of dichlorophenylphosphine and 100 g of phosphorus tribromide were placed in 250 - ml three-necked flask fitted with a gas inlet tube and an efficient reflux condenser provided with a calcium chloride drying tube. Anhydrous hydrogen bromide was passed from a cylinder through the mixture for a period of ten hours while the mixture was stirred magnetically and maintained at reflux with a heating mantle. The resulting yellow-orange solution was vacuum distilled and the unreacted phosphorus tribromide was removed by distillation at 48-50 °C / 12 mm. Hg, using an oil bath. The distillation flask was then fitted with a Vigreux column, well insulated with both glass wool and asbestos tape. The clear yellow oil boiling at 261-263 °C was collected. (Found : C, 26.93 ; H, 1.82%. PhPBr_2 requires C, 26.90 ; H, 1.88%). u. v. spectrum shows no tribromide absorption.

i. r. : - 3005(w), 1965(w), 1925(w), 1890(w), 1795(w), 1755(vm), 1670(w), 1580(m), 1480(m), 1435(s), 1380(vw), 1335(m), 1305(m), 1185(vw), 1155(vw), 1105(m), 1085(s), 1065(vw), 1025(w), 1000(s), 970(w), 840(w), 740(s), 685(s), 625(vw), 615(vw), 535(m), 475(s), 420(s), 405(s), 375(s), 330(m) cm^{-1} .

(II) Bromodiphenylphosphine

Bromodiphenylphosphine was prepared by the method outlined by Kuchen and Grunewald²⁶³. Chlorodiphenylphosphine (44.43 g) and phosphorus tribromide (111.67 g) were mixed in a 250 - ml three-necked flask fitted

with a gas inlet tube and an efficient reflux condenser provided with a calcium chloride drying tube. The mixture was refluxed under nitrogen for one hour at 130–150 °C using an oil bath. The resulting yellow solution was vacuum distilled at 12 mm. Hg to remove the unreacted materials. After the removal of the formed phosphorus trichloride the distillation flask was fitted with a Vigreux column, and the pressure was reduced to 0.9 mm. Hg. The clear pale yellow oil boiling at 153–154 °C/ 0.9 mm. Hg was collected. After further distillation at 0.9 mm. Hg, the product (Ph_2PBr) found to be analytically pure. (Found : C, 54.10; H, 3.62%. Ph_2PBr requires C, 54.37 ; H, 3.80%).

i. r. : 3045(m), 1950(wb), 1880(wb), 1800(wb), 1750(wb), 1780(m),
1470(m), 1430(s), 1380(wb), 1300(wb), 1271(vw), 1230(vw),
1180(vw), 1125(m), 1085(m), 1065(w), 990(m), 940(vw),
835(vw), 735(s), 685(s), 610(w), 495(m), 475(m), 425(m),
390(m), 320(vw) cm^{-1} .

(III) Phosphorus Tribromide

A. R. phosphorus tribromide was twice vacuum distilled at 12 mm. Hg pressure. The distillate was attached to vacuum line, cooled to liquid nitrogen temperature and pumped for one hour to remove the more volatile impurities and finally distilled by the method of freeze-drying. The phosphorus tribromide purified in this way was stored in a tightly stoppered flask in a desiccator containing phosphorus pentoxide. Before use, the phosphorus tribromide was further purified by fractionation under vacuum. (Found : Br, 87.99%. PBr_3 requires Br, 88.55%).

(IV) Diiodophenylphosphine

Various attempts to prepare diiodophenylphosphine were made using the methods reported by Feshchenko et al.¹⁴ as follows :-

(a) Reaction of dichlorophenylphosphine with lithium iodide in benzene

Lithium iodide (14.03 g) was stirred with 100 ml of benzene in a flat-bottomed flask fitted with a separating funnel containing dichlorophenylphosphine (9.38 g) in 30 ml of benzene. Dichlorophenylphosphine was added very slowly maintaining vigorous stirring in the reaction flask. The solution took up the colour of iodine. After complete addition of phosphine the mixture was stirred for another hour. The formed lithium chloride was filtered off and the solvent was evaporated under slightly reduced pressure to half volume. On cooling, yellow crystals of diiododiphenyldiphosphine ($\text{Ph}_2\text{P}_2\text{I}_2$) were precipitated. The crystals were filtered and then vacuum dried. When the mother solution was evaporated more of this product, $\text{Ph}_2\text{P}_2\text{I}_2$, was obtained. Thus, it was found not possible to isolate the expected diiodophenylphosphine, PhPI_2 , by this method. The yellow crystalline solid melted at 171°C . (Found : C, 30.63 ; H, 2.08%. $\text{Ph}_2\text{P}_2\text{I}_2$ requires C, 30.67 ; H, 2.14%). u.v. spectrum showed no trihalide ion absorption.

(b) Reaction of dichlorophenylphosphine with lithium iodide in carbon tetrachloride

Dichlorophenylphosphine (8.46 g) in 40 ml of carbon tetrachloride was added, as in the above reaction, to a suspension of lithium iodide (12.65) in carbon tetrachloride (150 ml). Once again only yellow crystalline solid was obtained. It was identical to that obtained in the above reaction (m.p. $169-171^\circ\text{C}$).

Various modifications of the overleaf reactions were attempted such as : refluxing the mixtures during the addition of dichlorophenylphosphine, addition of solid lithium iodide in portions to the solution of PhPCl_2 in benzene or carbon tetrachloride with reflux. But every time the compound $\text{Ph}_2\text{P}_2\text{I}_2$ was the only one isolated. (Found : C, 31.34; H, 2.15% . $\text{Ph}_2\text{P}_2\text{I}_2$ requires C, 30.67; H, 2.14%).

(c) Reaction of dichlorophenylphosphine with lithium iodide in absence of the solvent

Dichlorophenylphosphine (22.81 g) was added dropwise and with stirring from a separating funnel fitted to a three-necked flat bottomed flask containing lithium iodide (34.11g). The flask was also fitted with a gas inlet tube and an efficient reflux condenser provided with silica gel drying tube. When the addition was complete the mixture, which took up the iodine colour, was vigorously stirred for one hour. It was then diluted with benzene (40 ml), refluxed under nitrogen for two hours and the resultant mixture, which contained yellow crystals, was left to stand over-night in the dry-box before filtering. On evaporation of benzene by distillation of the filtrate further amount of yellow solid precipitated. This was separated and the final filtrate was vacuum distilled twice at 0.1 mm. Hg. The clear red-brown oil boiling at $136^\circ\text{C}/0.1$ mm. Hg was collected. This compound, PhPI_2 , was found to be analytically pure. This procedure when was repeated the same product, PhPI_2 , was isolated. (Found : C, 19.49 ; H, 1.41% . PhPI_2 requires C, 19.90 ; H, 1.39%). u.v. spectrum showed triiodide ions (peaks at $\lambda_{\text{max}} = 291, 361 \text{ m}\mu$).

i. r. :- 3060(m), 3040(m), 1945(wb), 1870(wb), 1790(wb), 1650(wb),
1575(m), 1565(w), 1475(m), 1430(s), 1375(wb), 1330(m),
1300(m), 1270(w), 1180(m), 1160(w), 1100(s), 1075(s), 1060(w),
1020(w), 997(s), 963(vw), 915(vw), 836(wb), 737(s), 682(s),
612(w), 467(s), 399(s), 363(s), 327(s) cm^{-1} .

(V) Dipenyliodophosphine

This compound, Ph_2PI , was prepared by the method of Issleib and Seidel²⁴⁴. Diphosphorus tetraphenyl, $\text{Ph}_2\text{P}-\text{P Ph}_2$ (from Digby Chemical Service, London), was dissolved in 100 ml of benzene contained in a three-necked flask fitted with a gas inlet tube (to pass nitrogen), silica gel drying tube, and electrical stirrer. To this, and with vigorous stirring, iodine (3.43g) solution in benzene (80 ml) was added dropwise. The reaction mixture was maintained at a temperature below 15°C using an ice-bath. The solution was brown in colour and contained small amounts of a dark coloured precipitate. This was filtered in the dry-box and the solvent was removed from the filtrate by distillation under atmospheric pressure. The resultant red solution was fractionated under reduced pressure. The fraction boiling at $169-170^\circ\text{C}/4.0\text{ mm. Hg}$ was collected. (Found: C, 46.22 ; H, 2.92% . Ph_2PI requires C, 46.18 ; H, 3.23%). u. v. spectrum shows no trihalide ion absorption.

i. r. :- 3060(m), 3043(m), 1942(wb), 1867(wb), 1789(wb), 1647(wb),
1575(wb), 1482(m), 1437(s), 1377(vw), 1330(w), 1308(w),
1273(vw), 1183(w), 1140(w), 1047(w), 1093(m), 1070(vw), 1028(m),
1000(s), 937(wb), 922(vw), 843(vw), 740(s), 690(s), 617(vw),
548(w), 503(m), 475(m), 428(m), 397(wb), 370(wb) cm^{-1} .

(VI) Phosphorus Triiodide

Phosphorus triiodide was prepared by the method of Malone and

Ferguson²⁶¹ from the reaction between elemental phosphorus and iodine. White phosphorus was purified by washing with hot dilute nitric acid (60 °C), rapidly followed by distilled water. It was further washed with methanol and finally with carbon tetrachloride. Phosphorus (1.13g) was weighed into 50 ml of carbon disulphide, and this was added immediately to 120 ml of carbon disulphide containing 13.80 grams of iodine. The reaction was carried out in a three-necked flask fitted with a gas inlet tube (to pass nitrogen during the course of the reaction) and an efficient reflux condenser provided with a calcium chloride drying tube. The resultant dark opaque solution was gently refluxed for one hour using a steam bath. After this stage the reaction mixture was filtered hot, and the filtrate reduced to small volume by distillation of the solvent. The solution was then cooled slowly to room temperature followed by further cooling in an ice-bath. Dark red crystals of phosphorus triiodide were deposited from the mother liquor. The crystals were filtered in the dry-box and washed with small amounts of cold carbon disulphide. After two recrystallisations from carbon disulphide the crystals were vacuum dried for a short period of time, to prevent decomposition. (m. p. 61 °C). (Found : I, 92.11 and 92.22% . PI_3 requires I, 92.47%). u. v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291, 361 \text{ m}\mu$). i. r. : $308(\text{s}) \text{ cm}^{-1}$.

(VII) Diphosphorus Tetraiodide (P_2I_4)

White phosphorus (3.1g) dissolved in carbon disulphide (65 ml) was added in portions with shaking, as in the above reaction, to a solution of iodine (25.39g) in carbon disulphide (280 ml)²¹⁶. The mixture was allowed to stand in the dark in a well-stoppered flask for twelve hours to complete

the reaction. The clear orange-red solution was distilled to remove most of the solvent. On cooling the solution to room temperature red crystals of P_2I_4 were deposited. The crystals were quickly filtered off in the dry-box and washed with small amounts of carbon disulphide and then dried for a short time in vacuum to prevent decomposition. (m.p. $125-126^\circ C$). (Found : I, 89.91% . P_2I_4 requires I, 89.12%) u.v. spectrum showed no triiodide ion absorption.

i. r. :- $330(s), 300(s) \text{ cm}^{-1}$.

(VIII) Triphenylphosphine

The commercial triphenylphosphine (B. D. H.) was recrystallised from 95% ethanol until a constant melting point was obtained (m.p. $79^\circ C$).

(IX) Triphenylarsine

Triphenylarsine was prepared by the Wartz reaction between arsenic trichloride and chlorobenzene ²⁶⁵, and the crude product was recrystallised from 95% ethanol to constant melting point (m.p. $61^\circ C$).

(X) Cyanogen Iodide ²¹⁶

A solution of sodium cyanide (27.06g) in water (100 ml) was allowed to cool to $0^\circ C$ in a 500-ml, ice-cooled three-neck flask provided with a stirrer and a thermometer. To this, solid iodine (127.1g) was added in portions of 3-4 g with vigorous stirring (each new portion was added only after the previous one had completely reacted). The cyanogen iodide was extracted ten minutes after the end of the addition, first with 120 ml, then with 100 ml and finally with 80 ml of ether. The combined ether extracts when were concentrated in vacuum at room temperature an impure,

light-brown product was separated. To remove the sodium iodide, which was soluble in ether solution of cyanogen iodide $\text{NaI}_2(\text{CN})$, the crude product was heated to 50°C with water (120 ml) and shaken for twenty minutes at slightly reduced pressure. After cooling at 0°C , the colourless, crystalline cyanogen iodide was separated from the yellow mother liquor by filtration, washed repeatedly with small amounts of ice water, and dried in air. This product was recrystallised twice from chloroform. The crystals were dissolved in 170 ml of boiling chloroform and slowly cooled to ca. -10°C . The crystals were filtered and washed with some ice-cold chloroform and then dried in air. The silky crystalline needles melted at $146-147^\circ\text{C}$. (Found : C, 7.74 ; N, 9.10%. CNI requires C, 7.85 ; N, 9.16%). u.v. spectrum showed no trihalide ion absorption.

i. r. :- 2187(s), 2137(w), 733(m) cm^{-1} .

(XI) Cyanogen Bromide²¹⁶

A solution of sodium cyanide (210g) in water (430 ml) was added to 160 ml of bromine, covered with water (150 ml) in a one-liter ground joint flask, at the rate of one drop per second with stirring. The temperature of the mixture was kept below 20°C . The last 150 ml of the sodium cyanide solution was diluted with twice that amount of water. In addition to the stirring, the flask was vigorously shaken by hand after every few minutes. When a persistent brown tint appeared the rest of the sodium cyanide solution was discarded. The flask containing the reaction mixture was then fitted with a small condenser well-isolated with both glass wool and asbestos. The cyanogen bromide was then distilled by heating the mixture on a water bath. To prevent the recrystallisation of cyanogen bromide

on the walls of the condenser, hot water was passed through the condenser. At a temperature of 50-53 °C, colourless crystals of cyanogen bromide were found to deposit around the container and then melted at 59-61 °C. When most of cyanogen bromide was distilled over, it was collected and redistilled under similar conditions, and then dried in a desiccator contained phosphorus pentoxide. Cyanogen bromide being very unstable compound, it was always redistilled before use. (m. p. 51-52 °C). (Found : C, 11.20 ; N, 13.25% . CNBr requires C, 11.34 ; N, 13.22%). u. v. spectrum showed no trihalide ion absorption. i. r. :- 2162 (m) cm⁻¹.

NOTE : The preparation of cyanogen iodide and cyanogen bromide were carried out under a good hood and in the case of the latter a gas-mask was also used.

(XII) 1,1-bis (diphenylarsino) methane

The 1,1-bis (diphenylarsino) methane (Aldrich Ralph N Emanuel Ltd.) was pumped on the vacuum line for several hours to remove any volatile impurities and moisture. (m. p. 97-98 °C). (Found : C, 63.47 ; H, 4.75% . Ph₂AsCH₂AsPh₂ requires C, 63.58 ; H, 4.70%).

i. r. :- 3045(s), 3017(vw), 2995(w), 2947(m), 2918(m), 1943(m), 1872(m), 1807(m), 1747(m), 1645(m), 1577(s), 1480(s), 1432(s), 1378(s), 1332(w), 1318(vw), 1305(s), 1267(m), 1183(s), 1156(m), 1085(s), 1078(s), 1047(m), 1027(s), 1000(s), 992(m), 968(m), 913(m), 845(m), 735(s), 710(s), 692(s), 665(sh) 619(s), 613(s), 588(s), 473(s), 461(s), 397(w), 322(s), 310(s), 298(s), 288(sh) cm⁻¹.

(XIII) 1,2-bis (diphenylarsino) ethane

The preparation of 1,2-bis (diphenylarsino) ethane was attempted using the method outlined by Hewertson and Watson^{241b}. Triphenylarsine (30.6g) was added in portions (ca. 5g) to a solution from sodium (4.6g) in

liquid ammonia (300 ml) at -75°C , (liquide ammonia was freeze-dried before use). A deep red solution was formed immediately. Addition of 1,2 - dichloroethane (10.0g, purified by fractionation at reduced pressure before use) in an equal volume of ether caused progressive loss of colour and formation of white precipitate. Water (200 ml) was added very cautiously and ammonia was allowed to boil from the mixture. Separation of the suspended solid followed by washing with methanol and recrystallisation from ethanol, afforded a white crystalline solid melted at $85-86^{\circ}\text{C}$. (Found : C, 64.61 ; H, 4.71 ; As, 30.54 and 30.69% . $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ requires C, 64.22 ; H, 4.94 ; As, 30.81%).

i. r. :- 3077(s), 3022(vw), 2098(w), 2947(m), 2907(m), 1950(m), 1870(m), 1803(m), 1753(wb), 1643(wb), 1573(s), 1478(s), 1432(s), 1325(m), 1302(m), 1222(w), 1186(m), 1160(s), 1138(m), 1081(s), 1070(s), 1060(m), 1028(s), 1002(s), 990(m), 917(w), 911(s), 853(m), 741(s), 730(s), 693(s), 678(s), 580(m), 485(s), 459(m), 442(m), 331(s), 322(s) cm^{-1} .

Because of the unexpected results obtained from the ^1H n.m.r. spectrum and the low melting point compared with the reported one ($100-101^{\circ}\text{C}$) (see discussion section), further attempts were made to prepare this compound (seven in all). The same product was obtained on each occasion. No improvement in melting point and ^1H n.m.r. spectra could be achieved on purifying by recrystallisation, sublimation and column chromatography. This compound was then labelled A.

3 - Preparations of Phosphine and Arsine - Halogen Adducts

All the procedures described in the following preparations were performed in the nitrogen filled dry-box. Samples were transferred between the dry-box and vacuum line and vice versa using a sealed adaptor to avoid contact with moisture.

(a) PART 1:A. $\text{Ph}_n\text{PBr}_{3-n}$ (n = 2, 1, 0) Adducts

(1) Dibromophenylphosphine adducts

1.1 - Br_2 - PhPBr_2

Mole ratio $\text{Br}_2 : \text{PhPBr}_2 = 1:1$. Bromine (0.372g) was dissolved in methyl cyanide (3 ml) and added dropwise to dibromophenylphosphine (0.624g) dissolved in the same solvent (15 ml). The bromine was decolourised as it was added and a yellow solid precipitated. This solid was filtered off, washed with anhydrous ether and allowed to stand in an open sample tube next to a tray of fresh phosphorus pentoxide for thirty minutes to dry.

m.p. 225-227 °C. (Found : C, 16.05 ; H, 1.20; Br, 74.70. PhPBr_4 requires C, 16.84; H, 1.18; Br, 74.73%). The ultra-violet spectrum showed traces of Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$).

i. r. :- 3023(vw), 1966(w), 1925(w), 1892(w), 1790(w), 1668(w), 1558(vw), 1570(vw), 1432(s), 1332(m), 1303(w), 1300(s), 1182(vw), 1103(s), 1083(m), 1026(vw), 1000(s), 970(vw), 927(vw), 837(vw), 742(s), 712(s), 684(s), 615(vw), 512(s), 498(s), 472(s), 435(m), 402(s), 378(m), 333(s) cm^{-1} .

The procedure above was repeated using petroleum-ether as solvent. When bromine (0.221g) dissolved in carbon tetrachloride (4 ml) was added to a solution of the phosphine (0.371g) in petroleum ether (40-60 °C) (10 ml) the yellow solid PhPBr_4 immediately precipitated. m.p. 224-226 °C

(Found : C, 17.11 ; H, 1.24 ; Br, 74.61. PhPBr_4 requires C, 16.84 ; H, 1.18 ; Br, 74.73%).

When the adduct PhPBr_4 was pumped on the vacuum line for 16 hours a suspension of yellow-orange solid in yellow solution resulted. This was filtered and the yellow-orange solid vacuum dried. m.p. 201-202^o C. (Found : C, 14.74 ; H, 1.20 ; PhPBr_5 requires C, 14.19 ; H, 0.99%). u.v. spectrum shows Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$).

Mole ratio $\text{Br}_2 : \text{PhPBr}_2 = 2:1$. Bromine (0.756g) was dissolved in methyl cyanide (5 ml) and added slowly to dibromophenylphosphine (0.634g) dissolved in the same solvent (10 ml). After addition was complete a yellow-orange crystalline solid separated from the pale orange solution. The crystalline solid was filtered off, well washed with anhydrous ether and vacuum dried. m.p. 201-203^o C. (Found : C, 14.32 ; H, 1.08 ; Br, 78.22%. PhPBr_5 requires C, 14.19 ; H, 0.99 ; Br, 78.71%). u.v. spectrum shows Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$).

i. r. :- 3027(vw), 1970(w), 1928(w), 1897(m), 1794(m), 1672(m), 1563(vw), 1564(s), 1438(s), 1336(s), 1312(s), 1292(m), 1253(s), 1196(m), 1182(w), 1172(w), 1107(m), 1072(s), 1064(vw), 1025(m), 998(s), 983(vw), 978(vw), 932(m), 841(vw), 746(s), 718(s), 677(s), 615(s), 512(sb), 463(s), 435(s), 404(w), 378(m), 335(w) cm^{-1} .

This reaction having failed to yield the expected adduct PhPBr_6 at the 2:1 mole ratio of $\text{Br}_2 : \text{PhPBr}_2$, the following preparations were attempted:
(I) A mixture of bromine (1.443g) and dibromophenylphosphine (1.210g) in methyl cyanide (15 ml and 10 ml respectively), 2:1 mole ratio of $\text{Br}_2 : \text{PhPBr}_2$, was attached to the vacuum line and then pumped. After the removal of the last traces of the solvent, a yellow-orange solid was deposited. This

solid was analysed immediately and once again it was found to be PhPBr_5 .
 (Found : C, 14.49 ; H, 1.24 ; Br, 78.41%. PhPBr_5 requires C, 14.19 ;
 H, 0.99 ; $\text{Br}_2 = 78.71\%$). u.v. shows Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$).

(II) Mole ratio $\text{Br}_2 : \text{PhPBr}_2 = 3:1$

When a solution of bromine (0.738g) in methyl cyanide (10 ml) was added to the phosphine (0.412g) dissolved in the same solvent (5 ml), a yellow-orange crystalline solid was immediately precipitated. After filtration and washing with anhydrous ether it was vacuum dried. m.p. 202-203 °C. (Found : C, 13.96 ; H, 1.01%. PhPBr_5 requires C, 14.19 ; H, 0.99%).

(III) On mixing the filtrates from the 1:1 and 2:1 reactions an identical product, PhPBr_5 , was isolated as a yellow-orange solid. (Found : C, 13.93 ; H, 1.01%. PhPBr_5 requires C, 14.19 ; H, 0.99%).

1.2 - I_2 - PhPBr_2

Mole Ratio $\text{I}_2 : \text{PhPBr}_2 = 1:1$. Iodine (1.016g), dissolved in methyl cyanide (20 ml), was added dropwise to dibromophenylphosphine (1.072g) dissolved in the same solvent (7 ml). The resulting solution was dark red, and as addition of dry diethyl ether failed to produce a precipitate, it was freeze dried. A dark red oil was obtained which ~~on~~ trituration with dry diethyl ether failed to produce a solid product. Although this oil was pumped on the vacuum line for several hours it was found not possible to remove the last traces of methyl cyanide. (Found : C, 15.57 ; H, 1.51 ; N, 1.35% ; total halogen, 4.12. $\text{Ph}_2\text{PBr}_2\text{I}_2 \cdot 0.5\text{CH}_3\text{CN}$ requires C, 15.51 ; H, 1.49 ; N, 1.35% ; total halogen, 4.00). u.v. spectrum contains peaks at $\lambda_{\text{max}} = 286$ and $356 \text{ m}\mu$ (I_2Br^- plus other trihalides).

i. r. :- 3043(vw), 2143(m), 1952(vw), 1925(vw), 1890(vw), 1790(vw),
1725(vw), 1667(wb), 1576(vw), 1437(s), 1365(vw), 1333(vw),
1230(mb), 1130(vw), 1105(s), 1000(m), 837(vw), 743(s), 715(m),
685(s), 617(vw), 518(sb), 475(w), 420(w), 370(w), cm^{-1} .

Mole Ratio $\text{I}_2 : \text{PhPBr}_2 = 2:1$. Iodine (1.386g) dissolved in methyl cyanide (30 ml) was added slowly to dibromophenylphosphine (0.731g) dissolved in the same solvent (7 ml). Again a dark red solution was formed and as normal methods of inducing precipitation failed, the solution was freeze dried leaving a very dark red oil. Repeated pumping on the vacuum line failed to remove all of the methyl cyanide. (Found : C, 12.76 ; H, 1.63 ; N, 1.71%, total halogen, 5.44. $\text{PhPBr}_2\text{I}_4 \cdot \text{CH}_3\text{CN}$ requires C, 11.77 ; H, 0.99 ; N, 1.69%; total halogen, 6.00). u. v. spectrum shows triiodide ions (peaks at $\lambda_m = 290, 362 \text{ m}\mu$).

These reactions also failed to yield solid products when petroleum-ether (40-60°C) or carbon tetrachloride were used as solvent in place of methyl cyanide.

1.3 - IBr - PhPBr_2

Mole Ratio $\text{IBr} : \text{PhPBr}_2 = 1:1$. Equimolar quantities of iodine monobromide (0.762g), dissolved in methyl cyanide (15 ml), and dibromophenylphosphine (0.987g), dissolved in methyl cyanide (5 ml), were combined using the same procedure outlined above. No precipitation was obtained either on ether addition or by freeze drying followed by trituration with ether. Although the resultant red oil was pumped on the vacuum line for several hours it still contained methyl cyanide. (Found : C, 19.90 ; H, 1.90 ; N, 3.19% , total halogen, 4.09. $\text{PhPBr}_3\text{I} \cdot 1.3\text{CH}_3\text{CN}$ requires C, 19.56 ; H, 1.70,

N, 3.45% ; total halogen, 4.00). u. v. spectrum shows I_2Br^- (peaks at $\lambda_m = 280$ and $350 \text{ m}\mu$). The i. r. spectrum was similar to that of $PhPBr_2I_2 \cdot 0.5CH_3CN$.

Mole Ratio IBr : $PhPBr_2 = 1.5:1$. The procedure was repeated as above using a mole ratio $IBr : PhPBr_2 = 1.5:1$. The resultant red solution was freeze dried to give a red oil. This oil was repeatedly pumped on the vacuum line, and even so traces of solvent were not completely removed. (Found : C, 15.45 ; H, 1.32 ; N, 1.00%. $PhPBr_3I \cdot 0.2CH_3CN$ requires C, 15.92 ; H, 1.17 ; N, 0.58%).

Mole Ratio IBr : $PhPBr_2 = 2:1$. On mixing methyl cyanide solutions of iodine monobromide (0.411g in 10 ml) and dibromophenylphosphine (0.266 g in 5 ml) a red solution was formed. Normal methods failed to produce a solid compound even on freeze drying and a red oil remained. This oil was shown by analysis to be identical to those obtained from the 1:1 and 1.5:1 reactions. (Found : C, 16.59 ; H, 1.32 ; N, 0.31% ; total halogen, 3.77. $PhPBr_3I \cdot 0.2CH_3CN$ requires C, 15.92 ; H, 1.17 ; N, 0.58% ; total halogen, 4.00). u. v. spectrum shows I_2Br^- ions (peaks at 280 and $351 \text{ m}\mu$).

Furthermore, attempts to isolate solids at the 1:1 and 2:1 mole ratios of $IBr : PhPBr_2$ were also made using petroleum-ether (40-60°C) as solvent, and these are described below.

Mole Ratio IBr : $PhPBr_2 = 1:1$. Iodine monobromide (0.337g) dissolved in petroleum-ether (40-60°C) (3 ml) was added dropwise to a solution of dibromophenylphosphine (0.436g) dissolved in the same solvent (15 ml). From the deep red solution a red oil precipitated which on trituration with dry ether turned into a red-brown solid. This solid was filtered, well washed

with successive amounts of dry ether and then vacuum dried for a short time to prevent decomposition or loss of halogen. m.p. 93-94 °C. (Found : C, 13.57 ; H, 0.94% , total halogen, 4.62. PhPBr_4I requires C, 13.00 ; H, 0.91% , total halogen, 5.00). u.v. spectrum contained a peak at $\lambda_{\text{max}} = 260 \text{ m}\mu$ (IBr_2^- plus traces of other trihalides).

i. r. :- 3040(vw), 1960(vw), 1888(vw), 1781(vw), 1660(vw), 1568(wb), 1436(s), 1331(s), 1308(m), 1248(s), 1190(w), 1100(m), 1085(s), 996(s), 930(vw), 742(s), 715(s), 671(s), 613(m), 512(sb), 465(s), 435(s), 375(vw), 335(vw) cm^{-1} .

Mole Ratio IBr : $\text{PhPBr}_2 = 2:1$. The procedure above was repeated using a mole ratio $\text{IBr} : \text{PhPBr}_2 = 2:1$ (0.806g IBr in 4 ml pet.-ether + 0.522g PhPBr_2 in 15 ml pet.-ether). The resultant dark red oil was separated by decantation and the deep red mother liquor was discarded. This oil gave a brown solid on trituration with dry ether. The brown solid was filtered, well washed with dry ether and vacuum dried for a short time. m.p. 87-89 °C. (Found : C, 11.58 ; H, 0.87% ; total halogen, 5.96. PhPBr_5I requires C, 11.36 ; H, 0.79% ; total halogen, 6.00. u.v. spectrum shows IBr_2^- ions (peak at $\lambda_{\text{max}} = 257 \text{ m}\mu$). i. r. spectrum was similar to that of PhPBr_4I .

2 - Bromodiphenylphosphine adducts

2.1 - $\text{Br}_2 - \text{Ph}_2\text{PBr}$

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{PBr} = 1:1$. Equimolar solutions of bromine (0.302g) in methyl cyanide (4 ml) and bromodiphenylphosphine (0.499g) dissolved in the same solvent (7 ml) were mixed to give a colourless solution from which an off-white crystalline solid was separated. These crystals were filtered and washed with dry ether. This compound was analysed immediately as the solid darkened to a yellow-orange colour in a matter of minutes even

though it was within the confines of the dry-box. m.p. 227-229 °C. (Found : C, 35.45 ; H, 2.55 ; Br, 55.52% . Ph_2PBr_3 requires C, 33.92 ; H, 2.37 ; Br, 56.42%). u.v. showed traces of Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$).
 i. r. :- 3040(vw), 1968(wb), 1890(w), 1807(m), 1672(m), 1570(s), 1432(s), 1335(s), 1315(s), 1290(wsh), 1222(sb), 1187(s), 1161(w), 1103(sb), 1070(wsh), 1023(m), 997(s), 976(w), 930(m), 840(w), 745(s), 720(s), 690(sb), 615(s), 520(sb), 472(sb), 432(s), 392(w), 344(wb) cm^{-1} .

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{PBr} = 2:1$. Bromine (0.610g) dissolved in methyl cyanide (5 ml) was added to the phosphine (0.506g) dissolved in the same solvent (12 ml) as in the above reaction. The yellow solid precipitated from the yellow solution was filtered off, well washed with petroleum-ether (40-60 °C) and vacuum dried. m.p. 95-97 °C. (Found : C, 29.55 ; H, 2.56% . Ph_2PBr_4 requires C, 28.55 ; H, 2.00%). u.v. spectrum showed Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$). The infra-red spectrum was identical to that of Ph_2PBr_3 .

This adduct, Ph_2PBr_4 , was also obtained from a similar reaction but in petroleum-ether (40-60 °C). (Found : C, 27.92 ; H, 2.07 ; Br, 63.45% . Ph_2PBr_4 requires C, 28.55 ; H, 2.00 ; Br, 63.22%). Moreover, Ph_2PBr_4 was also formed when the off-white solid Ph_2PBr_3 was pumped on the vacuum line for several hours.

2.2 - $\text{I}_2 - \text{Ph}_2\text{PBr}$

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{PBr} = 1:1$. Solid crystalline iodine (0.683g) was added directly to bromodiphenylphosphine (0.713g) dissolved in petroleum-ether (40-60 °C) (20 ml). When the mixture was thoroughly shaken, the iodine was all dissolved and a dark red oil precipitated from the dark red solution.

After shaking this mixture for 16 hours the oil was converted to a dark red solid which was filtered, washed with petroleum-ether (40-60 °C) and finally vacuum dried. m.p. 108-109 °C. (Found : C, 19.14 ; H, 1.37% ; total halogen, 4.79. Ph_2PBrI_4 requires C, 18.65 ; H, 1.30% ; total halogen, 5.00). u.v. spectrum shows I_3^- ions (peaks at $\lambda_{\text{max}} = 292$ and $361 \text{ m}\mu$).
 i. r. :- 3040(m), 1963(wb), 1880(vw), 1776(vw), 1660(wb), 1568(m), 1432(s), 1328(m), 1305(m), 1190(s), 1160(w), 1128(wb), 1082(s), 1040(vw), 1023(vw), 998(s), 967(vw), 830(w), 747(s), 737(s), 713(m), 677(s), 613(vw), 535(vw), 504(s), 470(m), 460(s), 433(m), 407(vw) cm^{-1} .

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{PBr} = 0.5:1$. As an attempt to prepare the 1:1 adduct, Ph_2PBrI_2 , the above procedure was repeated using a mole ratio $\text{I}_2 : \text{Ph}_2\text{PBr} = 0.5:1$ in both petroleum-ether (40-60 °C) and carbon tetrachloride, (0.281g solid iodine + 0.585g Ph_2PBr in 10 ml pet.-ether, and 0.152g solid iodine + 0.318g Ph_2PBr in 10 ml CCl_4 respectively). The resultant product from these reactions was also Ph_2PBrI_4 . [Found (from Pet.-ether) : C, 18.04 ; H, 1.25% , and found (from CCl_4) : C, 18.81 ; H, 1.36% . Ph_2PBrI_4 requires C, 18.65 ; H, 1.30%].

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{PBr} = 2:1$. When solid crystalline iodine (0.361g) was added to bromodiphenylphosphine (0.188g) dissolved in petroleum-ether (40-60 °C) (15 ml) and the mixture shaken overnight, a dark red solid remained in the iodine coloured mother liquor. It was filtered, washed and dried as before. m.p. 108-109 °C. Found (C, 18.78 ; H, 1.35% ; total halogen, 4.90. Ph_2PBrI_4 requires C, 18.65 ; H, 1.30% ; total halogen, 5.00). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 292, 361 \text{ m}\mu$).

The previous reactions between iodine and bromodiphenylphosphine

were also attempted in methyl cyanide but no solids were obtained.

2.3 - IBr - Ph₂PBr.

Mole Ratio IBr : Ph₂PBr = 1:1. To a solution of bromodiphenylphosphine (0.406g) in petroleum-ether (40-60 °C) (15 ml), was added a solution containing iodine monobromide (0.316g) dissolved in the same solvent (5 ml). After shaking for several hours, the initially formed red oil turned into a red-brown solid. This was separated from the red mother liquor, washed with small amounts of petroleum-ether (40-60 °C) and vacuum dried. m. p. 99-101 °C. (Found : C, 21.88 ; H, 1.55% ; total halogen, 5.36. Ph₂PBr₃I₂ requires C, 21.24 ; H, 1.49% ; total halogen, 5.00). u. v. spectrum contained peaks at $\lambda_{\max} = 278$ and $350 \text{ m}\mu$ (I₂Br⁻ ions plus other trihalides).

i. r. :- 3041(m), 1978(w), 1885(vw), 1786(wb), 1747(vw), 1660(wb), 1573(m), 1434(s), 1332(s), 1313(s), 1223(w), 1192(s), 1163(m), 1128(s), 1088(s), 1027(wsh), 997(s), 970(vw), 933(wb), 833(w), 786(vw), 752(wsh), 743(s), 722(s), 700(s), 678(s), 614(m), 517(sb), 472(s), 434(s), 347(m) cm⁻¹.

Mole Ratio IBr : Ph₂PBr = 0.5:1 and 1.5:1. Since the expected 1:1 addition adduct, Ph₂PBrI₂, was not obtained from the above reaction, the preparation was repeated using the mole ratios 0.5:1 and 1.5:1 of IBr : Ph₂PBr. The resultant solids in both cases were identical having the same empirical formula. m. p. 99-101 °C. (Found at 0.5:1 mole ratio : C, 20.97 ; H, 1.55% . and at 1.5:1 mole ratio : C, 20.98 ; H, 1.49% ; total halogen, 4.76. Ph₂PBr₃I₂ requires C, 21.24 ; H, 1.49% ; total halogen, 5.00).

Also, the same produce was isolated when the above reactions were repeated in carbon tetrachloride. The solids melted at 99-101 °C and their u. v. spectra contained peaks at $\lambda_{\max} = 278$ and $350 \text{ m}\mu$. (I₂Br⁻ ions

plus other trihalide ions).

Mole Ratio IBr : Ph₂PBr = 2:1. Iodine monobromide (0.421g), dissolved in petroleum-ether (4 ml) and bromodiphenylphosphine (0.270g), dissolved in the same solvent (15 ml), were reacted as in the above preparations. After shaking the mixture overnight a very dark red oil was precipitated which also on trituration with dry ether or carbon tetrachloride, after decanting the iodine coloured mother liquor, remained unchange. When this oil was left to stand in a very small amount of dry ether at a temperature below 0 °C for several hours, a sticky dark red solid resulted. It was filtered, well washed with dry ether and vacuum dried. (Found : C, 20.09 ; H, 1.67% ; total halogen, 4.65. Ph₂PBr₂I₃ requires C, 19.86 ; H, 1.36% ; total halogen, 5.00). u.v. spectrum showed I₃⁻ ions (peaks at $\lambda_{\text{max}} = 291$ and $361 \text{ m}\mu$). Its i.r. spectrum was similar to that of Ph₂PBr₃I₂.

3. Some phosphorus tribromide adducts

(I) I₂ - (PBr₃ + IBr), 1:1 mole ratio.

When a solution of iodine monobromide (0.357g) in petroleum-ether (2 ml) was added to phosphorus tribromide (0.468g) dissolved in the same solvent (6 ml), 1:1 mole ratio of IBr : PBr₃, a very dark solution was formed from which a dark red oil precipitated. To this and with stirring, solid crystalline iodine (0.425g) was added in portions. After shaking this mixture for several hours, the oil was dissolved and the resultant solution was dark red. Since normal methods failed to produce a solid or even an oil, the solution was freeze dried to remove the solvent. A slightly dark red oil resulted which on trituration with dry ether and cooling to below 0 °C for

several hours turned to red crystals. On filtration these crystals changed back to a red oil and therefore analysis was carried out immediately.

(Found : total halogen, 6.84. PBr_4I_3 requires total halogen, 7.00. u. v. spectrum contained peaks at $\lambda_{\text{max}} = 289$ and $359 \text{ m}\mu$) (I_3^- ions absorption). On repeating this preparation using methyl cyanide as solvent the same product was isolated as an oil.

(II). $\text{I}_2 - (\text{PBr}_3 + \text{Br}_2)$, 1:1 mole ratio.

Addition of bromine (1.558g) dissolved in methyl cyanide (8 ml) to phosphorus tribromide (2.936g) dissolved in the same solvent (12 ml), 1:1 mole ratio; produced a yellow solution from which a yellow solid precipitated (presumably PBr_5). To this mixture solid crystalline iodine (2.474g) was added in portions and after each addition the flask containing the reaction mixture was shaken vigorously. When the addition was complete, the solid dissolved and a dark red solution resulted. No product was obtained even on shaking overnight. On removal of the solvent by freeze drying a dark red oil remained, which on trituration with different solvents followed by cooling failed to yield a solid product. (Found : total halogen, 6.92.

PBr_5I_2 requires total halogen, 7.00). u. v. spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 278$ and $350 \text{ m}\mu$).

(III) $\text{IBr} - \text{PBr}_3$, 1:1 mole ratio.

On mixing equimolar solutions of iodine monobromide (1.041g) and phosphorus tribromide (1.363g) in methyl cyanide (7 ml and 15 ml respectively), a dark red solution was formed. The solution was freeze dried to give a dark red oil. (Found : total halogen, 7.25. PBr_6I requires total halogen,

7.00). u.v. spectrum showed IBr_2^- ions (peak at $\lambda_{\text{max}} = 258 \text{ m}\mu$).

(IV) $\text{IBr} - \text{PBr}_3$, 2:1 mole ratio.

The reaction was performed in a similar manner as described above. Iodine monobromide (0.329g) was dissolved in methyl cyanide (3 ml) and phosphorus tribromide (0.215g) was dissolved in the same solvent (10 ml). The mother liquor was deep red and the oil isolated by freeze drying was dark red. (Found : total halogen, 6.61. PBr_6I requires total halogen, 7.00). u.v. spectrum showed IBr_2^- ions (peak at $\lambda_{\text{max}} = 257 \text{ m}\mu$).

PART 1:B. $\text{Ph}_n\text{PI}_{3-n}$ (n = 2, 1, 0) Adducts

(1) Diiodophenylphosphine adducts

(1.1) Interaction of PhPI_2 with CH_3CN

On stirring a concentrated methyl cyanide (10 ml) solution of diiodophenylphosphine (0.982g) for several hours, a yellow solid was precipitated. This solid was separated from the dark red mother liquor by filtration, well washed with dry ether and then vacuum dried. The u.v. spectrum of the mother liquor contained peaks at $\lambda_{\text{max}} = 292$ and $362 \text{ m}\mu$ (I_3^- ions). The yellow solid melted at $170-172^\circ\text{C}$ and its u.v. spectrum showed no trihalide ion absorption. (Found : C, 30.94 ; H, 1.95% . $\text{Ph}_2\text{P}_2\text{I}_2$ requires C, 30.67 ; H, 2.14%).

(1.2) $\text{Br}_2 - \text{PhPI}_2$

Mole Ratio $\text{Br}_2 : \text{PhPI}_2 = 1:1$. The phosphine (0.738g), dissolved in methyl cyanide (10 ml), and bromine (0.326g), dissolved in the same solvent (3 ml), were mixed and the mixture shaken for a few hours. From the resultant

pale red solution an orange solid precipitated. This was filtered, washed with petroleum-ether (40-60 °C) and dried by pumping on the vacuum line for five minutes. This compound was analysed immediately as the solid turned into an oil in about thirty minutes even within the confines of the dry-box. (Found : C, 12.66 ; H, 1.60% ; total halogen, 4.5. PhPI_2Br_2 requires C, 13.81 ; H, 0.97% ; total halogen, 4.00). u.v. spectrum showed IBr_2^- ions (peak at $\lambda_{\text{max}} = 257 \text{ m}\mu$).

i. r. :- 3060(m), 1940(vw), 1900(wb), 1810(vw), 1673(m), 1583(m), 1436(s), 1384(w), 1363(vw), 1329(w), 1308(w), 1252(sb), 1208(vw), 1160(vw), 1103(s), 998(s), 958(vw), 927(vw), 870(wb), 822(vw), 748(s), 713(s), 684(s) cm^{-1} .

Mole Ratio $\text{Br}_2 : \text{PhPI}_2 = 2:1$. Bromine (0.510g), dissolved in carbon tetrachloride (4 ml), and diiodophenylphosphine (0.578g), dissolved in petroleum-ether (40-60 °C) (10 ml), were reacted as in the previous reactions.

A dark red solid was present in the dark mother liquor and when filtered was observed to be red in colour. It was washed and dried as before.

m.p. 94-96 °C. (Found : C, 10.87 ; H, 0.78% ; total halogen, 6.21. PhPI_2Br_4 requires C, 10.57 ; H, 0.74% ; total halogen, 6.00. u.v. spectrum showed IBr_2^- ions (peak at $\lambda_{\text{max}} = 257 \text{ m}\mu$). i. r. spectrum was identical to that of PhPI_2Br_2 .

(1.3). $\text{I}_2 - \text{PhPI}_2$.

Mole Ratio $\text{I}_2 : \text{PhPI}_2 = 1:1$. To a solution of diiodophenylphosphine (0.557g) in petroleum-ether (40-60 °C) (10 ml) was added solid crystalline iodine (0.390g) and the mixture mechanically shaken for one hour. A red solution resulted from which a red crystalline solid was obtained on standing for a

short time. After filtering and washing with carbon tetrachloride, the product was dried by pumping on the vacuum line for 15 minutes. m.p. 89-91 °C.

(Found : C, 12.99 ; H, 0.96 ; I, 80.69%. PhPI₄ requires C, 11.70 ; H, 0.82 ;

I, 82.45%). u.v. spectrum showed I₃⁻ ions (peaks at $\lambda_{\max} = 291$ and 361 m μ). This adduct, PhPI₄, was also isolated from a similar reaction

between iodine and PhPI₂ (equimolar amounts) in benzene. (Found :

C, 12.16 ; H, 0.68 ; I, 81.92%. PhPI₄ requires C, 11.70 ; H, 0.82 ; I, 82.45%).

Mole Ratio I₂ : PhPI₂ = 2:1. The reaction above was repeated with a mole

ratio I₂ : PhPI₂ = 2:1, (0.588g Solid I₂ + 0.419g PhPI₂ dissolved in 10 ml

pet.-ether). Again a dark red solid precipitated from the iodine coloured

solution. This solid was filtered and vacuum dried by pumping on the

vacuum line for 15 minutes. m.p. 75-76 °C. (Found : C, 8.36 ; H, 0.77 ;

I, 87.11%. PhPI₆ requires C, 8.29 ; H, 0.58 ; I, 87.57%). u.v. spectrum

showed I₃⁻ ions (peaks at $\lambda_{\max} = 291$ and 361 m μ).

(1.4) IBr - PhPI₂

Mole Ratio IBr : PhPI₂ = 1:1. When a solution of iodine monobromide (0.402g)

in methyl cyanide (10 ml), was added to diiodophenylphosphine (0.704g),

also dissolved in methyl cyanide (10 ml), a red oil precipitated from the

iodine coloured solution. As normal methods of inducing precipitation failed,

the solvent was removed by freeze drying and the resultant oil was triturated

with dry ether and cooled to give a dark red semi-solid product. The semi-

solid compound was filtered, well washed with anhydrous ether and vacuum

dried. (Found : C, 13.01 ; H, 1.21% ; total halogen, 3.81. PhPBrI₃ requires

C, 12.67 ; H, 0.89% ; total halogen, 4.00). u.v. spectrum showed I₃⁻ ions

(peaks at $\lambda_{\max} = 291$ and 361 m μ).

Mole Ratio IBr : PhPI₂ = 2:1. Iodine monobromide (0.630g), dissolved in carbon tetrachloride (6 ml), was added dropwise to diiodophenylphosphine dissolved in petroleum-ether (40-60 °C) (10 ml). From the resultant dark solution a dark coloured oil separated which on trituration with dry ether gave a very dark semi-solid product. This was filtered, well washed with dry ether and then vacuum dried. It was found that the semi-solid compound had lost some halogen during pumping on the vacuum line. (Found : C, 7.85 ; H, 0.61% . PhPBr₂I₄ requires C, 9.29 ; H, 0.65%). u.v. spectrum showed I₃⁻ ions (peaks at $\lambda_{\max} = 291$ and $361 \text{ m}\mu$).

(2) Diphenyliodophosphine Adducts.

(1.1) Br₂ - Ph₂PI

Mole Ratio Br₂ : Ph₂PI = 1:1. On mixing equimolar solutions of bromine (0.073g dissolved in 2 ml carbon tetrachloride) and diphenyliodophosphine (0.143g dissolved in 8 ml of pet.-ether) a red-brown oil precipitated from the yellow solution. After shaking overnight the oil turned into a red-brown solid. This was filtered, washed with dry ether and vacuum dried. m.p. 98-100 °C. (Found : C, 21.79 ; H, 1.48% ; total halogen, 5.02. PhPBr₃I₂ requires C, 21.24 ; H, 1.49% ; total halogen, 5.00). u.v. spectrum showed I₂Br⁻ ions (peak at $\lambda_{\max} = 280$ and $352 \text{ m}\mu$).

i. r. :- 3042(w), 1976(w), 1900(wb), 1803(w), 1665(wb), 1568(m), 1434(s), 1328(m), 1307(wb), 1258(wb), 1222(w), 1187(w), 1158(w), 1107(m), 1084(mb), 998(s), 965(w), 925(wb), 833(w), 740(s), 722(s), 675(s), 640(w), 610(m), 532(s), 500(s), 467(s), 432(s), 340(mb) cm⁻¹.

However, the experiment repeated in methyl cyanide failed to give a solid product.

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{PI} = 2:1$. The overleaf method was repeated using a mole ratio $\text{Br}_2 : \text{Ph}_2\text{PI} = 2:1$ (0.058g Br_2 in 2 ml CCl_4 + 0.056g Ph_2PI in 7 ml pet.-ether). From the resultant solution a yellow-orange oil precipitated. After shaking this mixture overnight an orange solid was obtained in the colourless mother liquor. This orange solid was filtered off, well washed with petroleum-ether (40-60°C) and then vacuum dried. m.p. 83-85°C. (Found : C, 22.72 ; H, 1.64% ; total halogen, 5.04. $\text{Ph}_2\text{PBr}_4\text{I}$ requires C, 22.82 ; H, 1.60% ; total halogen 5.00). u.v. spectrum showed IBr_2^- ions (peak at $\lambda_{\text{max}} = 257 \text{ m}\mu$).

i. r. :- 3044(w), 1970(wb), 1888(vw), 1802(vw), 1577(m), 1435(s), 1333(m), 1313(m), 1190(w), 1163(w), 1120(m), 1098(s), 998(s), 953(vw), 838(vw), 757(s), 742(m), 723(s), 705(s), 678(s), 613(m), 540(s), 518(s), 478(s), 433(m), 352(w) cm^{-1} .

(1.2) $\text{I}_2 - \text{Ph}_2\text{PI}$

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{PI} = 1:1$. When solid crystalline iodine (0.150g) was added to a petroleum-ether (10 ml) solution of diphenyliodophosphine (0.186g) a dark oil was formed. Trituration of this oil with the same solvent gave a brown solid. After filtration, the solid was well washed with dry ether and then vacuum dried. m.p. 125-128°C. (Found : C, 19.12 ; H, 1.31 ; I, 75.19% . Ph_2PI_5 requires C, 17.58 ; H, 1.32 ; I, 77.41%). Obviously this solid adduct had lost some iodine during pumping or washing with ether. u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 292$ and $362 \text{ m}\mu$).

Preparation of Ph_2PI_3

This 1:1 adduct, Ph_2PI_3 , which one would have expected to be a product in the above preparation was surprisingly isolated from the following reactions:

(I) Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{PI} = 0.5:1$. Bromine (0.037g) dissolved in carbon tetrachloride (3 ml) was added to diphenyliodophosphine (0.143g) in petroleum-ether (5 ml) to give a yellow solution. From this solution a red-brown oil precipitated, which on shaking overnight produced a pale brown solid. This solid was filtered off, well washed with dry ether and vacuum dried. m.p. 105-107. (Found : C, 25.27 ; H, 1.63 ; I, 67.26% . Ph_2PI_3 requires C, 25.47 ; H, 1.78 ; I, 67.28%). u.v. spectrum showed some I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $361 \text{ m}\mu$).

(II) Mole Ratio $\text{CNI} : \text{Ph}_2\text{PI} = 1:1$. On mixing equimolar solutions of cyanogen iodide and phosphine in methyl cyanide (0.103g CNI in 3 ml CH_3CN + 0.210g Ph_2PI in 10 ml CH_3CN), a pale brown crystalline solid remained in the pale yellow mother liquor. The crystalline solid was filtered, well washed with petroleum ether (40-60 $^{\circ}\text{C}$) and then vacuum dried. m.p. 105-106 $^{\circ}\text{C}$. (Found : C, 25.29 ; H, 1.83% . Ph_2PI_3 requires C, 25.47 ; H, 1.78%). u.v. spectrum showed some I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $362 \text{ m}\mu$). The i.r. spectrum was identical to that of Ph_2PI_5 .

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{PI} = 2:1$. Solid crystalline iodine (0.296g) was added directly to the phosphine (0.182g) dissolved in petroleum-ether (10 ml). After addition was complete a dark oil remained in the iodine coloured mother liquor. Shaking the mixture for one hour followed by trituration yielded a red crystalline solid which was then filtered, well washed with petroleum ether and vacuum dried. m.p. 131-132 $^{\circ}\text{C}$. (Found : C, 18.04 ; H, 1.19 ; I, 77.69% . Ph_2PI_5 requires C, 17.58 ; H, 1.23 ; I, 77.41%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $360 \text{ m}\mu$).

The same product, Ph_2PI_5 , was also isolated when a mixture of

iodine and diphenyliodophosphine in the mole ratio 3:1 ($I_2 : Ph_2PI$) was allowed to react in petroleum-ether (40-60°C). m.p. 130-132°C. (Found : C, 17.38 ; H, 1.17% . Ph_2PI_3 requires C, 17.58 ; H, 1.23%). u.v. spectrum also showed I_3^- ions.

(1.3) IBr - Ph_2PI

Mole Ratio IBr : Ph_2PI = 1:1. When iodine monobromide (0.082g), dissolved in methyl cyanide (3 ml), was added to diphenyliodophosphine (0.123g), dissolved in the same solvent (10 ml), a dark red oil remained in the red mother liquor. As normal methods failed to produce a solid, the dark red oil was pumped on the vacuum line for two hours before analysis. (This product was also obtained from the reaction between iodine monobromide and phosphine in methyl cyanide at a 2:1 mole ratio of $I_2 : Ph_2PI$). (Found : C, 20.82 ; H, 1.45% ; total halogen, 4.97. $Ph_2PBr_2I_3$ requires C, 19.86 ; H, 1.36% ; total halogen, 5.00). u.v. spectrum showed I_3^- ions (peaks at

$$\lambda_{\max} = 291 \text{ and } 360 \text{ m}\mu).$$

i. r. : - 3040(m), 2130(wb), 1973(wb), 1888(wb), 1792(vw), 1658(vw), 1572(s), 1471(m), 1432(s), 1380(wb), 1327(s), 1308(s), 1283(wsh), 1188(s), 1159(m), 1116(m), 1084(s), 1026(wsh), 997(s), 966(vw), 923(vw), 828(wsh), 748(s), 737(m), 725(vw), 713(vw), 692(wsh), 677(s), 612(m), 534(s), 504(sb), 470(sb), 432(m), 347(mb), cm^{-1} .

Mole Ratio IBr : Ph_2PI = 2:1. When a solution of iodine monobromide (0.091g) dissolved in carbon tetrachloride (2 ml) was added to diphenyliodophosphine (0.068g) dissolved in petroleum-ether (7 ml) and the mixture shaken for two hours, a dark red oil remained in the iodine coloured mother liquor. This oil on trituration with petroleum-ether and standing overnight gave a red-brown solid which was filtered off, washed with petroleum-ether

(40-60 °C) and vacuum dried for a very short time. m.p. 98-99 °C. (Found : C, 21.67 ; H, 1.53% ; total halogen, 4.82. $\text{Ph}_2\text{PBr}_3\text{I}_2$ requires C, 21.24 ; H, 1.49% ; total halogen, 5.00). u.v. spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 281$ and 352 m μ).

i. r. :- 3050(vw), 1985(vw), 1900(vw), 1880(vw), 1800(vw), 1740(vw), 1670(vw), 1578(m), 1437(s), 1332(m), 1312(m), 1282(vw), 1196(m), 1165(w), 1138(w), 1090(s), 1050(vw), 1023(vw), 1000(s), 970(vw), 923(vw), 840(w), 752(s), 744(s), 713(m), 695(m), 685(s), 614(w), 540(w), 508(s), 496(wsh), 478(w), 460(m) cm^{-1} .

(3) Attempts to prepare some adducts in the $\text{PI}_3 - \text{Hal}_2$ system

(I) Interaction of phosphorus triiodide with methyl cyanide

On stirring a concentrated solution of PI_3 (0.689g) in methyl cyanide (15 ml) for two hours, a yellow-orange crystalline solid was precipitated. This solid was separated from the dark red mother liquor by filtration, well washed with dry ether and vacuum dried. The mother liquor was shown by u.v. spectrum to contain I_3^- ions ($\lambda_{\text{max}} = 291$ and 361 m μ). m.p. 125-126 °C. (Found : I, 88.51% . P_2I_4 requires I, 89.12%). i. r. :- 331(s), 300(s) cm^{-1} .

This product, P_2I_4 , was also obtained when phosphorus triiodide was shaken for several hours with dichloromethane. m.p. 126 °C.

(II) Reaction of bromine and iodine monobromide with phosphorus triiodide in various solvents

The reactions between bromine or iodine monobromide and phosphorus triiodide were performed in a similar manner as described previously.

The solvents used in these attempted preparations were: methyl cyanide, carbon tetrachloride, petroleum-ether (40-60 °C), anhydrous ether, benzene

and carbon disulphide. Solutions of the starting materials dissolved in any of these solvents were mixed and the normal methods described earlier were attempted to isolate either solids or oils. However all these attempts failed to give any expected product. In some cases the yellow-orange solid, P_2I_4 , was isolated and on other occasions, the isolated product, always dark oil, gave analytical figures which did not fit the requirements of any single feasible product.

(III) $I_2 - PI_3$

Mole Ratio $I_2 : PI_3 = 1:1$ and $2:1$. When solutions of iodine and phosphorus triiodide in the mole ratio $1:1$ or $2:1$ ($I_2 : PI_3$) were mixed in carbon disulphide, very dark solutions resulted. Normal methods failed to produce any product and therefore the solutions were freeze dried, whereupon sticky solids remained. These adducts were pumped on the vacuum line for 30 minutes before analysis. m.p. $37-40^\circ C$. ($1:1$ adduct, Found : I, 94.08, 95.14 and 94.43% . $2:1$ adduct, Found : I, 94.68, 94.70 and 94.63% . PI_5 requires I, 95.35%).

It should be noted that this reaction was also attempted in methyl cyanide, carbon tetrachloride, petroleum-ether, ether and benzene. However in no case was a solid or an oil product isolated .

(b) PART 2 : 1 - Cyanogen Halide Adducts of Triphenylphosphine

(1.1) $CNI - Ph_3P$

Mole Ratio $CNI : Ph_3P = 1:1$.

(a) Solid triphenylphosphine (0.679g) was added to a suspension of cyanogen iodide (0.369g) in petroleum-ether ($40-60^\circ C$) (15 ml). After stirring for one

hour, the yellow powder formed in the solution was filtered and then discarded.

On shaking the pale red filtrate overnight, a brown oil (almost a tar)

precipitated which on trituration with fresh amount of petroleum-ether (40 -

60 °C) gave a dark red solid. This solid was filtered, washed with dry ether

and after drying it as usual was labelled (compound (II), Found : C, 40.03 ;

H, 2.70 ; N, 2.52%)* u.v. spectrum showed traces of I_3^- ions (peaks at

$\lambda_{\max} = 291 \text{ and } 361 \text{ m}\mu$).

i. r. :- 3048(vw), 2228(s), 2170(vw), 2092(w), 1960(vw), 1892(wb), 1820(wb),
1764(wb), 1668(wb), 1586(s), 1438(s), 1338(m), 1316(m), 1268(vw),
1173(sb), 1117(sb), 1078(w), 1033(m), 1004(s), 980(vw), 931(m),
848(m), 768(sb), 730(sb), 692(sb), 658(s) cm^{-1} .

(b) On addition of solid triphenylphosphine (0.410g) to petroleum-ether (20 ml) solution of CNI (0.223g) in the same way described above but without stirring, a yellow solid and a tar separated from the red solution. After a very short time the solid redissolved and the solution became a very pale yellow. The mother liquor was decanted and the oil was shaken with fresh petroleum-ether (40-60 °C) for two hours to give a yellow solid. This solid was filtered, washed with dry ether and after drying in vacuo labelled compound (III). On standing for two hours the filtrate produced a dark red oil which on treating with ether and cooling gave a brown-red solid labelled compound (I). After filtration, well washing with dry ether the solid was vacuum dried. (Compound III, found : C, 46.90 ; H, 3.23 ; N, 2.25%. Compound (I), found : C, 41.99 ; H, 2.65 ; N, 3.41%).

* Ph_3PI_2 requires C, 41.89 ; H, 2.93% .

Ph_3PCNI requires C, 54.57 ; H, 3.61 ; N, 3.35%.

$\text{Ph}_3\text{P}(\text{CN})_2$ requires C, 76.42 ; H, 4.81 ; N, 8.91%.

Infra-red spectrum :

Compound (I) :- 3063(vw), 2217(vw), 2175(m), 1980(vw), 1907(vw),
1880(vw), 1818(vw), 1653(vw), 1588(m), 1438(s),
1338(wb), 1317(w), 1189(s), 1160(wsh), 1108(s),
1075(vw), 1023(w), 1004(s), 970(wsh), 937(w), 852(w),
760(s), 735(s), 700(s) cm^{-1} .

Compound (III) : 3062(vw), 2215(s), 2170(vw), 2093(m), 1986(wb),
1900(w), 1810(w), 1675(wb), 1583(s), 1437(s), 1338(m),
1317(m), 1187(sb), 1115(sb), 1077(m), 1032(m),
1002(s), 986(wsh), 933(wb), 866(vw), 848(wb), 759(s),
732(s), 700(sb) 657(m) cm^{-1} .

(c) Solid crystalline cyanogen iodide (1.576g) was added directly to a solution of triphenylphosphine (2.703g) in petroleum-ether (20 ml). After shaking for 48 hours and then standing overnight a brown solid remained in the pale red mother liquor. The solid, labelled (IV), was filtered off, well washed with petroleum-ether (40-60°C) and vacuum dried. (Found : C, 47.25 ; H, 3.07 ; N, 3.22%). u.v. spectrum showed traces of I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $361 \text{ m}\mu$).

i. r. : - 2225(m), 2175(w), 1583(m), 1442(sb), 1339(w), 1318(m), 1194(s),
1170(w), 1120(s), 1080(vw), 1033(w), 1005(s), 980(vw), 937(vw),
848(m), 763(s), 740(sb), 694(s), 663(m) cm^{-1} .

(d) Preparation of $\text{Ph}_3\text{P}(\text{CN})_2$

Solid crystalline triphenylphosphine (1.689g) and cyanogen iodide (0.985g), dissolved in benzene (20 ml), were reacted and the mixture containing a brown-yellow solid stirred for two hours. After standing overnight the brown-yellow solid was filtered off, well washed with dry ether and labelled (VI) after drying in vacuo. (Compound VI : found C, 51.30 ; H, 3.41 ;

N, 2.27%).

i. r. :- 3047(w), 2237(s), 2173(vw), 2164(w), 2090(w), 1975(wb), 1890(vw), 1810(wb), 1760(vw), 1673(w), 1584(s), 1437(s), 1340(m), 1313(m), 1278(w), 1190(s), 1170(m), 1115(sb), 1076(wsh), 1029(m), 1003(s), 931(m), 848(m), 760(s), 733(sb), 707(wsh) 690(s), 660(s) cm^{-1} .

To the yellow filtrate (resulting from the above reaction) a large volume of anhydrous ether (120 ml) was added, and slowly white crystals began to separate from solution. These were filtered, well washed with anhydrous ether and dried as usual, by pumping on the vacuum line. m.p. 117-118^o C. (Found C, 76.27 ; H, 4.81 ; N, 8.58% . $\text{Ph}_3\text{P}(\text{CN})_2$ requires C, 76.42 ; H, 4.81 ; N, 8.91%). u. v. spectrum showed no trihalide absorption.

i. r. :- 3043(w), 2175(s), 1975(wb), 1890(vw), 1810(wb), 1760(vw), 1673(w), 1584(s), 1437(s), 1340(m), 1320(w), 1195(wb), 1123(s), 1115(sh), 1080(w), 1037(w), 1010(m), 765(s), 747(s), 705(s) cm^{-1} .

This compound, $\text{Ph}_3\text{P}(\text{CN})_2$, was reproduced when the above reaction was repeated under similar conditions. m.p. 117-118^o C. (Found : C, 75.89; H, 4.52 ; N, 8.46% . $\text{Ph}_3\text{P}(\text{CN})_2$ requires C, 76.42 ; H, 4.81 ; N, 8.91%).

The original precipitate formed in this reaction was yellow solid and labelled VII. (Found C, 50.97 ; H, 3.72 ; N, 0.91). u. v. spectrum showed traces of I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $362 \text{ m}\mu$). The i. r. spectrum of this substance was similar to those of the other impure compounds.

(e) Preparation of Ph_3PI_2 .

Solid triphenylphosphine (2.897g) was added in portions to cyanogen iodide (1.689g) dissolved in methyl cyanide (15 ml). The yellow crystals

which separated immediately from the yellow mother liquor was filtered off, well washed with ether and dried under vacuum. m.p. 190-191.

(Found : C, 41.87 ; H, 2.90 ; I, 49.02%. Ph_3PI_2 requires C, 41.89 ; H, 2.93 ; I, 49.18%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 292$ and $362 \text{ m}\mu$).

i. r. :- 3046(vw), 1960(vw), 1892(wb), 1820(w), 1764(w), 1577(m), 1434(s), 1383(vw), 1313(m), 1180(m), 1167(vw), 1157(vw), 1105(s), 1027(vw), 1001(s), 935(vw), 846(vw), 757(s), 730(s), 694(s) cm^{-1} .

(f) Preparation of hydrogen (1+) bis (triphenylphosphine oxide) - triiodide

Cyanogen iodide (0.473g) dissolved in methyl cyanide (3 ml) was added to triphenylphosphine (0.811g) suspended in petroleum-ether (15 ml). The solution was complete soon after the addition of cyanogen iodide began and then fine yellow crystals precipitated. The crystals were filtered, well washed with dry ether and then vacuum dried. m.p. 111-113 $^{\circ}\text{C}$. (Found : C, 47.83 ; H, 3.32 ; I, 40.47%. $(\text{Ph}_3\text{PO})_2\text{H}^+ \text{I}_3^-$ requires C, 47.71 ; H, 3.45 ; I, 40.57%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 292$ and $361 \text{ m}\mu$).

i. r. :- 1315(m), 1187(s), 1170(w), 1160(w), 1130(s), 1107(s), 1077(m), 1030(m), 1005(s), (940-840)(b), 760(s), 733(s), 695(s) cm^{-1} .

The broad peak at (940-840) cm^{-1} is indicative of the hydrogen bonded cation.

To the yellow filtrate (obtained from the above reaction), an excess amount of petroleum-ether (40-60 $^{\circ}\text{C}$) was added and on standing overnight yellow crystals were formed in the colourless mother liquor. These crystals were filtered, washed with dry ether and then vacuum dried. (Found : C, 43.63 ; H, 3.00%). u.v. spectrum showed I_3^- and the i. r. spectrum was very similar to that of Ph_3PI_2 .

Mole Ratio CNI : Ph₃P = 2:1.

(a) In benzene

The reaction was performed in a similar manner as described overleaf. Solid triphenylphosphine (0.500g) was added to the benzene (20 ml) solution of cyanogen iodide (0.583g). After stirring overnight, the mother liquor was red and the solid isolated was yellow-brown (called compound VIII). (Found : C, 41.18 ; H, 2.81% . Ph₃PI₂ requires C, 41.89 ; H, 2.93%).

(b) In petroleum-ether (40-60 °C).

On mixing solutions of cyanogen iodide (0.664g) and triphenylphosphine (0.570g) in petroleum-ether (15 ml and 20 ml respectively), a dark red solution was formed. When the normal methods failed to produce any product the solution was freeze dried to yield a brown solid (called compound V) which was further pumped to dryness. (Found : C, 43.19 ; H, 2.93 ; N, 2.02%). Infra-red and u.v. spectra were similar to those of the other compounds containing nitrogen.

(1.2) CNBr - Ph₃P

Mole Ratio CNBr : Ph₃P = 1:1.

(a) To a suspension of the phosphine (0.532g) in methyl cyanide (5 ml) was added a solution of cyanogen bromide (0.215g) in the same solvent (7 ml). The resultant red solution was divided into two portions.

To the first portion, excess dry ether was added and when the addition was complete a very pale yellow solid remained in the colourless mother liquor. This was filtered off, well washed with dry ether and vacuum dried. m.p. 250-253 °C. (Found : C, 52.35 ; H, 3.74 ; Br, 37.68. Ph₃PBr₂ requires

C, 51.22 ; H, 3.58 ; Br, 37.86).

The second portion was freeze dried to give an off white solid which was further pumped on the vacuum line. m.p. 242-244 °C. (Found: C, 60.41; H, 4.05 ; N, 3.08 ; Br, 22.39%. Ph_3PCNBr requires C, 61.98 ; H, 4.11 ; N, 3.80 ; Br, 21.70%). u.v. spectrum showed no trihalide absorption.

(b) On mixing equimolar solutions of cyanogen bromide and triphenylphosphine in benzene (0.226g CNBr in 8 ml benzene + 0.560g Ph_3P in 10 ml benzene) an off white solid immediately separated from the yellow-brown mother liquor. This was filtered, washed with dry ether and vacuum dried. m.p. 258-265 °C. (Found: C, 50.94 ; H, 3.50 ; N, 1.24 ; Br, 32.88%).

PART 2:2 - Cyanogen Halide Adducts of Triphenylarsine

(2.1) CNI - Ph_3As

Mole Ratio CNI : Ph_3As = 1:1.

(a) In methyl cyanide.

When equimolar solutions of cyanogen iodide (0.296g) and triphenylarsine (0.592g), in methyl cyanide (8 ml and 12 ml respectively), were mixed a red solution formed. On standing for 48 hours, orange crystals separated from the solution. These crystals were filtered off, well washed with dry ether and then vacuum dried. m.p. 135-136 °C. (Found: C, 38.75 ; H, 2.66%. Ph_3AsI_2 requires C, 38.60 ; H, 2.70%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $360 \text{ m}\mu$).
i. r. :- 3048(w), 1974(vw), 1875(vw), 1800(vw), 1720(vw), 1640(vw).

1574(m), 1432(s), 1327(vw), 1305(m), 1268(vw), 1220(vw),
1180(wb), 1150(w), 1078(s), 1008(m), 911(wb), 850(wb), 758(m),
748(s), 698(s) cm^{-1} .

On addition of excess dry ether to the filtrate, obtained from the reaction directly above, dark violet crystals were formed in the colourless solution. These crystals were filtered, washed with dry ether and vacuum dried. m. p. 174-176 $^{\circ}\text{C}$. (Found : C, 42.71 ; H, 2.84 ; N, 1.53 ; I, 38.16% . $(\text{Ph}_3\text{As})_2\text{CNI}_3$ requires C, 43.60 ; H, 2.97 ; N, 1.37 ; I, 37.35%). u. v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $361 \text{ m}\mu$).

i. r. :- 3045(vw), 2164(m), 1970(vw), 1890(vw), 1810(vw), 1705(vw),
1650(vw), 1580(vw), 1443(m), 1341(vw), 1311(w), 1185(vw),
1167(vw), 1090(m), 1030(w), 1007(m), 972(s), 933(vw), 860(w),
774(vw), 757(s), 748(s), 702(s), 680(wsh) cm^{-1} .

(b) In petroleum-ether (40-60 $^{\circ}\text{C}$)

A solution of cyanogen iodide (0.219g), dissolved in petroleum ether (5 ml) was added to triphenylarsine (0.439g), dissolved in the same solvent (15 ml). A red oil was formed in the pale red mother liquor. On discarding the filtrate and trituration of the oil with dry ether (30 ml), dark violet crystals were precipitated. These were filtered, well washed with dry ether and then vacuum dried. (Found : C, 41.30 ; H, 2.90 ; N, 0.83%)*. u. v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $362 \text{ m}\mu$). The infra-red spectrum was identical to that of $(\text{Ph}_3\text{As})_2\text{CNI}_3$.

* Ph_3AsI_2 requires C, 38.60 ; H, 2.70% .

Ph_3AsCNI requires C, 49.70 ; H, 3.29 ; N, 3.05% .

$(\text{Ph}_3\text{As})_2\text{CNI}_3$ requires C, 43.60 ; H, 2.97 ; N, 1.37% .

(c) In benzene

The procedure directly overleaf was repeated in benzene, with a mole ratio $\text{CNI} : \text{Ph}_3\text{As} = 1:1$ (0.555g CNI in 5 ml C_6H_6 + 1.112g Ph_3As in 20 ml C_6H_6). Addition of excess unhydrous ether to the resultant pale red solution caused the separation of dark violet crystals which were filtered, washed with dry ether and vacuum dried before analysis. (Found : C, 42.40 ; H, 3.04 ; I, 37.06%. $(\text{Ph}_3\text{AsO})_2\text{HI}_3$ requires C, 42.14 ; H, 3.05 ; I, 37.10%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $361 \text{ m}\mu$).

i. r. :- 3060(vw), 1970(vw), 1890(vw), 1810(vw), 1705(vw), 1650(vw), 1572(wb), 1443(s), 1340(vw), 1317(w), 1202(vw), 1150(wb), 1100(s), 1020(wb), 1008(m), (900-850)(mb), 787(mb), 768(s), 753(m), 705(s) cm^{-1} . Also the spectrum showed a strong broad absorption in the range 1250-850 cm^{-1} . Thus the spectra demonstrates the presence of the hydrogen bonded cation, $[\text{Ph}_3\text{AsOHOAsPh}_3]^+$.

Mole Ratio CNI : $\text{Ph}_3\text{As} = 2:1$.

(a) In methyl cyanide: When solutions of cyanogen iodide (0.206g) and triphenylarsine (0.206g) in methyl cyanide (8 ml and 10 ml respectively) were mixed, a red solution resulted. Orange crystals were precipitated when the solution left to stand in the dry-box for 48 hours. These crystals were filtered off, washed with dry ether and then vacuum dried. m.p. $135-136^\circ\text{C}$. (Found : C, 38.21 ; H, 2.52%. Ph_3AsI_2 requires C, 38.60 ; H, 2.70%).

Addition of excess dry ether to the filtrate of the above reaction caused the separation of dark violet crystals. These crystals were washed

and dried as usual before analysis. m.p. 187-189 °C. (Found : C, 40.80 ; H, 2.82 ; N, 1.40%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\max} = 291$ and $360 \text{ m}\mu$). The infra-red spectrum was similar to that of $(Ph_3As)_2^- CNI_3$.

(b) In petroleum-ether (40-60 °C). The reaction above was repeated using petroleum-ether as solvent, (0.455g CNI in 8 ml pet.-ether + 0.456 g Ph_3As in 20 ml pet.-ether). The resultant red oil was separated by decantation and on trituration with dry ether (100 ml) the oil turned into dark violet crystals. The crystals were filtered, washed with dry ether, and then vacuum dried. (Found : C, 39.77 ; H, 2.65 ; N, 0.50%). u.v. spectrum showed I_3^- ions (peaks at $\lambda_{\max} = 290$ and $360 \text{ m}\mu$).

(c) In benzene. Solid crystalline cyanogen iodide (0.600g) was added to the arsine (0.601g), dissolved in benzene (15 ml). A pale orange solution resulted from which dark violet crystals were obtained after the removal of approximately half the volume of the solvent on the vacuum line and addition of dry ether. After filtration and thorough washing with dry ether, the crystals were vacuum dried. (Found : C, 42.32 ; H, 2.96% . $(Ph_3AsO)_2^- HI_3$ requires C, 42.14 ; H, 3.05%). The u.v. and i.r. spectra were identical to that of $[Ph_3AsOHOAsPh_3]^+ I_3^-$ previously described.

(2.2). $CNBr - Ph_3As$

Mole Ratio $CNBr : Ph_3As : 1:1$

(a) In methyl cyanide : To a suspension of the arsine (0.567g) in methyl cyanide (5 ml) was added (dropwise and with stirring) a solution of cyanogen bromide (0.169) in the same solvent (5 ml). After the addition was complete,

a cream coloured solid remained in the pale orange mother liquor. This solid was filtered off, well washed with anhydrous ether and then vacuum dried. m.p. $> 300^{\circ}\text{C}$. (Found : C, 56.24 ; H, 3.45 ; N, 2.99 ; Br, 20.37% . Ph_3AsCNBr requires C, 55.37 ; H, 3.67 ; N, 3.40 ; Br, 19.39%). u.v. spectrum showed no trihalide absorption.

i. r. :- 3068(vw), 2183(m), 1956(wb), 1880(wb), 1740(wb), 1660(vw), 1578(m), 1445(s), 1338(m), 1314(m), 1282(w), 1183(m), 1167(m), 1080(m), 1034(s), 1008(s), 980(wb), 920(vw), 853(vw), 842(vw), 750(s), 700(s), 692(s) cm^{-1} .

(b) In benzene : The reaction above was repeated using benzene in place of methyl cyanide, (0.403g Ph_3As in 7 ml C_6H_6 + 0.139g CNBr in 5 ml C_6H_6). The resultant solution was orange in colour and when excess anhydrous ether was added a cream coloured solid precipitated from the solution. This was filtered, well washed with dry ether and then vacuum dried. m.p. $> 300^{\circ}\text{C}$. (Found : C, 53.13 ; H, 3.23 ; N, 3.64 ; Br, 21.10% . Ph_3AsCNBr requires C, 55.37 ; H, 3.67 ; N, 3.40 ; Br, 19.39%). The u.v. and i. r. spectra were similar to the above mentioned adduct, Ph_3AsCNBr .

(c) PART 3 : A - Halogen Adducts of 1,1 - bis(diphenylarsino) methane

(1) $\text{Br}_2 - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 2:1$. Addition of bromine (0.359g), dissolved in methyl cyanide (4 ml), to the arsine (0.53g), suspended in the same solvent (5 ml), produced a pale yellow solution. The cream coloured solid obtained after freeze drying was well washed with dry ether and then vacuum dried. m.p. 163-165 $^{\circ}\text{C}$. (Found : C, 34.57 ; H, 2.84 ; Br, 42.60% . $(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{O})_2\text{HBr}_9$ requires C, 35.39 ; H, 2.67 ; Br, 42.39%). u.v. spectrum showed Br_3^- ions ($\lambda_{\text{max}} = 269 \text{ m}\mu$).

i. r. :- 3076(m), 3028(w), 3005(w), 2954(m), 2917(m), 2580(wb),
1968(w), 1890(w), 1810(w), 1770(vw), 1662(wb), 1576(w),
1443(s), 1337(m), 1312(vw), 1283(vw), 1200(m), 1170(m),
1090(s), 1026(w), 1220-1000(b) , 1000(s), 978(w), 922(w),
844(vw), 771(s), 763(s), 745(s), 693(vw), 682(s) 800-650(b) ,
588(m), 462(s), 355(s), 323(s), 302(m) cm^{-1} . The i. r. spectrum

is therefore indicating the presence of the hydrogen bonded cation.

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 3:1$ When a methyl cyanide solution
(7 ml) of bromine (0.278g) was added to the arsine (0.274g) suspended in
the same solvent (5 ml), a pale yellow solid separated from the colourless
solution. This was filtered, well washed with dry ether and vacuum dried.
m.p. 122-124 $^{\circ}\text{C}$. (Found : C, 29.23 ; H, 2.15 ; Br, 53.99%. $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$
 Br_7 requires C, 29.11 ; H, 2.15 ; Br, 54.22%). u. v. showed Br_3^- ions
($\lambda_{\text{max}} = 269 \text{ m}\mu$).

i. r. :- 3072(m), 3022(w), 3005(vw), 2954(m), 2917(m), 1948(m), 1872(m),
1791(m), 1738(w), 1648(w), 1575(m), 1442(s), 1362(s), 1338(s),
1330(m), 1304(m), 1280(m), 1190(s), 1183(s), 1173(s), 1160(s),
1123(w), 1100(w), 1083(s), 1078(s), 1063(s), 1021(s), 999(s),
978(m), 920(w), 912(vw), 831(m), 791(s), 762(w), 744(s), 733(s),
690(s), 680(s), 660(vw), 610(m), 566(s), 463(s), 350(s), 310(s)
 cm^{-1} .

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 4:1$ On mixing directly methyl cyanide
solutions of the two reagents in the 4:1 mole ratio (0.314g arsine suspended
in 7 ml $\text{CH}_3\text{CN} + 0.422\text{g Br}_2$ dissolved in 5 ml CH_3CN), a yellow solid
precipitated. This solid was filtered off, well washed with dry ether and
then vacuum dried. m.p. 111-113 $^{\circ}\text{C}$. The u. v. and i. r. spectra were
similar to that of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{Br}_7$ isolated at the 3:1 mole ratio.
(Found : C, 25.95 ; H, 1.84 ; Br, 59.01% . $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{Br}_8$ requires

C, 27.01 ; H, 1.99 ; Br, 57.51%).

Mole Ratio $\text{Br}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 6:1$. To a suspension of the arsine (0.310g), in methyl cyanide (5 ml), was added (as before) a solution of bromine (0.629g) dissolved in methyl cyanide (4 ml). When addition was complete an orange crystalline solid remained in the pale orange mother liquor. The crystals were filtered, washed with dry ether and vacuum dried. m.p. 103-105 °C. The u.v. and i.r. spectra were identical to that of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{Br}_8$. (Found : C, 23.31 ; H, 1.54 ; Br, 62.31% .

$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{Br}_{10}$ requires C, 23.62 ; H, 1.74 ; Br, 62.85 %).

(2) $\text{I}_2 - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 2:1$. Iodine (0.430g), dissolved in methyl cyanide (10 ml), was added dropwise to a suspension of 1,1 - bis(diphenylarsino) methane (0.401g) in methyl cyanide (4 ml) and the flask placed on the mechanical shaker overnight. A red solution resulted from which a brown solid was obtained after the removal of approximately half the volume of the solvent on the vacuum line. After filtering and thorough washing with anhydrous ether, the brown solid was vacuum dried. m.p. 113-115 °C.

(Found : C, 30.90 ; H, 2.16 ; I, 51.16%. $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_4$ requires C, 30.64; H, 2.26 ; I, 51.18%). u.v. spectrum showed I_3^- ions ($\lambda_{\text{max}} = 360$ and 290 m μ).

i. r. :- 3076(s), 3012(w), 2998(w), 2950(m), 2913(m), 1974(w), 1948(w), 1875(wb), 1787(w), 1642(w), 1567(m), 1433(s), 1332(s), 1303(s), 1270(m), 1187(m), 1164(m), 1157(m), 1103(m), 1087(m), 1076(s), 1043(s), 1025(s), 1021(m), 998(s), 986(w), 973(w), 958(vw), 918(m), 907(m), 901(w), 835(w), 740(s), 730(s), 707(s), 690(s), 680(s), 653(wsh), 610(w), 573(w), 564(s), 472(s), 462(w), 457(m),

448(s), 398(vw), 331(s), 320(s), 315(vw), 305(s) cm^{-1} .

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 4:1$. Iodine (0.602g) dissolved in methyl cyanide (10 ml), was added (as in the above reaction) to the arsine (0.280g) suspended in the same solvent (4 ml). After shaking for several hours, a dark red oil separated from the dark red solution. When most of the solvent was removed an oil resulted. This oil on scraping, converted into a dark solid which was filtered, well washed with methyl cyanide and then vacuum dried. m.p. 90-92 $^{\circ}\text{C}$. (Found : C, 25.05 ; H, 1.81 ; I, 61.58% .

$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_6$ requires C, 24.34 ; H, 1.80 ; I, 61.72%). The u. v. and i. r. spectra were similar to that of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_4$. This adduct, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_6$, was also isolated when the above reaction repeated using the mole ratio 3:1 of $\text{I}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$.

Mole Ratio $\text{I}_2 : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 6.67:1$. The solution obtained from the conductometric titration of the $\text{I}_2 - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ system which contained iodine (1.390g) and arsine (0.280g) dissolved in methyl cyanide (30 ml and 32 ml respectively), was freeze dried. On removal of most of the solvent a dark (almost black) oil was observed. Trituration of this oil with fresh methyl cyanide resulted in the formation of a black solid. The solid was filtered, well washed with methyl cyanide and finally vacuum dried for a short time to prevent decomposition. m.p. 67 $^{\circ}\text{C}$. (Found : C, 16.51 ; H, 1.34 ; I, 73.33% . $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_{10}$ requires C, 17.24 ; H, 1.27 ; I, 72.88%). u. v. spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and 361 $\text{m}\mu$).

(3) $\text{IBr} - \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$

Mole Ratio $\text{IBr} : \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 1:1, 2:1$ and $3:1$. On mixing methyl

cyanide solutions of arsine and iodine monbromide in the 1:1, 2:1 and 3:1 mole ratios, (1:1 - 0.362g arsine in 5 ml CH_3CN + 0.159g IBr in 4 ml CH_3CN ; 2:1 - 0.290g arsine in 3 ml CH_3CN + 0.254g IBr in 2 ml CH_3CN ; 3:1 - 0.139g arsine in 4 ml CH_3CN + 0.183g IBr in 2 ml CH_3CN), three clear red solutions were formed. These solutions were freeze dried to give red oils which on trituration with petroleum-ether (40-60°C), produced identical brown-yellow solids. m.p. 156-158°C. (Found C, 27.44; H, 2.27%; total halogen, 5.8. $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_3\text{Br}_3$ requires C, 27.47; H, 2.03%; total halogen, 6.00). u.v. spectrum contained peaks at $\lambda_{\text{max}} = 272$ and $356 \text{ m}\mu$ (I_2Br^- plus other trihalides).

i. r. :- 3068(m), 3027(w), 3000(w), 2953(m), 2916(m), 1980(w), 1950(w), 1878(m), 1790(w), 1743(w), 1647(w), 1565(m), 1436(s), 1330(s), 1303(m), 1270(w), 1180(m), 1153(m), 1092(m), 1066(s), 1016(m), 997(s), 990(w), 967(w), 917(m), 830(m), 754(vw), 730(s), 700(vw), 670(s), 603(w), 453(s), 446(s), 352(s), 336(s), 308(s) cm^{-1} .

Mole Ratio IBr : $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2 = 4:1$. The preparative procedure was exactly as in the above reaction. The arsine (0.260g) was suspended in methyl cyanide (3 ml) and the iodine monobromide (0.455g) was freshly prepared in methyl cyanide (4.5 ml). The resulting dark red solution was freeze dried to give a dark red oil. Since trituration of this oil with petroleum-ether (40-60°C) failed to give a solid, it was repeatedly pumped on the vacuum line to remove traces of solvent. (Found C, 26.37; H, 2.04; N, 0.80%; total halogen, 6.3. $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{I}_3\text{Br}_3 \cdot 0.65 \text{ CH}_3\text{CN}$ requires C, 26.82; H, 2.15; N, 0.81%; (total halogen, 6.00). u.v. spectrum contained peaks at $\lambda_{\text{max}} = 272$ and $356 \text{ m}\mu$ (I_2Br^- plus other trihalides).

Mole Ratio IBr : Ph₂AsCH₂AsPh₂ = 6.2:1. The solution obtained from the conductometric-titration of the IBr - Ph₂AsCH₂AsPh₂ system, which contained iodine monobromide (0.925g) and arsine (0.310g) dissolved in methyl cyanide (23 ml and 29 ml, respectively), was freeze dried. The resultant dark red oil was repeatedly pumped on the vacuum line to remove traces of solvent. (Found : C, 21.34 ; H, 1.89% ; total halogen, 7.82. Ph₂AsCH₂AsPh₂I₃Br₂ requires C, 21.55; H, 1.59% ; total halogen, 8.00). u.v. spectrum showed I₃⁻ ions ($\lambda_{\text{max}} = 292 \text{ and } 362 \text{ m}\mu$). The i.r. spectrum was similar to that of Ph₂AsCH₂AsPh₂I₃Br₃.

PART 3 : B- Halogen Adducts of Substance A.

(1) Br₂ - A. (Where A is assumed to be Ph₂AsCH₂CH₂AsPh₂).

When methyl cyanide solutions of bromine and substance A were mixed in the mole ratios 1:1, 2:1, 3:1, 4:1 and 6:1, five solids (which are listed in Table 87 page 170) were isolated. In addition, A.Br₃ and A.Br₈ were isolated at the 2:1 and 4:1 mole ratios when benzene was used as solvent. The i.r. spectra of these adducts were similar to those of the bromine adducts of Ph₂AsCH₂AsPh₂.

(2) I₂ - A.

Six solids were isolated when iodine and substance A were mixed in methyl cyanide, as in the previous reactions, in mole ratios 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1 of I₂ : A. These adducts are listed in Table 87 page 170 . It should be noted that the substances A.I₆ and A.I₈ were also isolated when the reagents (I₂ and A) were mixed in benzene in the mole ratios 2:1 and 4:1 respectively. Once again, the i.r. spectra of these adducts were similar to the iodine adducts of Ph₂AsCH₂AsPh₂ mentioned earlier.

(3) IBr - A

On repeating the procedure overleaf with mole ratios IBr : A of 2:1, 3:1 and 4:1, three compounds were isolated. Details of the colour, m. p. analysis and u. v. spectra of these adducts are summarised in Table 87 page 170. Their i. r. spectra were similar to those of the iodine monobromide adducts of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$.

4. Experimental Data(a) Conductometric Titration Data of the Systems $\text{Ph}_n\text{PX}_{3-n}\text{-X}_2$ Table 6. Br_2 - PhPBr_2 in Methyl Cyanide

Mole Ratio (Br_2 : PhPBr_2)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio (Br_2 : PhPBr_2)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	6.90	2.1505	26.63
0.0935	7.35	2.2440	27.88
0.1870	7.84	2.3375	29.48
0.2805	8.22	2.4310	30.42
0.3740	8.75	2.5245	31.85
0.4675	9.17	2.6180	33.07
0.5610	9.41	2.7115	34.26
0.6545	9.72	2.8050	35.27
0.748	10.00	2.8985	36.38
0.8415	10.28	2.9920	37.46
0.9350	10.63	3.0855	38.61
1.0285	11.15	3.1790	39.52
1.1220	12.30	3.2725	40.36
1.2155	13.56	3.3660	41.23
1.3090	14.74	3.4595	42.06
1.4025	16.03	3.5530	42.87
1.4960	17.39	3.6465	43.63
1.5895	18.61	3.7400	44.26
1.6830	19.97	3.8335	44.75
1.7765	21.40	3.9270	45.37
1.8700	22.72	4.0205	45.79
1.9635	24.05	4.1140	46.28
2.0570	25.37	4.2075	46.69

Table 6. continued.

Mole Ratio (Br ₂ : PhPBr ₂)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (Br ₂ : PhPBr ₂)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
4.3010	46.98	5.5165	49.91
4.3945	47.26	5.6100	50.01
4.488	47.54	5.7035	50.08
4.5815	47.85	5.7970	50.08
4.6750	48.16	5.8905	50.11
4.7685	48.34	5.9840	50.15
4.8620	48.62	6.0775	50.36
4.9555	48.82	6.1710	50.39
5.0490	49.03	6.2645	50.29
5.1425	49.24	6.4515	50.39
5.2360	49.38	6.6385	50.39
5.3295	49.59	6.8270	50.36
5.4250	49.77	7.0140	50.18

Table 11. $\text{Br}_2^-(\text{PhPBr}_5)_2$ in Methyl Cyanide

Mole Ratio $\text{Br}_2^-(\text{PhPBr}_5)_2$	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio $\text{Br}_2^-(\text{PhPBr}_5)_2$	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	16.36	2.2824	37.91
0.1268	19.27	2.4092	38.72
0.2536	20.54	2.5360	39.54
0.3804	21.81	2.6628	40.31
0.5072	23.09	2.7896	41.04
0.6340	24.32	2.9164	41.72
0.7608	25.54	3.0432	42.41
0.8876	26.72	3.1700	43.04
1.0144	27.91	3.2968	43.63
1.1412	29.04	3.4236	44.22
1.2680	30.18	3.5504	44.63
1.3948	31.27	3.6772	45.22
1.5216	32.31	3.8040	45.77
1.6484	33.31	3.9308	46.13
1.7752	34.31	4.0576	46.31
1.9020	35.27	4.1844	46.45
2.0288	36.13	4.3112	46.54
2.1556	36.99		

Table 13. I_2^- PhPBr₂ in Methyl Cyanide

Mole Ratio (I_2^- : PhPBr ₂)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (I_2^- : PhPBr ₂)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.000	5.91	2.128	27.68
0.076	7.23	2.204	28.27
0.152	8.14	2.280	28.77
0.228	8.82	2.356	29.36
0.304	9.73	2.432	30.09
0.380	10.59	2.508	30.77
0.456	11.59	2.584	31.36
0.532	12.14	2.660	32.04
0.608	13.04	2.736	32.68
0.684	13.91	2.812	33.59
0.760	14.73	2.888	34.45
0.836	15.23	2.964	35.50
0.912	16.00	3.040	36.59
0.988	16.77	3.116	37.36
1.064	17.59	3.192	38.27
1.140	18.41	3.268	39.04
1.216	19.18	3.344	39.91
1.292	19.91	3.420	40.54
1.368	20.63	3.496	41.31
1.444	21.18	3.572	41.18
1.520	21.91	3.648	41.95
1.596	22.54	3.724	42.54
1.672	23.31	3.800	43.18
1.748	23.82	3.876	43.72
1.824	24.59	3.952	44.22
1.900	25.45	4.028	44.59
1.976	26.18	4.104	44.86
2.052	26.91	4.180	45.18

Table 13 continued.

Mole Ratio (I ₂ : PhPBr ₂)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (I ₂ : PhPBr ₂)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
4. 256	45. 50	4. 636	46. 27
4. 332	45. 68	4. 712	46. 31
4. 408	45. 86	4. 788	46. 36
4. 484	46. 00	4. 864	46. 40
4. 560	46. 13		

Table 14. Solid I₂⁻ PhPBr₂ in Methyl cyanide

Mole Ratio I ₂ : PhPBr ₂	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0. 0000	7. 23
0. 223	10. 08
0. 332	11. 91
0. 585	14. 77
0. 749	16. 54
0. 944	17. 51
1. 130	21. 82
1. 493	27. 86
1. 799	33. 50
2. 001	37. 50
2. 175	40. 03
2. 209	43. 18
2. 568	47. 59
2. 906	50. 50

Table 16. IBr - PhPBr₂ in Methyl Cyanide

Mole Ratio (IBr : PhPBr ₂)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (IBr : PhPBr ₂)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.0000	6.94	2.4280	30.74
0.1214	7.70	2.5494	32.55
0.2428	8.71	2.6708	34.08
0.3642	9.58	2.7922	35.83
0.4856	10.49	2.9136	37.53
0.6070	11.43	3.0350	39.38
0.7284	12.37	3.1564	40.77
0.8498	13.24	3.2778	41.92
0.9712	14.15	3.3992	43.39
1.0926	14.95	3.5206	44.61
1.2140	15.89	3.6420	45.65
1.3354	16.83	3.7634	46.63
1.4568	17.56	3.8848	47.43
1.5782	18.75	4.0062	48.13
1.6996	20.21	4.1276	48.82
1.8210	21.85	4.2490	49.35
1.9424	23.56	4.3704	49.84
2.0638	25.34	4.4918	50.32
2.1852	27.25	4.6132	50.71
2.3066	29.06	4.7346	51.09

Table 19. Br_2 - Ph_2PBr in Methyl Cyanide

Mole Ratio ($\text{Br}_2 : \text{Ph}_2\text{PBr}$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($\text{Br}_2 : \text{Ph}_2\text{PBr}$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.00	2.98	2.53	21.09
0.11	3.42	2.64	22.18
0.22	4.01	2.75	23.32
0.33	4.40	2.86	24.22
0.44	4.86	2.97	25.18
0.55	5.23	3.08	26.18
0.66	5.64	3.19	27.22
0.77	6.00	3.30	28.13
0.88	6.32	3.41	29.00
0.99	6.64	3.52	29.86
1.10	7.36	3.63	30.68
1.21	8.36	3.74	31.45
1.32	9.27	3.85	32.04
1.43	10.32	3.96	32.63
1.54	11.36	4.07	33.27
1.65	12.41	4.18	33.91
1.76	13.50	4.40	35.00
1.87	14.60	4.62	35.93
1.98	15.63	4.84	36.13
2.09	16.73	5.06	36.38
2.20	17.82	5.28	36.5
2.31	18.91	5.50	36.5
2.42	20.04		

Table 22. $I_2 - Ph_2PBr$ in Methyl Cyanide

Mole Ratio ($I_2 : Ph_2PBr$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)	Mole Ratio ($I_2 : Ph_2PBr$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.0000	3.32	2.1230	22.91
0.0965	5.41	2.2195	23.63
0.1930	6.82	2.3160	24.41
0.2895	8.23	2.4125	25.18
0.3860	9.36	2.5090	25.82
0.4825	10.54	2.6055	26.54
0.5790	11.59	2.7020	27.27
0.6755	12.54	2.7985	28.13
0.7720	13.27	2.8950	28.77
0.8685	13.86	2.9915	29.77
0.9650	14.50	3.0880	30.72
1.0615	15.13	3.1845	31.95
1.1580	15.82	3.2810	33.27
1.2545	16.50	3.3755	34.31
1.3510	17.23	3.4740	35.41
1.4475	17.77	3.5705	36.36
1.5440	18.54	3.6670	37.09
1.6405	19.23	3.7635	37.54
1.7370	19.95	3.8600	38.00
1.8335	20.63	3.9565	38.45
1.9300	21.41	4.0530	38.68
2.0265	22.13	4.1495	38.81

Table 23. Solid $I_2 - Ph_2PBr$ in Methyl Cyanide

Mole Ratio ($I_2 : Ph_2PBr$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.0000	4.50
0.2225	9.59
0.5254	15.13
0.7122	17.32
0.9408	19.55
1.0828	20.03
1.1439	20.38
1.3682	24.01
1.6562	29.22
1.9626	33.50
2.2623	37.77
2.6987	46.31

Table 25. $I_2 - Ph_2PBr$ in Methyl Cyanide

Mole Ratio ($I_2 : Ph_2PBr$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)	Mole Ratio ($I_2 : Ph_2PBr$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.0000	2.97	2.6828	22.63
0.1412	3.96	2.8240	24.13
0.2824	5.23	2.9652	25.41
0.4236	6.36	3.1064	27.00
0.5648	7.59	3.2476	28.22
0.7060	8.54	3.3888	29.54
0.8472	9.45	3.5300	31.04
0.9884	10.09	3.6712	32.31
1.1296	10.64	3.8124	33.41
1.2708	10.91	3.9536	34.41
1.4120	11.09	4.0948	35.50
1.5532	11.32	4.2360	36.13
1.6944	12.23	4.3772	36.41
1.8356	13.64	4.5184	36.54
1.9768	15.23	4.6596	36.59
2.1180	16.68	4.8008	36.50
2.2592	18.04	4.9420	36.41
2.4004	19.68	5.0832	36.22
2.5416	21.13	5.2244	36.00

Table 26. $\text{Br}_2 - \text{PBr}_3$ in Methyl Cyanide

Mole Ratio $\text{Br}_2 : \text{PBr}_3$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$	Mole Ratio $\text{Br}_2 : \text{PBr}_3$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$
0.0000	7.04	1.5936	16.32
0.0664	7.27	1.6600	16.82
0.1328	7.45	1.7264	17.23
0.1992	7.64	1.7928	17.68
0.2656	7.82	1.8592	18.23
0.3320	8.04	1.9256	18.73
0.3984	8.23	1.9920	19.32
0.4648	8.41	2.0584	19.86
0.5312	8.54	2.1248	20.45
0.5976	8.77	2.1912	20.95
0.7304	9.25	2.2576	21.50
0.7968	9.77	2.3240	21.91
0.8632	10.00	2.3904	22.41
0.9296	11.14	2.4568	22.91
0.9960	11.64	2.5232	23.41
1.0624	12.14	2.6560	24.41
1.1288	12.64	2.7888	25.27
1.1952	13.14	2.9216	26.18
1.2616	13.68	3.2496	27.51
1.3280	14.23	3.4992	28.02
1.3944	14.77	3.7488	28.25
1.4608	15.41	3.9984	28.51
1.5272	15.86		

Table 27. $I_2 - PBr_3$ in Methyl Cyanide

Mole Ratio ($I_2 : PBr_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($I_2 : PBr_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.000	9.03	2.071	23.11
0.109	10.52	2.180	23.45
0.218	11.85	2.289	24.05
0.327	13.31	2.398	24.81
0.436	14.78	2.507	25.58
0.545	16.24	2.616	26.45
0.654	17.70	2.725	27.32
0.763	19.24	2.824	28.37
0.872	20.67	2.933	29.20
0.981	22.06	3.012	30.35
1.090	23.24	3.121	31.54
1.199	24.36	3.230	32.62
1.308	25.48	3.339	33.56
1.417	26.80	3.448	34.36
1.526	28.02	3.557	35.09
1.635	29.03	3.666	35.62
1.744	29.52	3.775	36.10
1.853	23.07	3.884	36.66
1.962	22.23		

Table 29. IBr - PBr₃ in Methyl Cyanide

Mole Ratio (IBr : PBr ₃)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (IBr : PBr ₃)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0.0000	7.88	2.4293	40.50
0.1429	8.85	2.5722	41.79
0.2858	10.56	2.7151	42.66
0.4287	12.41	2.8580	43.35
0.5716	14.25	3.0009	43.67
0.7145	16.45	3.1438	44.05
0.8574	18.30	3.2867	44.12
1.0003	20.35	3.4296	44.50
1.1432	22.51	3.5725	44.64
1.2861	24.67	3.7154	44.68
1.4290	26.76	3.8583	44.75
1.5719	28.82	4.0012	44.82
1.7148	30.88	4.1441	44.89
1.8577	33.11	4.2870	44.89
2.0006	34.92	4.4299	44.78
2.1435	37.18	4.5728	44.75
2.2864	39.00	4.7157	44.68

Table 30. I₂ - (PBr₃ + IBr) in Methyl Cyanide

Mole Ratio (I ₂ : PBr ₃ IBr)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (I ₂ : PBr ₃ IBr)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0.0000	26.97	1.313	39.10
0.101	28.54	1.414	40.01
0.202	30.04	1.515	41.31
0.303	31.09	1.616	42.10
0.404	32.27	1.717	42.59
0.505	33.28	1.818	43.14
0.606	34.33	1.919	43.60
0.707	35.41	2.020	44.09
0.808	36.35	2.121	44.40
0.909	37.36	2.222	44.43
1.010	38.02	2.323	44.29
1.111	38.42	2.424	43.95
1.212	38.86	2.525	43.67

Table 37. $\text{Br}_2 - \text{PhPI}_2$ in Methyl Cyanide

Mole Ratio $\text{Br}_2 : \text{PhPI}_2$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$	Mole Ratio $\text{Br}_2 : \text{PhPI}_2$	$K \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$
0.0000	12.27	1.9509	28.50
0.0929	12.82	2.0438	29.72
0.1858	13.27	2.1367	31.09
0.2787	13.68	2.2296	32.68
0.3716	14.09	2.3225	34.36
0.4645	14.45	2.4154	34.27
0.5574	14.86	2.5083	34.27
0.6503	14.91	2.6012	34.27
0.7432	14.95	2.6941	34.27
0.8361	15.00	2.7870	34.31
0.9290	15.23	2.8799	34.41
1.0219	15.77	2.9728	34.59
1.1148	16.91	3.0657	34.72
1.2077	18.27	3.1586	34.81
1.3006	19.63	3.2515	34.91
1.3935	20.95	3.3444	35.04
1.4864	22.32	3.4373	35.18
1.5793	23.63	3.5302	35.27
1.6722	24.86	3.6231	35.36
1.7651	26.09	3.7160	35.41
1.8580	27.32		

Table 39. $I_2 - PhPI_2$ in Methyl Cyanide

Mole Ratio $I_2 : PhPI_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio $I_2 : PhPI_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.0000	13.50	1.4355	31.68
0.0957	14.59	1.5312	32.36
0.1914	15.59	1.6269	32.86
0.2871	16.73	1.7226	33.31
0.3828	17.86	1.8183	33.81
0.4785	19.00	1.9140	34.22
0.5742	20.18	2.0097	34.45
0.6699	21.50	2.1054	34.59
0.7656	22.82	2.2011	34.72
0.8613	24.09	2.2968	34.81
0.9570	25.59	2.3925	34.77
1.0527	27.54	2.4882	34.72
1.1484	29.22	2.5839	34.72
1.2441	30.18	2.6796	34.68
1.3398	30.86	2.7753	34.63

Table 40. Solid $I_2 - PhPI_2$ in Methyl Cyanide

Mole Ratio $I_2 : PhPI_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$	Mole Ratio $I_2 : PhPI_2$	$K \times 10^4$ $ohm^{-1} cm^{-1}$
0.0000	14.45	1.2052	33.41
0.2417	17.91	1.3546	34.04
0.5495	22.63	1.4538	35.03
0.6875	24.77	1.6351	35.75
0.8153	26.68	1.8462	36.25
0.9209	28.36	2.0325	36.51
1.0511	29.51	2.3435	36.45
1.0771	31.09		

Table 41. IBr - PhPI₂ in Methyl Cyanide

Mole Ratio IBr : PhPI ₂	$K \times 10^4$ ohm ⁻¹ cm ⁻¹	Mole Ratio IBr : PhPI ₂	$K \times 10^4$ ohm ⁻¹ cm ⁻¹
0.0000	15.36	3.4884	51.01
0.2052	17.40	3.6936	52.05
0.4104	19.48	3.8988	52.90
0.6156	21.44	4.1040	53.71
0.8208	23.45	4.3092	54.29
1.0260	25.26	4.5144	54.71
1.2312	26.80	4.7196	55.13
1.4364	28.18	4.9248	55.44
1.6416	29.57	5.1300	55.75
1.8468	31.19	5.3352	55.98
2.0520	32.96	5.5404	56.17
2.2572	37.19	5.7456	56.33
2.4624	40.43	5.9508	56.44
2.6676	43.66	6.1560	56.52
2.8728	46.39	6.3612	56.60
3.0780	48.47	6.5664	56.67
3.2832	49.63		

Table 42. $\text{Br}_2 - \text{Ph}_2\text{PI}$ in Methyl Cyanide

Mole Ratio ($\text{Br}_2 : \text{Ph}_2\text{PI}$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($\text{Br}_2 : \text{Ph}_2\text{PI}$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	9.91	2.2032	17.86
0.0918	9.95	2.2950	18.68
0.1836	10.00	2.3868	19.50
0.2754	10.04	2.4786	20.32
0.3672	10.09	2.5704	21.09
0.4590	10.18	2.6622	21.86
0.5508	10.18	2.7540	22.68
0.6426	10.04	2.8458	23.50
0.7348	9.86	2.9376	24.22
0.8262	9.68	3.0294	24.95
0.9180	9.50	3.1212	25.68
1.0098	9.36	3.2130	26.36
1.1016	9.45	3.3048	27.09
1.1934	9.54	3.3966	27.72
1.2852	9.64	3.4884	28.32
1.3770	10.00	3.5802	28.95
1.4688	10.54	3.6720	29.50
1.5606	11.50	3.7638	30.00
1.6524	12.36	3.8556	30.50
1.7442	13.27	3.9474	30.95
1.8360	14.13	4.0392	31.41
1.9278	15.04	4.1310	31.77
2.0196	16.00	4.2228	32.09
2.1114	16.91	4.3146	32.31

Table 44. $I_2 - Ph_2PI$ in Methyl Cyanide

Mole ratio ($I_2 : Ph_2PI$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)	Mole ratio ($I_2 : Ph_2PI$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.0000	9.91	2.3583	29.18
0.1123	11.00	2.4706	30.000
0.2246	11.73	2.5829	30.91
0.3369	12.27	2.6952	31.82
0.4492	12.86	2.8075	32.63
0.5615	13.50	2.9198	33.54
0.6738	14.18	3.0321	34.59
0.7861	14.86	3.1444	35.63
0.8984	15.54	3.2567	36.45
1.0107	16.27	3.3690	37.22
1.1230	17.00	3.4813	37.91
1.2353	17.77	3.5936	38.59
1.3476	19.73	3.7059	39.09
1.4599	20.73	3.8182	39.50
1.5722	21.86	3.9305	39.63
1.6845	22.95	4.1551	39.63
1.7968	24.04	4.3797	38.86
1.9091	25.13	4.6043	38.36
2.0214	26.18	4.8289	37.86
2.1337	27.22	5.0535	37.36
2.2460	28.18		

Table 46. Solid $I_2 - Ph_2PI$ in Methyl Cyanide

Mole ratio ($I_2 : Ph_2PI$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)	Mole ratio ($I_2 : Ph_2PI$)	$K \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.0000	10.00	2.1865	29.63
0.2886	12.36	2.3949	31.77
0.4100	13.18	2.5129	33.13
0.5475	14.00	2.8508	37.09
0.7548	15.45	3.0604	39.50
0.9209	16.63	3.2665	41.63
1.1270	18.41	3.4899	42.77
1.3641	20.50	3.7751	43.00
1.4935	21.91	4.0099	42.81
1.6802	24.13	4.4668	42.31
1.8417	25.95		

Table 47. IBr - Ph₂PI in Methyl Cyanide

Mole Ratio (IBr : Ph ₂ PI)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (IBr : Ph ₂ PI)	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.0000	12.34	1.9602	20.60
0.0891	12.80	2.0493	21.71
0.1782	13.24	2.1384	22.97
0.2673	13.56	2.2275	24.26
0.3564	13.77	2.3166	25.61
0.4455	13.94	2.4057	26.80
0.5346	14.22	2.4948	28.02
0.6237	14.46	2.5839	29.20
0.7128	14.71	2.6730	30.32
0.8019	14.95	2.7621	31.43
0.8910	15.16	2.8512	32.52
0.9801	15.40	2.9403	33.49
1.0692	15.82	3.0294	34.47
1.1583	16.24	3.1185	35.34
1.2474	16.66	3.2076	36.24
1.3365	17.08	3.2967	37.01
1.4256	17.53	3.3858	37.67
1.5147	18.02	3.4749	38.20
1.6038	18.47	3.5640	38.75
1.6929	18.92	3.6531	39.10
1.7820	19.41	3.7422	39.42
1.8711	19.93		

Table 48. Solid I_2-PI_3 in Methyl Cyanide

Mole Ratio ($I_2:PI_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($I_2:PI_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	19.13	1.8568	40.59
0.2764	21.95	2.0291	41.86
		2.2143	42.81
0.6972	24.77	2.4578	44.09
0.8012	26.00	2.7481	48.45
0.9103	27.32	3.0137	50.86
1.0658	29.91	3.2942	51.81
1.3722	33.59	3.5013	52.00
1.6021	37.04		

Table 49. I_2-PI_3 in Methyl Cyanide

Mole Ratio ($I_2:PI_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($I_2:PI_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	19.73	2.0440	41.36
0.1022	21.13	2.1462	42.45
0.2044	22.36	2.2484	43.59
0.3066	23.77	2.3506	44.22
0.4088	25.00	2.4528	44.90
0.5110	26.27	2.5550	46.04
0.6132	27.50	2.6572	46.90
0.7154	28.72	2.7594	47.81
0.8176	30.00	2.8616	49.31
0.9198	31.27	2.9638	50.77
1.0226	32.63	3.0660	51.54
1.1242	34.09	3.1682	52.04
1.2264	35.27	3.2704	52.31
1.3286	36.45	3.3726	52.40
1.4308	37.45	3.4747	52.45
1.5330	38.41	3.5770	52.54
1.6352	39.27	3.7814	52.45
1.7374	39.81	3.9858	52.18
1.8396	40.18	4.1902	51.86
1.9418	41.00		

Table 51. I_2-PI_3 in Nitrobenzene

Mole Ratio ($I_2:PI_3$)	$K \times 10^6$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($I_2:PI_3$)	$K \times 10^6$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.0000	29.09	1.8612	34.13
0.1034	29.45	1.9646	34.18
0.2068	29.63	2.0680	34.22
0.3102	29.81	2.1714	34.32
0.4136	30.00	2.2748	34.32
0.5170	30.09	2.3782	34.39
0.6204	30.45	2.4816	34.39
0.7238	30.72	2.5850	34.40
0.8272	31.02	2.7918	34.56
0.9306	31.45	2.9986	34.75
1.0340	31.72	3.2054	34.91
1.1374	32.09	3.4122	34.95
1.2408	32.36	3.6190	35.00
1.3442	32.72	3.8258	35.04
1.4476	33.09	4.0326	35.09
1.5510	33.36	4.2394	35.22
1.6544	33.63	4.4462	35.22
1.7578	34.00		

Table 52. IBr : PI₃ in Methyl Cyanide

Mole Ratio (IBr : PI ₃)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole Ratio (IBr : PI ₃)	K x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0.000	17.95	3.120	37.64
0.156	19.03	3.276	39.10
0.312	19.86	3.432	40.36
0.468	20.53	3.588	41.37
0.624	21.15	3.744	42.17
0.780	22.00	3.900	42.80
0.936	22.65	4.056	43.46
1.092	23.28	4.212	44.09
1.248	23.87	4.368	44.57
1.404	24.40	4.524	44.82
1.560	25.02	4.680	45.13
1.716	25.82	4.836	45.51
1.872	26.73	4.992	45.76
2.028	27.81	5.148	45.97
2.184	29.27	5.304	46.14
2.340	30.39	5.460	46.21
2.496	31.92	5.616	46.32
2.652	33.25	5.772	46.35
2.808	35.09	5.928	46.39
2.964	36.28		

Table 53. $\text{Br}_2\text{-PI}_3$ in Methyl Cyanide

Mole Ratio ($\text{Br}_2:\text{PI}_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Mole Ratio ($\text{Br}_2:\text{PI}_3$)	$K \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)
0.000	18.12	1.890	25.55
0.105	18.33	1.995	26.49
0.210	18.33	2.100	27.32
0.315	18.33	2.205	28.30
0.420	18.37	2.310	29.24
0.525	18.37	2.415	30.18
0.630	18.44	2.520	31.16
0.735	18.54	2.625	32.17
0.840	18.68	2.730	33.21
0.945	18.82	2.835	34.26
1.050	18.89	2.940	35.30
1.155	19.48	3.045	36.24
1.260	20.14	3.150	37.22
1.365	20.88	3.255	38.30
1.470	21.71	3.360	39.49
1.575	22.69	3.465	39.83
1.680	23.66	3.675	40.25
1.785	24.64	3.885	41.01

b. Conductometric Titration Data of the Systems $\text{Ph}_3\text{M-CN X}$ ($\text{M} = \text{P}$,As ; X = Br, I)Table 63. CNI - Ph_3P in Methyl Cyanide

Mole ratio ICN: Ph_3P	$k \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$	Mole ratio ICN: Ph_3P	$k \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$
0.0000	0.0182	1.4724	10.41
0.0818	1.46	1.5542	9.23
0.1636	3.59	1.6360	8.36
0.2454	5.54	1.7178	7.82
0.3272	7.27	1.7996	7.50
0.4090	8.77	1.8814	7.18
0.4908	10.27	1.9632	6.91
0.5726	11.73	2.0450	6.73
0.6544	12.82	2.1268	6.54
0.7362	13.45	2.2086	6.41
0.8180	31.32	2.2904	6.27
0.8998	13.04	2.3722	6.14
0.9816	12.91	2.4540	6.00
1.0634	12.73	2.5358	5.86
1.1452	12.50	2.6176	5.73
1.2270	12.41	2.6994	5.59
1.3088	12.09	2.7812	5.50
1.3906	11.45	2.8630	5.45

Table 65 Solid CNI - Ph_3P in Methyl Cyanide

Mole ratio ICN: Ph_3P	$k \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$	Mole ratio ICN: Ph_3P	$k \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$
0.0000	0.043	1.8822	5.136
0.4722	7.545	2.0207	4.863
0.7876	9.999	2.1075	4.727
1.0629	9.726	2.3861	4.454
1.2982	9.408	2.5947	4.272
1.4267	8.681		

Table 69. BrCN-Ph₃P in Methyl Cyanide

Mole ratio BrCN:Ph ₃ P	K x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio BrCN:Ph ₃ P	K x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.0000	0.076	1.4336	18.044
0.1024	1.959	1.5360	17.907
0.2048	3.777	1.6384	17.771
0.3072	5.909	1.7408	17.589
0.4096	7.999	1.8432	17.453
0.5120	9.999	1.9456	17.316
0.6144	11.908	2.0480	17.180
0.7168	13.59	2.1504	17.044
0.8192	15.226	2.2528	16.907
0.9216	16.771	2.3552	16.726
1.0240	18.271	2.4576	16.589
1.1264	18.498	2.5600	16.498
1.2288	18.362		
1.3312	18.225		

Table 70. CNI-Ph₃As in Methyl Cyanide

Mole ratio ICN:Ph ₃ As	K x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio ICN:Ph ₃ As	K x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.0000	0.0067	1.5589	9.12
0.0917	1.45	1.6506	9.05
0.1834	2.33	1.7423	8.98
0.2751	3.04	1.8340	8.94
0.3668	3.70	1.9257	8.87
0.4585	4.40	2.0174	8.80
0.5502	5.00	2.1091	8.73
0.6419	5.67	2.2008	8.69
0.7336	6.23	2.3842	8.55
0.8253	6.79	2.5676	8.45
0.9170	7.32	2.7510	8.34
1.0087	7.78	2.9344	8.24
1.1004	8.24	3.1178	8.13
1.1921	8.66	3.3012	8.03
1.2838	9.08	3.4846	7.92
1.3755	9.40	3.6680	7.85

Table 71. Solid CNI - Ph₃As in Methyl Cyanide

Mole ratio ICN:Ph ₃ As	$k \times 10^4$ ohm ⁻¹ cm ⁻¹
0.0000	0.005
0.0451	1.268
0.4059	6.090
0.5964	8.181
0.7449	9.635
0.902	11.09
1.0373	12.226
1.0847	12.635
1.1415	13.044
1.3055	14.317
1.5012	15.023
1.7254	15.271
2.0489	15.226
2.2573	15.226
2.4656	15.226

Table 74. CNBr - Ph₃As in Methyl Cyanide

Mole ratio BrCN:Ph ₃ As	K x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio BrCN:Ph ₃ As	K x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.000	0.103	1.261	2.668
0.097	0.691	1.358	2.695
0.194	1.045	1.455	2.709
0.291	1.314	1.552	2.718
0.388	1.536	1.649	2.727
0.485	1.741	1.746	2.735
0.582	1.909	1.843	2.739
0.679	2.073	1.940	2.746
0.776	2.218	2.037	2.759
0.873	2.341	2.134	2.765
0.970	2.45	2.328	2.782
1.067	2.532	2.522	2.794
1.164	2.609		

c-Conductometric Titration Data of the Systems Ph₂As(CH₂)_nAsPh₂-Hal₂Table 75. Br₂-Ph₂AsCH₂As₂Ph₂ in Methyl Cyanide

Mole ratio (Br ₂ : Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole ratio (Br ₂ : Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0.000	0.013	0.618	1.52
0.103	0.54	0.721	1.70
0.206	0.80	0.824	1.80
0.309	1.04	0.927	1.96
0.412	1.20	1.030	2.09
0.515	1.38	1.133	2.16

continued overleaf.

Mole ratio (Br ₂ : Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole ratio (Br ₂ : Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
1.236	2.16	4.120	27.23
1.339	2.19	4.223	27.82
1.442	2.21	4.326	28.41
1.545	2.25	4.429	29.00
1.648	2.24	4.532	29.59
1.751	2.48	4.635	30.18
1.854	3.37	4.738	30.72
1.957	4.64	4.841	31.27
2.060	6.23	4.944	31.86
2.163	7.77	5.047	32.36
2.266	9.32	5.150	32.77
2.369	11.04	5.253	33.18
2.472	12.68	5.356	33.68
2.575	14.04	5.459	34.04
2.678	15.23	5.562	34.41
2.781	16.68	5.665	34.68
2.884	17.82	5.768	34.95
2.987	18.82	5.871	35.18
3.090	19.82	5.974	35.32
3.193	20.77	6.077	35.50
3.296	21.68	6.180	35.59
3.399	22.36	6.283	35.68
3.502	23.23	6.386	35.72
3.605	23.86	6.489	35.82
3.708	24.59	6.592	35.82
3.811	25.23	6.695	35.82
3.914	25.86	6.798	35.82
4.017	26.59	6.901	35.82

Table 76. $I_2 - Ph_2AsCH_2AsPh_2$ in Methyl Cyanide

Mole ratio ($I_2 : Ph_2AsCH_2AsPh_2$)	$k \times 10^4$ ($ohm^{-1} cm^{-1}$)	Mole ratio ($I_2 : Ph_2AsCH_2AsPh_2$)	$k \times 10^4$ ($ohm^{-1} cm^{-1}$)
0.000	0.012	2.742	21.57
0.091	0.93	2.833	21.59
0.183	1.75	2.925	21.68
0.274	2.40	3.016	21.73
0.366	3.09	3.108	21.73
0.457	3.79	3.199	21.82
0.548	4.52	3.290	21.86
0.640	5.23	3.382	21.91
0.731	5.95	3.473	21.91
0.823	6.54	3.565	21.95
0.914	7.27	3.656	21.95
1.004	8.00	3.747	21.95
1.097	8.73	3.839	21.95
1.188	9.54	3.930	22.00
1.280	10.36	4.022	22.00
1.371	11.09	4.113	22.00
1.462	11.95	4.296	22.00
1.554	12.77	4.479	22.04
1.645	13.73	4.661	22.04
1.737	14.68	4.844	22.09
1.828	15.73	5.027	22.13
1.919	16.82	5.210	22.13
2.011	18.00	5.393	22.18
2.102	19.00	5.575	22.23
2.194	19.68	5.758	22.27
2.285	20.36	5.941	22.27
2.376	20.77	6.124	22.32
2.468	21.04	6.307	22.32
2.559	21.22	6.489	22.36
2.651	21.36	6.672	22.41

Table 77. IBr-Ph₂AsCH₂AsPh₂ in Methyl Cyanide

Mole ratio (IBr:Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)	Mole ratio (IBr:Ph ₂ AsCH ₂ AsPh ₂)	k x 10 ⁴ (ohm ⁻¹ cm ⁻¹)
0.000	0.006	3.390	17.59
0.113	0.56	3.503	18.04
0.226	0.92	3.616	18.45
0.339	1.23	3.729	18.95
0.452	1.59	3.842	19.36
0.565	1.92	3.955	19.86
0.678	2.26	4.068	20.27
0.791	2.69	4.181	20.73
0.904	3.03	4.294	21.18
1.017	3.50	4.407	21.59
1.130	4.05	4.520	22.00
1.243	4.74	4.633	22.50
1.356	5.54	4.746	22.91
1.469	6.50	4.859	23.32
1.582	7.36	4.972	23.77
1.695	7.95	5.085	24.27
1.808	8.68	5.198	24.68
1.921	9.36	5.311	25.13
2.034	10.09	5.424	25.50
2.147	10.73	5.537	25.91
2.260	11.41	5.650	26.22
2.373	12.27	5.763	26.59
2.486	13.09	5.876	27.04
2.599	13.73	5.989	27.41
2.712	14.59	6.102	27.77
2.825	15.32	6.215	28.13
2.938	16.00	6.328	28.50
3.051	16.45	6.441	28.91
3.164	16.86	6.554	29.27
3.277	17.23	6.667	29.63

Table 84. Br₂-A in Methyl Cyanide

Mole ratio (Br ₂ -Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio (Br ₂ -Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.0000	0.03	2.8840	6.86
0.1442	0.60	3.0282	8.27
0.2884	0.80	3.1724	9.45
0.4326	1.04	3.3166	10.91
0.5768	1.07	3.4608	11.95
0.7210	1.06	3.6050	13.09
0.8652	1.12	3.7492	14.13
1.0094	1.39	3.8934	15.04
1.1536	1.62	4.0376	16.04
1.2978	1.80	4.1818	17.00
1.4420	1.97	4.3260	17.77
1.5862	1.96	4.4702	18.63
1.7304	1.89	4.7586	20.23
1.8746	1.82	5.0470	21.82
2.0188	1.79	5.3354	23.36
2.1630	1.94	5.6238	24.86
2.3072	2.33	5.9122	26.41
2.4514	2.83	6.4890	27.96
2.5956	3.91	7.0658	28.54
2.7398	5.36		

Table 85. I₂-A in Methyl Cyanide

Mole ratio (I ₂ : Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio (I ₂ : Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.0000	0.0051	1.2340	8.23
0.1234	0.96	1.3574	8.82
0.2468	1.73	1.4808	9.36
0.3702	2.63	1.6042	9.82
0.4936	3.66	1.7276	10.14
0.6170	4.77	1.8501	10.36
0.7404	5.68	1.9744	10.59
0.8638	6.41	2.0978	10.82
0.9872	7.00	2.2212	10.95
1.1106	7.64	2.3446	11.09

continued overleaf.

Table 85 continued.

Mole ratio (I ₂ :Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio (I ₂ :Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹
2.4680	11.23	3.9488	12.36
2.5914	11.32	4.1956	12.50
2.7148	11.45	4.4424	12.64
2.8382	11.54	4.6892	12.82
2.9616	11.64	4.9360	12.91
3.0850	11.73	5.1828	13.04
3.2084	11.82	5.4296	13.14
3.4552	12.00	5.6764	13.27
3.7020	12.18	5.9232	13.36

Table 86. IBr - A in Methyl Cyanide

Mole ratio (IBr:Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹	Mole ratio (IBr:Ph ₂ AsCH ₂ CH ₂ AsPh ₂)	k x 10 ⁴ ohm ⁻¹ cm ⁻¹
0.000	0.01	2.838	18.82
0.142	0.93	2.982	19.45
0.284	1.88	3.124	20.18
0.426	2.74	3.266	20.77
0.568	4.64	3.408	21.27
0.710	5.91	3.548	21.27
0.851	7.23	3.692	21.41
0.994	8.54	3.834	21.63
1.136	10.04	3.976	21.77
1.278	11.68	4.118	22.09
1.419	12.73	4.257	22.36
1.562	13.50	4.399	22.63
1.846	14.41	4.686	23.36
1.988	14.91	4.970	24.27
2.129	15.45	5.254	25.27
2.272	16.18	5.538	26.36
2.414	16.77	5.822	27.54
2.556	17.45	6.106	28.72
2.698	18.09		

Table 7. The Mass Spectra of the Compounds PhPBr_2 , PhPBr_4 and PhPBr_5

PhPBr_2			PhPBr_4 and PhPBr_5		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
			286	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{O}^+$	10(w)*
			284	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrO}^+$	19(10)
			282	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{O}^+$	10(w)
270	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	14	270	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^+$	vw(vw)
268	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}^+$	32	268	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}^+$	w(w)
266	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2^+$	14	266	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2^+$	vw(vw)
			205	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	100(100)
			203	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrO}^+$	100(100)
189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	98	189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	16(10)
187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	100	187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	16(10)
108	$\text{C}_6\text{H}_5\text{P}^+$	49	108	$\text{C}_6\text{H}_5\text{P}^+$	10(w)
82	H^{81}Br^+	22	82	H^{81}Br^+	41(37)
81	$^{81}\text{Br}^+$	17	81	$^{81}\text{Br}^+$	21(17)
80	H^{79}Br^+	29	80	H^{79}Br^+	42(38)
79	$^{79}\text{Br}^+$	14	79	$^{79}\text{Br}^+$	22(17)
78	C_6H_6^+	vw	78	C_6H_6^+	15(13)
77	C_6H_5^+	13	77	C_6H_5^+	100(100)
31	P^+	26	31	P^+	vw(vw)

* The relative intensities in brackets correspond to PhPBr_5 .

Relative intensity between 0 and 3 -----vw (very weak).

Relative intensity between 3 and 10 -----w (weak).

Table 15. The Mass Spectra of the Compounds PhPBr_2I_2 and $(\text{PhPBr}_2\text{I}_4)^*$

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
524	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{I}_2^+$	w	254	I_2^+	100
522	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrI}_2^+$	w	235	$\text{C}_6\text{H}_5\text{PI}^+$	23
520	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{I}_2^+$	w	205	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	90
443	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrI}_2^+$	w	203	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrO}^+$	91
441	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrI}_2^+$	w	189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	100
397	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{I}^+$	vw	187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	100
395	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrI}^+$	w	128	HI^+	100
393	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{I}^+$	vw	127	I^+	100
362	$\text{C}_6\text{H}_5\text{PI}_2^+$	vw	108	$\text{C}_6\text{H}_5\text{P}^+$	85
316	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrI}^+$	w	82	H^{81}Br^+	100
314	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrI}^+$	w	81	$^{81}\text{Br}^+$	100
286	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	w	80	H^{79}Br^+	100
284	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrO}^+$	10	79	$^{79}\text{Br}^+$	100
282	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{O}^+$	w	78	C_6H_6^+	10
270	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^+$	20	77	C_6H_5^+	100
268	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}^+$	44	31	P^+	w
266	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2^+$	20			

* The relative intensity of PhPBr_2I_4 is not included.

Table 17. The Mass Spectrum of the Compound PhPBr_3I

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
286	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{O}^+$	18	128	HI^+	57
284	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrO}^+$	40	127	I^+	58
282	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{O}^+$	19	108	$\text{C}_6\text{H}_5\text{P}^+$	9
270	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^+$	vw	82	H^{81}Br^+	100
268	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}^+$	vw	81	$^{81}\text{Br}^+$	100
266	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2^+$	vw	80	H^{79}Br^+	100
254	I_2^+	59	79	$^{79}\text{Br}^+$	100
205	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	100	78	C_6H_6^+	34
203	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrO}^+$	100	77	C_6H_5^+	100
189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	10	31	P^+	14
187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	10			

Table 18. The Mass Spectrum of the Compound PhPBr_4I .

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
570	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrI}_3^+$	vw	314	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrI}^+$	vw
568	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrI}_3^+$	vw	286	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{O}^+$	w
524	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{I}_2^+$	vw	284	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrO}^+$	11
522	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrI}_2^+$	w	282	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{O}^+$	w
520	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{I}_2^+$	vw	270	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^+$	vw
478	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_3\text{I}^+$	w	268	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}^+$	vw
476	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^{79}\text{BrI}^+$	w	266	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2^+$	vw
474	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}_2\text{I}^+$	w	254	I_2^+	100
472	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_3\text{I}^+$	w	205	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	100
441	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrI}_2^+$	vw			
443	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrI}_2^+$	vw			
432	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_4^+$	vw	203	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrO}^+$	100
430	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_3^{79}\text{Br}^+$	w	189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	19
428	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^{79}\text{Br}_2^+$	w	187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	19
426	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}_3^+$	w	128	HI^+	14
424	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_4^+$	vw	127	I^+	82
397	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2\text{I}^+$	vw	108	$\text{C}_6\text{H}_5\text{P}^+$	14
395	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{BrI}^+$	w	82	H^{81}Br^+	91
393	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_2\text{I}^+$	vw	81	$^{81}\text{Br}^+$	54
351	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_3^+$	vw	80	H^{79}Br^+	98
349	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}_2^{79}\text{Br}^+$	w	79	$^{79}\text{Br}^+$	55
347	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^{79}\text{Br}_2^+$	w	78	C_6H_6^+	23
345	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}_3^+$	vw	77	C_6H_5^+	100
316	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrI}^+$	vw	31	P^+	w

Table 21. The Mass Spectra of the Compounds Ph_2PBr_3 and $(\text{Ph}_2\text{PBr}_4)_2$

Ph_2PBr_3			$(\text{Ph}_2\text{PBr}_4)_2$		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
			428	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_3^+$	vw
			426	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^{79}\text{Br}^+$	vw
			424	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}_2^+$	vw
			422	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_3^+$	vw
			347	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^+$	vw
			345	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}^+$	vw
			343	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_2^+$	vw
282	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrO}^+$	vw			
280	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrO}^+$	vw			
266	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^+$	15	266	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^+$	10
264	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}^+$	15	264	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}^+$	10
201	$(\text{C}_6\text{H}_5)_2\text{P O}^+$	100	201	$(\text{C}_6\text{H}_5)_2\text{P O}^+$	100
189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	vw	189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	vw

To be continued overleaf.

Table 21 continued.

Ph_2PBr_3			$(\text{Ph}_2\text{PBr}_4)_2$		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	vw	187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	vw
185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	42	185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	44
162	$^{81}\text{Br}_2^+$	13	162	$^{81}\text{Br}_2^+$	21
160	$^{81}\text{Br}^{79}\text{Br}^+$	27	160	$^{81}\text{Br}^{79}\text{Br}^+$	43
158	$^{79}\text{Br}_2$	13	158	$^{79}\text{Br}_2$	21
108	$\text{C}_6\text{H}_5\text{P}^+$	13	108	$\text{C}_6\text{H}_5\text{P}^+$	11
82	H^{81}Br^+	43	82	H^{81}Br^+	37
81	$^{81}\text{Br}^+$	25	81	$^{81}\text{Br}^+$	33
80	H^{79}Br^+	43	80	H^{79}Br^+	37
79	$^{79}\text{Br}^+$	25	79	$^{79}\text{Br}^+$	33
78	C_6H_6^+	w	78	C_6H_6^+	10
77	C_6H_5^+	72	77	C_6H_5^+	100
31	P^+	vw	31	P^+	vw

Table 24. The Mass Spectrum of the Compound Ph_2PBrI_4

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
393	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrI}^+$	vw	127	I^+	100
391	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrI}^+$	vw	108	$\text{C}_6\text{H}_5\text{P}^+$	17
312	$(\text{C}_6\text{H}_5)_2\text{P I}^+$	vw	82	H^{81}Br^+	15
266	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^+$	w	81	$^{81}\text{Br}^+$	18
264	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}^+$	w	80	H^{79}Br^+	15
254	I_2^+	100	79	$^{79}\text{Br}^+$	10
235	$\text{C}_6\text{H}_5\text{PI}^+$	vw	78	C_6H_6^+	w
201	$(\text{C}_6\text{H}_5)_2\text{PO}^+$	w	77	C_6H_5^+	41
185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	41	31	P^+	vw
128	HI^+	vw			

Table 33. The Mass Spectrum of the Compound PhPBr₅I.

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
570	$C_6H_5P^{81}BrI_3^+$	vw	314	$C_6H_5P^{79}BrI^+$	vw
568	$C_6H_5P^{79}BrI_3^+$	vw	286	$C_6H_5P^{81}Br_2O^+$	w
524	$C_6H_5P^{81}Br_2I_2^+$	vw	284	$C_6H_5P^{81}Br^{79}BrO^+$	20
522	$C_6H_5P^{81}Br^{79}BrI_2^+$	w	282	$C_6H_5P^{79}Br_2O^+$	w
520	$C_6H_5P^{79}Br_2I_2^+$	vw	270	$C_6H_5P^{81}Br_2^+$	w
478	$C_6H_5P^{81}Br_3I$	vw	268	$C_6H_5P^{81}Br^{79}Br^+$	20
476	$C_6H_5P^{81}Br_2^{79}BrI^+$	w	266	$C_6H_5P^{79}Br_2^+$	w
474	$C_6H_5P^{81}Br^{79}Br_2I^+$	w	254	I_2^+	100
472	$C_6H_5P^{79}Br_3I^+$	vw	235	$C_6H_5PI^+$	w
443	$C_6H_5P^{81}BrI_2^+$	vw			
441	$C_6H_5P^{79}BrI_2^+$	vw			
432	$C_6H_5P^{81}Br_4^+$	vw	205	$C_6H_5P^{81}BrO^+$	100
430	$C_6H_5P^{81}Br_3^{79}Br^+$	w	203	$C_6H_5P^{79}BrO^+$	100

To be continued overleaf.

Table 33 continued.

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
428	$C_6H_5P^{81}Br_2^{79}Br_2^+$	w	189	$C_6H_5P^{81}Br^+$	60
426	$C_6H_5P^{81}Br^{79}Br_3^+$	w	187	$C_6H_5P^{79}Br^+$	60
424	$C_6H_5P^{79}Br_4^+$	w	128	HI^+	15
			127	I^+	100
397	$C_6H_5P^{81}Br_2I^+$	vw	108	$C_6H_5P^+$	40
395	$C_6H_5P^{81}Br^{79}BrI^+$	w	82	$H^{81}Br^+$	92
393	$C_6H_5P^{79}Br_2I^+$	vw	81	$^{81}Br^+$	48
378	$C_6H_5PI_2O^+$	vw	80	$H^{79}Br^+$	94
362	$C_6H_5PI_2^+$	vw	79	$^{79}Br^+$	48
332	$C_6H_5P^{81}BrIO^+$	w	78	$C_6H_6^+$	18
330	$C_6H_5P^{79}BrIO^+$	w	77	$C_6H_5^+$	100
316	$C_6H_5P^{81}BrI^+$	vw	31	P^+	w

Table 34. The Mass Spectrum of the Compound $\text{Ph}_2\text{PBr}_3\text{I}_2$.

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
474	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2\text{I}^+$	vw	201	$(\text{C}_6\text{H}_5)_2\text{PO}^+$	46
472	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{BrI}^+$	vw	185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	58
470	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_2\text{I}^+$	vw	128	HI^+	w
428	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_3^+$	vw	127	I^+	100
426	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^{79}\text{Br}^+$	vw	108	$\text{C}_6\text{H}_5\text{P}^+$	46
424	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}_2^+$	vw	82	H^{81}Br^+	63
422	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_3^+$	vw	81	$^{81}\text{Br}^+$	32
393	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrI}^+$	vw	80	H^{79}Br^+	64
391	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrI}^+$	vw	79	$^{79}\text{Br}^+$	32
347	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^+$	vw	78	C_6H_6^+	w
345	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}^+$	w	77	C_6H_5^+	47
343	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_2^+$	vw	31	P^+	w
266	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^+$	25			
264	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}^+$	25			
254	I_2^+	100			
208	I^{81}Br^+	26			
206	I^{79}Br^+	26			

Table 35. The Mass Spectrum of the Compound $\text{Ph}_2\text{PBr}_2\text{I}_3$.

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
520	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrI}_2^+$	vw	266	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^+$	100
518	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrI}_2^+$	vw	264	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}^+$	100
474	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2\text{I}^+$	vw	254	I_2^+	100
472	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{BrI}^+$	w	235	$\text{C}_6\text{H}_5\text{PI}^+$	17
470	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_2\text{I}^+$	vw	208	I^{81}Br^+	100
455	$(\text{C}_6\text{H}_5)_2\text{PI}_2\text{O}^+$	vw	206	I^{79}Br^+	100
428	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_3^+$	vw	201	$(\text{C}_6\text{H}_5)_2\text{PO}^+$	100
426	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^{79}\text{Br}^+$	vw	185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	100
424	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}_2^+$	vw	128	HI^+	20
422	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_3^+$	vw	127	I^+	100
409	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrIO}^+$	vw	108	$\text{C}_6\text{H}_5\text{P}^+$	100
407	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrIO}^+$	vw	82	H^{81}Br^+	100
393	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrI}^+$	vw	81	$^{81}\text{Br}^+$	100
391	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrI}^+$	vw	80	H^{79}Br^+	100
347	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}_2^+$	vw	79	$^{79}\text{Br}^+$	100
345	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{Br}^{79}\text{Br}^+$	w	78	C_6H_6^+	60
343	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{Br}_2^+$	vw	77	C_6H_5^+	100
282	$(\text{C}_6\text{H}_5)_2\text{P}^{81}\text{BrO}^+$	w	31	P^+	vw
280	$(\text{C}_6\text{H}_5)_2\text{P}^{79}\text{BrO}^+$	w			

Table 55. The Mass Spectrum of PhPI_2

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
362	$\text{C}_6\text{H}_5\text{PI}_2^+$	100	185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	90
343	$(\text{C}_6\text{H}_5)_2\text{P}_2\text{I}^+$	70	158	PI^+	25
316	P_2I_2^+	v. w.	139	$\text{C}_6\text{H}_5\text{P}_2^+$	36
312	$(\text{C}_6\text{H}_5)_2\text{PI}^+$	16	128	HI^+	100
285	PI_2^+	v. w.	127	I^+	100
262	$(\text{C}_6\text{H}_5)_3\text{P}^+$	18	108	$\text{C}_6\text{H}_5\text{P}^+$	100
254	I_2^+	13	78	C_6H_6^+	95
235	$\text{C}_6\text{H}_5\text{PI}^+$	100	77	C_6H_5^+	98
216	$(\text{C}_6\text{H}_5)_2\text{P}_2^+$	80	31	P^+	13

Table 56. The Mass Spectrum of Ph_2PI

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
312	$(\text{C}_6\text{H}_5)_2\text{PI}^+$	v. w.	108	$\text{C}_6\text{H}_5\text{P}^+$	15
254	I_2^+	v. w.	78	C_6H_6^+	v. w.
185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	w.	77	C_6H_5^+	v. w.
128	HI^+	100	31	P^+	v. w.
127	I^+	61			

Table 57. The Mass Spectrum of PI_3

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
412	PI_3^+	100	127	I^+	100
285	PI_2^+	65	124	P_4^+	55
254	I_2^+	35	62	P_2^+	58
158	PI^+	43	31	P^+	15
128	HI^+	100			

Table 58. The Mass Spectrum of $\text{Ph}_2\text{P}_2\text{I}_2$

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
470	$(\text{C}_6\text{H}_5)_2\text{P}_2\text{I}_2^+$	w.	158	PI^+	v. w.
362	$\text{C}_6\text{H}_5\text{PI}_2^+$	31	139	$\text{C}_6\text{H}_5\text{P}_2^+$	94
343	$(\text{C}_6\text{H}_5)_2\text{P}_2\text{I}^+$	54	128	HI^+	98
316	P_2I_2^+	14	127	I^+	93
262	$(\text{C}_6\text{H}_5)_3\text{P}^+$	w.	108	$\text{C}_6\text{H}_5\text{P}^+$	100
254	I_2^+	v. w.	78	C_6H_6^+	30
235	$\text{C}_6\text{H}_5\text{PI}^+$	100	77	C_6H_5^+	100
216	$(\text{C}_6\text{H}_5)_2\text{P}_2^+$	35	31	P^+	w.
185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	30			

Table 59. The Mass Spectrum of P_2I_4

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
570	$P_2I_4^+$	12	128	HI^+	100
442	$P_2I_3^+$	39	127	I^+	100
412	PI_3^+	46	124	P_4^+	100
316	$P_2I_2^+$	15	112		20
285	PI_2^+	65	109		21
254	I_2^+	62	62	P_2^+	100
189	P_2I^+	63	31	P^+	77
158	PI^+	100			

Table 60. The Mass Spectrum of $PhPI_4$

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
490	$C_6H_5PI_3^+$	w.	128	HI^+	100
362	$C_6H_5PI_2^+$	100	127	I^+	100
312	$(C_6H_5)_2PI^+$	w.	78	$C_6H_6^+$	v.w.
254	I_2^+	100	77	$C_6H_5^+$	64
235	$C_6H_5PI^+$	80	31	P^+	w.
185	$(C_6H_5)_2P^+$	13			

Table 61. The Mass Spectrum of Ph_2PI_3

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
312	$(\text{C}_6\text{H}_5)_2\text{PI}^+$	27	127	I^+	100
254	I_2^+	100	108	$\text{C}_6\text{H}_5\text{P}^+$	57
218	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})_2\text{H}^+$	85	78	C_6H_6^+	24
201	$(\text{C}_6\text{H}_5)_2\text{PO}^+$	93	77	C_6H_5^+	91
185	$(\text{C}_6\text{H}_5)_2\text{P}^+$	91	31	P^+	w.
128	HI^+	100			

Table 62. The Mass Spectrum of PhPBrI_3

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
570	$\text{C}_6\text{H}_5\text{PI}_3^{81}\text{Br}^+$	v. w.	187	$\text{C}_6\text{H}_5\text{P}^{79}\text{Br}^+$	60
568	$\text{C}_6\text{H}_5\text{PI}_3^{79}\text{Br}^+$	v. w.	158	PI^+	w.
443	$\text{C}_6\text{H}_5\text{PI}_2^{81}\text{Br}^+$	v. w.	128	HI^+	100
441	$\text{C}_6\text{H}_5\text{PI}_2^{79}\text{Br}^+$	v. w.	127	I^+	100
362	$\text{C}_6\text{H}_5\text{PI}_2^+$	100	108	$\text{C}_6\text{H}_5\text{P}^+$	85
316	$\text{C}_6\text{H}_5\text{PI}^{81}\text{Br}^+$	w.	82	H^{81}Br^+	63
314	$\text{C}_6\text{H}_5\text{PI}^{79}\text{Br}^+$	w.	81	$^{81}\text{Br}^+$	25
285	PI_2^+	11	80	H^{79}Br^+	64
254	I_2^+	100	79	$^{79}\text{Br}^+$	25
235	$\text{C}_6\text{H}_5\text{PI}^+$	100	78	C_6H_6^+	w.
205	$\text{C}_6\text{H}_5\text{P}^{81}\text{BrO}^+$	w.	77	C_6H_5^+	20
203	$\text{C}_6\text{H}_5\text{P}^{79}\text{BrO}^+$	w.	31	P^+	v. w.
189	$\text{C}_6\text{H}_5\text{P}^{81}\text{Br}^+$	60			

Table 67. The Mass Spectrum of the Compound $\text{Ph}_3\text{P}(\text{CN})_2$

m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
278	Ph_3PO^+	11	78	C_6H_6^+	3
262	Ph_3P^+	89	77	C_6H_5^+	18
201	Ph_2PO^+	6	57	PCN^+	11
185	Ph_2P^+	100	52	$(\text{CN})_2^+$	27
152	PhPCNOH	15	31	P^+	1
134	PhPCN^+	9	27	HCN^+	8
108	PhP^+	25	26	CN^+	4

Table 68. The Mass Spectra of the Compound Ph_3PI_2 and Sample (IV)

Ph_3PI_2			Sample IV (see Table 66)		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
406	Ph_3PIOH^+	2			
278	Ph_3PO^+	24	278	Ph_3PO^+	26
262	Ph_3P^+	100	262	Ph_3P^+	100
254	I_2^+	96	254	I_2^+	100
201	Ph_2PO^+	8	201	Ph_2PO^+	8
185	Ph_2P^+	64	185	Ph_2P^+	58
			152	PhPCNOH	40
			134	PhPCN^+	22

To be continued overleaf.

Table 68 continued.

Ph ₃ PI ₂			Sample IV (see Table 66)		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
128	HI ⁺	58	128	HI ⁺	28
127	I ⁺	100	127	I ⁺	80
108	PhP ⁺	100	108	PhP ⁺	93
78	C ₆ H ₆ ⁺	14	78	C ₆ H ₆ ⁺	11
77	C ₆ H ₅ ⁺	48	77	C ₆ H ₅ ⁺	40
			57	PCN ⁺	26
			52	(CN) ₂ ⁺	68
31	P ⁺	2	31	P ⁺	1
			27	HCN ⁺	16
			26	CN ⁺	5

Table 73. The Mass Spectra of the Compounds Ph_3AsI_2 and $(\text{Ph}_3\text{As})_2\text{CNI}_3$

Ph_3AsI_2			$(\text{Ph}_3\text{As})_2\text{CNI}_3$		
m/e	Proposed ion	Relative Intensity	m/e	Proposed ion	Relative Intensity
306	Ph_3As^+	26	306	Ph_3As^+	5
254	I_2^+	9	254	I_2^+	3
229	Ph_2As^+	90	229	Ph_2As^+	3
152	PhAs^+	100	152	PhAs^+	100
128	HI^+	11	128	HI^+	13
127	I^+	37	127	I^+	22
			101	AsCN^+	6
78	C_6H_6^+	21	78	C_6H_6^+	7
77	C_6H_5^+	55	77	C_6H_5^+	18
75	As^+	7	75	As^+	2
			52	$(\text{CN})_2^+$	22
			27	HCN^+	9
			26	CN^+	4

Table 80. The Mass Spectrum results of $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ and $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2\text{Br}_8^*$

$(\text{Ph}_2\text{As-CH}_2\text{-AsPh}_2)$			$(\text{Ph}_2\text{As-CH}_2\text{-AsPh}_2\text{Br}_8)$		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
472	$\text{Ph}_2\text{AsCH}_2\text{AsPh}_2^+$	7			
458	$\text{Ph}_2\text{As-AsPh}_2^+$	7			
			350	$\text{PhAsCH}_2\text{AsPh}_2(\text{O})_2^+$	2
			310	$\text{Ph}_2\text{As}^{81}\text{Br}^+$	24
			308	$\text{Ph}_2\text{As}^{79}\text{Br}^+$	24
306	Ph_3As^+	13			
			250	$\text{PhAs}^{81}\text{BrOH}^+$	100
			248	$\text{PhAs}^{79}\text{BrOH}^+$	100
243	$\text{Ph}_2\text{AsCH}_2^+$	30			
			233	$\text{PhAs}^{81}\text{Br}^+$	28
			231	$\text{PhAs}^{79}\text{Br}^+$	29
229	Ph_2As^+	100	229	Ph_2As^+	100
			174	$\text{C}^{81}\text{Br}_2^+$	18
			172	$\text{C}^{81}\text{Br}^{79}\text{Br}^+$	36
			170	$\text{C}^{79}\text{Br}_2^+$	18
152	PhAs^+	47	152	PhAs^+	100
			82	H^{81}Br^+	100
			81	$^{81}\text{Br}^+$	100
			80	H^{79}Br^+	100
			79	$^{79}\text{Br}^+$	100
78	C_6H_6^+	14	78	C_6H_6^+	22
77	C_6H_5^+	58	77	C_6H_5^+	79
75	As^+	4	75	As^+	10

* The hydrolysis product isolated at the 2:1 ratio (Br_2 : biarsine) and the other bromides exhibited similar spectra.

Table 82. The Mass Spectra of the Substance A and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$

COMPOUND (A)			$\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$		
m/e	Proposed ions	Relative Intensity	m/e	Proposed ions	Relative Intensity
			487		8
486	$\text{C}_{26}\text{H}_{24}\text{As}_2^+$	12	486	$\text{C}_{26}\text{H}_{24}\text{As}_2^+$	25
458	$\text{C}_{24}\text{H}_{20}\text{As}_2^+$	8	458	$\text{C}_{24}\text{H}_{20}\text{As}_2^+$	11
409	$\text{C}_{26}\text{H}_{17}\text{As}_2^+$	1	409	$\text{C}_{20}\text{H}_{17}\text{As}_2^+$	0.3
381	$\text{C}_{18}\text{H}_{15}\text{As}_2^+$	2	381	$\text{C}_{18}\text{H}_{15}\text{As}_2^+$	1
333	$\text{C}_{20}\text{H}_{18}\text{As}^+$	1	333	$\text{C}_{20}\text{H}_{18}\text{As}^+$	0.3
306	$\text{C}_{18}\text{H}_{15}\text{As}^+$	14	306	$\text{C}_{18}\text{H}_{15}\text{As}^+$	6
229	$\text{C}_{12}\text{H}_{10}\text{As}^+$	100	229	$\text{C}_{12}\text{H}_{10}\text{As}^+$	100
227	$\text{C}_{12}\text{H}_8\text{As}^+$	50	227	$\text{C}_{12}\text{H}_8\text{As}^+$	41
154	$\text{C}_{12}\text{H}_{10}^+$	20	154	$\text{C}_{12}\text{H}_{10}^+$	15
152	$\text{C}_6\text{H}_5\text{As}^+$	30	152	$\text{C}_{12}\text{H}_8^+; \text{C}_6\text{H}_5\text{As}^+$	22
151	$\text{C}_6\text{H}_4\text{As}^+$	17	151	$\text{C}_6\text{H}_4\text{As}^+$	10
115	C_9H_7^+	4	115	C_9H_7^+	2
78	C_6H_6^+	9	78	C_6H_6^+	5
77	C_6H_5^+	13	77	C_6H_5^+	6
75	As^+	2			
51	C_4H_3^+	11	51	C_4H_3^+	6
28	C_2H_4^+	13			

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