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SOME STUDIES OF ALKYLPHOSPHINE-HALOGEN ADDUCTS AND  
POLYHALIDES

A Thesis

presented for the degree of

Master of Science

in the Faculty of Science of the

University of St. Andrews

by

James Stuart McKechnie

January, 1972

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



I declare that this thesis is my own composition and that the work, which was carried out part-time by myself, 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 St. Andrews University during the three years beginning October 1st, 1968, under the supervision of Dr. G.S. Harris.

I hereby certify that James Stuart McKechnie has spent seven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 51 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Master of Science.

Director of Research

## ACKNOWLEDGEMENTS

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PART I

HALOGEN ADDUCTS OF SOME TRIALKYLPHOSPHINES

INTRODUCTION

## INTRODUCTION

### I. HALIDES OF THE PHOSPHORUS GROUP ELEMENTS

Since the early years of the nineteenth century it has been known that when elements of the Phosphorus Group (P, As, Sb, Bi) react with halogens two distinct series of compounds - trihalides and pentahalides - are formed. For example, the tri- and pentachlorides of phosphorus could be very easily synthesised from the basic starting materials, of yellow (or red) phosphorus and elemental chlorine. These compounds were extremely reactive to moisture and their ease of hydrolysis to more stable compounds, whilst hindering reliable studies of their chemical and physical properties, gave a simple method of analysis which firmly established their formulas. The existence of these two well defined series of compounds, the tri- and penta-halides was thus of great general interest in the development of chemical ideas, particularly in connection with valency.

The chemistry of the halides of the Phosphorus Group continues to be one of much interest to inorganic chemists, and in recent years much new information has been obtained through the application of the many new physical and manipulative techniques now at the chemists disposal.

Trihalides of the Phosphorus Group Elements:

All of the simple trihalides of the Phosphorus Group elements P, As, Sb and Bi have been isolated and characterised; in contrast the mixed trihalides, of which a large number are possible, are relatively sparse and only a few compounds have been prepared and characterised. The trihalides which have been isolated and whose individual properties have been recognised are set out in table I below.

TABLE I: The Trihalides of P, As, Sb and Bi.<sup>1</sup>

| Phosphorus         | Arsenic           | Antimony           | Bismuth           |
|--------------------|-------------------|--------------------|-------------------|
| PF <sub>3</sub>    | AsF <sub>3</sub>  | SbF <sub>3</sub>   | BiF <sub>3</sub>  |
| PCl <sub>3</sub>   | AsCl <sub>3</sub> | SbCl <sub>3</sub>  | BiCl <sub>3</sub> |
| PBr <sub>3</sub>   | AsBr <sub>3</sub> | SbBr <sub>3</sub>  | BiBr <sub>3</sub> |
| PI <sub>3</sub>    | AsI <sub>3</sub>  | SbI <sub>3</sub>   | BiI <sub>3</sub>  |
| PF <sub>2</sub> Cl |                   | SbBrI <sub>2</sub> |                   |
| PFCl <sub>2</sub>  |                   |                    |                   |
| PF <sub>2</sub> Br |                   |                    |                   |
| PBr <sub>2</sub>   |                   |                    |                   |

Other mixed trihalides have been identified in the course of nuclear magnetic resonance studies by Van Wazer and co-workers<sup>2</sup>. They identified PCl<sub>2</sub>Br and PClBr<sub>2</sub> when mixtures of PBr<sub>3</sub>-PCl<sub>3</sub> were

allowed to reorganise at room temperature. Similarly with the  $\text{PBr}_3\text{-PI}_3$  system there is evidence for the formation of  $\text{PBr}_2\text{I}$  and  $\text{PBrI}_2$  in an equilibrium mixture<sup>3</sup>. There is also Raman spectral evidence for the formation of a chlorobromofluoride of phosphorus,  $\text{PFClBr}$ , when  $\text{PFCl}_2$  and  $\text{PFBr}_2$  are mixed<sup>4</sup>. However none of these compounds has ever been isolated.

No mixed trihalides of arsenic have so far been prepared but like phosphorus there is physical evidence, using techniques such as n.m.r., of the formation of  $\text{AsFCl}_2$  and  $\text{AsF}_2\text{Cl}$  in exchange equilibria set up by  $\text{AsF}_3$  and  $\text{AsCl}_3$  mixtures. Compared to phosphorus, little work has been done on mixed trihalides of As, Sb and Bi. The compound  $\text{SbBrI}_2$  reported by Clark<sup>5</sup> is the only mixed halide of tervalent antimony to be described. It exists as a yellow crystalline solid and surprisingly, is moderately stable in air. The trihalides of the Phosphorus Group elements are structurally simple, all being pyramidal molecules similar to ammonia.

#### Pentahalides of the Phosphorus Group Elements.

While all the simple trihalides of P, As, Sb and Bi are known the same cannot be said for the simple pentahalides. Those which have been isolated and whose individual properties have been recognised are set out in the top part of Table II below which lists the known simple and mixed pentahalides of the

Phosphorus Group Elements.

TABLE II: The Pentahalides of P, As, Sb and Bi.<sup>1</sup>

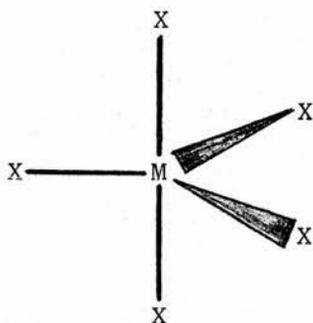
| Phosphorus                      | Arsenic                          | Antimony                         | Bismuth          |
|---------------------------------|----------------------------------|----------------------------------|------------------|
| PF <sub>5</sub>                 | AsF <sub>5</sub>                 | SbF <sub>5</sub>                 | BiF <sub>5</sub> |
| PCl <sub>5</sub>                |                                  | SbCl <sub>5</sub>                |                  |
| PBr <sub>5</sub>                |                                  |                                  |                  |
| PF <sub>4</sub> Cl              |                                  |                                  |                  |
| PF <sub>3</sub> Cl <sub>2</sub> | AsF <sub>3</sub> Cl <sub>2</sub> | SbF <sub>3</sub> Cl <sub>2</sub> |                  |
| PF <sub>2</sub> Cl <sub>3</sub> |                                  |                                  |                  |
| PFCl <sub>4</sub>               |                                  | SbFCl <sub>4</sub>               |                  |
| PF <sub>3</sub> Br <sub>2</sub> |                                  |                                  |                  |
| PF <sub>2</sub> Br <sub>3</sub> |                                  |                                  |                  |
| PFBBr <sub>4</sub>              |                                  |                                  |                  |

Some of these compounds have been known for a long time but it is noteworthy that BiF<sub>5</sub> was first reported as recently as 1959<sup>6</sup>. The possible number of species which might be obtained allowing for simple and mixed fluorides, chlorides, bromides and iodides of phosphorus, arsenic, antimony and bismuth being well over 150, and the fact that less than a tenth have so far been prepared is an indication of the difficulties involved. As one can see from the table phosphorus dominates the series yet even here only the

fluorochlorides can be said to be well known. In the case of arsenic,  $\text{AsCl}_2\text{F}_3$  appears to be the only well substantiated mixed pentahalide. The formation of  $\text{SbCl}_4\text{F}$  and  $\text{SbCl}_2\text{F}_3$  are well established although a fairly recent investigation<sup>10</sup> found this system difficult to interpret. No mixed pentahalides of bismuth have been reported.

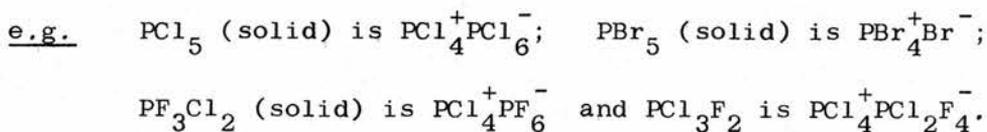
Many of the pentahalides in this group are found to be capable of existing in two different structural forms, one of which is molecular the other ionic. For example the liquid chloro-fluorophosphorane  $\text{PCl}_3\text{F}_2$  changes on standing to a white crystalline form which Kolditz and co-workers<sup>9</sup> have shown to display ionic properties.

Structural investigations have demonstrated the presence of trigonal bipyramidal units:



in the molecular forms. In these molecules axial bonds are invariably longer than equatorial bonds. Examples of this type of structure are found in  $\text{PF}_5$  (gas and liquid);  $\text{PCl}_5$  (gas);  $\text{AsF}_5$  (gas and liquid);  $\text{SbF}_5$  (gas) and  $\text{SbCl}_5$  (gas and solid).

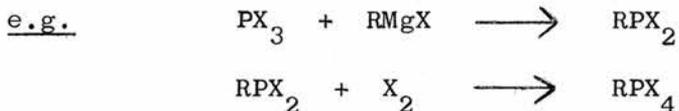
The ionic forms of these pentahalides contain a tetrahalogeno.....onium cation.

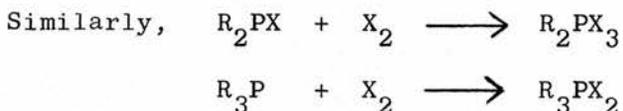


It can be seen that reference to a specific pentahalide is in many cases only a reference to its stoichiometric composition and in no way reflects the structural state of the compound concerned. Some of the pentahalides like  $\text{PF}_5$  appear to exist only in a molecular form whereas others are capable of existing as ionic species under certain conditions and molecular under others. For example  $\text{PCl}_5$  in the solid state is ionic whilst in the liquid and vapour phase is molecular in structure. This quality of duality of behaviour of these compounds extends to their existence in different types of solvent where it is found that in non-polar solvents the molecular form is present<sup>11</sup> whereas in polar solvents the ionic form predominates<sup>12,13</sup>.

#### Substituted Phosphorus Pentahalides.

Substitution of one or more halogen atoms in a phosphorus pentahalide by an organic group can be readily achieved by standard procedures. It is usual for an organic group to be introduced at first to a P(III) compound which is then further reacted with halogen.

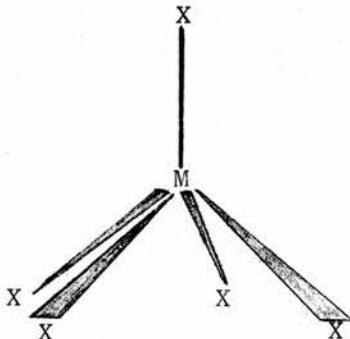




Typical compounds which have been prepared in this way are  $C_2H_5PCl_4$ <sup>24</sup>,  $(C_6H_5)_2PCl_3$ <sup>25</sup>, and  $(C_6H_5)_3PCl_2$ <sup>26</sup>. Thus the series  $PHal_5$ ,  $RPHal_4$ ,  $R_2PHal_3$ ,  $R_3PHal_2$ ,  $R_4PHal$ ,  $R_5P$  can be obtained.

Known compounds of the fully substituted pentahalides  $R_5P$  are not common; the best known is the phenyl derivative<sup>14</sup>.

Pentaphenyl phosphorus is a molecular substance which like the pentahalides, adopts a trigonal bipyramidal structure in which the axial bonds are slightly longer than the equatorial (1.987 Å and 1.8506 Å respectively)<sup>15</sup>. It is of considerable interest to note here that although pentaphenyl arsenic is isomorphous with  $Ph_5P$ <sup>16</sup> Wheatley has shown that the pentaphenyl antimony molecule adopts the geometry of a tetragonal pyramid<sup>17</sup>:



This seems to be the only well established example of this stereochemistry in a five coordinate compound of a group V element although theory predicts that the stability of the two geometries is comparable<sup>7</sup>.

Many examples of quaternary substituted compounds,  $R_4\text{P}^+\text{Hal}^-$ , are known. They tend to be high melting, crystalline solids, soluble in polar solvents in which they give highly conducting solutions, suggesting therefore that they are ionic both in the solid state and in solution. A crystal structure analysis of  $\text{Ph}_4\text{PI}^{18}$  has shown that the structure is built from  $\text{Ph}_4\text{P}^+$  and  $\text{I}^-$  ions. Indeed, there is no evidence to be found in the literature of any  $R_4\text{P}^+\text{Hal}^-$  type of compound exhibiting a covalent structure.

Discussion of the intermediate members of the series,  $\text{RPHal}_4$ ,  $\text{R}_2\text{PHal}_3$  and  $\text{R}_3\text{PHal}_2$  is not so clear cut and conflicting viewpoints have been put forward concerning their nature. For the  $\text{RPHal}_4$  and  $\text{R}_2\text{PHal}_3$  compounds, low melting points and ease of solubility in organic solvents led Rochow et.al.<sup>19</sup> to deduce that they are molecular. Van Wazer<sup>20</sup> however, in discussing this series of compounds, suggests they are likely to have ionic structures by analogy with the phosphorus pentahalides. They exhibit the same reactions as the phosphorus pentahalides and he assumes an ionic formulation with the organic groups in the cation.

e.g.  $\text{RPCl}_4$  is assumed to be  $[\text{RPCl}_3^+][\text{Cl}^-]$

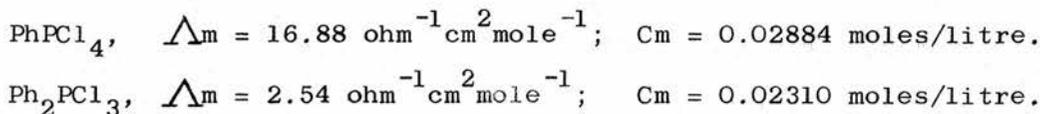
Although no direct determination of structures of these compounds has been carried out in the solid state, some recent work has thrown some light on their nature. Goubeau and

Baumgärtner<sup>35</sup> have carried out spectroscopic studies on the dihalides of trimethyl phosphine,  $\text{Me}_3\text{P}\text{Hal}_2$  (Hal = Cl, Br and I) which indicate that in the solid state ionic structures of the type  $\text{Me}_3\text{P}^+\text{X}^-$  are adopted. Kosolapoff<sup>21</sup> also stresses ionic character of these compounds from their ability to add another mole of halogen to give a derivative of a phosphorus heptahalide.

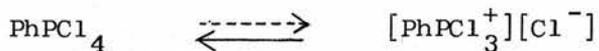


It is reasonable to assume that  $\text{PhPBr}_6$  is in fact  $\text{PhPBr}_3^+\text{Br}_3^-$  as it has recently been shown that  $\text{PBr}_7$  is  $\text{PBr}_4^+\text{Br}_3^-$ . Also  $\text{R}_2\text{PHal}_3$  (R =  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ) reacts with halogens to form  $\text{R}_2\text{PHal}_5$ , which have been shown to give highly conducting solutions when dissolved in polar solvents indicating a dihalophosponium salt type of structure ( $\text{R}_2\text{PHal}_2^+\text{Hal}_3^-$ ) for these compounds<sup>23</sup>. However although,  $\text{RPX}_6$  and  $\text{R}_2\text{PX}_5$  appear to be ionic it does not seem a valid assumption that the original halide is necessarily ionic too.

However, McPherson<sup>1</sup> has recently carried out some careful conductivity measurements on the systems  $\text{Ph}_2\text{PCl}-\text{Cl}_2$  and  $\text{PhPCl}_2-\text{Cl}_2$  in methyl cyanide, and has found that values of molar conductance are low at compositions corresponding to  $\text{Ph}_2\text{PCl}_3$  and  $\text{PhPCl}_4$ :



$\text{PhPCl}_4$  and  $\text{Ph}_2\text{PCl}_3$  can therefore be regarded as weak electrolytes in methyl cyanide, thus:-



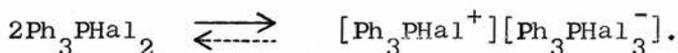
It seems reasonable to assume that in the solid state these compounds are covalent in character and that partial ionisation occurs in solutions of high dielectric constant.

The derivatives,  $\text{R}_3\text{PHal}_2$  have received much more study than others in the series  $\text{R}_n\text{PHal}_{5-n}$ . Conductometric studies in methyl cyanide of the phenyl derivatives have shown that the phosphorus dihalides are strong electrolytes whereas the antimony and bismuth dihalides are non-electrolytes, suggesting that the solids are respectively ionic and covalent<sup>30</sup>. The arsenic derivatives on the other hand are weak electrolytes and therefore probably covalent in the solid state<sup>31</sup>.

The mode of ionisation of triphenyl phosphorus dihalides in methyl cyanide has recently been shown, by <sup>31</sup>P n.m.r. study<sup>32</sup>, and from reactions with the strong chloride ion donor, tetraethylammonium chloride,  $\text{Et}_4\text{N}^+\text{Cl}^-$ <sup>33</sup>, to be as follows:-



and there is no evidence for the alternative possibility:-



The existence of the halotriorganophosphonium cation,  $[\text{R}_3\text{PHal}^+]$ , in the tertiary phosphorus dihalides,  $\text{R}_3\text{PHal}_2$  (R =  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ , iso-amyl, cyclohexyl or  $\text{C}_6\text{H}_5$ ) has also been

inferred from their solubility behaviour, their high decomposition temperatures and the electrical conductivities of their solutions in nitrobenzene<sup>34</sup>.

There now appears to be fairly firm evidence for both ionic and covalent forms in the  $RPhal_4$  and  $R_2Phal_3$  groups of compounds. Fairly recently  $^{31}P$  n.m.r. studies of the compounds  $[Ph_nPCl_{4-n}]ClO_4$  and  $[Ph_nPCl_{4-n}]SbCl_6$ <sup>27</sup> have shown the presence of chloro-organo phosphonium cations of the type postulated for the ionic forms of  $RPhal_4$  and  $R_2Phal_3$ . Also, recent  $^{19}F$  n.m.r. investigations of a number of fluorophosphoranes,

e.g.  $RPF_4$  where  $R = CH_3, C_2H_5, n-C_4H_9, C_6H_5,$

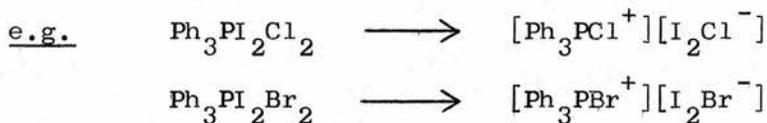
and a few of the analogous arsenic and antimony compounds suggest trigonal bipyramidal structure for these compounds<sup>28,29</sup>.

II. PHOSPHINE-HALOGEN ADDUCTS - RECENT STUDIES

An extensive study of organo phosphine-halogen systems using mainly conductometric techniques has been made by Harris and co-workers who have shown that the properties of these compounds, which may be represented  $R_n P Hal_{5-n}$ , are strongly dependent on the nature of the organic group R. The group R most frequently incorporated in the adducts studied has been phenyl.

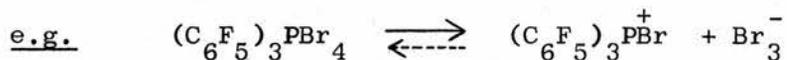
Beveridge and Harris<sup>30</sup> found that triphenylphosphine readily forms dihalides when it reacts with the simple halogens chlorine, bromine and iodine. Solutions of these dihalides (1:1 adducts) in methyl cyanide were found to be highly conducting. The dihalides are easily converted to the tetrahalides (1:2 adducts) by addition of another mole of halogen and the solutions of these tetrahalides were also found to be highly conducting.

Ali<sup>8</sup> has studied the systems  $Ph_3P-Hal_2$  (Hal = ICl or  $ICl_3$ ) and  $Ph_3PCl_2-Hal_2$  ( $Hal_2 = Br_2, I_2, ICl, IBr, ICl_3$ ) by conductometric titration and has demonstrated the existence in methyl cyanide of triphenylphosphorus tetrahalides of the series  $Ph_3PCl_n I_{4-n}$  and  $Ph_3PCl_n Br_{4-n}$ . They are strong 1:1 electrolytes and their modes of ionisation parallel that of the analogous compounds of general formula  $Ph_3PBr_n I_{4-n}$ ; that is ionisation occurs to give the cation containing the halogen atom of lower atomic number<sup>31</sup>.



Harris and Inglis<sup>22</sup> have drawn attention to a correlation between the electronegativity of the aryl groups and the molar conductances of the compounds. Along the same lines Ali<sup>8</sup> made a study of some of the reactions of halogens and interhalogens with tertiary phosphines containing R groups of widely differing electronegativity. The phosphines he used were tris(dimethylamino)phosphine and tris(pentafluorophenyl)phosphine. It was hoped to obtain information about the way the strongly electron donating  $\text{Me}_2\text{N}$  group affected the nature of the reactions and products as opposed to the electron withdrawing  $\text{C}_6\text{F}_5$  groups. He found that tris(dimethylamino)phosphine reacted with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) and interhalogens ( $\text{ICl}$ ,  $\text{IBr}$ ,  $\text{ICl}_3$ ) to form simple 1:1 adducts, e.g.  $(\text{Me}_2\text{N})_3\text{PCl}_2$ ,  $(\text{Me}_2\text{N})_3\text{PClI}$  and the 1:2 adducts, e.g.  $(\text{Me}_2\text{N})_3\text{PCl}_n\text{I}_{4-n}$  ( $n = 0$  to 4) and  $(\text{Me}_2\text{N})_3\text{PBr}_n\text{I}_{4-n}$  ( $n = 0$  to 4). From conductometric studies, in methyl cyanide, of the dihalides and tetrahalides the molar conductance values were compared with the corresponding triphenylphosphine compounds. All the 1:1 and 1:2 adducts were found to be strong electrolytes and ionised as halogeno tris(dimethylamino)phosphonium salts. Ali then studied the reactions of tris(pentafluorophenyl)phosphine,  $(\text{C}_6\text{F}_5)_3\text{P}$ , with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) and interhalogens ( $\text{IBr}$ ,  $\text{ICl}$ ,  $\text{ICl}_3$ ) and his results when compared with the tris(dimethylamino)phosphine are of considerable interest. The only dihalide so far isolated is the dichloride  $(\text{C}_6\text{F}_5)_3\text{PCl}_2$ , which he showed to behave as a non-electrolyte in methyl cyanide solution. The formation of  $(\text{C}_6\text{F}_5)_3\text{PBr}_2$  has been indicated in

solution, under suitable conditions, by conductometric titration of bromine and tris(pentafluorophenyl)phosphine.  $(C_6F_5)_3PBr_2$  behaves as a weak electrolyte in methyl cyanide. Vapour pressure study of the system  $(C_6F_5)_3P-Br_2$  demonstrated the existence of two additional bromides of tris(pentafluorophenyl)phosphine -  $(C_6F_5)_3PBr_{10}$  and  $(C_6F_5)_3PBr_4$ . The tetrabromide was isolated as a yellow unstable compound. Evidence has also been provided for the existence in solution of the following adducts of tris(pentafluorophenyl)phosphine -  $(C_6F_5)_3PI_2Br_2$ ,  $(C_6F_5)_3PIBr_3$  etc. but these interhalogen adducts have not been isolated as crystalline solids. Solutions of the tetrahalides are highly conducting indicating strong electrolyte behaviour. The ions are halogeno tris(pentafluorophenyl)phosphonium halide and trihalide.



Ali in this way has substantiated the opinion of Harris and Inglis that the molar conductance of dihalides of the type  $R_3PX_2$  increases with the decrease in the electronegativity of the substituent organic group attached to phosphorus.

In practically all the previous conductance work on tertiary phosphine-halogen and interhalogen systems the substituent group R has been aryl. It was therefore of interest to continue to vary the group R by investigating more fully the effect on the properties of the halogen adducts when electron releasing groups are attached

to the phosphorus atom. Part I of this thesis deals with the investigation, principally using conductometric methods, of the reactions and the stability of the adducts formed when various tertiary alkyl phosphines are reacted with the halogens, iodine and bromine and the interhalogen iodine monobromide.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

I. THE REACTIONS OF HALOGENS WITH TRI(n-BUTYL)PHOSPHINE.

The techniques used by Harris and co-workers in previous studies of phosphine-halogen adducts were employed in the present investigation. However since the tertiary alkyl phosphine-halogen systems proved to be extremely labile, certain modifications of these techniques have been made, the principal one being the development of a system whereby conductometric titrations could be carried out wholly within a nitrogen filled dry-box. Exposure of compounds to moisture was thus completely eliminated. The Appendix contains full descriptions of the specialised pieces of apparatus developed in the present work.

It must also be pointed out that many of the compounds formed are potential halogenating agents and consequently the use of apparatus incorporating rubber parts and tap grease was undesirable. Likewise the choice of solvents was severely limited. Carbon tetrachloride (for preparative work), nitrobenzene and methyl cyanide (for conductometric studies) were chiefly used and steps had to be taken to ensure that these were of very high purity and thoroughly dry.

(1) THE REACTION OF BROMINE WITH TRI(n-BUTYL)PHOSPHINE.

The results of the conductometric titration of bromine with

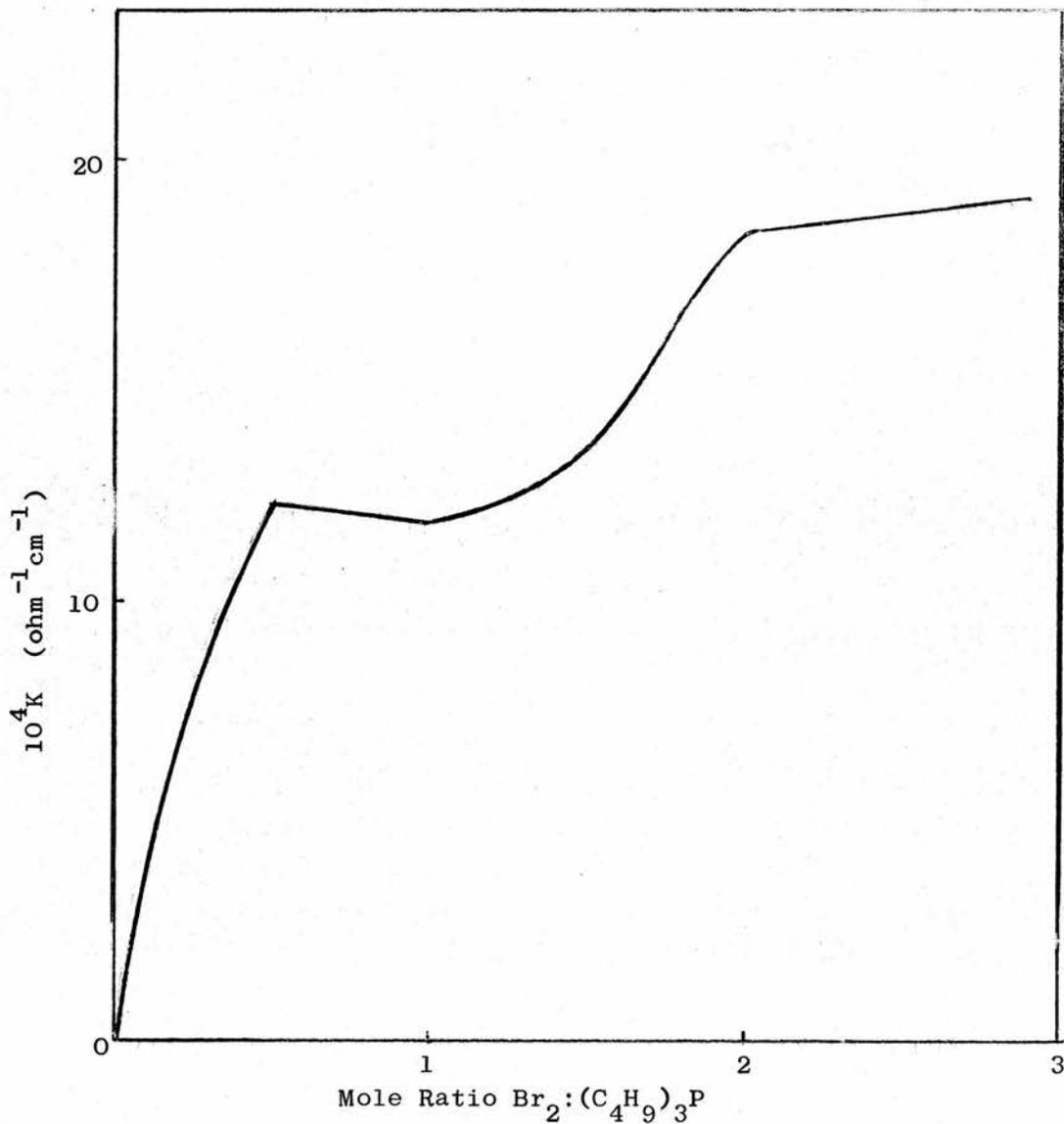


Figure I: Conductometric Analysis of the System  $\text{Br}_2-(\text{C}_4\text{H}_9)_3\text{P}$  in Methyl Cyanide.

tri(n-butyl)phosphine in methyl cyanide are recorded in Table III and illustrated graphically in Figure I.

TABLE III: Conductometric Analysis of the System  $\text{Br}_2 - (\text{C}_4\text{H}_9)_3\text{P}$  in Methyl Cyanide.

| Mole Ratio $\text{Br}_2 : (\text{C}_4\text{H}_9)_3\text{P}$ | $\text{K} \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_4\text{H}_9)_3\text{P}$ | $\text{K} \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_4\text{H}_9)_3\text{P}$ | $\text{K} \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_4\text{H}_9)_3\text{P}$ | $\text{K} \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.000   | 0.08  | 1.020   | 12.62   | 2.040   | 18.27   | 3.060   | 18.58   |
| 0.102   | 4.06  | 1.122   | 12.90   | 2.142   | 18.23   | 3.162   | 18.64   |
| 0.204   | 6.74  | 1.224   | 13.14   | 2.244   | 18.34   | 3.264   | 18.61   |
| 0.306   | 8.26  | 1.326   | 13.38   | 2.346   | 18.37   | 3.366   | 18.64   |
| 0.408   | 9.74  | 1.428   | 13.76   | 2.448   | 18.37   | 3.468   | 18.68   |
| 0.510   | 11.18   | 1.530   | 14.24   | 2.550   | 18.40   | 3.570   | 18.71   |
| 0.612   | 12.45   | 1.632   | 15.14   | 2.652   | 18.47   | 3.672   | 18.78   |
| 0.714   | 12.42   | 1.734   | 16.34   | 2.754   | 18.47   | 3.774   | 18.82   |
| 0.816   | 12.28   | 1.836   | 17.41   | 2.856   | 18.54   | 3.876   | 18.82   |
| 0.918   | 12.42   | 1.938   | 18.16   | 2.958   | 18.51   |   |   |

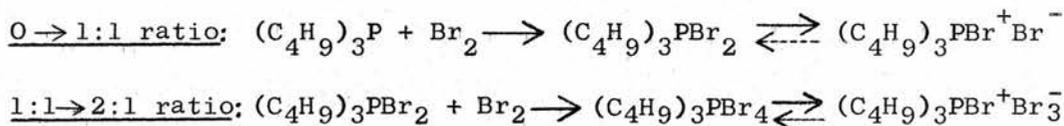
The graph shows a pronounced break at the 1:1 ratio, at which point during the titration the colourless solution turned pale yellow.

The solution then darkened progressively up to and beyond the second break at the 2:1 ratio. The molar conductance values at these

breaks were:

$$\begin{aligned} \underline{1:1} \quad \Lambda_m &= 81.39 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} & (\text{C}_m &= 0.01526 \text{ moles/litre}) \\ \underline{2:1} \quad \Lambda_m &= 129.99 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} & (\text{C}_m &= 0.01397 \text{ moles/litre}) \end{aligned}$$

These molar conductance values indicate strong electrolytes and the species present at these breaks must have the stoichiometries  $(C_4H_9)_3PBr_2$  and  $(C_4H_9)_3PBr_4$  respectively. Thus we can write the following scheme for the reactions occurring in solution:

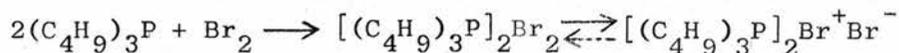


The fact that the solution develops colour after the 1:1 break is in keeping with the formation of the tribromide ion.

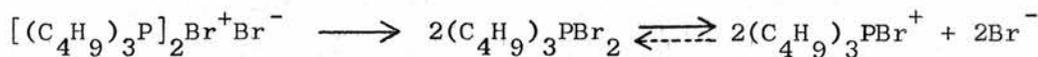
During addition of bromine solution at the beginning of the titration small quantities of white fumes were produced above the liquid in the titration flask; this was not observed after the 0.5:1 ratio. As can be seen from the graph there is a fairly distinct break at this ratio, but no colour change was observed. It was thought possible that an intermediate of stoichiometry  $[(C_4H_9)_3P]_2Br_2$ , was being formed in solution. However from solutions containing  $(C_4H_9)_3P$  and  $Br_2$  in 1:0.5 ratios the dibromide only, was obtained.

A likely reaction scheme for a two stage process up to the 1:1 ratio is the following:

0 → 0.5:1 ratio:

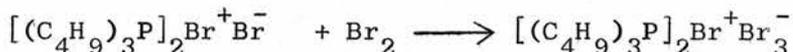


0.5:1 → 1:1 ratio:



The absence of tribromide ion formation (colourless solution)

below the 1:1 mole ratio rules out the reaction;



for the 0.5:1  $\longrightarrow$  1:1 stage. Cations of type  $(R_3P)_2X^+$  are not common but have been reported by Harris and Ali<sup>36</sup> when reacting triphenyl phosphine with IBr and ICl resulting in the isolation of compounds of the formula  $[(Ph_3P)_2Hal]^+I_3^-$ .

Graphs similar in form to that obtained for this system were obtained by Ali<sup>8</sup> in the titration of iodine monochloride and iodine trichloride against triphenylphosphine, and also by McPherson<sup>1</sup> in his investigation of the reactions of bromine, iodine and iodine monobromide with tri(p-tolyl)phosphine. These authors both postulate similar reaction schemes to that outlined above.

Examination of the ultraviolet spectra of solutions containing bromine and tri(n-butyl)phosphine in a range of mole ratios indicated that up to the 1:1 mole ratio the only absorbing species was the phosphine. When greater amounts of bromine are present the very strong tribromide ion absorption band ( $\lambda_{max} = 269 \text{ m}\mu$ ), begins to appear. As in the conductometric titrations great care was taken to exclude moisture during the preparation of all the solutions for U.V. work.

Attempts to prepare solid adducts consistent with the conductometric titration resulted in the isolation of a solid dibromide,  $(C_4H_9)_3PBr_2$ , and tetrabromide,  $(C_4H_9)_3PBr_4$ , both of which were very unstable. As well as being hydrolytically unstable the tetrabromide

loses bromine readily on standing which makes it extremely difficult to obtain the compound in a state of high purity. As already mentioned several attempts were made to prepare an intermediate 0.5:1 compound but in each instance the solid dibromide  $(C_4H_9)_3PBr_2$  was obtained.

Electrolytic Conductance of  $(C_4H_9)_3PBr_2$  in Methyl Cyanide.

The electrolytic conductance of the dibromide was measured using methyl cyanide as solvent. The solutions were prepared in the dry-box and two separate conductance measurements made at 25°C. The molar conductance values which decrease with increasing concentration were found to be:

$$\Lambda_m = 96.67 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.0106 \text{ moles/litre})$$

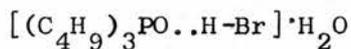
$$\Lambda_m = 105.08 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.0036 \text{ moles/litre})$$

Molar conductance values in the region of  $100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  at the concentrations used are indicative of a strong 1:1 electrolyte. This together with the compounds relatively high melting point ( $\sim 200^\circ$ ) would seem to suggest that in the solid state the compound may well have an ionic structure  $(C_4H_9)_3PBr^+Br^-$ .

Atmospheric Hydrolysis of  $(C_4H_9)_3PBr_2$ .

Tri(n-butyl)phosphine dibromide is an extremely labile compound, appearing to decompose during manipulation, even in the nitrogen filled dry-box. To examine the decomposition further, a

specimen was exposed to the open atmosphere for two days. After this period a clear viscous oil remained which, after pumping on the vacuum line for several hours, was analysed straight away. Analysis of the liquid suggested that the product was the hydrated hydroxybromide -  $(C_4H_9)_3POHBr \cdot H_2O$ . It is believed the compound obtained after vacuum drying was the anhydrous hydroxybromide and gained a molecule of water of hydration during weighing in the analysis. The infra-red spectrum of the hydrolysis product contained a very broad absorption band in the region  $3500-2000 \text{ cm}^{-1}$  indicative of both free  $H_2O$  and hydrogen bonded  $-OH$ , similar to that found by Inglis<sup>22</sup> in his work on triarylarsonic hydroxyhalides,  $Ar_3AsOHHal$ . Inglis has shown that hydroxyhalides of this type are more correctly represented as simple hydrogen bonded adducts of the oxide and hydrogen halide, thus  $Ph_3\overset{\delta+}{As} \dots O \dots H \dots \overset{\delta-}{Hal}$ , where  $\dots$  represented a bond order of less than one and all bonds are covalent, though polar. The most prominent feature of the infra-red spectra of this type of compound is very strong absorption in the region  $2750-2000 \text{ cm}^{-1}$  attributed to an O-H stretching mode under the influence of very strong hydrogen bonding. In the hydrolysed dibromide there was also a strong peak at  $980 \text{ cm}^{-1}$ . It seems likely that this is the P=O stretching frequency lowered considerably on account of hydrogen bonding. By analogy with the structure proposed by Inglis, the hydrolysed product of  $(C_4H_9)_3PBr_2$  is probably:-



(2) THE REACTION OF IODINE WITH TRI(n-BUTYL)PHOSPHINE

The shape of the conductance-composition graph was very similar to that of the corresponding bromine system. The results are recorded in Table IV and illustrated graphically in Figure II - plot 1.

TABLE IV: Conductometric Analysis of the  $I_2-(C_4H_9)_3P$  System in Methyl Cyanide

| Mole Ratio $I_2:(C_4H_9)_3P$ | $K \times 10^4$ ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio $I_2:(C_4H_9)_3P$ | $K \times 10^4$ ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio $I_2:(C_4H_9)_3P$ | $K \times 10^4$ ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio $I_2:(C_4H_9)_3P$ | $K \times 10^4$ ohm <sup>-1</sup> cm <sup>-1</sup> |
|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|
| 0.000                        | 0.04   | 1.060                        | 11.18  | 2.120                        | 15.24  | 3.286                        | 14.07  |
| 0.106                        | 4.64   | 1.166                        | 11.56  | 2.226                        | 15.10  | 3.498                        | 13.86  |
| 0.212                        | 7.16   | 1.272                        | 12.07  | 2.332                        | 15.00  | 3.710                        | 13.66  |
| 0.318                        | 8.19   | 1.378                        | 12.59  | 2.438                        | 14.90  | 3.922                        | 13.45  |
| 0.424                        | 8.98   | 1.484                        | 13.14  | 2.544                        | 14.79  | 4.134                        | 13.28  |
| 0.530                        | 9.70   | 1.590                        | 13.76  | 2.650                        | 14.69  | 4.346                        | 13.07  |
| 0.636                        | 10.18  | 1.696                        | 14.41  | 2.756                        | 14.59  | 4.558                        | 12.87  |
| 0.742                        | 10.15  | 1.802                        | 15.20  | 2.862                        | 14.48  | 4.770                        | 12.69  |
| 0.848                        | 10.42  | 1.908                        | 15.41  | 2.986                        | 14.38  | 5.194                        | 12.52  |
| 0.954                        | 10.77  | 2.014                        | 15.38  | 3.074                        | 14.28  |                              |  |

The graph in this instance does not have a clear cut break at the 0.5:1 ratio but again shows definite breaks at the 1:1 and

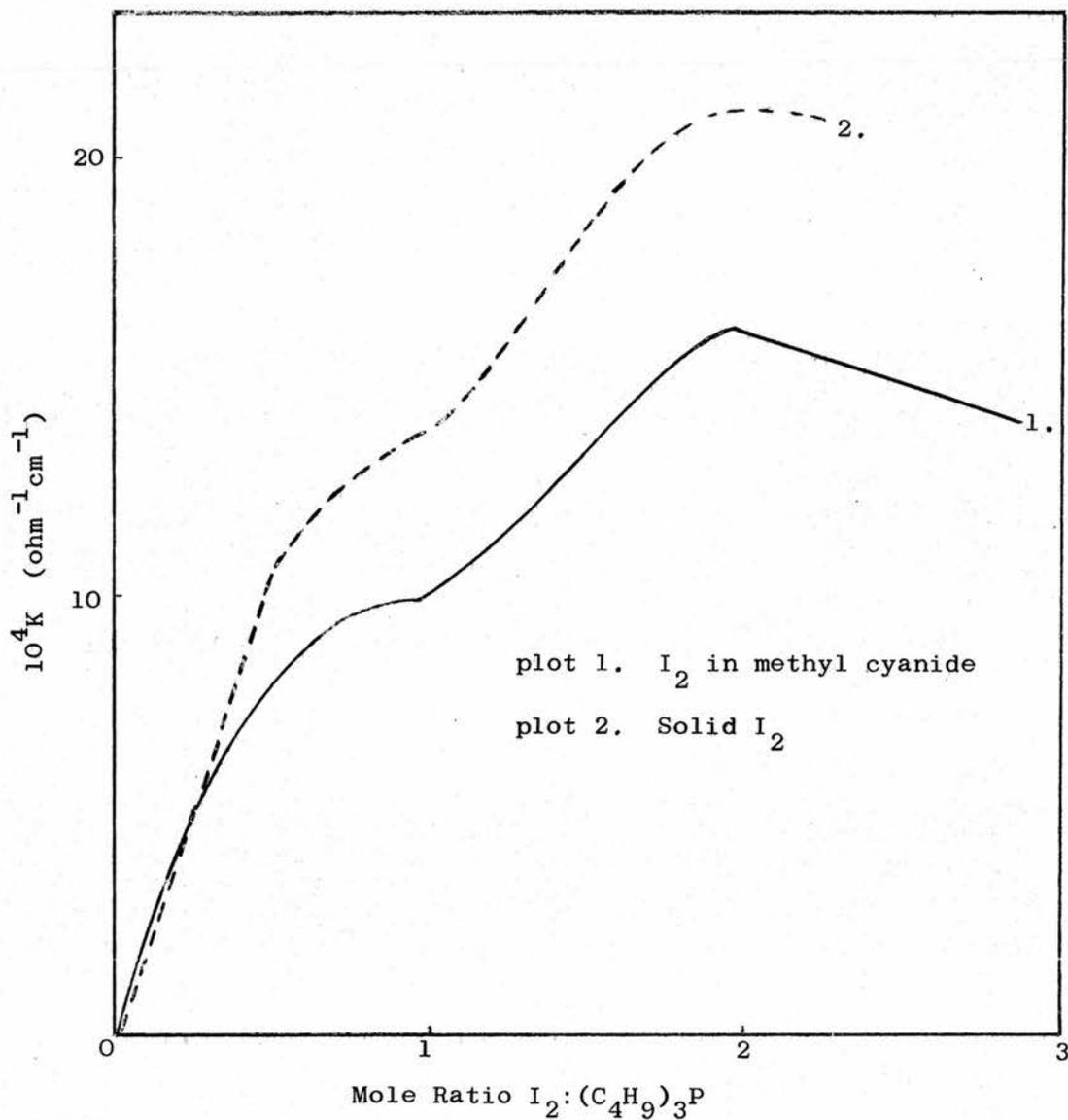


Figure II: Conductometric Analysis of the I<sub>2</sub>-(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P System in  
Methyl Cyanide.

2:1 mole ratios at which points the respective molar conductances are:

$$\begin{array}{ll} \underline{1:1} \quad \Lambda_m = 85.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} & (\text{C}_m = 0.01243 \text{ moles/litre}) \\ \underline{2:1} \quad \Lambda_m = 134.64 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} & (\text{C}_m = 0.01145 \text{ moles/litre}) \end{array}$$

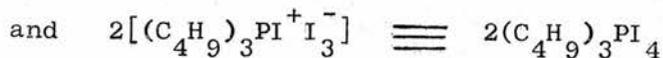
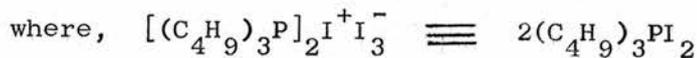
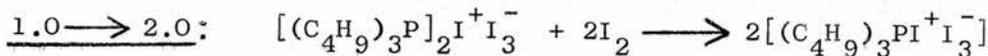
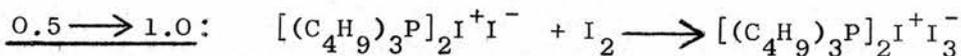
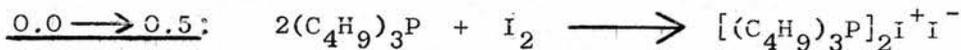
Formation of a diiodide and tetraiodide, both of which are strong electrolytes, is indicated in solution. Although the shape of the graph is similar to that obtained for the corresponding bromine system a notable difference was the observation of a colour change, from colourless to yellow, just after the 0.5:1 mole ratio after which the solution progressively darkened with successive additions of iodine solution. This change in colour would suggest triiodide ion formation. This system appears therefore to differ from the  $\text{Br}_2-(\text{C}_4\text{H}_9)_3\text{P}$  system in which trihalide ion did not begin to appear until the 1:1 ratio had been attained.

#### Ultra-violet Spectroscopic Study of the $\text{I}_2-(\text{C}_4\text{H}_9)_3\text{P}$ System.

A systematic U.V. study at different mole ratios of iodine to phosphine was carried out in an attempt to ascertain exactly when the formation of triiodide ion begins. Strict precautions were taken to prepare all solutions in the dry-box and the findings are summarised as follows:

| $I_2:(C_4H_9)_3P$ ratio | U.V. indicated   |
|-------------------------|--|
| 0.2:1                   | $I_3^-$ ion absent, only phosphine absorption detected.  |
| 0.4:1                   | $I_3^-$ ion absent, only phosphine absorption detected.  |
| 0.5:1                   | Trace of $I_3^-$ ion ( $\lambda_{max} = 291, 360 \text{ m}\mu$ ), still strong phosphine absorption. |
| 1.0:1                   | Strong absorption due to $I_3^-$ ion, no phosphine.  |
| 1.5:1                   | Strong absorption due to $I_3^-$ ion, no phosphine.  |
| 2.0:1                   | Strong absorption due to $I_3^-$ ion, no phosphine.  |

The conclusion must be made that triiodide ion formation begins at the 0.5:1 mole ratio. From the U.V. analysis and conductometric titration data a three stage reaction in dilute solution is suggested as follows:-



Solids of stoichiometry  $(C_4H_9)_3PI_2$  and  $(C_4H_9)_3PI_4$  were obtained from solution at the 1:1 and 2:1 ratios respectively.

Attempts to isolate a solid at the 0.5:1 ratio yielded only  $(C_4H_9)_3PI_2$ . This parallels the behaviour of the tri(n-butyl) phosphine-bromine system which again emphasises the equilibrium nature of these reactions. The solids like their bromine analogues were very unstable.

It was thought worthwhile to repeat the conductometric titration study of the iodine-tri(n-butyl)phosphine system introducing a variation of technique. Addition of titrant solution results in dilution of the solution whose conductance is being measured and this can often lead to indistinctness of breaks in the titration graph. The technique was therefore modified in such a way that the titrant was added as solid crystalline iodine, the experiment being done in the dry-box. Table V and Figure II - plot 2 contain the results and graph for this titration.

TABLE V: Conductometric Analysis of the Solid  $I_2-(C_4H_9)_3P$  System.

| Mole Ratio<br>$I_2:(C_4H_9)_3P$ | $K \times 10^4$<br>$ohm^{-1}cm^{-1}$ |
|---------------------------------|--------------------------------------|
| 0.000                           | 0.11                                 |
| 0.102                           | 5.08                                 |
| 0.252                           | 7.51                                 |
| 0.393                           | 9.27                                 |
| 0.597                           | 10.99                                |
| 1.005                           | 13.63                                |
| 1.304                           | 16.81                                |
| 1.509                           | 19.66                                |
| 1.809                           | 20.88                                |
| 2.118                           | 20.88                                |

In the titration graph the portion between 0 and 1:1 is straightened out and there is no break at the 0.5:1 ratio of iodine to phosphine, but a definite inflection at the 1:1 ratio and a sharp break at the 2:1 ratio was observed. The respective molar conductances at these ratios were:

$$\underline{1:1} \quad \Lambda_m = 62.61 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.02177 \text{ moles/litre})$$

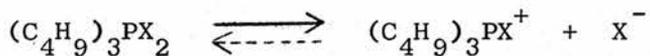
$$\underline{2:1} \quad \Lambda_m = 95.91 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.02177 \text{ moles/litre})$$

White fumes were evolved on adding the solid iodine up to the 0.5:1 ratio at which point a definite colour change to yellow was again observed indicating triiodide ion formation. It would seem clear from the results of this experiment that the shape of the titration curve of systems of the type under study does depend on whether the concentration varies or not during the titration.

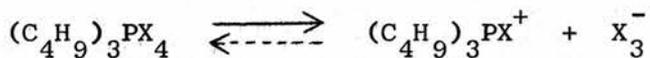
### (3) Summary.

Tri(n-butyl)phosphine has been shown to react with the halogens, bromine and iodine to give the 1:1 adducts  $(C_4H_9)_3PBr_2$  and  $(C_4H_9)_3PI_2$ , and the 1:2 adducts  $(C_4H_9)_3PBr_4$  and  $(C_4H_9)_3PI_4$ ; these halogen compounds are all very unstable. Conductometric titration studies of the systems  $Br_2-(C_4H_9)_3P$  and  $I_2-(C_4H_9)_3P$  in dilute methyl cyanide solution resulted in conductance-composition graphs which exhibited well defined breaks at the halogen:phosphine ratios of 1:1 and 2:1. In addition the  $Br_2-(C_4H_9)_3P$  system gave a definite break at the 0.5:1 ratio.

Measurement of molar conductance has shown that both the 1:1 and 2:1 adducts are strong 1:1 electrolytes in methyl cyanide solution. They have been shown to ionise as halogeno-tris(n-butyl) phosphonium salts thus:



and



Hydrolysis of tri(n-butyl)phosphine dibromide,  $(\text{C}_4\text{H}_9)_3\text{PBr}_2$ , gives rise to the hydroxybromide,  $(\text{C}_4\text{H}_9)_3\text{POHBr}$ .

## II. THE REACTIONS OF HALOGENS WITH TRIOCTYLPHOSPHINE.

Since trioctylphosphine is sparingly soluble in methyl cyanide, in the following conductometric titration studies involving reaction of the phosphine with halogens and inter-halogen, suspensions of trioctylphosphine were used. In all cases complete solution was observed after the second or third addition of halogen (approximate mole ratio 0.2-0.3) and always well below the 0.5:1 mole ratio; the solutions at this stage were colourless.

### (1) THE REACTION OF BROMINE WITH TRIOCTYLPHOSPHINE.

The conductance-composition graph of this system had the same general shape as those obtained for the previous systems. The results are tabulated in Table VI and illustrated graphically in Figure III - plot 1.

The graph shows pronounced breaks at the 0.5:1, 1:1 and 2:1 mole ratios and the originally colourless solution turned yellow at the 0.5:1 ratio showing tribromide ion to be present from this point. The molar conductance values at the latter two breaks were:

$$\underline{1:1} \quad \Lambda_m = 64.55 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.00804 \text{ moles/litre})$$

$$\underline{2:1} \quad \Lambda_m = 116.66 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.00735 \text{ moles/litre})$$

These molar conductance values indicate the presence of a fairly strong electrolyte at the 1:1 ratio and a very highly

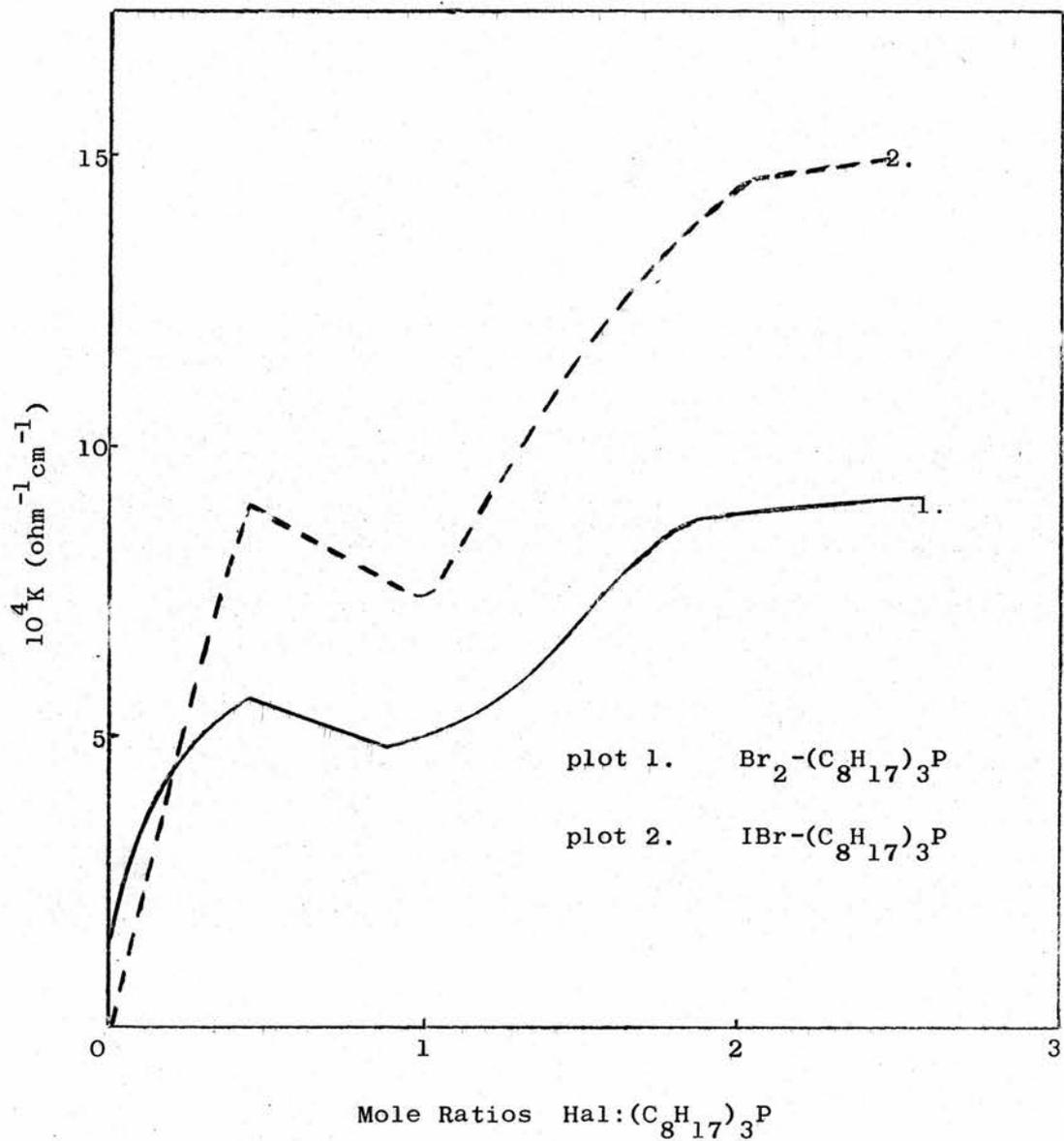


Figure III: Conducometric Analysis of the Systems  $\text{Br}_2-(\text{C}_8\text{H}_{17})_3\text{P}$  and

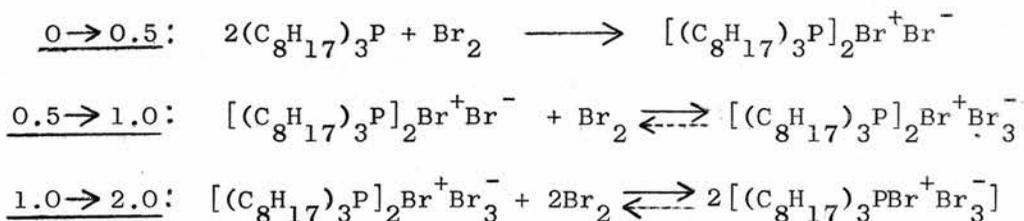
$\text{IBr}-(\text{C}_8\text{H}_{17})_3\text{P}$  in Methyl Cyanide

TABLE VI: Conductometric Analysis of the System  $\text{Br}_2 - (\text{C}_8\text{H}_{17})_3\text{P}$  in

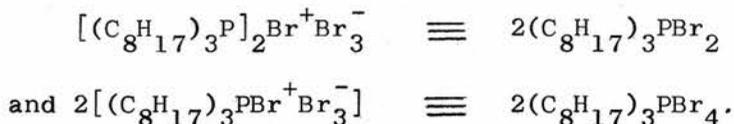
Methyl Cyanide.

| Mole Ratio<br>$\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P}$ | $\text{K} \times 10^4$<br>$\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio<br>$\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P}$ | $\text{K} \times 10^4$<br>$\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio<br>$\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P}$ | $\text{K} \times 10^4$<br>$\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio<br>$\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P}$ | $\text{K} \times 10^4$<br>$\text{ohm}^{-1} \text{cm}^{-1}$ |
|---|--|---|--|---|--|---|--|
| 0.000   | 1.78   | 1.096   | 5.54   | 2.191   | 8.60   | 3.486   | 8.67   |
| 0.0996  | 3.54   | 1.195   | 5.88   | 2.291   | 8.60   | 3.685   | 8.74   |
| 0.199   | 4.58   | 1.295   | 6.36   | 2.390   | 8.60   | 3.884   | 8.80   |
| 0.299   | 5.16   | 1.394   | 6.91   | 2.490   | 8.60   | 4.084   | 8.84   |
| 0.398   | 5.57   | 1.494   | 7.36   | 2.590   | 8.60   | 4.283   | 8.88   |
| 0.498   | 5.26   | 1.594   | 7.88   | 2.689   | 8.60   | 4.482   | 8.91   |
| 0.598   | 5.09   | 1.693   | 8.26   | 2.789   | 8.63   | 4.681   | 8.94   |
| 0.697   | 5.09   | 1.793   | 8.46   | 2.888   | 8.63   |   |  |
| 0.797   | 5.13   | 1.892   | 8.57   | 2.988   | 8.63   |   |  |
| 0.896   | 5.19   | 1.992   | 8.57   | 3.088   | 8.63   |   |  |
| 0.996   | 5.30   | 2.092   | 8.57   | 3.287   | 8.67   |   |  |

conducting species at the 2:1 ratio, corresponding to the respective stoichiometries  $(\text{C}_8\text{H}_{17})_3\text{PBr}_2$  and  $(\text{C}_8\text{H}_{17})_3\text{PBr}_4$ . Therefore from the observed formation of tribromide ion at the 0.5:1 mole ratio and the data obtained from the conductometric titration graph, the following scheme for the reaction in dilute methyl cyanide is suggested:



where stoichiometrically,



Compounds corresponding to the stoichiometries of the dibromide and tetrabromide were prepared. The dibromide,  $(\text{C}_8\text{H}_{17})_3\text{PBr}_2$ , was an unstable white solid but the tetrabromide, although existing as an amorphous solid below  $0^\circ$ , was an orange oil at room temperatures. In fact, none of the trioctylphosphine tetrahalides prepared, in contrast to the other phosphine tetrahalides studied, were isolated as crystalline solids; they remained as oils even after standing for periods of more than one month. The reluctance of these adducts to crystallise is probably due to the presence of the long alkyl chains. This is perhaps not surprising as this type of behaviour is a well known characteristic of long chain organic compounds. Attempts to isolate a solid at the 0.5:1 ratio yielded only the dibromide,  $(\text{C}_8\text{H}_{17})_3\text{PBr}_2$ .

## (2) THE REACTION OF IODINE WITH TRIOCTYLPHOSPHINE

The conductometric analysis of this system gave a result quite different from that of the corresponding bromine and iodine

monobromide (described later) systems. The graph illustrated in Figure IV - plot 1 was obtained from the results tabulated in Table VII. To verify this result and confirm the position of the breaks in the graph, a further titration was carried out using direct (solvent free) addition of solid iodine to the phosphine suspension, the technique being the same as described for the iodine-tri(n-butyl)phosphine system. The graph of this titration is also illustrated in Figure IV - plot 2 and the results given in Table VIII.

TABLE VII: Conductometric Analysis of the  $I_2-(C_8H_{17})_3P$  System in

Methyl Cyanide.

| Mole Ratio<br>$I_2:$<br>$(C_8H_{17})_3P$ | $K \times 10^4$<br>$ohm^{-1}$<br>$cm^{-1}$ |
|--|--|--|--|--|--|--|--|
| 0.000                                    | 1.67                                       | 0.900                                    | 6.60                                       | 1.800                                    | 7.57                                       | 2.800                                    | 7.16                                       |
| 0.100                                    | 3.54                                       | 1.000                                    | 6.81                                       | 1.900                                    | 7.57                                       | 3.000                                    | 7.09                                       |
| 0.200                                    | 4.44                                       | 1.100                                    | 7.09                                       | 2.000                                    | 7.53                                       | 3.200                                    | 6.98                                       |
| 0.300                                    | 5.57                                       | 1.200                                    | 7.36                                       | 2.100                                    | 7.50                                       | 3.400                                    | 6.88                                       |
| 0.400                                    | 5.95                                       | 1.300                                    | 7.50                                       | 2.200                                    | 7.46                                       | 3.600                                    | 6.78                                       |
| 0.500                                    | 6.02                                       | 1.400                                    | 7.57                                       | 2.300                                    | 7.40                                       | 3.800                                    | 6.67                                       |
| 0.600                                    | 6.12                                       | 1.500                                    | 7.57                                       | 2.400                                    | 7.36                                       | 4.000                                    | 6.57                                       |
| 0.700                                    | 6.26                                       | 1.600                                    | 7.57                                       | 2.500                                    | 7.33                                       | 4.200                                    | 6.47                                       |
| 0.800                                    | 6.40                                       | 1.700                                    | 7.57                                       | 2.600                                    | 7.26                                       | 4.400                                    | 6.40                                       |

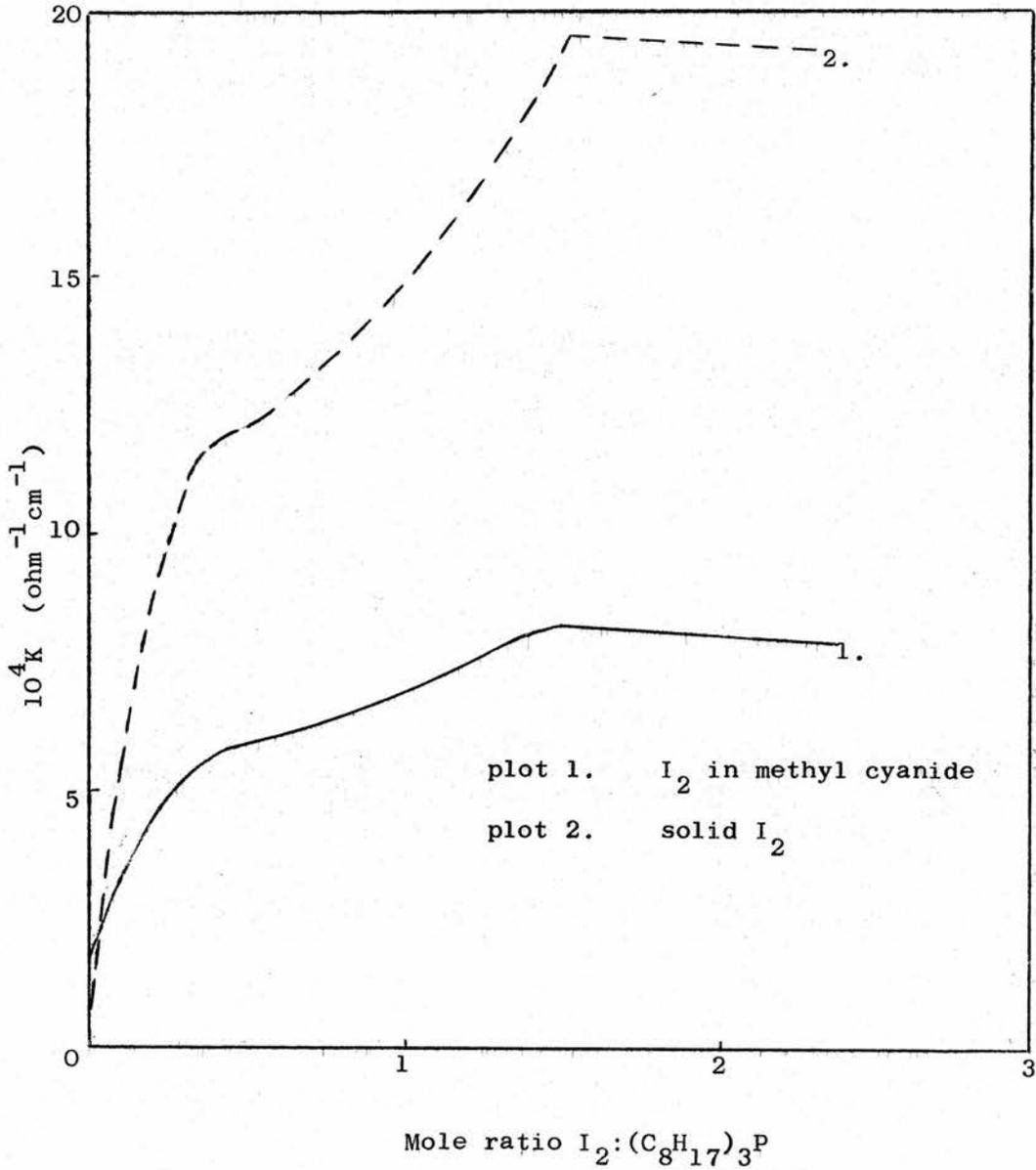


Figure IV: Conductometric Analyses of the  $I_2:(C_8H_{17})_3P$  System

TABLE VIII: Conductometric Analysis of the Solid  $I_2-(C_8H_{17})_3P$

System.

| Mole Ratio $I_2:(C_8H_{17})_3P$ | $K \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ |
|---------------------------------|--|
| 0.000                           | 0.97   |
| 0.197                           | 8.81   |
| 0.428                           | 12.11  |
| 0.639                           | 12.14  |
| 0.844                           | 13.11  |
| 1.092                           | 14.96  |
| 1.304                           | 17.17  |
| 1.501                           | 19.54  |
| 1.726                           | 19.61  |
| 1.965                           | 19.57  |
| 2.197                           | 19.47  |
| 2.452                           | 19.37  |

As can be seen from the graphs good reproducibility was obtained. Definite breaks occurred at the 0.5:1 and 1.5:1 mole ratios respectively and the originally colourless solution changed to yellow at the first break. Again, it should be noted that more pronounced titration graph breaks were obtained in the experiment involving direct addition of iodine, dilution effects being eliminated. The respective molar conductance values for both titrations were:

(a) Iodine added in methyl cyanide solution.

$$\underline{0.5:1} \quad \Lambda_m = 71.98 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.00836 \text{ moles/litre})$$

$$\underline{1.5:1} \quad \Lambda_m = 98.32 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.00770 \text{ moles/litre})$$

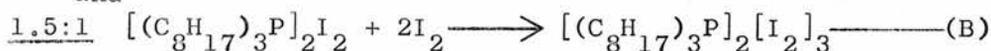
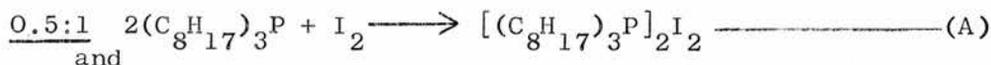
(b) Iodine added as solid.

$$\underline{0.5:1} \quad \Lambda_m = 60.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.02006 \text{ moles/litre})$$

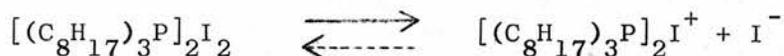
$$\underline{1.5:1} \quad \Lambda_m = 97.41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (C_m = 0.02006 \text{ moles/litre})$$

From the molar conductance values the species present at the 0.5:1 and 1.5:1 mole ratios of iodine to trioctylphosphine are clearly both strong electrolytes and, in addition, with the solution developing colour around the 0.5:1 ratio polyiodide ion must start forming at this point. Compounds of stoichiometry  $(C_8H_{17})_3PI_2$ ,  $(C_8H_{17})_3PI_3$  and  $(C_8H_{17})_3PI_4$  were isolated from solution containing the phosphine and iodine in the appropriate mole ratios.

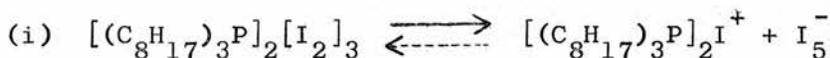
Interpretation of these experimental data is not straightforward. The absence of a 1:1 break in the conductometric titration graph coupled with the isolation of a 1:1 adduct from solution is especially difficult to explain. It would seem likely that in dilute solution a series of equilibria is set up, the predominant ones as the reaction proceeds corresponding to the following stoichiometries:



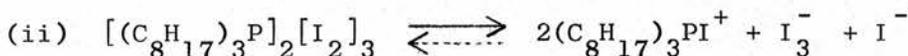
The nature of the product present at the 0.5:1 ratio is likely to be,



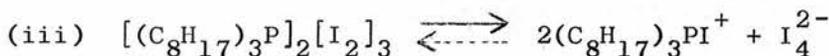
but that present at the 1.5:1 ratio is not so clear cut: there would seem to be three possibilities.



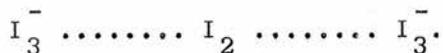
i.e. direct formation of penta-iodide ion from iodide ion. Although this seems not impossible all previous work on similar systems indicates initial formation of triiodide ion when iodine is added to a solution containing iodide ion.



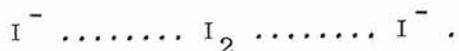
i.e. only half of the iodide present has been converted to tri-iodide. It is difficult to see why the remaining iodide would not add on iodine to produce triiodide ion unless some kind of interaction between triiodide and iodide ions in solution prevented this from happening [see (iii) below].



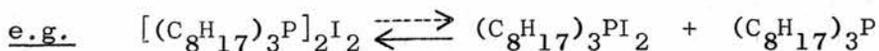
Although the even polyhalide ion,  $I_4^{2-}$ , has not been reported previously the species  $I_8^{2-}$  is mentioned in the literature<sup>37</sup>. It is postulated that this ion is made from two triiodide ions bridged by an iodine molecule thus:



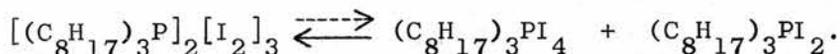
By analogy an  $I_4^{2-}$  ion could be built from two iodide ions and an iodine molecule:



Since the diiodide and tetraiodide are isolated as solids from the  $I_2-(C_8H_{17})_3P$  system it is clear that more than two equilibria are present in solution and the above is a simplified picture. The diiodide and tetraiodide must be formed in equilibria of minor significance.



and



Details of the materials isolated from solution are:

| Ratio of components             | Formula of product isolated | Nature of substance                   | Suggested structure               |
|---------------------------------|-----------------------------|---------------------------------------|-----------------------------------|
| $I_2:(C_8H_{17})_3P$<br>= 0.5:1 | $(C_8H_{17})_3PI_2$         | Unstable white solid<br>M.p. 155-165° | $(C_8H_{17})_3PI^+I^-$            |
| 1:1                             | $(C_8H_{17})_3PI_2$         | Unstable white solid<br>M.p. 155-165° | $(C_8H_{17})_3PI^+I^-$            |
| 1.5:1                           | $(C_8H_{17})_3PI_3$         | Dark red semi-solid                   | $[(C_8H_{17})_3PI^+]_2I^-I_3^- *$ |
| 2:1                             | $(C_8H_{17})_3PI_4$         | Dark red mobile oil                   | $(C_8H_{17})_3PI^+I_3^-$          |

\* Solids containing simple halide ion and trihalide ion have been reported previously<sup>38</sup>. An example of such a structure is the compound  $[(C_6H_5)_3AsOH^+]_2Br^-Br_3^-$ .

(3) THE REACTION OF IODINE MONOBROMIDE WITH TRIOCTYLPHOSPHINE.

The general form of the conductance-composition graph for this system was very similar to that obtained for the corresponding bromine titration. The graph is illustrated in Figure III - plot 2 from data listed in Table IX.

TABLE IX: Conductometric Analysis of the  $\text{IBr}-(\text{C}_8\text{H}_{17})_3\text{P}$  System in Methyl Cyanide.

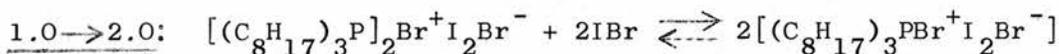
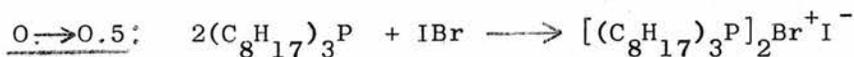
| Mole Ratio<br>IBr:<br>$(\text{C}_8\text{H}_{17})_3\text{P}$ | $\text{K} \times 10^4$<br>$\text{ohm}^{-1}$<br>$\text{cm}^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.000   | 0.05  | 0.930   | 7.60  | 1.860   | 14.48   | 3.069   | 14.79   |
| 0.093   | 3.30  | 1.023   | 7.91  | 1.953   | 14.52   | 3.255   | 14.76   |
| 0.186   | 5.57  | 1.116   | 8.43  | 2.046   | 14.55   | 3.441   | 14.76   |
| 0.279   | 7.77  | 1.209   | 9.39  | 2.139   | 14.59   | 3.627   | 14.72   |
| 0.372   | 8.98  | 1.302   | 10.32   | 2.232   | 14.65   | 3.813   | 14.69   |
| 0.465   | 8.67  | 1.395   | 11.39   | 2.325   | 14.72   | 3.999   | 14.69   |
| 0.558   | 8.26  | 1.488   | 12.21   | 2.418   | 14.79   | 4.185   | 14.69   |
| 0.651   | 7.98  | 1.581   | 13.11   | 2.511   | 14.83   | 4.371   | 14.65   |
| 0.744   | 7.71  | 1.674   | 13.93   | 2.697   | 14.83   |   |   |
| 0.837   | 7.57  | 1.767   | 14.28   | 2.883   | 14.79   |   |   |

Breaks were observed at the mole ratios of interhalogen to trioctylphosphine of 0.5:1, 1:1 and 2:1 and the corresponding molar conductance values at the latter two ratios were:

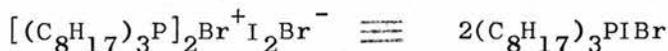
$$\underline{1:1} \quad \Lambda_m = 59.12 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01290 \text{ moles/litre})$$

$$\underline{2:1} \quad \Lambda_m = 123.57 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01175 \text{ moles/litre})$$

The colourless solution turned distinctly yellow at the 0.5:1 ratio, again showing the existence of trihalide ion from this point in the titration. By analogy with the corresponding trioctylphosphine-bromine system, which behaved identically, the following reaction scheme is suggested:



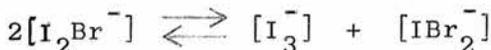
where stoichiometrically,



and



From the 0.5:1 ratio onward the ultra-violet spectrum of the solution showed the presence of a mixture of  $\text{I}_2\text{Br}^-$  and  $\text{I}_3^-$  ions up to and beyond the 1:1 ratio of interhalogen to phosphine. However at the 2:1 ratio only  $\text{I}_2\text{Br}^-$  ion ( $\lambda_{\text{max}} = 280, 351 \text{ m}\mu$ ) could be detected. The presence of triiodide ion in the U.V. spectra can be explained by the dissociation of the diiodobromide ion as follows:



Compounds of the stoichiometry  $(\text{C}_8\text{H}_{17})_3\text{PIBr}$  and

$(C_8H_{17})_3PI_2Br_2$  were prepared. The dihalide was precipitated from methyl cyanide solution by addition of anhydrous ether. It is an unstable pale yellow solid. The tetrahalide crystallised from methyl cyanide at temperatures below  $0^\circ$  but when the solvent was removed and room temperature attained a deep red oil remained.

#### (4) SUMMARY.

Trioctylphosphine has been shown to react in concentrated solution with the halogens bromine and iodine and the interhalogen iodine monobromide to give 1:1 adducts  $(C_8H_{17})_3PBr_2$ ,  $(C_8H_{17})_3PI_2$  and  $(C_8H_{17})_3PIBr$  and 1:2 adducts  $(C_8H_{17})_3PBr_4$ ,  $(C_8H_{17})_3PI_4$  and  $(C_8H_{17})_3PI_2Br_2$ . All of these are extremely unstable compounds. In the iodine system an adduct of the intermediate 1.5:1 composition,  $1.5 I_2(C_8H_{17})_3P$ , was isolated. Conductometric titration studies of the  $Br_2-(C_8H_{17})_3P$  and  $IBr-(C_8H_{17})_3P$  systems in dilute methyl cyanide give titration graphs with breaks at the ratios 0.5:1, 1:1 and 2:1. Compounds corresponding to the 0.5:1 stoichiometry were never isolated but the reproducibility of a break at this point in the graphs does point to the formation of an intermediate of this composition in dilute methyl cyanide solution. All attempts to isolate such a compound yielded only the 1:1 adducts. In the  $I_2-(C_8H_{17})_3P$  system, distinct breaks were obtained only at ratios 0.5:1 and 1.5:1 in the titration graphs. 1:1 and 2:1 adducts were however isolated and it would therefore seem that this system

is more complex than that involving bromine or iodine monobromide; a series of complex equilibria in solution is postulated. Measurement of molar conductances has shown that all these adducts are strong 1:1 electrolytes in methyl cyanide.

### III. THE REACTIONS OF HALOGENS WITH TRICYCLOHEXYLPHOSPHINE.

Tricyclohexylphosphine unlike the other two phosphines studied is a solid under normal conditions, thus its handling was somewhat easier. The solubility of this phosphine in methyl cyanide was again not very great, so that suspensions were used in its reactions with halogens. The halogen adducts isolated from the systems  $\text{Br}_2-(\text{C}_6\text{H}_{11})_3\text{P}$ ,  $\text{I}_2-(\text{C}_6\text{H}_{11})_3\text{P}$  and  $\text{IBr}-(\text{C}_6\text{H}_{11})_3\text{P}$  proved to be considerably more stable than those involving tri(n-butyl)phosphine and trioctylphosphine.

#### (1) THE REACTION OF BROMINE WITH TRICYCLOHEXYLPHOSPHINE.

A conductometric titration study of the  $\text{Br}_2-(\text{C}_6\text{H}_{11})_3\text{P}$  system in methyl cyanide gave the results recorded in Table X and graph illustrated in Figure V - plot 1.

The graph showed definite breaks at the 0.5:1, 1:1 and 2:1 mole ratios at which points the respective molar conductance values were:

$$\underline{0.5:1} \quad \Lambda_m = 74.34 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01152 \text{ moles/litre})$$

$$\underline{1:1} \quad \Lambda_m = 74.88 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01116 \text{ moles/litre})$$

$$\underline{2:1} \quad \Lambda_m = 124.75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01053 \text{ moles/litre})$$

(The molar conductance value at the 0.5:1 ratio is included to show how little it changes between this ratio and the 1:1 ratio. This is typical for all previous conductometric titrations discussed).

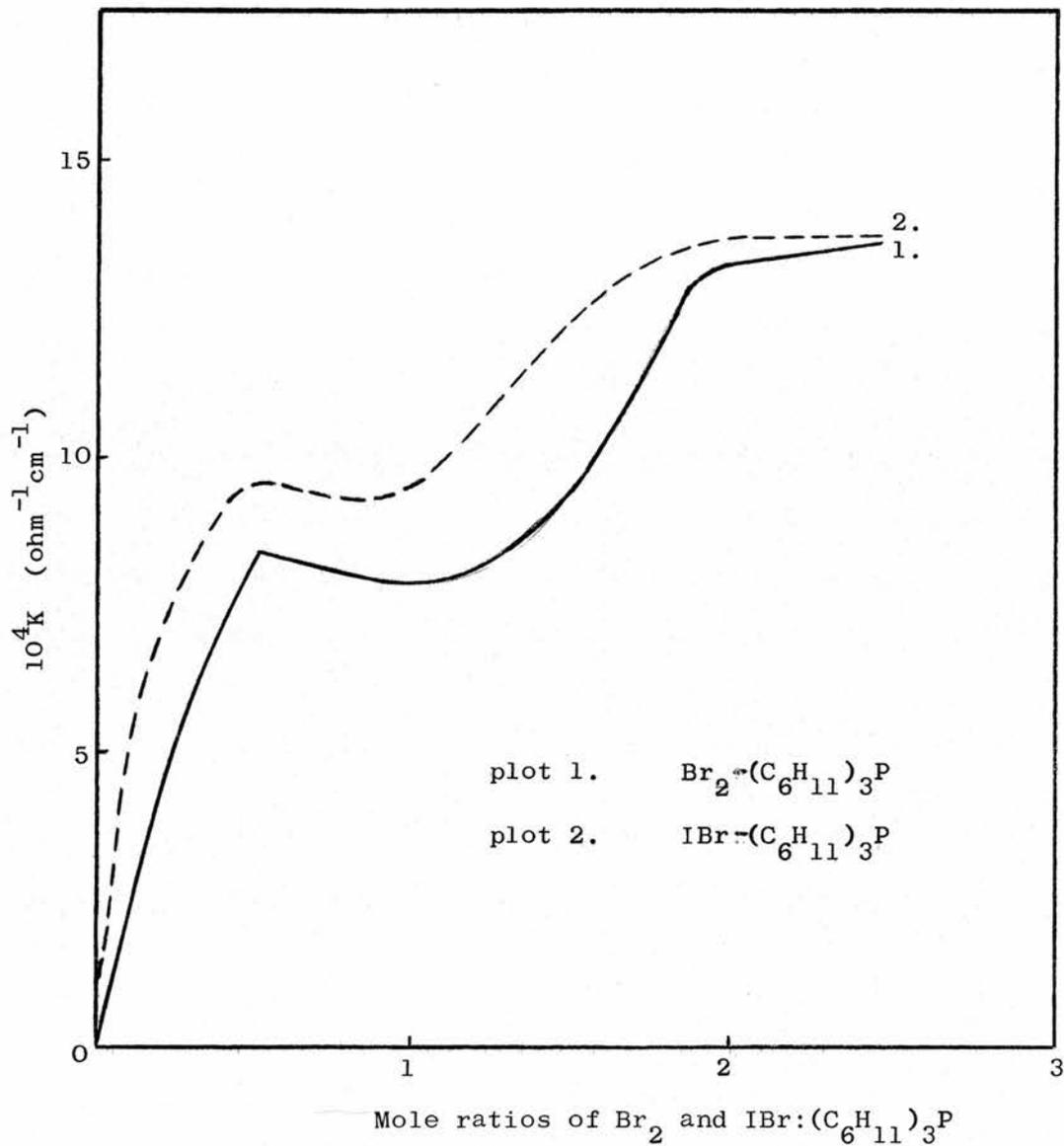
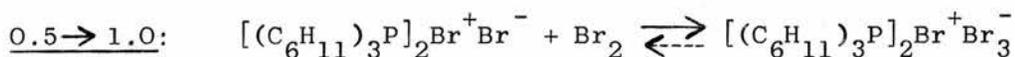
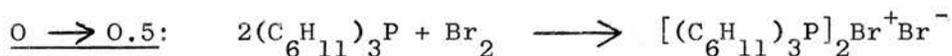


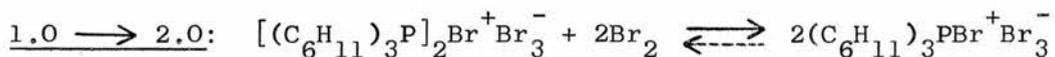
Figure V: Conductometric Analysis of the Systems  $\text{Br}_2 \cdot (\text{C}_6\text{H}_{11})_3\text{P}$   
and  $\text{IBr} \cdot (\text{C}_6\text{H}_{11})_3\text{P}$  in Methyl Cyanide.

TABLE X: Conductometric Analysis of the System  $\text{Br}_2 - (\text{C}_6\text{H}_{11})_3\text{P}$  in Methyl Cyanide.

| Mole Ratio $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P}$ | $\text{K} \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P}$ | $\text{K} \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P}$ | $\text{K} \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$ | Mole Ratio $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P}$ | $\text{K} \times 10^4$ $\text{ohm}^{-1} \text{cm}^{-1}$ |
|--|---|--|---|--|---|--|---|
| 0.000  | 0.16  | 0.891  | 8.29  | 1.782  | 13.14   | 2.673  | 13.93   |
| 0.099  | 3.23  | 0.990  | 8.36  | 1.881  | 13.24   | 2.772  | 14.00   |
| 0.198  | 5.16  | 1.089  | 8.50  | 1.980  | 13.35   | 2.871  | 14.07   |
| 0.297  | 6.78  | 1.188  | 8.77  | 2.079  | 13.45   | 2.970  | 14.14   |
| 0.396  | 7.91  | 1.287  | 9.15  | 2.178  | 13.52   | 3.069  | 14.21   |
| 0.495  | 8.57  | 1.386  | 9.84  | 2.277  | 13.59   | 3.168  | 14.28   |
| 0.594  | 8.46  | 1.485  | 10.84   | 2.376  | 13.69   | 3.267  | 14.34   |
| 0.693  | 8.26  | 1.584  | 11.73   | 2.475  | 13.79   |  |   |
| 0.792  | 8.26  | 1.683  | 12.76   | 2.574  | 13.86   |  |   |

The colourless solution turned distinctly yellow at the 0.5:1 ratio and appeared to darken considerably at the 2:1 ratio. These high molar conductance values are again indicative of strong electrolyte behaviour and of the formation of tribromide ion from the 0.5:1 ratio; the same reaction scheme as postulated for the previous systems is suggested to explain this present reaction:





Solids of stoichiometry  $(\text{C}_6\text{H}_{11})_3\text{PBr}_2$  and  $(\text{C}_6\text{H}_{11})_3\text{PBr}_4$  were obtained by addition of anhydrous ether to methyl cyanide solutions containing bromine and the phosphine in the ratios 1:1 and 2:1 respectively. When a suspension of the phosphine in a limited amount of methyl cyanide was shaken overnight with an equimolar quantity of bromine complete solution was not obtained, but the crystalline form of the solid changed. Analysis and the infra-red spectrum of this solid suggested that it was the solvated dibromide containing one molecule of methyl cyanide,  $[(\text{C}_6\text{H}_{11})_3\text{PBr}_2] \cdot \text{CH}_3\text{CN}$ . The unsolvated dibromide was precipitated on addition of anhydrous ether to the filtrate from this reaction. Attempts to isolate a solid at the 0.5:1 ratio, once again, yielded only the dibromide.

In the next system to be discussed, namely  $\text{I}_2 - (\text{C}_6\text{H}_{11})_3\text{P}$ , adducts with a halogen to tricyclohexylphosphine ratio greater than 2 were isolated. An attempt was therefore made to prepare higher adducts of the  $\text{Br}_2 - (\text{C}_6\text{H}_{11})_3\text{P}$  system. Addition of anhydrous ether to solutions containing a high proportion of bromine always yielded the relatively stable tetrabromide,  $(\text{C}_6\text{H}_{11})_3\text{PBr}_4$ , but from a methyl cyanide solution which contained bromine and tricyclohexylphosphine in the ratio of 4:1, large orange crystals were obtained on slow evaporation of the solvent. Analysis of this material indicated the stoichiometry  $(\text{C}_6\text{H}_{11})_3\text{PBr}_8$ ; this can be formulated as a compound containing the heptabromide ion,  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_7^-$ . When this compound was exposed to the atmosphere of the dry-box it rapidly

lost bromine, gradually transforming to the more stable 2:1 adduct,  $(C_6H_{11})_3PBr_4$ ,  $[(C_6H_{11})_3PBr^+Br_3^-]$ .

(2) VAPOUR PRESSURE STUDY OF THE  $Br_2-(C_6H_{11})_3P$  SYSTEM.

In view of the facile decomposition of the tricyclohexylphosphine-bromine adducts described, it was thought that a vapour pressure study of the system might provide valuable information about the stoichiometry of the solid phases in this system.

The interaction of bromine and tricyclohexylphosphine was studied by measurement of the vapour pressures of different compositions of the mixture at  $15^\circ$ . A spiral gauge system was used for the pressure measurements. The phase diagram constructed from the dissociation pressure data is reproduced in Figure VI.

From mole ratio 0 to 4, the vapour pressure of the system was too low (ca. 2 mm) for reliable determination of the stoichiometry of the solid phases present. Thus the compounds already isolated,  $(C_6H_{11})_3PBr_2$  and  $(C_6H_{11})_3PBr_4$  were not detected. From mole ratio 4 onwards, however, pressures were much higher, and the presence of three distinct vertical portions (at mole ratios 4:1, 5:1 and 6:1) on the isotherm of the system are indicative of solid phases of composition  $(C_6H_{11})_3PBr_8$ ,  $(C_6H_{11})_3PBr_{10}$  and  $(C_6H_{11})_3PBr_{12}$ . The former of these corresponds to the unstable polybromide mentioned above. McPherson<sup>1</sup> when carrying out a vapour pressure study on the bromine-tri(p-tolyl)phosphine system at  $15^\circ$  obtained evidence

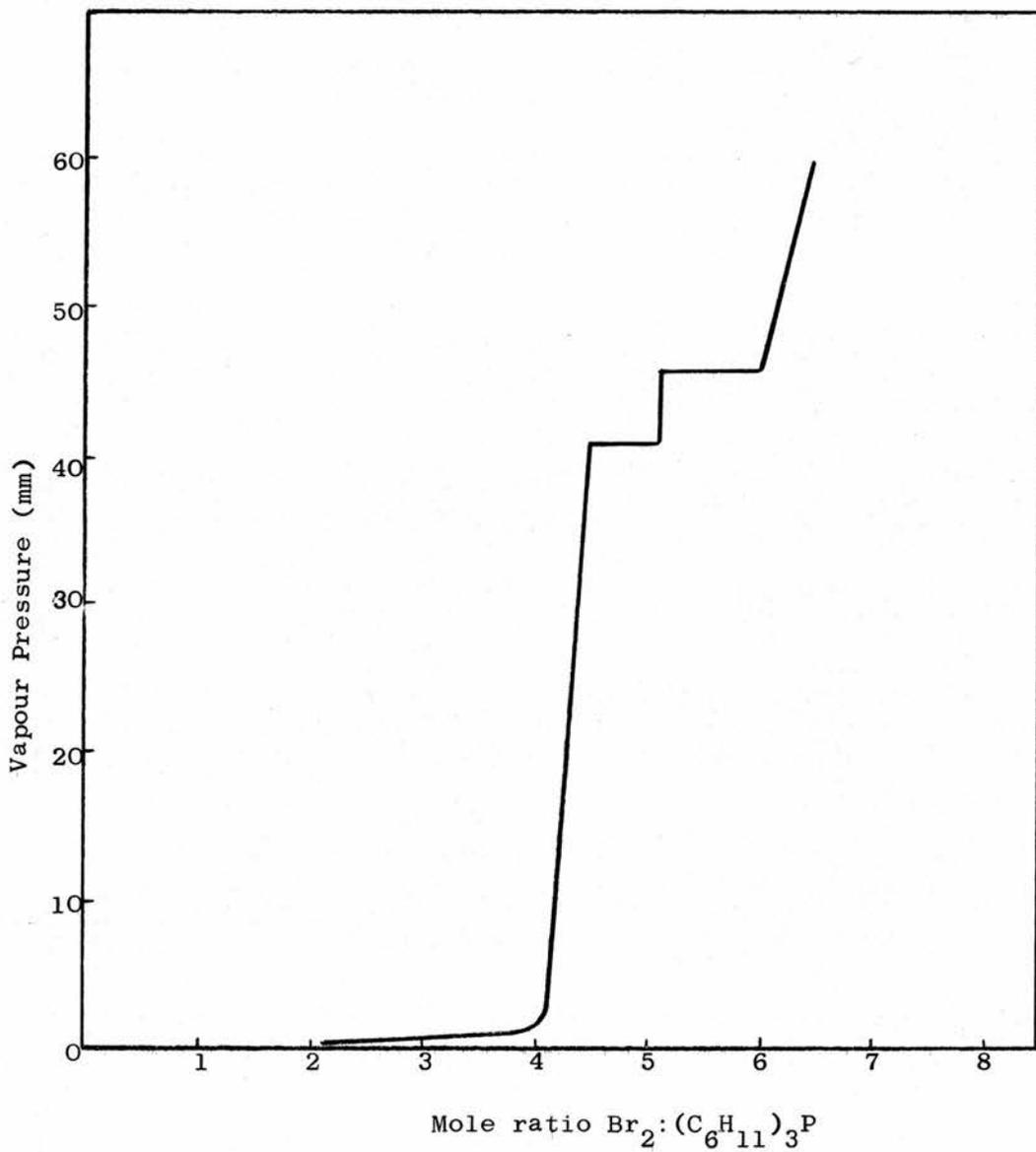


Figure VI: Vapour Pressure Study of the  $\text{Br}_2-(\text{C}_6\text{H}_{11})_3\text{P}$  System at  $15^\circ$ .

---

for a 6:1 adduct,  $(p\text{-tol})_3\text{PBr}_{12}$ , for which he postulated the structure  $(p\text{-tol})_3\text{PBr}^+\text{Br}_{11}^-$ , although no conclusive evidence for the  $\text{Br}_{11}^-$  ion has, as yet, been presented. Furthermore Ali<sup>8</sup>, in a study of the vapour pressure of the bromine-tris(pentafluorophenyl) phosphine system at  $0^\circ$ , showed the formation of a decabromide,  $(\text{C}_6\text{F}_5)_3\text{PBr}_{10}$ , which, by analogy with  $\text{Me}_4\text{N}^+\text{Br}_9^-$ <sup>39</sup>, he described as  $(\text{C}_6\text{F}_5)_3\text{PBr}^+\text{Br}_9^-$ . It would seem reasonable then, that for the bromine-tricyclohexylphosphine system described above there is a strong indication of the existence of the ionic compounds  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_{11}^-$ ,  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_9^-$  and  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_7^-$ .

From the high molar conductance values of the tetrabromide and dibromide in solution, obtained from the conductometric titration, these may be formulated  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_3^-$  and  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}^-$  respectively.

The evidence then, points to the formation of a series of ionic adducts formed between bromine and tricyclohexylphosphine, ranging from the dibromide,  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}^-$ , to the duodecabromide,  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{Br}_{11}^-$ .

### (3) ATMOSPHERIC HYDROLYSIS OF $(\text{C}_6\text{H}_{11})_3\text{PBr}_2$ .

As already noted, the halogen adducts of tricyclohexylphosphine appeared to be hydrolytically more stable than those isolated from the previous systems. However on exposure to the atmosphere the tricyclohexylphosphine dibromide began to decompose and in order to examine this decomposition further, a specimen of

the dibromide was exposed to the open atmosphere for one week. After this period there remained a sticky, yellow solid. On vacuum drying a yellow powder was produced. This solid, although hygroscopic, could be handled readily and analysis indicated that it was the hydroxybromide,  $(C_6H_{11})_3POHBr$ . This behaviour parallels the hydrolysis product of tri(n-butyl)phosphine dibromide which was very hygroscopic. The infra-red spectrum of the sticky, yellow solid clearly showed absorption due to water but in the spectrum of the vacuum-pumped solid all the water absorption had disappeared. The spectrum showed the characteristic strong absorption in the region  $2,600-2,000\text{ cm}^{-1}$  (-OH stretch) reported by Inglis<sup>22</sup> for  $Ar_3AsOHBr$  compounds. There was a strong peak at  $970\text{ cm}^{-1}$ , which was absent in the anhydrous dibromide; this is presumed to be P=O stretching frequency, lowered considerably on account of hydrogen bonding. Therefore, again by analogy with the structures proposed by Inglis for triarylarsonic hydroxyhalides,  $Ar_3AsOHHal$ , the hydrolysed product of  $(C_6H_{11})_3PBr_2$  is probably  $[(C_6H_{11})_3PO..H-Br]$ .

#### (4) THE REACTION OF IODINE WITH TRICYCLOHEXYLPHOSPHINE.

A conductometric titration study of the  $I_2-(C_6H_{11})_3P$  system in methyl cyanide gave the results recorded in Table XI and graph illustrated in Figure VII.

The graph shows an inflection at the 0.5:1 ratio at which

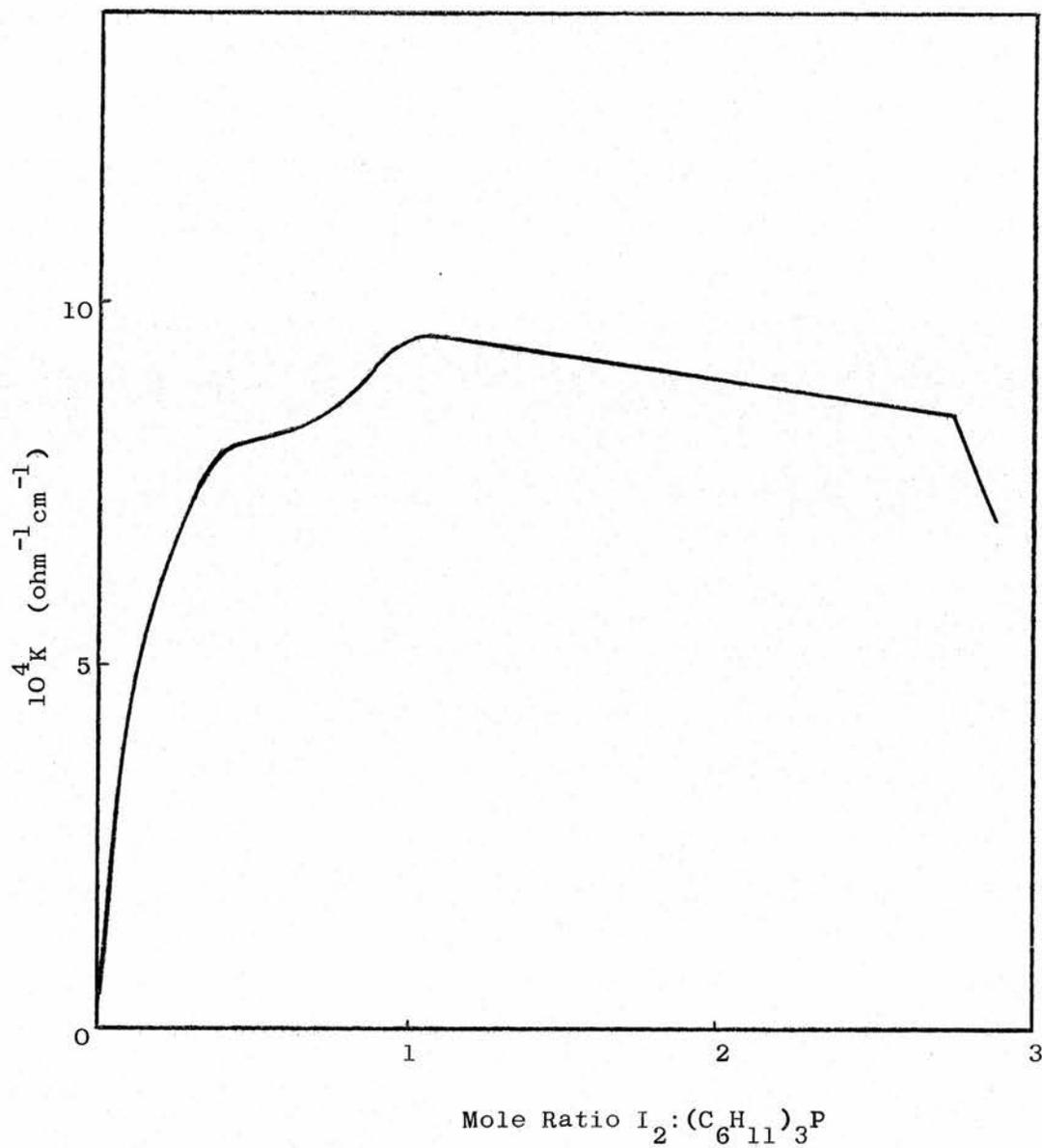


Figure VII: Conductometric Analysis of the System  $I_2-(C_6H_{11})_3P$  in  
Methyl Cyanide.

TABLE XI: Conductometric Analysis of the System  $I_2-(C_6H_{11})_3P$  in

Methyl Cyanide.

| Mole Ratio<br>$I_2:$<br>$(C_6H_{11})_3P$ | $K \times 10^4$<br>$ohm^{-1}$<br>$cm^{-1}$ |
|--|--|--|--|--|--|--|--|
| 0.000                                    | 0.37                                       | 1.133                                    | 9.36                                       | 2.266                                    | 8.70                                       | 3.399                                    | 6.67                                       |
| 0.103                                    | 4.61                                       | 1.236                                    | 9.36                                       | 2.369                                    | 8.67                                       | 3.502                                    | 6.60                                       |
| 0.206                                    | 6.78                                       | 1.339                                    | 9.29                                       | 2.472                                    | 8.60                                       | 3.605                                    | 6.54                                       |
| 0.309                                    | 7.71                                       | 1.442                                    | 9.22                                       | 2.575                                    | 8.57                                       | 3.708                                    | 6.50                                       |
| 0.412                                    | 8.08                                       | 1.545                                    | 9.15                                       | 2.678                                    | 8.50                                       | 3.811                                    | 6.47                                       |
| 0.515                                    | 8.19                                       | 1.648                                    | 9.08                                       | 2.781                                    | 8.43                                       | 3.914                                    | 6.43                                       |
| 0.618                                    | 8.36                                       | 1.751                                    | 8.98                                       | 2.884                                    | 7.09                                       | 4.017                                    | 6.36                                       |
| 0.721                                    | 8.57                                       | 1.854                                    | 8.94                                       | 2.987                                    | 7.02                                       | 4.120                                    | 6.30                                       |
| 0.824                                    | 8.84                                       | 1.957                                    | 8.91                                       | 3.090                                    | 6.91                                       | 4.223                                    | 6.26                                       |
| 0.927                                    | 9.15                                       | 2.060                                    | 8.84                                       | 3.193                                    | 6.85                                       | 4.326                                    | 6.19                                       |
| 1.030                                    | 9.29                                       | 2.163                                    | 8.77                                       | 3.296                                    | 6.78                                       | 4.429                                    | 6.16                                       |

point the colourless solution turned yellow indicating the appearance of triiodide ion. There was a distinct break at the 1:1 ratio and on approaching the 3:1 ratio a sudden drop in the conductance took place accompanied by the precipitation of a greenish-black crystalline solid which subsequently proved to be the octaiodide  $(C_6H_{11})_3PI_8$ , i.e.  $(C_6H_{11})_3PI^+I_7^-$ . In this titration the absence of

a break at the 2:1 ratio and the fact that the octaiodide precipitated before even the 3:1 ratio was reached, gives an indication of the complex equilibria which must be present in these dilute methyl cyanide solutions.

The molar conductance values at the 0.5:1 and 1:1 ratios were:

$$\underline{0.5:1} \quad \Lambda_m = 59.03 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01387 \text{ moles/litre})$$

$$\underline{1:1} \quad \Lambda_m = 71.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \quad (\text{Cm} = 0.01310 \text{ moles/litre})$$

These values are indicative of fairly strong electrolyte behaviour, especially at the 1:1 ratio. A solid of stoichiometry

$[(\text{C}_6\text{H}_{11})_3\text{PI}_2] \cdot \text{CH}_3\text{CN}$  was isolated in reactions carried out at both

of the above ratios. The solvation of the diiodide parallels the

occurrence of solvation in the corresponding bromine system but in

this instance the unsolvated adduct could not be prepared. Ether

addition to the filtrate did not yield a solid product although the

reactions were performed in an identical manner. A tetraiodide,

hexaiodide and octaiodide were all prepared with ease; none of these

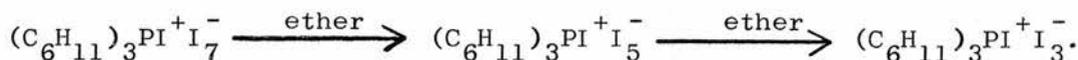
compounds contained solvated molecules of methyl cyanide. The

tetraiodide,  $(\text{C}_6\text{H}_{11})_3\text{PI}^+\text{I}_3^-$ , was the most stable of the polyhalides

prepared and on thorough shaking of the octaiodide,  $(\text{C}_6\text{H}_{11})_3\text{PI}^+\text{I}_7^-$ ,

with anhydrous ether, iodine was gradually extracted according to

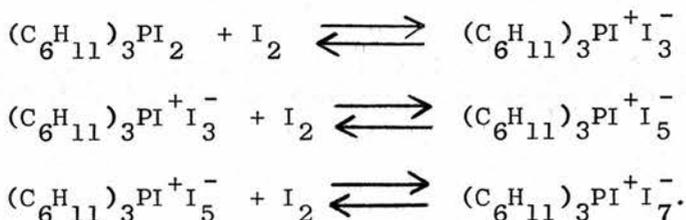
the following scheme:



On prolonged extracted with ether, the tetraiodide did not change.

It would appear then, that the absence of a break in the

conductometric titration graph at the 2:1 ratio may be due to the occurrence of several overlapping equilibria involving 2:1, 3:1 and 4:1 adducts. It is envisaged that up to the 1:1 ratio the reaction occurring is identical to that in the bromine-tricyclohexylphosphine system outlined previously. Beyond the 1:1 ratio the following equilibria are presumably involved:



(5) THE REACTION OF IODINE MONOBROMIDE WITH TRICYCLOHEXYLPHOSPHINE.

A conductometric titration study of the  $\text{IBr}-(\text{C}_6\text{H}_{11})_3\text{P}$  system in methyl cyanide gave the results recorded in Table XII and graph illustrated in Figure V - plot 2.

The conductometric titration graph was very similar to that obtained for the  $\text{Br}_2-(\text{C}_6\text{H}_{11})_3\text{P}$  system and contained breaks at the 0.5:1, 1:1 and a rather indistinct one at the 2:1 ratio. The conductance rise after the 1:1 ratio "tails off" from about the 1.6:1 ratio onward but the maximum conductance reading was not attained until close to the 2:1 ratio. The indistinct nature of this break in the graph is indicative of the product being in equilibrium with non-conducting or less-well conducting species. It may well be that the equilibrium,

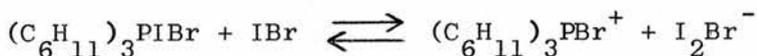
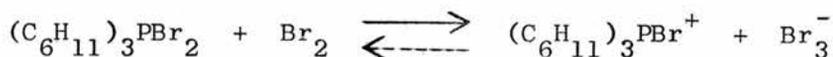


TABLE XII: Conductometric Analysis of the System IBr-(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>P in

Methyl Cyanide.

| Mole Ratio IBr: (C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> P | Kx10 <sup>4</sup> ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio IBr: (C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> P | Kx10 <sup>4</sup> ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio IBr: (C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> P | Kx10 <sup>4</sup> ohm <sup>-1</sup> cm <sup>-1</sup> | Mole Ratio IBr: (C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> P | Kx10 <sup>4</sup> ohm <sup>-1</sup> cm <sup>-1</sup> |
|--|--|--|--|--|--|--|--|
| 0.000  | 0.43   | 1.212  | 11.63  | 2.424  | 13.42  | 3.636  | 13.42  |
| 0.101  | 4.20   | 1.313  | 12.59  | 2.525  | 13.42  | 3.737  | 13.45  |
| 0.202  | 6.64   | 1.414  | 12.90  | 2.626  | 13.42  | 3.838  | 13.45  |
| 0.303  | 8.12   | 1.515  | 13.11  | 2.727  | 13.42  | 3.939  | 13.55  |
| 0.404  | 9.05   | 1.616  | 13.24  | 2.828  | 13.38  | 4.040  | 13.59  |
| 0.505  | 9.36   | 1.717  | 13.35  | 2.929  | 13.38  | 4.141  | 13.59  |
| 0.606  | 9.36   | 1.818  | 13.38  | 3.030  | 13.38  | 4.242  | 13.55  |
| 0.707  | 9.29   | 1.919  | 13.45  | 3.131  | 13.42  | 4.343  | 13.59  |
| 0.808  | 9.25   | 2.020  | 13.45  | 3.232  | 13.42  | 4.444  | 13.59  |
| 0.909  | 9.43   | 2.121  | 13.45  | 3.333  | 13.38  | 4.545  | 13.59  |
| 1.010  | 9.80   | 2.222  | 13.45  | 3.434  | 13.38  |  |  |
| 1.111  | 10.46  | 2.323  | 13.45  | 3.535  | 13.42  |  |  |

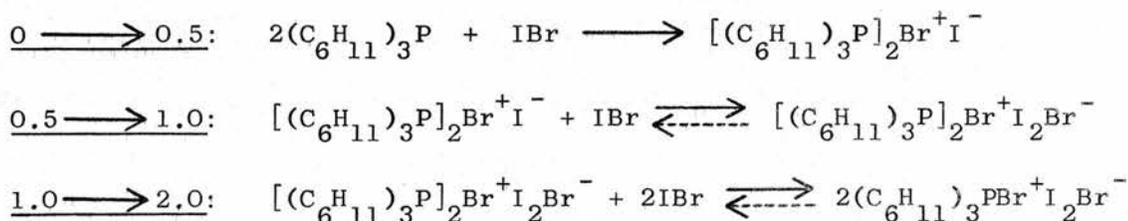
lies less far to the right hand side than the corresponding one involving bromine, namely,



The colourless solution turned pale orange at the 0.5:1 ratio, indicative of trihalide ion formation, and the molar conductance values at the three breaks were:

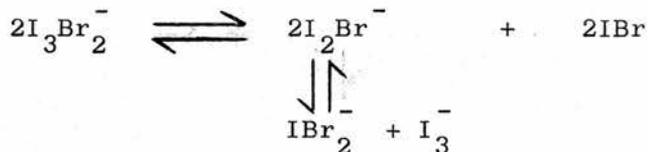
|              |   |                            |
|--------------|---|----------------------------|
| <u>0.5:1</u> | $\Lambda_m = 52.50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ | (Cm = 0.01783 moles/litre) |
| <u>1:1</u>   | $\Lambda_m = 54.99 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ | (Cm = 0.01715 moles/litre) |
| <u>2:1</u>   | $\Lambda_m = 85.83 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ | (Cm = 0.01567 moles/litre) |

The values at the 1:1 and 2:1 ratios are indicative of medium-strong and strong electrolyte behaviour respectively. Ultra-violet spectra were obtained for the adducts isolated,  $(\text{C}_6\text{H}_{11})_3\text{PIBr}$  and  $(\text{C}_6\text{H}_{11})_3\text{PI}_2\text{Br}_2$ . The results from this and from the conductometric titration graph, leads to the suggestion that the same reaction scheme as for the corresponding bromine and iodine systems applies to the iodine monobromide system:

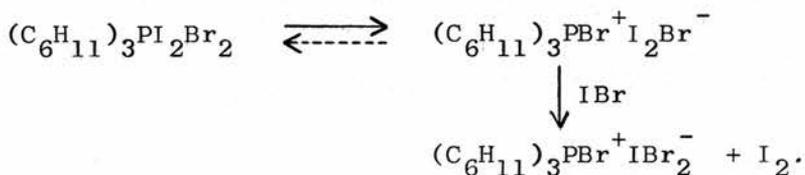


Solids corresponding to the stoichiometries  $[(\text{C}_6\text{H}_{11})_3\text{PIBr}] \cdot \text{CH}_3\text{CN}$  and  $(\text{C}_6\text{H}_{11})_3\text{PI}_2\text{Br}_2$  were isolated when halogen solutions and suspensions of the phosphine were mixed in the 1:1 and 2:1 ratios respectively. The unsolvated 1:1 adduct could not be prepared. When tricyclohexylphosphine was reacted with iodine monobromide in the ratios of 1:3 and 1:4, solids of stoichiometry  $(\text{C}_6\text{H}_{11})_3\text{PI}_3\text{Br}_3$  and  $(\text{C}_6\text{H}_{11})_3\text{PI}_4\text{Br}_4$  were formed. Formulation of these as containing higher polyhalide ions requires the existence of  $\text{I}_3\text{Br}_2^-$  and  $\text{I}_4\text{Br}_3^-$  ions which have not been reported previously. Since these ions are mixed halogen analogues of the  $\text{I}_5^-$  and  $\text{I}_7^-$  ions, which have been reported<sup>37</sup>, there seems no reason to doubt that such ions can exist.

The ultra-violet absorption spectra of methyl cyanide solutions of these compounds had a strong broad absorption band at 275 mμ. This does not correspond with the absorption band of a trihalide ion. It seems likely that ions such as  $I_3Br_2^-$  and  $I_4Br_3^-$  would break down, to a greater or lesser degree, in solution to simpler polyhalide ions, thus:



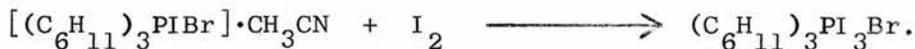
From the filtrate of the 1:4 reaction orange crystals were obtained on addition of anhydrous ether. These proved to be the tetrahalide adduct,  $(C_6H_{11})_3PIBr_3$ . A possible explanation for the unexpected precipitation of this compound is that  $(C_6H_{11})_3PI_2Br_2$ , which could be present in solution, further reacts with excess iodine monobromide in the following manner:



where,  $(C_6H_{11})_3PBr^+IBr_2^- \equiv (C_6H_{11})_3PIBr_3$ .

Therefore with the isolation of this adduct, four members of the series of compounds  $(C_6H_{11})_3PI_nBr_{4-n}$  have now been prepared -  $(C_6H_{11})_3PBr_4$ ;  $(C_6H_{11})_3PIBr_3$ ;  $(C_6H_{11})_3PI_2Br_2$  and  $(C_6H_{11})_3PI_4$ . The missing member,  $(C_6H_{11})_3PI_3Br$ , was prepared by the 1:1 reaction of the solvated dihalide  $[(C_6H_{11})_3PIBr] \cdot CH_3CN$  and iodine, in methyl

cyanide. (See Experimental Section for further details).



### (6) SUMMARY.

Tricyclohexylphosphine has been shown to react with bromine, iodine and iodine monobromide to give a variety of crystalline adducts, all of which appear to be considerably more stable and easier to handle than the adducts of the other two phosphines studied, although they come into the category of moisture sensitive compounds. The dihalide adducts have been prepared containing one molecule of methyl cyanide of solvation, and only in the case of dibromide was the unsolvated adduct obtained. Both the bromine and iodine systems are capable of forming higher adducts - a 4:1 was isolated - and from the vapour pressure study of the bromine-tricyclohexylphosphine system, a 6:1 adduct has been indicated.

Conductometric titration studies in dilute methyl cyanide show, as expected, a 0.5:1 break with all three halogens, together with a break at the 1:1 ratio. However a break at the 2:1 ratio was observed with bromine and iodine monobromide only. The dihalides are medium-strong electrolytes whilst all the tetrahalides have been shown to be highly conducting.

Hydrolysis of tricyclohexylphosphine dibromide,  $(C_6H_{11})_3PBr_2$ , gives rise to the hydroxybromide,  $(C_6H_{11})_3POHBr$ .

#### IV. SOME GENERAL COMMENTS.

A significant factor emerging from the results of this study would seem to be the relative stability, and large number, of adducts formed by the halogen-tricyclohexylphosphine systems when compared with the corresponding halogen-tri(n-butyl)- and trioctylphosphine reactions. It is difficult to see any obvious electronic factor in the phosphines which might account for this and so it is concluded that steric effects must be responsible. The bulky cyclohexyl rings around the phosphorus atom may play an important part in protecting the phosphorus atom from attack. The straight chain alkyl groups would offer less protection, enabling moisture and oxygen to attack the central phosphorus atom in the cation of these adducts more readily. A comparison could be made with the corresponding triphenylphosphine adducts. They are also relatively stable and the steric effects of the phenyl rings must be somewhat similar to the cyclohexyl system although, of course, electronic differences will exist here.

All attempts to prepare an intermediate compound at the 0.5:1 ratio of halogen to phosphine resulted in the isolation of 1:1 adducts, but the consistently reproducible breaks obtained at this ratio in the conductometric titration studies points to such an intermediate being formed in dilute methyl cyanide solution. The conductance work has also shown that most of the dihalides and all the tetrahalides are strong 1:1 electrolytes in methyl cyanide and in no instance was non-electrolyte behaviour observed.

EXPERIMENTAL

## EXPERIMENTAL

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EXPERIMENTAL

I. GENERAL TECHNIQUES.

(1) 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 trays 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 in a partially evacuated desiccator over phosphorus pentoxide or silica gel.

(2) 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.

Vapour Pressure Measurement.

For the vapour pressure study of the system  $\text{Br}_2 - (\text{C}_6\text{H}_{11})_3\text{P}$  a special all glass system was used (Figure VIII). The spiral gauge (C) in this system was used as a null instrument in which the deflection of the pointer was magnified by the optical lever principle. The pointer of the gauge was made to actuate a small delicately balanced mirror which reflected a parallel beam of light on to a scale situated at a distance of 1 metre. The zero point of the instrument on the scale was adjusted.

The tricyclohexylphosphine under investigation was placed in flask A to which was then added a known excess of bromine by weight. An exothermic reaction occurred and, after cooling, the resultant dark solution was shaken for several minutes to ensure thorough mixing. It was then cooled in liquid nitrogen before attaching to the vacuum line and evacuated (0.002 mm Hg). Before the vapour pressure titration began, bulb B was evacuated and weighed in preparation for receiving aliquots of the excess bromine over the phosphine. The tap and joints which would come into contact with the bromine vapour had been carefully greased with the halogen resistant 'Kel-F' fluorocarbon grease. For vapour pressure readings during the titration, flask A was kept immersed in a Dewar vessel containing water at  $15^\circ$ . The vapour pressure of the contents of tube A having deflected the mirror on gauge C, this pressure was compensated by admitting air through capillary leak E and the surge chamber D. Full compensation was monitored by the return of the light signal to the original zero point

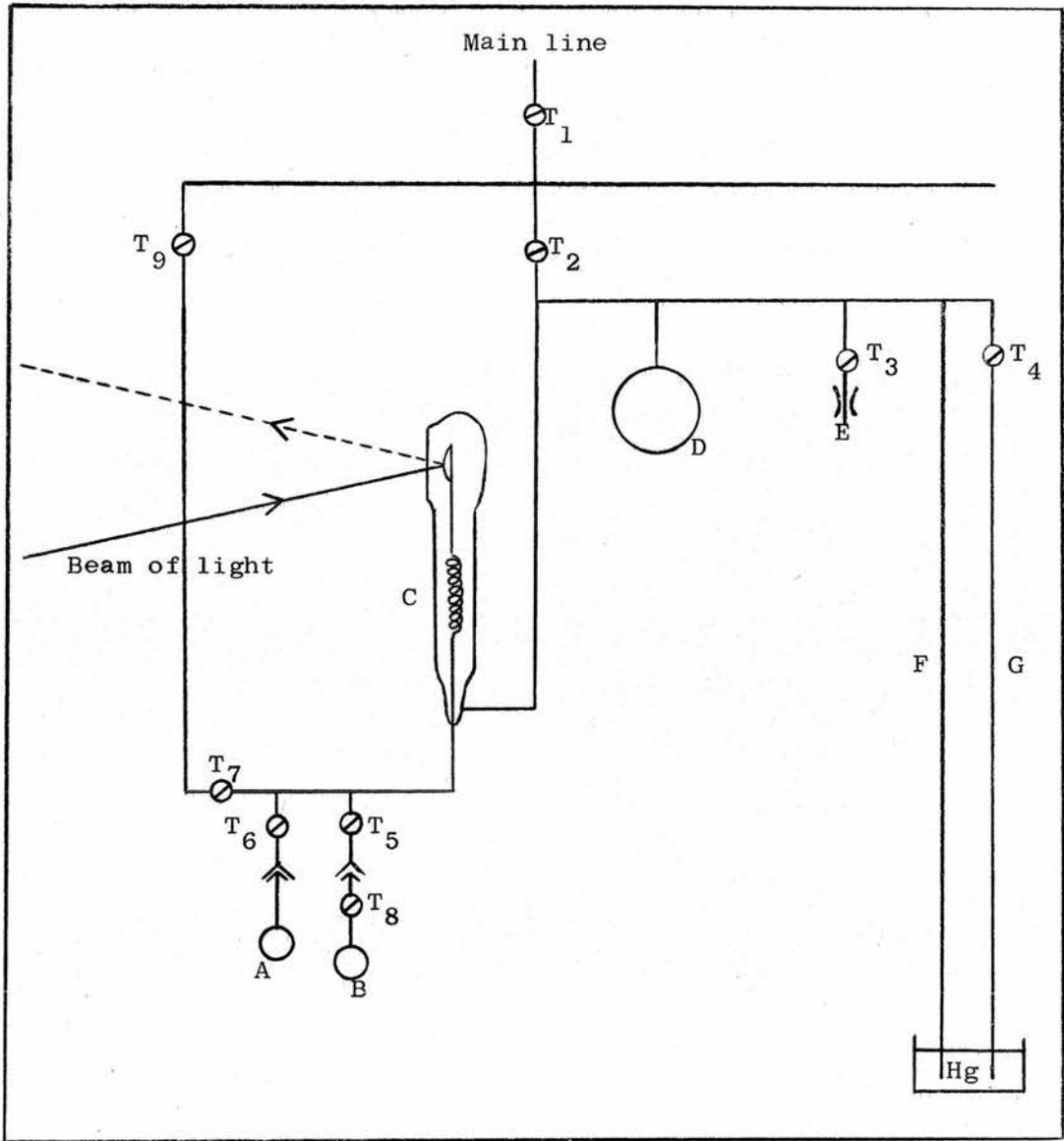


Figure VIII: Vacuum System for Vapour Pressure Study.

on the scale. Vapour pressure could then be obtained as a difference in mercury levels between manometers F and G, arranged close to one another and using a common mercury reservoir. Having closed tap  $T_4$  before the start of the titration, with tube G fully evacuated, manometer G was employed as an ordinary barometer. A cathetometer was used to obtain accurate measurement of mercury levels.

Having read the vapour pressure for given contents of tube A, some of the excess bromine was then distilled off into tube B by temperature difference, liquid nitrogen being used to surround B during this process. Tube B was allowed to assume room temperature, after closing taps  $T_5$  and  $T_8$ , and re-weighed. Thus the new mole ratio of bromine to phosphine in tube A could be ascertained, and the process of obtaining the vapour pressure repeated as before. When it was necessary to reduce the pressure in, or pump directly, any part of the system, taps  $T_2$  and  $T_1$ , which gave access to the main line, were used.

### (3) Conductance Measurements.

Conductance measurements were made at  $25^\circ$  in a sealed cell. A standard pair of smooth dipping electrodes (cell constant  $0.344 \text{ cm}^{-1}$ ) was used. Solutions of known concentration were prepared by adding a weighed amount of dry solvent to the cell which contained a known weight of solid. When solution was complete, the cell was placed in a thermostat bath at  $25^\circ$  and the specific conductance measured using a Wayne Kerr B641 Autobalance Bridge. Molar conductances were then calculated.

#### (4) Conductometric Titrations.

A convenient technique for studying the reactions of triarylphosphines, and their derivatives, with halogens has been shown to be the conductometric titration<sup>30,31</sup>. Information may be obtained not only on the stoichiometry of the reaction products but also on their electrolytic behaviour.

Methyl cyanide was usually employed as a solvent as its high dielectric constant (36.7 at 25<sup>o</sup>) results in high conductances of electrolytes and consequent easy distinction between non-electrolytes and strong and weak electrolytes. Strong 1:1 electrolytes have  $\Delta\Lambda_m = \text{ca. } 100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  and weak electrolytes  $\Delta\Lambda_m = \text{ca. } 10\text{-}20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  in methyl cyanide. Nitrobenzene was also used occasionally (see Appendix), but since compounds have much lower conductances in this solvent than in methyl cyanide it was not so useful.

The apparatus used was specially designed so that all the conductometric titrations could be performed wholly within the dry-box (for a description of this apparatus see Appendix). The dipping electrodes and the conductance bridge used were the same ones previously mentioned for conductometric measurements. The conductance was measured when equilibrium had been attained after each addition of halogen solution.

#### (5) Infra-red Spectra.

Infra-red spectra were recorded on a Perkin-Elmer Model 621

grating spectrophotometer over the range 4000-400  $\text{cm}^{-1}$ . A Perkin-Elmer Model 137 infracord fitted with sodium chloride optics was also occasionally used. Although infra-red spectroscopy was extensively used throughout this work, it was really only with respect to the hydrolysis experiments and in the identification of the solvated 1:1 adducts of the halogen-tricyclohexylphosphine systems, that much useful information could be obtained. For example, the spectra of a series of adducts such as  $(\text{C}_6\text{H}_{11})_3\text{PI}_4$ ,  $(\text{C}_6\text{H}_{11})_3\text{PI}_6$  and  $(\text{C}_6\text{H}_{11})_3\text{PI}_8$  did not change, to any degree, from one adduct to the other. The samples were generally prepared in the dry-box as mulls in nujol or hexachlorobutadiene, and then placed between plates of sodium chloride, potassium bromide or caesium iodide. The plates were then bound around the edge with sellotape to prevent attack by atmospheric moisture. Potassium bromide pressed discs were also used and could be prepared in the dry box using a Wilks Scientific Corporation Mini-Press, but once the disc was removed from the dry-box there was no way of protecting it from air attack.

#### (6) Ultra-violet Spectra.

Ultra-violet spectra were recorded on a Unicam SP800 B U.V./visible recording spectrophotometer. Stoppered silica cells of 1 cm or 0.5 cm path length were used. The measurements were made at room temperature (ca.  $18^\circ$ ).

(7) 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. Samples of the unstable halogen-alkyl phosphine adducts were transferred from the sample tubes, in which they were stored, to previously weighed aluminium pans and sealed using a special press. This procedure was done wholly within the nitrogen filled dry-box and the sealed pans containing the sample were then re-weighed before analysis, thus avoiding exposure of the sample to air or atmospheric moisture.

Halogen analyses were carried out potentiometrically using an adaptation of the method described by Lingane<sup>40</sup>. A description of the method developed is as follows:

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 0.1 M 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 barium nitrate was added to remove sulphate ion present and also to help prevent adsorption of halide ion, especially in the case of iodide, on the silver halide precipitate. The acetone reduces the solubility product of the silver halide being precipitated and results in sharper end-points. Finally, it was found, especially in the case of iodide, that addition of more than a few drops of 6M nitric acid resulted in the oxidation of halide to halogen, giving low results.

The electrode potential (mV) of the initial halide solution was determined, and corresponding measurements taken at 0.1 ml intervals of silver nitrate until the end-point was being approached. This was detected by a more rapid increase in the change in potential and, when this was observed, the additions of silver nitrate solution were reduced to 0.02 ml for each reading. A graph of mV readings against ml of silver nitrate added was plotted, the points of inflection being regarded as the end-points of the titration.

Before each titration the silver wire indicator electrode was

cleaned by immersing in 50% nitric acid for one minute, washed with distilled water, then immersed in concentrated ammonia for two minutes before a final thorough washing with distilled water.

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.

## II. SOURCE AND PURIFICATION OF MATERIALS.

### (1) Solvents.

#### (i) Methyl Cyanide.

Pure anhydrous methyl cyanide suitable for conductance studies was prepared by a modification of the method described by Smith and Witten<sup>41</sup>. 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) when it was stirred 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 Sieves, using a nine inch column of glass helices which had also been oven dried. The fraction boiling between 81-82° was collected and after tightly stoppering the flask, using a 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.  $10^{-7}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°.

(ii) Nitrobenzene.

A.R. grade nitrobenzene was distilled twice, once at atmospheric pressure, when the fraction boiling at 207-208<sup>o</sup> was collected, and the other at reduced pressure (ca. 2 mm) incorporating a nitrogen leak and a Vigreux column. The fraction boiling at 67<sup>o</sup> was collected. The specific conductance of this nitrobenzene was less than 10<sup>-7</sup> ohm<sup>-1</sup> cm<sup>-1</sup> at 25<sup>o</sup>.

(iii) Carbon Tetrachloride.

The method used to obtain pure carbon tetrachloride was a variation of that described by Popov and Schmor<sup>42</sup>. 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<sup>o</sup>, 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) Chloroform.

The commercial grade solvent was washed with a large volume of water to remove ethanol and dried by passing through a column of alumina. It was stored over silica gel and distilled before use.

(2) Reagents.

(i) Bromine.

A.R. bromine was first stored over calcium bromide. It was filtered into a small flask under a nitrogen hood, attached to the vacuum system and pumped off to remove the more volatile impurities. The bromine was then cooled to  $0^{\circ}$  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.

(3) Starting Materials.

(i) Tri(n-butyl)phosphine.

The commercial grade material (Kodak Limited, London via Eastman Chemicals, U.S.A.) was distilled using a Claisen head containing a Vigreux column, under water pump pressure. An air leak attached to a dry nitrogen supply was incorporated and the fraction used was collected at 120°.

(ii) Trioctylphosphine.

The commercial trioctylphosphine (Kodak Limited, London via Eastman Chemicals, U.S.A.) was a colourless liquid which contained a white crystalline solid in the bottom of the reagent bottle. Several values as to its boiling point at 1 mm pressure were obtained ranging from 190° to 234°<sup>43,44</sup>. These references also quoted melting points for the phosphine of 48° and 30° respectively. Since the boiling ranges were very high it was decided to attempt to purify the commercial trioctylphosphine by the method of fractional freezing.

Approximately 30 ml of the phosphine was placed in a 100 ml conical flask, filled with dry nitrogen, tightly stoppered and cooled slowly in an ice bath. Single crystals did not form and the whole mass gradually began to solidify. Once solid, it was warmed up very slowly until about five per cent of the mass had liquefied. This liquid was decanted off and the procedure repeated three times. The remaining phosphine, which was still a liquid containing some fine needles, was found to be analytically pure and so no further purification

steps were required. (Found: C, 77.99; H, 14.02.  $(C_8H_{17})_3P$  requires: C, 77.77; H, 13.87%).

(iii) Tricyclohexylphosphine.

The tricyclohexylphosphine (Geigy (U.K.) Limited) was very impure and was recrystallised several times from dry A.R. acetone, under an atmosphere of nitrogen. The pale crystals were filtered off in the dry box and washed with a small volume of cold acetone. M.p.  $80-81^{\circ}$ . (Found: C, 77.20; H, 12.17.  $(C_6H_{11})_3P$  requires: C, 77.09; H, 11.86%).

### III. PREPARATIONS OF HALOGEN-ALKYL PHOSPHINE ADDUCTS.

#### Preliminary Note.

All the procedures described in the following preparations were performed in the nitrogen filled dry-box. These included the preparation of solutions, mixing of reactants, filtering and drying. The trays which contained the phosphorus pentoxide were regularly replaced. When a prepared adduct was to be removed from the dry-box, so that it could be pumped on the vacuum line, it was done so in a rounded-off B.34 cone which held a small sample tube containing the adduct. The B.34 socket cap contained a greased tap and a B.19 cone which attached directly to the vacuum line. The apparatus was of suitable size to facilitate entry to the dry-box.

Melting point determinations were carried out in sealed tubes which had been stored in the dry-box. Melting points of many of the crystalline compounds were diffuse, due to decomposition at elevated temperature, but reproducible within a few degrees and therefore characteristic of the compounds without indicating their purity.

(1) Preparation of Halogen-Tri(n-butyl)phosphine Adducts

(i)  $\text{Br}_2-(\text{C}_4\text{H}_9)_3\text{P}$

Mole ratio  $\text{Br}_2:(\text{C}_4\text{H}_9)_3\text{P} = 0.5:1$ . Bromine (0.266 g) was dissolved in methyl cyanide (3ml) and added dropwise to tri(n-butyl)phosphine (0.678 g) suspended in the same solvent (3 ml). The bromine was decolourised as it was added and dense white fumes evolved. Addition of anhydrous ether to the colourless solution precipitated a waxy, white solid which was filtered off, washed with ether and pumped to dry. M.p. 186-190°.

Mole ratio  $\text{Br}_2:(\text{C}_4\text{H}_9)_3\text{P} = 1:1$ . Bromine (0.347 g), dissolved in methyl cyanide (4 ml), was added dropwise, with shaking, to a suspension of tri(n-butyl)phosphine (0.442 g) in methyl cyanide (2 ml). Dense white fumes were evolved and when the addition was complete a colourless solution remained. Addition of anhydrous ether yielded a waxy, white solid which after filtering off and washing with ether was pumped on the vacuum line for several hours. M.p. 184-190° decomp. (Found: C, 40.82; H, 7.96; Br, 42.96.  $\text{C}_{12}\text{H}_{27}\text{PBr}_2$  requires: C, 39.80; H, 7.53; Br, 44.13%).

Mole ratio  $\text{Br}_2:(\text{C}_4\text{H}_9)_3\text{P} = 2:1$ . Bromine (0.833 g) was dissolved in methyl cyanide (4 ml) and added, as in the above reaction, to a suspension of the phosphine (0.413 g) in methyl cyanide (4 ml). Addition of anhydrous ether, carbon tetrachloride and chloroform to portions of the resultant orange solution failed to precipitate a

product. The remaining orange solution was freeze dried on the vacuum line to remove the solvent and, after pumping to remove the last traces of methyl cyanide, an orange semi-solid remained. (Found: C, 28.91; H, 5.52; Br, 57.87.  $C_{12}H_{27}PBr_4$  requires: C, 27.61; H, 5.22; Br, 61.24%). It would appear that in pumping to remove the last traces of solvent, which was quite tightly held, the unstable tetrabromide lost halogen. This was substantiated by observation of an orange colouration in the sludge trap.

(ii)  $I_2-(C_4H_9)_3P$ .

Mole Ratio  $I_2:(C_4H_9)_3P = 0.5:1$ . Solid crystalline iodine (0.283 g) was added directly to a suspension of tri(n-butyl)phosphine (0.452 g) in methyl cyanide (4 ml). After addition was complete a sticky, white solid remained in the pale yellow mother liquor. The solid was filtered off, well washed with anhydrous ether and allowed to stand in an open sample tube next to a tray of fresh phosphorus pentoxide for fifteen minutes to dry. M.p. 190-195°. (Found: C, 32.33; H, 6.37.  $C_{12}H_{27}PI_2$  requires: C, 31.60; H, 5.92%).

Mole Ratio  $I_2:(C_4H_9)_3P = 1:1$ . Solid crystalline iodine (0.648 g) was added, as in the above reaction, to a suspension of the phosphine (0.517 g) in methyl cyanide (5 ml). Initially a white solid was formed and when approximately three quarters of the iodine had been added it was necessary to add more methyl cyanide (5 ml) because the whole mass had turned almost completely solid. The iodine addition

was then completed. The pale solid which remained was filtered off and washed and dried as in the above reaction. M.p. 190-195°.

(Found: C, 31.57; H, 6.33; I, 56.53.  $C_{12}H_{27}PI_2$  requires: C, 31.60; H, 5.92; I, 55.65%).

Mole ratio  $I_2:(C_4H_9)_3P = 2:1$ . As in the previous two reactions solid iodine (1.201 g) was added directly to the phosphine (0.416 g) which was suspended in methyl cyanide (8 ml) to give a resultant dark solution. When anhydrous ether was added to this dark solution and the mixture cooled in the refrigerator for several days, reddish-brown needles crystallised out. However on the attainment of room temperature the crystals had changed to a dark oil, indicating the product to be a low melting solid. The liquid was decanted off to leave the dark oil which was then pumped under vacuum to remove the last traces of solvent. (Found: C, 20.22; H, 4.10; I, 69.68.

$C_{12}H_{27}PI_4$  requires: C, 20.28; H, 3.80; I, 71.50%).

(2) Preparation of Halogen-Trioctylphosphine Adducts.

(i)  $\text{Br}_2 \cdot (\text{C}_8\text{H}_{17})_3\text{P}$

Mole ratio  $\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P} = 0.5:1$ . Bromine (0.092 g), dissolved in methyl cyanide (1 ml), was added dropwise to a suspension of trioctylphosphine (0.424 g) in methyl cyanide (5 ml), the flask containing the phosphine being shaken as the halogen was added. After decanting the resultant colourless solution from a little unreacted phosphine, anhydrous ether was added to a portion of the solution in an attempt to precipitate a product, but this proved unsuccessful. The remaining solution was freeze dried to leave a waxy, white solid which, after filtering off and washing with anhydrous ether, was immediately transferred to a tightly stoppered sample tube. The solid appeared quite stable in the stoppered sample tube but the portion remaining in the sintered filter funnel rapidly decomposed to a colourless oil in the nitrogen filled dry-box. The product was analysed immediately. M.p. 150-155° decomp. (Found: C, 53.80; H, 10.57.  $\text{C}_{24}\text{H}_{51}\text{PBr}_2$  requires: C, 54.34; H, 9.69%).

Mole ratio  $\text{Br}_2 : (\text{C}_8\text{H}_{17})_3\text{P} = 1:1$ . A solution of bromine (0.190 g) in methyl cyanide (2 ml) was added, as in the above reaction, to a suspension of the phosphine (0.426 g) in methyl cyanide (5 ml). The resultant pale orange solution was freeze dried, to remove the solvent, and a fawn coloured solid remained. This solid was washed with anhydrous ether and filtered, followed by a further washing with ether;

the solid was now white. As before, it was rapidly transferred to a small sample tube which was then tightly stoppered. Analysis was carried out immediately. M.p. 150-158<sup>o</sup> decomp. (Found: C, 53.89; H, 10.13; Br, 29.52.  $C_{24}H_{51}PBr_2$  requires: C, 54.34; H, 9.69; Br, 30.13%).

Mole ratio  $Br_2:(C_8H_{17})_3P = 2:1$ . An excess of bromine (0.339 g), dissolved in methyl cyanide (3 ml), was added, as in the above reactions, to the phosphine (0.393 g) which was suspended in the same solvent (3 ml). An orange solution resulted from which no solid could be isolated on the addition of the previously mentioned non-polar solvents to separate portions of the solution. On freeze drying the remaining solution it was observed that when most of the solvent had been removed, and the flask was still cold, an orange crystalline solid was present. However, after the complete removal of methyl cyanide and attainment of room temperature, only a mobile orange oil remained. This oil was pumped for a short time before immediate analysis. (Found: C, 42.50; H, 8.00; Br, 44.22.  $C_{24}H_{51}PBr_4$  requires: C, 41.76; H, 7.45; Br, 46.31%). From the analysis, and presence of bromine in the sludge trap, to remove all traces of solvent results in the loss of some bromine from the unstable adduct.

(ii)  $I_2-(C_8H_{17})_3P$

Mole ratio  $I_2:(C_8H_{17})_3P = 0.5:1$ . To trioctylphosphine (0.356 g), suspended in methyl cyanide (5 ml), was added a solution containing

iodine (0.122 g) in the same solvent (10 ml). After vigorous shaking (using a mechanical shaker) a very pale yellow solution resulted and when the solvent was removed by freeze drying, a sticky, pale yellow solid remained. The solid was washed with anhydrous ether, which extracted the colour, and the finely divided white solid was filtered and washed in the usual manner. The product was very unstable and even before it could be transferred to a sample tube it had started to darken. After pumping on the vacuum line the solid was analysed immediately. (Found: C, 46.95; H, 8.91.  $C_{24}H_{51}PI_2$  requires: C, 46.16; H, 8.23%).

Mole ratio  $I_2:(C_8H_{17})_3P = 1:1$ . To a suspension of the phosphine (0.472 g) in methyl cyanide (11 ml) was added solid crystalline iodine (0.320 g) and the mixture mechanically shaken overnight. A red solution resulted from which a pale solid was obtained after the removal of approximately half the volume of solvent on the vacuum line. After filtering and thorough washing with anhydrous ether, the pale 'off-white' solid was transferred to a sample tube and tightly stoppered. Again, it was very unstable and darkened immediately it was exposed, even in the atmosphere of the dry-box. M.p. 155-165<sup>o</sup> decomp. (Found: C, 46.43; H, 8.34; I, 41.12.  $C_{24}H_{51}PI_2$  requires: C, 46.16; H, 8.23; I, 40.64%).

Mole ratio  $I_2:(C_8H_{17})_3P = 1.5:1$ . Iodine (0.517 g) was added, as in the above reaction, to the phosphine (0.503 g) which was suspended in methyl cyanide (7 ml). After shaking overnight, a dark red

solution resulted from which a dark, very viscous oil separated on cooling. The supernatant liquid was decanted off and last traces of solvent were removed on the vacuum line. A dark red semi-solid remained which was further pumped for thirty minutes before analysis. (Found: C, 38.67; H, 6.83; I, 48.96.  $C_{24}H_{51}PI_3$  requires: C, 38.37; H, 6.84; I, 50.67%).

Mole ratio  $I_2:(C_8H_{17})_3P = 2:1$ . A slight excess of iodine (0.619 g) was added to a suspension of the phosphine (0.446 g) in methyl cyanide (7 ml), exactly as in the previous two reactions. The reddish-brown solution which resulted after shaking overnight was cooled to precipitate a mobile dark oil. This oil was treated similarly to the product from the above reaction. (Found: C, 32.01; H, 5.98; I, 56.91.  $C_{24}H_{51}PI_4$  requires: C, 32.82; H, 5.85; I, 57.80%).

(iii)  $I\text{Br}-(C_8H_{17})_3P$

Mole ratio  $I\text{Br}:(C_8H_{17})_3P = 1:1$ . A slight excess of iodine monobromide (0.330 g), dissolved in methyl cyanide (3.5 ml), was added to a suspension of trioctylphosphine (0.575 g) in the same solvent (3 ml). A red solution resulted after shaking the mixture for one hour. A sticky, brown solid remained when the solvent was removed by freeze drying. Shaking with anhydrous ether extracted most of the colour from the solid but it appeared to be slowly dissolving and so the ether was quickly decanted off. This procedure was repeated after which the now pale yellow solid was transferred to a sample tube

and pumped on the vacuum line for one hour. As in the previous 1:1 reactions, the dihalide isolated was very unstable and rapidly decomposed when removed from the tightly stoppered sample tube. M.p. 130-140° decomp. (Found: C, 49.98; H, 9.01; total halogen, 1.93 moles.  $C_{24}H_{51}PIBr$  requires: C, 49.92; H, 8.90%; total halogen 2.00 moles).

Note: Individual iodine and bromine percentages are not quoted since in the mixed halide potentiometric determinations co-precipitation of bromide and iodide occurred resulting in high iodine and low bromine values. However a total halogen analysis based on the total number of moles present per formula unit could be accurately calculated, and it is these values which are quoted for the mixed halide determinations of the iodine monobromide adducts of both the trioctylphosphine and tricyclohexylphosphine systems.

Mole ratio  $I Br : (C_8H_{17})_3P = 2:1$ . An excess of iodine monobromide (0.717 g), dissolved in methyl cyanide (5 ml), was added directly to the phosphine (0.647 g) and the mixture thoroughly shaken as before. Complete solution was obtained and after standing in the dry-box for two days, the solvent was slowly removed by freeze drying. It was observed that crystallisation took place below 0° when most of the solvent had been removed. However on reaching room temperature the dark crystals had changed to a deep red oil and so the remainder of the solvent was removed, after which the oil was pumped on the vacuum line for two hours. (Found: C, 36.23; H, 6.83; total halogen, 3.90.  $C_{24}H_{51}PI_2Br_2$  requires: C, 36.75; H, 6.56%; total halogen, 4.00).

(3) Preparation of Halogen-Tricyclohexylphosphine Adducts.

(i)  $\text{Br}_2 \cdot (\text{C}_6\text{H}_{11})_3\text{P}$ .

Mole ratio  $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P} = 0.5:1$ . Bromine (0.059 g), dissolved in methyl cyanide (1 ml), was added dropwise, with shaking, to a suspension of tricyclohexylphosphine (0.204 g) in methyl cyanide (6 ml). The bromine was decolourised as it was added and when addition was complete a pale yellow solid remained in the colourless mother liquor. After shaking overnight the solid was filtered, well washed with anhydrous ether, transferred to a sample tube and dried by leaving the open sample tube next to a dish of phosphorus pentoxide for one hour. M.p.  $245-247^\circ$ . (Found: C, 49.98; H, 7.86; N, 2.24.  $\text{C}_{20}\text{H}_{36}\text{NPBr}_2$  requires: C, 49.91; H, 7.54; N, 2.91%).

i.e. Compound is  $[(\text{C}_6\text{H}_{11})_3\text{PBr}_2] \cdot \text{CH}_3\text{CN}$ .

When more anhydrous ether was added to the filtrate a white, finely crystalline solid precipitated. This solid was treated as above. M.p.  $234-240^\circ$ . (Found: C, 49.37; H, 8.09.  $\text{C}_{18}\text{H}_{33}\text{PBr}_2$  requires: C, 49.11; H, 7.56%).

Mole ratio  $\text{Br}_2 : (\text{C}_6\text{H}_{11})_3\text{P} = 1:1$ . The preparative procedure was exactly as in the above reaction. The phosphine (0.202 g) was suspended in methyl cyanide (7 ml) and the bromine (0.117 g) was dissolved in the same solvent (1 ml). A pale yellow solid remained in the light orange mother liquor. The solid was filtered, washed and dried as in the above reaction. M.p.  $240-245^\circ$ . (Found: C, 49.78; H, 7.89; N, 2.71;

Br, 33.26.  $C_{20}H_{36}NPBr_2$  requires: C, 49.91; H, 7.54; N, 2.91; Br, 33.21%).

A white, finely crystalline solid separated out when anhydrous ether was added to the filtrate. M.p. 241-242<sup>o</sup>. (Found: C, 49.49; H, 7.70; Br, 36.11.  $C_{18}H_{33}PBr_2$  requires: C, 49.11; H, 7.56; Br, 36.30%).

i.e. The compound is  $(C_6H_{11})_3PBr_2$

Mole ratio  $Br_2:(C_6H_{11})_3P = 2:1$ . To a suspension of the phosphine (0.206 g) in methyl cyanide (8 ml) was added a solution of bromine (0.237 g) in the same solvent (2 ml). On prolonged shaking all the phosphine dissolved to leave a clear orange solution. Addition of anhydrous ether precipitated pale orange crystals which were filtered, washed and dried as before. M.p. 156-157<sup>o</sup>. (Found: C, 35.69; H, 5.56; Br, 53.63.  $C_{18}H_{33}PBr_4$  requires: C, 36.03; H, 5.54; Br, 53.27%).

Mole ratio  $Br_2:(C_6H_{11})_3P = 3:1$ . Several attempts were made to prepare the 3:1 adduct, all of which resulted in the isolation of the tetrabromide.

Mole ratio  $Br_2:(C_6H_{11})_3P = 4:1$ . A dark bromine coloured solution resulted when bromine (0.420 g), dissolved in methyl cyanide (3 ml), was added to a suspension of the phosphine (0.183 g) in the same solvent (1 ml). The solvent was slowly evaporated in the dry-box and gradually dark orange chunks began to separate out. From experience

gained from the previous reaction, addition of ether or washing the crystals with ether, would only have resulted in the formation of the tetrabromide and so the orange chunks were filtered but not washed. They were dried as before. M.p. 68-75°. (Found: C, 25.20; H, 4.05.  $C_{18}H_{33}PBr_8$  requires: C, 23.51; H, 3.62%.  $C_{18}H_{33}PBr_6$  requires: C, 28.45; H, 4.38%).

The adduct isolated is obviously the unstable octahalide which has lost some bromine during the drying process. A sample was exposed to the atmosphere of the nitrogen filled dry-box when it lightened considerably in colour, and after two days a further melting point and analysis were performed. M.p. 150-152°. (Found: C, 36.00; H, 5.81.  $C_{18}H_{33}PBr_4$  requires: C, 36.03; H, 5.54%).

(ii)  $I_2-(C_6H_{11})_3P$ .

Mole ratio  $I_2:(C_6H_{11})_3P = 0.5:1$ . Iodine (0.064 g), dissolved in methyl cyanide (4 ml), was added dropwise to a suspension of tri-cyclohexylphosphine (0.137 g) in methyl cyanide (1 ml) and the flask placed on the mechanical shaker overnight. A very pale yellow solid, of obvious different crystalline form to that of the starting phosphine, remained in the colourless mother liquor. After filtering and thorough washing with anhydrous ether, the pale solid was dried by standing in an open sample tube next to a dish containing phosphorus pentoxide for one hour. M.p. 265-270°. (Found: C, 41.55; H, 6.46; N, 2.84.  $C_{20}H_{36}NPI_2$  requires: C, 41.75; H, 6.31; N, 2.44%).

The unsolvated diiodide could not be isolated.

Mole ratio  $I_2:(C_6H_{11})_3P = 1:1$ . The reaction was performed in a similar manner as described above. Iodine (0.090 g) was dissolved in methyl cyanide (5 ml) and the phosphine (0.097 g) was suspended in the same solvent (1 ml). The mother liquor was deep red and the solid isolated a buff colour. M.p. 260-265°. (Found: C, 42.50; H, 6.44; N, 2.26; I, 43.07.  $C_{20}H_{36}NPI_2$  requires: C, 41.75; H, 6.31; N, 2.44; I, 44.12%).

Again, this was the only adduct isolated from the reaction.

Mole ratio  $I_2:(C_6H_{11})_3P = 2:1$ . When a solution of iodine (0.213 g) in methyl cyanide (5 ml) was added to a suspension of the phosphine (0.117 g) in the same solvent and the mixture shaken overnight, a dark brown, finely crystalline material remained in the iodine coloured mother liquor. This solid when washed with anhydrous ether lightened considerably. It was dried as before. M.p. 204-206°. (Found: C, 27.75; H, 4.36; I, 62.03.  $C_{18}H_{33}PI_4$  requires: C, 27.44; H, 4.22; I, 64.42%).

Mole ratio  $I_2:(C_6H_{11})_3P = 3:1$ . Iodine (0.245 g), dissolved in methyl cyanide (5 ml), was added as in previous reactions, to a suspension of the phosphine (0.090 g) in methyl cyanide (1 ml). After shaking, a greenish-black crystalline solid was present in the dark solution. This solid was filtered but not washed since it had earlier been shown that washing with anhydrous ether removed halogen to form the more stable tetraiodide adduct. It was then pumped on the vacuum line for three hours after which it appeared to have lost its greenish appearance and was now almost black. However, the melting

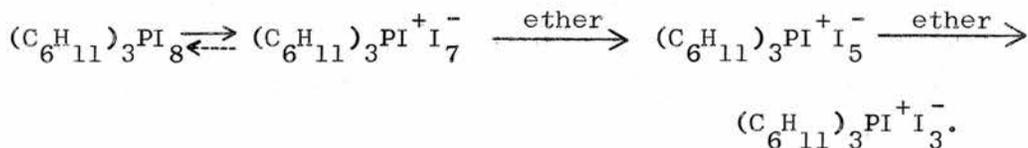
point before and after pumping did not change. M.p. 136-138°.

(Found: C, 19.60; H, 3.04; I, 74.09.  $C_{18}H_{33}PI_6$  requires: C, 20.75; H, 3.19; I, 73.09%).

Mole ratio  $I_2:(C_6H_{11})_3P = 4:1$ . Solution was not obtained on the addition of iodine (0.263 g), dissolved in methyl cyanide (6 ml), to a suspension of the phosphine (0.072 g) in the same solvent (3 ml). After shaking overnight, a dark green, finely crystalline solid remained which was filtered and dried by standing in an open sample tube next to a tray containing phosphorus pentoxide, for one hour. M.p. 150-155°. (Found: C, 17.22; H, 2.74; I, 76.28.  $C_{18}H_{33}PI_8$  requires: C, 16.69; H, 2.57; I, 78.36%).

Extraction of  $(C_6H_{11})_3PI_8$  with anhydrous ether.

A sample of the dark green octaiodide was shaken with successive portions of anhydrous ether, within the dry-box, until the ether washings were colourless. A light brown solid remained which was subsequently shown to be the tetraiodide. The ether must extract iodine in the following manner:



(iii)  $I\text{Br}-(C_6H_{11})_3P$ .

Mole ratio  $I\text{Br}:(C_6H_{11})_3P = 0.5:1$ . To a suspension of tricyclohexylphosphine (0.075 g), in methyl cyanide (4 ml), was added a solution

containing iodine monobromide (0.030 g) dissolved in methyl cyanide (1 ml). After shaking overnight, a finely divided white solid remained in the colourless mother liquor. The white solid was filtered, washed and dried in the usual manner. M.p. 230-232<sup>o</sup>. (Found: C, 44.49; H, 7.02; N, 2.81.  $C_{20}H_{36}NPIBr$  requires: C, 45.47; H, 6.87; N, 2.65%).

This was the only adduct isolated from the reaction.

Mole ratio IBr:( $C_6H_{11}$ )<sub>3</sub>P = 1:1. Iodine monobromide (0.073 g), dissolved in methyl cyanide (2 ml), and tricyclohexylphosphine (0.098 g), suspended in the same solvent (4 ml), were reacted as in the above preparation. The pale, almost white, solid which remained after shaking was filtered, washed and dried as before. M.p. 238-240<sup>o</sup>. (Found: C, 45.13; H, 7.15; N, 2.65; total halogen, 2.00.  $C_{20}H_{36}NPIBr$  requires: C, 45.47; H, 6.87; N, 2.65%; total halogen, 2.00).

Mole ratio IBr:( $C_6H_{11}$ )<sub>3</sub>P = 2:1. To a suspension of the phosphine (0.088 g), in methyl cyanide (3 ml), was added as before, a solution of iodine monobromide (0.134 g) dissolved in methyl cyanide (3 ml). After shaking overnight a dark reddish-brown solution remained which, when treated with anhydrous ether, precipitated dark orange needles. These were filtered, washed and dried in the usual manner. M.p. 132-133<sup>o</sup>. (Found: C, 31.17; H, 5.02; total halogen, 3.94.  $C_{18}H_{33}PI_2Br_2$  requires: C, 31.15; H, 4.79%; total halogen, 4.00).

Mole ratio IBr:( $C_6H_{11}$ )<sub>3</sub>P = 3:1. Iodine monobromide (0.280 g), dissolved in methyl cyanide (3 ml), and the phosphine (0.123 g), suspended in the

same solvent (5 ml), were reacted as in the previous reactions. A crystalline solid was present in the dark mother liquor and when filtered was observed to be reddish-brown in colour. It was dried as before. M.p. 111-113°. (Found: C, 24.66; H, 3.95; total halogen, 5.46.  $C_{18}H_{33}PI_3Br_3$  requires: C, 24.01; H, 3.69%; total halogen, 6.00).

Mole ratio  $IBr:(C_6H_{11})_3P = 4:1$ . The phosphine (0.094 g), suspended in methyl cyanide (3 ml), and iodine monobromide (0.290 g), dissolved in methyl cyanide (5 ml), were reacted and the mixture shaken overnight. Finely divided, dark crystals remained on the sides of the flask but in relatively small bulk. These were scraped off, filtered and dried. The crystals were almost black in colour but had a slight violet tinge to them. M.p. 123-124°. (Found: C, 19.18; H, 3.10; total halogen, 7.56.  $C_{18}H_{33}PI_4Br_4$  requires: C, 19.52; H, 3.00%; total halogen, 8.00).

To the dark filtrate was added a large volume of anhydrous ether (150 ml) and slowly orange crystals began to separate from solution. After several days these were filtered, washed with ether and dried as usual, by standing in an open sample tube in the dry-box. M.p. 115-117°. (Found: C, 32.97; H, 5.10; total halogen, 3.87.  $C_{18}H_{33}PIBr_3$  requires: C, 33.41; H, 5.14%; total halogen, 4.00).

(iv)  $[(C_6H_{11})_3PIBr] \cdot CH_3CN \cdot I_2$  (Mole ratio = 1:1).

This reaction was carried out in an attempt to complete the series  $(C_6H_{11})_3PBr_4$ ,  $(C_6H_{11})_3PIBr_3$ ,  $(C_6H_{11})_3PI_2Br_2$ ,  $(C_6H_{11})_3PI_3Br$ ,

$(C_6H_{11})_3PI_4$ . (See Results and Discussion).

Iodine (0.068 g), dissolved in methyl cyanide (3 ml), was added as in the previous reactions, to a suspension of  $[(C_6H_{11})_3PIBr] \cdot CH_3CN$  (0.141 g), in the same solvent (2 ml), and the mixture shaken overnight. A finely divided, brown solid remained which was filtered off in the dry-box and dried in the usual way without washing. M.p. 185-187°. (Found: C, 28.42; H, 4.72; total halogen, 3.90.

$C_{18}H_{33}PI_3Br$  requires: C, 29.18; H, 4.49%; total halogen, 4.00).

(4) Atmospheric Hydrolysis of the Dibromides of Tri(n-butyl)phosphine and Tricyclohexylphosphine.

(i)  $(C_4H_9)_3PBr_2$ .

A sample of tri(n-butyl)phosphine dibromide was exposed to the open atmosphere for two days after which time a clear viscous oil remained. The oil was pumped on the vacuum line for several hours before analysis. The weighing of the sample for analysis, was carried out in an open platinum boat and it was observed that the sample gained weight on the microbalance. It was left on the balance until equilibrium was attained before the final weight reading was taken. (Found: C, 46.17; H, 9.80.  $C_{12}H_{30}O_2PBr$  requires: C, 45.43; H, 9.53%). From this analysis and the infra-red spectral evidence it is believed the compound obtained after the vacuum drying process was the anhydrous hydroxybromide,  $(C_4H_9)_3POHBr$ , which being hygroscopic, picked up a molecule of water of hydration during the weighing process.

(ii)  $(C_6H_{11})_3PBr_2$ .

The procedure described above was repeated on a specimen of tricyclohexylphosphine dibromide and after several days a sticky, yellow solid remained. After pumping on the vacuum line for several hours the sticky solid had become quite dry and easy to work. Again, the sample for analysis was weighed into an open platinum boat. It appeared to be much more stable than the corresponding

tri(n-butyl)phosphine hydrolysis product, but it also gained weight on the microbalance, although very slowly. A fresh sample was then rapidly weighed out and analysed immediately. (Found: C, 56.42; H, 9.36.  $C_{18}H_{34}OPBr$  requires: C, 57.30; H, 9.08%). Therefore the compound is  $(C_6H_{11})_3POHBr$  which is much less hygroscopic than the  $(C_4H_9)_3POHBr$  product. The infra-red spectrum of the anhydrous hydroxybromide, prepared in the dry-box as a nujol mull and protected from moisture by sealing the edges of the plates with sellotape, showed the characteristic strong hydrogen bonding absorption typical of this class of compound. No free -OH absorption could be detected.

APPENDIX TO PART I

APPENDIX TO PART I.

On the initiation of the work of this part of the thesis, the conductometric titration studies of the halogen-tri(n-butyl)phosphine systems were performed with the apparatus which had successfully been used by Harris and co-workers in their studies of halogen-triaryl-phosphine systems. This apparatus was so designed that the titration could be carried out in an atmosphere of dry air, on a small scale, without the solutions coming into contact with tap grease or atmospheric moisture. A description of the apparatus and its operation has been published<sup>45</sup>.

However the halogen-tri(n-butyl)phosphine systems proved too labile for this apparatus, resulting in conductometric titration graphs in which the breaks did not correspond to the adducts isolated from preparations carried out wholly within the dry-box. It would appear then, that dry air was not a sufficiently inert atmosphere for halogen-alkyl phosphine conductometric titration studies. The titrations were repeated several times using both methyl cyanide and nitrobenzene as solvents, but in all cases the results were unsatisfactory. It should also be noted that the solid adducts isolated from the above system proved to be very unstable to both moisture and oxygen and so it was decided to carry out a solid iodine-tri(n-butyl)phosphine titration in the nitrogen filled dry-box, by adding weighed samples of iodine to the phosphine solution contained in a B.24 round bottomed tube which held the platinum electrodes. A

totally different titration graph was obtained in this experiment and the results agreed with the adducts isolated from this system; breaks at 1:1 and 2:1 ratios were observed on the resultant graph. Therefore it was shown to be essential that a system be devised whereby all the conductometric titration studies of halogen-alkyl phosphine systems could be carried out in the dry-box. The apparatus is illustrated in Figure IX and described below.

The phosphine under investigation was dissolved or suspended in approximately 30 ml of methyl cyanide, in the titration vessel A. The vessel was weighed on a top pan balance before and after addition of methyl cyanide and from this weight an accurate volume of solvent could be calculated ( $\pm 0.01$  g). The vessel A was of such a size that it could be taken in and out of the dry-box with ease. In the cases where the phosphines were liquids, accurate weights ( $\pm 0.0005$  g) could be added to the solvent using a weight pipette. When the phosphine was solid, it was weighed directly into the empty vessel A before addition of solvent.

The halogen solutions were prepared so that addition of 3 ml of solution gave approximately a 1:1 mole ratio of halogen to phosphine. The halogen was dissolved in approximately 15 ml of methyl cyanide, again an accurate volume being calculated from the weight, and transferred to the 10 ml, grade A, burette (greased with halogen resistant 'Kel-F' fluorocarbon grease) with a dropping pipette. Stirring was effected using a P.T.F.E-enclosed magnet driven by a Toyo Magnetic Mini-Stirrer MS/16B. The total height

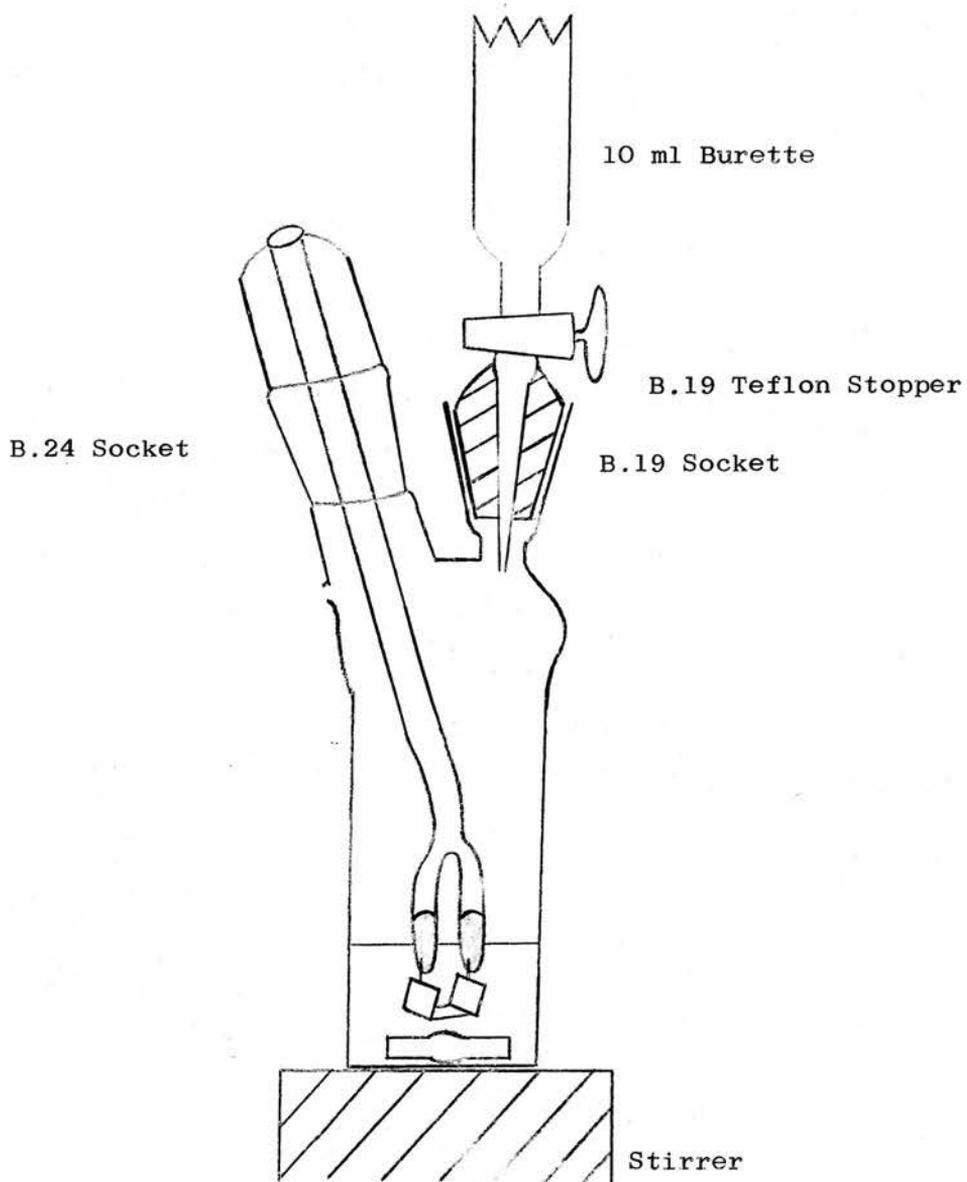


Figure IX: Dry Box Conductometric Titration Apparatus.

of the apparatus with the burette in position was 27 cm (not including the height of the stirrer).

The halogen solution was added from the burette in 0.3 ml aliquots and the solution allowed to attain equilibrium before its specific conductance was measured directly using the bridge previously mentioned in the Experimental Section. When a solid iodine addition titration was to be performed, the aliquots of iodine were added from specially constructed long necked flasks which were weighed before and after addition.

The standard pair of smooth dipping platinum electrodes were angled in such a way that they were situated in the centre of the reaction vessel a few millimetres above the teflon enclosed magnet. Electrical contact from the bridge (which was situated outside the dry-box) to the electrodes was made through a pair of co-axial sockets and a 13-amp switch socket was fitted to the back of the dry-box for mains connection to the stirrer.

Thus, using the apparatus described above, conductometric titrations of the three alkyl phosphines studied could be carried out wholly within a nitrogen filled dry-box, thus eliminating any possibility of hydrolysis due to moisture or air attack.

PART II

THE STABILITY OF SOME POLYHALIDES

INTRODUCTION

## INTRODUCTION

### POLYHALIDES.

#### Classification.

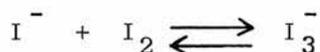
Polyhalides can, according to the number of atoms in their ions, be divided into trihalides, pentahalides, heptahalides etc. They are complexes of halogen atoms which contain negatively charged polyhalide ions. In most cases it is clear from the formulas that the polyhalide ion must contain an even number of electrons; the lowest possible formula weight of the polyhalide ion contains an odd number of atoms and hence, because of its charge, an even number of electrons. Only the formulas of the group of "even" polyhalides, such as  $\text{CsI}_4$  and  $\text{N}(\text{CH}_3)_4\text{I}_{10}^-$ , do not allow this conclusion to be drawn. On the contrary, if the ion in, say,  $\text{CsI}_4$  had the formula  $\text{I}_4^-$ , the number of electrons would be odd, and the substance would be paramagnetic. From the diamagnetism of this compound it can be concluded that the formula should at least be doubled<sup>46</sup>. The result of the structure determination of  $\text{CsI}_4$  shows indeed, that  $\text{I}_4^-$  complexes do not occur in this substance, but that instead planar  $\text{I}_8^{=}$  complexes may be distinguished<sup>47</sup>. The compound is built from two triiodide ions bridged by an iodine molecule.

#### Preparations and Reactions.

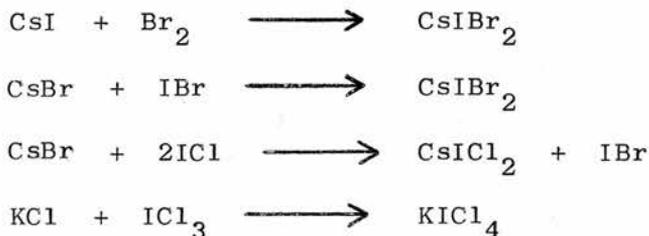
In spite of their unusual composition many of the polyhalides

are easily prepared; some of them have been known as long as the halogens themselves. In fact the first crystalline polyhalide, strychnine triiodide, was prepared by Pelletier and Caventou in 1819<sup>48</sup>. Polyhalide formation appears to be restricted to cases where a large cation, such as an alkali metal ion, an alkaline earth metal ion, a coordination complex such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , or an organic base like an alkaloid or a quaternary ammonium ion is present, and it is more characteristic of iodides than of any of the other halides. These restrictions are of course more rigidly applicable to solid materials than to those existing in solution.

It has been known for many years that iodine, which is only very slightly soluble in water, readily dissolves in solutions of iodides because of the formation of triiodide,



This is not an isolated phenomenon<sup>49</sup>. The ability of halide ions, either in solution or in solid salts, to associate with molecular halogens or interhalogen compounds to yield univalent ions containing an abundance of halogen has been recognised for many years, particularly since the pioneering researches of Wells and his co-workers<sup>50-55</sup>. The literature on this subject is extensive, the best general reference being Gmelin's Handbuch<sup>56</sup>. The following are some typical examples of the preparations of polyhalides analogous to the formation of triiodide described above:



Often the crystalline polyhalides can be obtained from solution by the evaporation of solvent or by cooling. Also, reactions between gaseous halogen or interhalogen and solid monohalides, in the absence of solvent, can be successfully used for preparing many crystalline polyhalides. As regards the solid polyhalides, Grace<sup>57</sup> noticed that in such ionic crystals the greatest thermal stability results when anion and cation approach each other in size. If polyiodides are considered, then, it is apparent only cations which are large in their own right, e.g.,  $\text{Cs}^+$  and  $(\text{C}_2\text{H}_5)_4\text{N}^+$ , or are made large by solvation, e.g., with water or benzene, should form stable compounds with ions such as  $\text{I}_3^-$  and  $\text{I}_7^-$ . That this is true is evidenced by the formulas for typical solid polyhalides given in Table XIII<sup>58</sup>.

### Properties.

Dissociation is perhaps the most characteristic property of polyhalide ions. All polyhalides decompose to some extent into a halogen or interhalogen compound and a lower halide. In many cases (e.g.  $\text{CsI}_2\text{Br}$ ) the dissociation pressure is already appreciable at room temperature. The chemical reactions of the polyhalides are

TABLE XIII.

| TYPICAL SOLID POLYHALIDES        |                      |                   |
|----------------------------------|----------------------|-------------------|
| Type $X_n^-$                     | Type $XX'_n^-$       | Type $XX'X''_n^-$ |
| $NaI_3 \cdot 2H_2O$              | $NH_4IBr_2$          | $CsFIBr$          |
| $KI_3 \cdot H_2O$                | $KICl_2$             | $RbFICl_3$        |
| $NH_4I_3 \cdot 3H_2O$            | $RbIBr_2$            | $CsFICl_3$        |
| $RbI_3$                          | $RbICl_2$            | $KClIBr$          |
| $CsI_3$                          | $RbBrCl_2$           | $RbClIBr$         |
| $CsI_4$                          | $CsICl_2$            | $CsClIBr$         |
| $NH_4I_5 \cdot H_2O$             | $CsBrCl_2$           |                   |
| $KI_7 \cdot H_2O$                | $CsClBr_2$           |                   |
| $RbI_7 \cdot H_2O$               | $(CH_3)_3NHIBr_2$    |                   |
| $RbBr_3$                         | $(CH_3)_4NIBr_2$     |                   |
| $CsBr_3$                         | $C_5H_5NHIBr_2$      |                   |
| $(CH_3)_4NI_9$                   | $C_5H_5NCH_3IBr_2$   |                   |
| $(C_2H_5)_4NI_7$                 | $HICl_4 \cdot 4H_2O$ |                   |
| $KI_9 \cdot 3C_6H_6$             | $KIF_6$              |                   |
| $RbI_9 \cdot 2C_6H_6$            |                      |                   |
| $CsI_9 \cdot 1\frac{1}{2}C_6H_6$ |                      |                   |

mostly those of the dissociation products. The tendency of the polyhalide to dissociate into monohalides and halogen or halogen halide has a considerable influence on their reactions in the absence of a solvent. Although some of the reactions are apparently due to the reactivity of the polyhalide compound, in many cases the

reacting substance is really one of the products of dissociation usually the halogen or halogen halide and, when the polyhalide reacts with another solid, one may be reasonably certain that reaction occurs through the vapour phase. When a gas acts on a solid polyhalide, however, both types of reaction are possible; reaction by way of the dissociation products being most frequent in the case of compounds of high dissociation pressure.

The existence of polyhalide ions in solutions of the polyhalides in polar solvents has been adequately proved for all trihalide ions consisting of iodine, bromine and/or chlorine atoms. The evidence has been obtained from measurement of freezing point depressions, electrical conductivities, distribution equilibria with non-polar solvents, absorption spectra, exchange of radioactive isotopes between halide ions and halogen molecules, oxidation-reduction potentials, and reactions of the polyhalide ions in solution<sup>59</sup>.

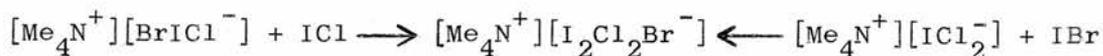
For the more complex polyhalides only the existence of  $\text{ICl}_4^-$  in solution has been established; other polyhalide ions probably exist in concentrated solutions, but their composition is not certain.

#### Stability of the Polyhalides.

It has been pointed out that the polyhalides are generally not stable with respect to dissociation into a monohalide and halogen or interhalogen compound. It is found that the dissociation

always takes place in such a way that the halogen or interhalogen molecules formed contain the heaviest halogen atoms. For instance,  $\text{CsICl}_2$  dissociates into  $\text{CsCl} + \text{ICl}$  and not into  $\text{CsI} + \text{Cl}_2$ . Similarly, in solution the  $\text{ICl}_2^-$  ion dissociates into  $\text{Cl}^-$  and  $\text{ICl}$ , and the  $\text{ICl}_4^-$  ion into  $\text{ICl}_2^- + \text{Cl}_2$ .

Considering briefly the reverse process, Cremer and Duncan<sup>60</sup> observed that while it was possible to add a halogen molecule to a trihalide ion, such as  $\text{ICl}_2^- + \text{Cl}_2 \longrightarrow \text{ICl}_4^-$ , their attempts to add an interhalogen molecule to a polyhalide ion were unsuccessful, e.g.  $\text{ICl}_2^- + \text{ICl} \not\longrightarrow \text{I}_2\text{Cl}_3^-$ . Recently, however, it has been shown that this generalisation is incorrect<sup>61</sup>, and the following reactions have been successfully performed:



It should also be noted that Cornog and Bauer<sup>62</sup> did report a very unstable compound  $\text{KCl} \cdot 2\text{ICl}$  while Ray and Majumdar<sup>63</sup> prepared a fairly stable tetraalkylammonium salt  $(\text{Et})_4\text{NIBrCl}_3$ . In both cases, it seems, new pentahalide ions had been obtained.

The heaviest halogen atom in the given polyhalide ion has always been observed to occupy the central position. Thus  $[\text{I}_2\text{Br}^-]$  is  $[\text{I}-\text{I}-\text{Br}^-]$  and not  $[\text{I}-\text{Br}-\text{I}^-]$ <sup>64</sup>. Similarly, symmetry is important, and it is found that  $\text{IBr}_2^-$  which is  $[\text{Br}-\text{I}-\text{Br}^-]$  is indeed more stable than  $[\text{I}-\text{I}-\text{Br}^-]$ .

A number of attempts have been made to arrange polyhalide ions in order of their stabilities. For the crystalline trihalides stability has been determined by the measurement of the temperature

at which the dissociation pressure reached one atmosphere<sup>65</sup>. When the dissociation pressures of trihalides containing the same trihalide ion but different cations were compared, it appeared that, irrespective of the anion, the stability of a trihalide compound with respect to dissociation is greater when the cation is larger and more symmetrical. This rule was also established by bringing the solid polyhalide into contact with carbon tetrachloride at 25<sup>o</sup>, after which the equilibrium concentration of the halogen or interhalogen in this solvent was measured<sup>66</sup>. From the fact that polyhalides with dipositive or tripositive cations are found to exist only when these cations are very large, it may be inferred that polyhalides are less stable when the charge density on the cation is higher.

A likely possible explanation of the dependence of the stability of a crystalline polyhalide on the nature of its cation is the fact that the lattice energy of the monohalide formed in the dissociation reaction will be large for small, highly charged and symmetrical cations. It is difficult to prove, however, that this will be the dominating factor since the standard free enthalpy of dissociation must also be taken into account in a rigorous treatment of the dissociation process. Even if the influence of the entropy is neglected, the difference between the lattice energies of the different polyhalides considered cannot be expected to be negligible, especially when their crystals are not isomorphous.

The stabilities of trihalides which contain the same cation but different trihalide ions have been compared. These stabilities have been determined from measurements of dissociation pressures as

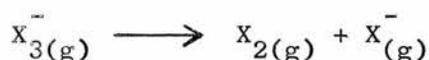
well as from measurements of the equilibrium concentration of the halogen or interhalogen formed in carbon tetrachloride. In this case the order of stability obtained by the two methods was different, which is not surprising, because in the second method the interaction between halogen or interhalogen and the solvent must play a role. Again, a somewhat different order of stability may be expected when the degrees of dissociation of different trihalide ions in solution are compared. The order of stabilities, which have been determined by the three different methods, and the results for trihalides of the same cation are shown in Table XIV<sup>59</sup>.

TABLE XIV: Trihalides of the Same Cation Listed in Order of Decreasing Stability.

| Dissociation pressure <sup>65</sup> | CCl <sub>4</sub> method <sup>66</sup> | Dissociation in H <sub>2</sub> O <sup>67</sup> |
|-------------------------------------|---------------------------------------|--|
| I <sub>3</sub> <sup>-</sup>         | ICl <sub>2</sub> <sup>-</sup>         | I <sub>3</sub> <sup>-</sup>                    |
| IBr <sub>2</sub> <sup>-</sup>       | IBr <sub>2</sub> <sup>-</sup>         | IBr <sub>2</sub> <sup>-</sup>                  |
| ICl <sub>2</sub> <sup>-</sup>       | I <sub>3</sub> <sup>-</sup>           | BrCl <sub>2</sub> <sup>-</sup>                 |
| I <sub>2</sub> Br <sup>-</sup>      | IBrCl <sup>-</sup>                    | ICl <sub>2</sub> <sup>-</sup>                  |
| Br <sub>3</sub> <sup>-</sup>        |                                       | Br <sub>3</sub> <sup>-</sup>                   |
| BrCl <sub>2</sub> <sup>-</sup>      |                                       | I <sub>2</sub> Br <sup>-</sup>                 |
| Br <sub>2</sub> Cl <sup>-</sup>     |                                       | I <sub>2</sub> Cl <sup>-</sup>                 |
|                                     |                                       | Cl <sub>3</sub> <sup>-</sup>                   |

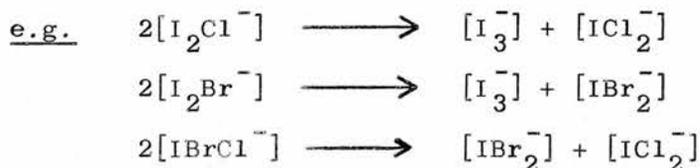
All three methods of determining stability confirm the regularity, already mentioned, that on dissociation the monohalide

formed contains the lightest halogen atom. This regularity may be explained in a way similar to that given for the dependence of the stability on the nature of the cation. It may then be ascribed to the large lattice energy of the monohalide formed when this monohalide contains the small halide ion. Here, however, a further complication arises because, for the different ways of dissociation of the polyhalide which are possible in principle, the halogen or interhalogen formed is also different. Therefore, in addition to lattice energy and entropy changes in the process  $\text{MX}_{3(s)} \longrightarrow \text{MX}_{(s)}$  the energy and entropy change in the reaction,



is also important. An explanation of the dissociation trends of polyhalides in solution may be given along the same lines, if lattice energy is replaced by energy of hydration.

It is of interest to note that the unstable trihalide ions,  $\text{I}_2\text{Cl}^-$ ,  $\text{I}_2\text{Br}^-$ , and  $\text{IBrCl}^-$  are all found to undergo re-organisation reactions (especially in solution),



In this part of the thesis there are three sections, each of which deals with an aspect of polyhalide chemistry. The first section stems from the observation that when one mole of tricyclohexylphosphine and four moles of iodine monobromide are allowed to react the adduct  $(\text{C}_6\text{H}_{11})_3\text{PIBr}_3$ , i.e.  $(\text{C}_6\text{H}_{11})_3\text{PBr}^+\text{IBr}_2^-$ , is formed,

and in interpreting this result it was assumed that an initially formed compound containing  $I_2Br^-$  ion was converted by excess iodine monobromide to the above one containing the  $IBr_2^-$  ion, i.e. the reaction conversion  $I_2Br^- + IBr \longrightarrow IBr_2^- + I_2$  was postulated to have occurred in methyl cyanide. The cations chosen for the series of polyhalides investigated were  $Cs^+$  and  $(C_2H_5)_4N^+$  because of their solubility in methyl cyanide and the stability of the resulting solutions.

The second section describes accurate vapour pressure measurements of caesium polyhalides. Although vapour pressure studies have previously been recorded by Ephraim<sup>65</sup>, it was believed that improvement in the technique of vapour pressure measurement would yield more consistent and reliable data. Confirmation or otherwise of stability orders given by Ephraim could then be made. The vapour pressures were measured using an all glass system, incorporating greaseless taps and a spiral gauge.

In the third section some thermo-analytical studies of polyhalides are described. It was thought worthwhile to investigate the suitability of techniques such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) for stability studies of these compounds since the nature of the dissociation occurring could easily be determined by weight loss measurements. Also it was thought that decomposition temperatures would give a measure of the stability of the polyhalides.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

1. Qualitative Ultra-Violet Spectroscopic Studies of the Reactions of Tetraethylammonium and Caesium Polyhalides with Halogens, in Methyl Cyanide.

Cremer and Duncan<sup>60</sup> have examined the behaviour of certain solid polyhalides towards halogens, in the absence of a solvent and mainly using the gaseous halogen. They conclude that a halogen atom in a polyhalide ion may be replaced by a more electronegative one except that the central atom is not replaceable. Thus chlorine replaces bromine in  $\text{IBr}_2^-$  to give  $\text{ICl}_2^-$  but will not replace iodine. Similarly, bromine converts  $\text{I}_3^-$  to  $\text{IBr}_2^-$  but not to  $\text{Br}_3^-$ .

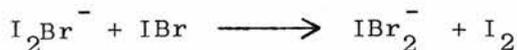
In this chapter the reactions of halogens and interhalogens with the polyhalides tetraethylammonium diiodobromide,  $(\text{C}_2\text{H}_5)_4\text{NI}_2\text{Br}$ , and tetraethylammonium triiodide,  $(\text{C}_2\text{H}_5)_4\text{NI}_3$ , together with the corresponding caesium compounds,  $\text{CsI}_2\text{Br}$  and  $\text{CsI}_3$ , have been studied in methyl cyanide solution to confirm that the conclusions drawn by Cremer and Duncan from solvent-free reactions are applicable to reactions in methyl cyanide. This, as has been mentioned, is of particular relevance to the study of reactions of  $\text{R}_3\text{P}$  compounds with halogens particularly when these are carried out with halogen/phosphine mole ratios exceeding 2:1.

The reaction of the dibromiodides with iodine, bromine and iodine monobromide were studied together with the reactions of the triiodides with bromine and iodine monobromide. It was found that

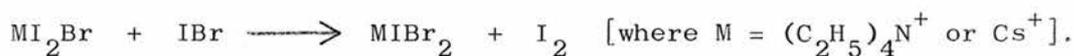
the tetraethylammonium and caesium polyhalides which contained the same anion behaved identically; they will therefore be discussed together.

(i) The reaction of  $(C_2H_5)_4NI_2Br$  and  $CsI_2Br$  with iodine monobromide.

When methyl cyanide solutions of the diiodobromides were reacted with iodine monobromide, also dissolved in methyl cyanide, the ultra-violet spectra of the resultant solutions at the 1:1 mole ratio showed a strong broad absorption band with a maximum at 263  $m\mu$ . This lies between the absorption maxima for the  $I_2Br^-$  and  $IBr_2^-$  ions ( $\lambda_{max} I_2Br^- = 280 m\mu$ ;  $\lambda_{max} IBr_2^- = 256 m\mu$ ), but is closer to the latter. On account of the closeness in absorption maxima of the peaks for the  $IBr_2^-$  and  $I_2Br^-$  ions it would be expected that the spectrum of a solution containing a mixture of these would consist of a broad unresolved peak at a  $\lambda$  value somewhere between the two, the exact position depending on the proportions present<sup>68</sup>. Thus the reaction,



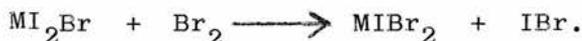
had not gone to completion. However, on addition of a slight excess of the interhalogen the spectra showed only the presence of  $IBr_2^-$  ion. The weak absorption band in the spectra of the  $IBr_2^-$  ion, at 370  $m\mu$ , was difficult to locate due to its being masked by the free iodine formed which strongly absorbs in the visible region of the spectrum at 460  $m\mu$ . The reaction may thus be written,



The solid dibromiodides were isolated from solution in both cases and identified by their U.V. spectra in methyl cyanide.

(ii) The reaction of  $(C_2H_5)_4NI_2Br$  and  $CsI_2Br$  with bromine.

Formation of the dibromiodide compounds was inferred from examination of the ultra-violet spectra of the resultant solutions when the respective diiodobromides were reacted with bromine in the mole ratio of 1:1. The spectra remained unaltered on the addition of a two fold excess of bromine and so the reaction taking place may be written,



The solid products were again isolated and identified as in the previous reaction.

(iii) The reaction of  $(C_2H_5)_4NI_2Br$  and  $CsI_2Br$  with iodine.

Even when a two fold excess of iodine in methyl cyanide was thoroughly mixed with solutions of the diiodobromides, in the same solvent, the main peak in the spectra showed only a very slight shift from that of the  $I_2Br^-$  ion absorption towards the higher wavelengths of the  $I_3^-$  ion. However, this slight shift was definite and the two peaks occurring at 284 and 354  $m\mu$  indicated partial conversion of the  $I_2Br^-$  ion to  $I_3^-$  ion,

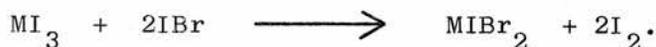


Similarly the solids isolated gave spectra which clearly showed a slight shift towards  $I_3^-$  ion absorption. It must be concluded

from this reaction that in methyl cyanide solution, the equilibrium shown above lies well to the left-hand side.

(iv) The reaction of  $(C_2H_5)_4NI_3$  and  $CsI_3$  with iodine monobromide.

When methyl cyanide solutions of the above triiodides were each thoroughly shaken with iodine monobromide in the ratio of 1:1, the ultra-violet spectra of the resultant solutions showed the presence of a broad peak in the region of 265-270 m $\mu$ . This lies between that of the ions  $I_3^-$  and  $IBr_2^-$ . However when the mole ratio of interhalogen to polyhalide was increased to 2:1, absorption due to  $IBr_2^-$  alone was present. Again there was some difficulty in obtaining the weak absorption band of  $IBr_2^-$  at 370 m $\mu$  because of the free iodine liberated in the reaction. Since the solution appeared to contain  $I_3^-$  ion up to the 2:1 stage the following scheme may be written,



The solid dibromiodides were isolated from solution and identified as before.

(v) The reaction of  $(C_2H_5)_4NI_3$  and  $CsI_3$  with bromine.

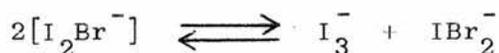
On thorough mixing of 1:1 mixtures of these triiodides with bromine, in methyl cyanide, the ultra-violet spectra of the resultant solutions indicated that partial formation of dibromiodide ion had taken place. The absorption bands were however very broad and had a maximum at about 266 m $\mu$ ; i.e. approximately

10  $\mu$  higher than that of the  $\text{IBr}_2^-$  ion. The presence of other ions was therefore indicated but when the mole ratio was increased to 2:1 by the further addition of bromine solution, only  $\text{IBr}_2^-$  ion absorption could be detected. There was no difficulty in obtaining the weak absorption band at 370  $\mu$  which was indicative of the absence of free iodine and thus the following equation is postulated for the reaction,



The solid dibromiodides were successfully isolated from solution and identified from their U.V. spectra in methyl cyanide.

The conclusions drawn by Cremer and Duncan from their polyhalide-halogen reactions carried out in the absence of a solvent would therefore appear to be paralleled when they are carried out in methyl cyanide. However, there is some indication, in the case of the diiodobromide-iodine reactions, of triiodide ion formation, but only to a very small extent. This being so, it would mean that some displacement of a bromine atom by the less electronegative iodine atom had occurred in solution. The upwards shift in the spectra cannot simply be due to dissociation of the  $\text{I}_2\text{Br}^-$  ion in solution as follows,



because from the wavelengths of the absorption bands of the  $\text{I}_3^-$  and  $\text{IBr}_2^-$  ions and from their relative intensities the net effect, if any, would be to shift the peaks to lower wavelengths, which is the reverse of what is observed.

A number of people have examined the ultra-violet spectra of

polyhalide ions and values of absorption maxima for characteristic peaks recorded. The values found by Popov and Swensen<sup>69</sup>, using methyl cyanide as solvent, are arranged in Table XV.

TABLE XV: Maximum Absorption Characteristics of Polyhalide Ions in Methyl Cyanide.

| Anion                          | Max <sub>1</sub> (mμ) | Max <sub>2</sub> (mμ) |
|--------------------------------|-----------------------|-----------------------|
| I <sub>3</sub> <sup>-</sup>    | 360                   | 291                   |
| I <sub>2</sub> Br <sup>-</sup> | 370                   | 256                   |
| I <sub>2</sub> Br <sup>-</sup> | 351                   | 280                   |
| Br <sub>3</sub> <sup>-</sup>   | 269                   | ...                   |
| ICl <sub>2</sub> <sup>-</sup>  | 336                   | 227                   |
| I <sub>2</sub> Cl <sup>-</sup> | 360                   | 288                   |
| I <sub>2</sub> Cl <sup>-</sup> | 261                   | 227                   |

Some additional reactions of tetraethylammonium polyhalides with iodine and iodine monochloride were carried out since they were of some interest in the general context of reactions of halogen molecules and polyhalide ions.

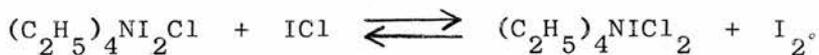
(vi) The reaction of  $(C_2H_5)_4NI_3$  with iodine monochloride.

Since iodine monobromide is capable of brominating triiodide to give dibromiodide it would be expected that iodine monochloride would chlorinate triiodide and form dichloriodide. The ultra-violet spectrum of a methyl cyanide solution containing tetraethylammonium triiodide and iodine monochloride in the mole ratio 1:1 showed only the presence of the  $I_2Cl^-$  ion indicating the following reaction having gone to completion,



On the addition of a further mole of ICl the spectrum contained absorption bands due to both  $I_2Cl^-$  and  $ICl_2^-$  ions and even at the 4:1 mole ratio of interhalogen to polyhalide there was still a considerable amount of  $I_2Cl^-$  ion present. The ultra-violet spectrum of both the 2:1 and 4:1 mixtures, even after shaking overnight, gave absorptions at 228 and 332  $m\mu$  attributable to the  $ICl_2^-$  ion, and also at 260  $m\mu$  due to the  $I_2Cl^-$  ion. The visible spectrum showed free iodine absorption at 460  $m\mu$ . Therefore it must be concluded that with excess iodine monochloride, beyond the 1:1 mole ratio, the following equilibrium reaction is set up and even at the 4:1

ratio there is still some  $(C_2H_5)_4NI_2Cl$  present:



This is a rather surprising result in view of the relative instability of the  $I_2Cl^-$  ion. It should be noted that the only solid product isolated from the 2:1 and 4:1 solutions was the more stable tetraethylammonium dichloroiodide compound,  $(C_2H_5)_4N^+ICl_2^-$ .

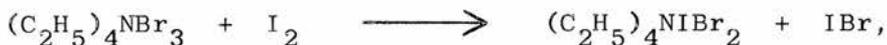
(vii) The reaction of  $(C_2H_5)_4NBr_3$  with iodine.

Moeller<sup>58</sup> states the general rule that in solid state reactions the centre atom of a trihalide ion cannot be replaced by any other halogen atom, even if it is heavier, except in the case of the solid state reaction between the tribromide ion and iodine,



To confirm that the above replacement takes place in methyl cyanide the reaction between tetraethylammonium bromide and iodine was performed.

When tetraethylammonium tribromide and iodine were dissolved in methyl cyanide and thoroughly mixed in the mole ratio of 1:1, the resultant ultra-violet spectrum of the solution contained only  $IBr_2^-$  ion absorption indicative of the following reaction having taken place,



thus confirming that an iodine atom displaces the central bromine



the spectrum being that of the original tetraethylammonium diiodobromide. Even at the 2:1 ratio of halide to polyhalide there was no change in the spectrum. Thus the above reaction did not occur.

(ix) The reaction of  $(C_2H_5)_4NI_3$  with  $(C_2H_5)_4NBr$ .

A similar negative result as in the above reaction was obtained when tetraethylammonium triiodide and bromide were thoroughly mixed in the 1:1 and 1:2 mole ratios, in methyl cyanide solution. That is, no change in the ultra-violet spectra was detected, the spectra being that of the triiodide.

Table XVI summarises the results of the reactions studied in this section.

Table XVI

| REACTANTS                          | PRODUCTS        | COMMENTS  |
|------------------------------------|-----------------|---|
| $MI_2Br + IBr$                     | $IBr_2^- + I_2$ | Reaction complete when slight excess of IBr over the 1:1 ratio was added  |
| $MI_2Br + Br_2$                    | $IBr_2^- + IBr$ | Reaction complete at 1:1 stage  |
| $MI_2Br + I_2$                     | $I_2Br^- + I_2$ | Evidence of small amounts of $I_3^-$ formed, but not to any significant degree  |
| $MI_3 + IBr$                       | $IBr_2^- + I_2$ | Reaction not complete until 2:1 ratio of IBr:MI <sub>3</sub> was reached  |
| $MI_3 + Br_2$                      | $IBr_2^- + IBr$ | Reaction not complete until 2:1 ratio of IBr:MI <sub>3</sub> was reached  |
| $(C_2H_5)_4NI_3 + ICl$             | $I_2Cl^- + I_2$ | Reaction complete at 1:1 stage. With excess ICl, beyond the 1:1 mole ratio, there was distinct evidence of a mixture of $I_2Cl^-$ and $ICl_2^-$ ions in solution, even up to the 4:1 stage. |
| $(C_2H_5)_4NBr_3 + I_2$            | $IBr_2^- + IBr$ | Reaction complete at 1:1 stage  |
| $(C_2H_5)_4NI_2Br + (C_2H_5)_4NBr$ | no reaction     |   |
| $(C_2H_5)_4NI_3 + (C_2H_5)_4NBr$   | no reaction     |   |

[M = Cs<sup>+</sup> or (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>]

## 2. Dissociation Pressure Study.

In view of the fairly ready loss of halogen which generally occurs with solid trihalides,



these compounds exert a partial pressure of halogen at room temperature. It was thought worthwhile to make an accurate dissociation pressure study of a series of caesium trihalides, namely  $\text{CsI}_3$ ,  $\text{CsI}_2\text{Br}$ ,  $\text{CsI}\text{Br}_2$  and  $\text{CsBr}_3$ , from which could be obtained data on the thermodynamic stability of these compounds, and also data on the ease of dissociation of the trihalide ions,



A vapour pressure study of caesium trihalides was carried out by Ephraim<sup>65</sup> in 1917 and from the temperatures at which these compounds exerted a dissociation pressure of one atmosphere, Ephraim constructed an order of stability for the compounds. This was:



The apparatus used by Ephraim was, by present day standards, rather crude and an attempt was made in the present work to improve the measuring system.

The vapour pressure measurements were carried out in an all-glass system, incorporating a sensitive glass spiral null-meter and wide-bore mercury manometers. The dissociation pressure data obtained are given in Tables XVII-XX and illustrated graphically in Figure X.

Table XVII: CsI<sub>3</sub>

| Pressure (mm) | Temperature °K | log p  | $\frac{1}{T}$ |
|---------------|----------------|--------|---------------|
| 8.54          | 354.65         | 0.9315 | 0.002820      |
| 20.70         | 373.15         | 1.3160 | 0.002680      |
| 46.88         | 394.35         | 1.6709 | 0.002536      |
| 95.69         | 414.65         | 1.9809 | 0.002412      |
| 138.68        | 435.15         | 2.1422 | 0.002298      |

Table XVIII: CsI<sub>2</sub>Br

|        |        |        |          |
|--------|--------|--------|----------|
| 22.77  | 297.95 | 1.3574 | 0.003356 |
| 53.23  | 313.15 | 1.7261 | 0.003193 |
| 142.65 | 334.15 | 2.1544 | 0.002993 |
| 212.94 | 343.95 | 2.3281 | 0.002907 |
| 346.41 | 356.15 | 2.5395 | 0.002808 |
| 447.81 | 363.65 | 2.6511 | 0.002750 |
| 593.45 | 371.95 | 2.7735 | 0.002689 |

Table XIX: CsIBr<sub>2</sub>

|        |        |        |          |
|--------|--------|--------|----------|
| 15.93  | 382.95 | 1.2022 | 0.002611 |
| 29.68  | 402.65 | 1.4725 | 0.002484 |
| 50.39  | 430.95 | 1.7024 | 0.002320 |
| 106.44 | 467.15 | 2.0274 | 0.002141 |

Table XX: CsBr<sub>3</sub>

|        |        |        |          |
|--------|--------|--------|----------|
| 6.95   | 292.15 | 0.8420 | 0.003423 |
| 25.50  | 313.65 | 1.4065 | 0.003188 |
| 61.84  | 332.65 | 1.7913 | 0.003006 |
| 146.84 | 351.95 | 2.1668 | 0.002841 |
| 194.39 | 362.65 | 2.2887 | 0.002757 |
| 298.84 | 372.65 | 2.4754 | 0.002683 |
| 576.45 | 393.65 | 2.7609 | 0.002540 |

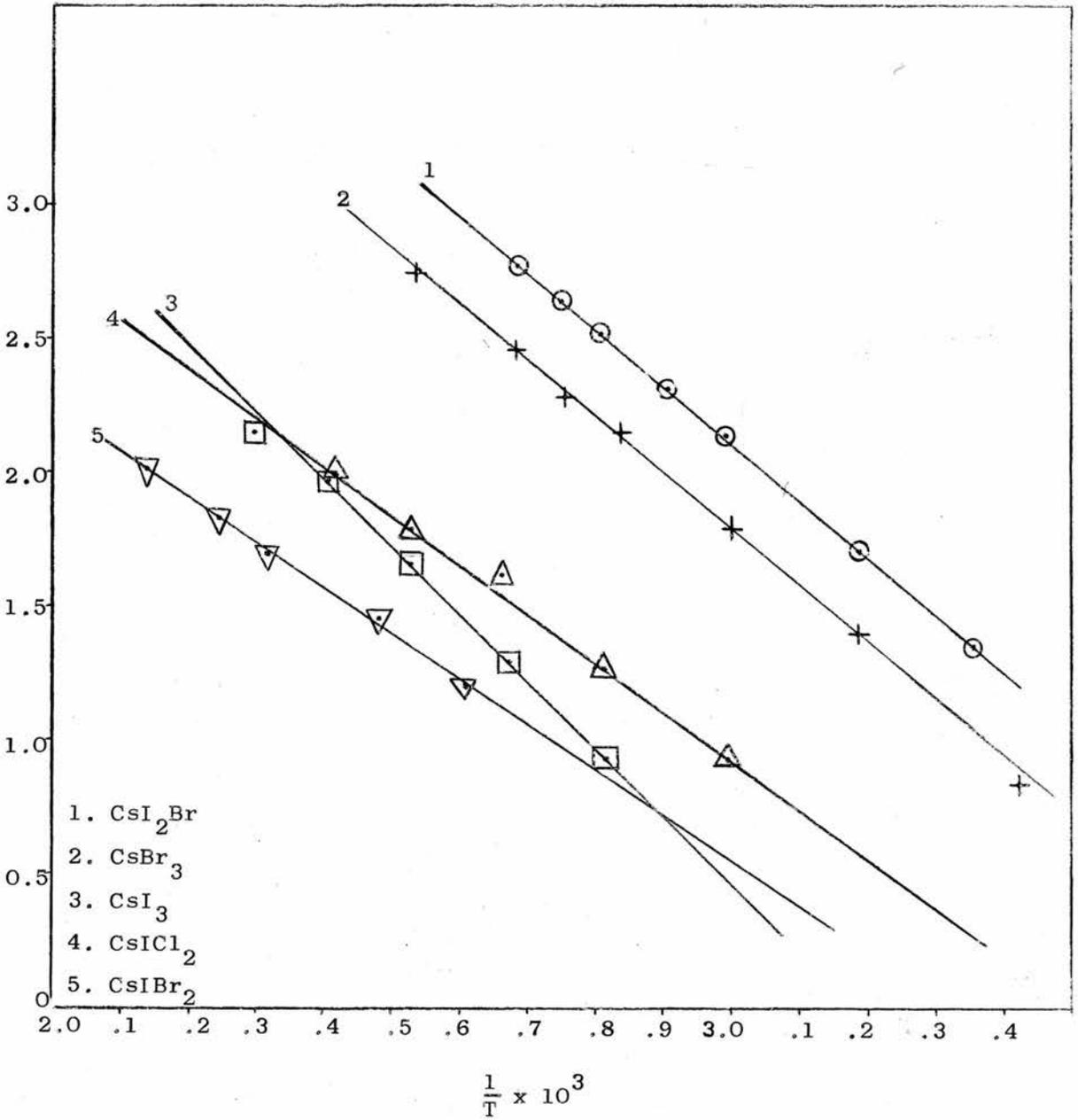


Figure X: The Dissociation Pressure of Caesium Trihalides

In each case within the temperature range studied, the plot of  $\log_{10} p$  against  $\frac{1}{T}$  was linear.

The equations of these lines are:

$$\underline{\text{CsI}_3} \quad \log_{10} p(\text{mm}) = - \frac{2600.0}{T} + 8.27$$

$$\underline{\text{CsIBr}_2} \quad \log_{10} p(\text{mm}) = - \frac{1816.7}{T} + 5.96$$

$$\underline{\text{CsI}_2\text{Br}} \quad \log_{10} p(\text{mm}) = - \frac{2116.4}{T} + 8.46$$

$$\underline{\text{CsBr}_3} \quad \log_{10} p(\text{mm}) = - \frac{2221.4}{T} + 8.47$$

Thermodynamic functions may be calculated for these data since in each case the dissociation of the caesium trihalide is of the type,



and equilibrium constants ( $K_p$ ) are given by,

$$K_p = p(\text{atmos})$$

where  $p$  is the measured dissociation pressure.

The general form of the Van't Hoff Equation is

$$\log_{10} K_p = - \frac{\Delta H}{2.303RT} + \text{const.}$$

Therefore for the present system,

$$\log_{10} p = - \frac{\Delta H}{2.303RT} + \text{const.}$$

$\Delta H$  values may thus be calculated from the experimental dissociation pressure data. Using the values of  $\Delta H$  found, in the following equations:

$$\Delta G^\circ = -2.303 RT \log_{10} K_p \quad \text{and}$$

$$\Delta G = \Delta H - T\Delta S$$

allows values of  $\Delta G$  and  $\Delta S$  to be derived for the dissociations studied. The values calculated are given in Table XXI.

Table XXI.

| Compound            | $\Delta H$ expt.<br>(Kcal mole <sup>-1</sup> ) | $\Delta G_{298}^{\circ}$<br>(Kcal mole <sup>-1</sup> ) | $\Delta S$<br>(cal deg <sup>-1</sup> mole <sup>-1</sup> ) |
|---------------------|--|--|---|
| CsI <sub>3</sub>    | 11.90  | 4.54   | 24.96   |
| CsI <sub>2</sub> Br | 9.68   | 2.07   | 25.54   |
| CsIBr <sub>2</sub>  | 8.31   | 4.12   | 14.06   |
| CsBr <sub>3</sub>   | 10.16  | 2.55   | 25.54   |

Although values of  $\Delta G^{\circ}$  at 25° are fairly close to one another the indicated order of thermodynamic stability of the caesium trihalides studied (with respect to the dissociation  $\text{CsX}_3(\text{g}) \rightarrow \text{CsX}(\text{s}) + \text{X}_2(\text{g})$ ) is:



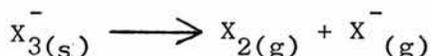
It is of interest to note, from inspection of the temperature versus pressure graphs, that at higher temperatures (> 70°C) the order is slightly different and is:



Also, it should be noted that neither of these orders of stability corresponds exactly with that obtained by Ephraim. However the method used by the latter in obtaining his sequence is of doubtful thermodynamic significance.

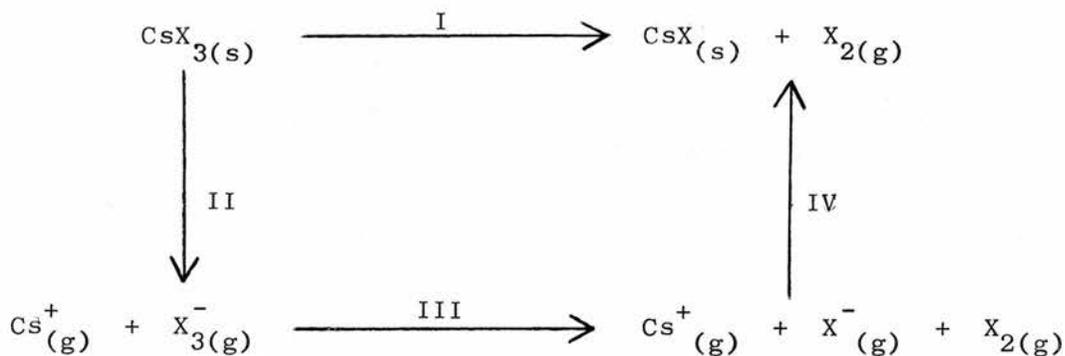
These stability sequences (comparison of  $\Delta G^{\circ}$  values) represent

the thermodynamic stability of the solid caesium polyhalides studied and not the stability of the trihalide ions they contain. To obtain information on this one has to consider a thermodynamic cycle which incorporates the step



and there also has to be available data for each of the other steps in the cycle.

One such cycle is:-



Re-examination of thermodynamic data listed in Table X reveals that trends in  $\Delta H$  values do not parallel those in  $\Delta G_{2980}^{\circ}$  values. Thus in considering the above thermodynamic cycle in a discussion of trihalide ion stability it would not be permissible to use enthalpy data (lattice energies etc) for each step; free energy data would have to be employed.

The steps in the cycle are the following:

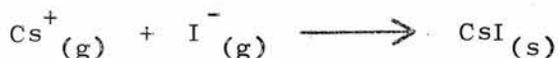
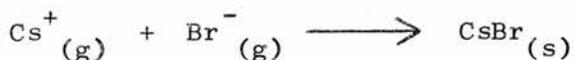
I. Dissociation of the caesium trihalide for which free energy data have been calculated above for  $CsI_3$ ,  $CsI_2Br$ ,  $CsIBr_2$  and  $CsBr_3$ .

II. Dispersion of the ions forming the  $\text{CsX}_3$  lattice to infinity (lattice energy is the enthalpy change associated with this step). Free energy data are, unfortunately, not available for this step. However the trihalides  $\text{CsI}_3$ ,  $\text{CsI}_2\text{Br}$ ,  $\text{CsIBr}_2$  and  $\text{CsBr}_3$  are isomorphous, and since they each contain a large anion, and these are of comparable sizes, the lattice energies of the compounds would be expected to be about equal. It is therefore assumed, for the present purposes, that the free energy change in this step is the same for each caesium trihalide studied (say  $x \text{ Kcal mole}^{-1}$ ).

III. Dissociation of the gaseous trihalide ion to gaseous halogen molecule and gaseous halide ion. To obtain information about this step is the object of this discussion.

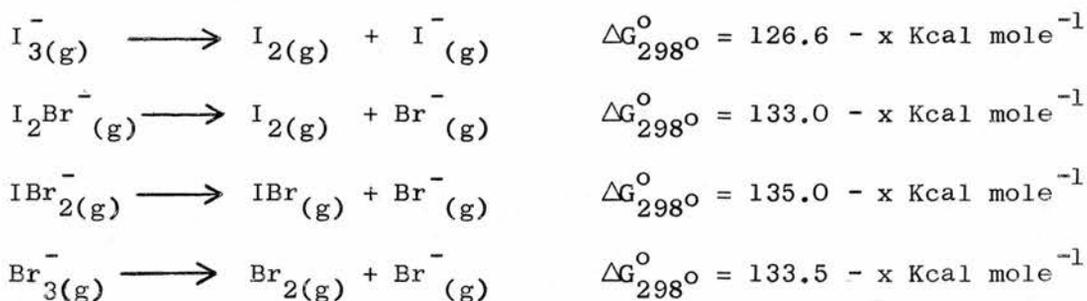
IV. Formation of the  $\text{CsX}$  lattice from the constituent gaseous ions at infinity (the enthalpy change associated with this step is the lattice energy of the  $\text{CsX}$  compound).

Free energy changes for the steps



have been calculated indirectly as  $-130.9 \text{ Kcal mole}^{-1}$  and  $-122.1 \text{ Kcal mole}^{-1}$  respectively from published data<sup>70,71,72</sup>.

Calculation of free energy data for step III gives the following results:



The order of thermodynamic stability suggested by these  $\Delta G_{298^\circ}^\circ$  values is therefore:



In view of the closeness of the values (especially for  $\text{CsI}_2\text{Br}$ ,  $\text{CsIBr}_2$  and  $\text{CsBr}_3$ ) and the assumption that  $x$  is constant, too much reliance cannot be placed on such an order of stability. However the general conclusion may be made that the trihalide ions are of comparable stabilities.

As an addendum to these measurements the dissociation pressure of  $\text{CsICl}_2$  was measured. The data are given in Table XXII and included in the graph illustrated in Figure X.

Table XXII:  $\text{CsICl}_2$

| Pressure(mm) | Temperature (°K) | log p  | $\frac{1}{T}$ |
|--------------|------------------|--------|---------------|
| 8.68         | 333.65           | 0.9385 | 0.002997      |
| 18.99        | 355.15           | 1.2786 | 0.002816      |
| 44.10        | 374.45           | 1.6444 | 0.002671      |
| 63.22        | 393.95           | 1.8008 | 0.002538      |
| 99.88        | 412.65           | 1.9999 | 0.002423      |

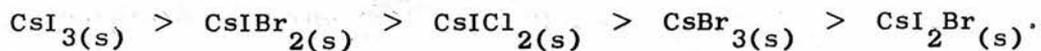
Values of thermodynamic functions derived from experimental data are:

$$\Delta H = 8.62 \text{ Kcal mole}^{-1}$$

$$\Delta G_{2980}^{\circ} = 3.57 \text{ Kcal mole}^{-1}$$

$$\Delta S = 16.94 \text{ Kcal mole}^{-1}$$

Therefore including  $\text{CsICl}_2$  in the order of stabilities of the caesium trihalides gives:



3. Thermal Analytical Studies of Caesium Trihalides.

The two main techniques of thermal analysis are thermogravimetric analysis (TGA) and differential thermal analysis (DTA), in which changes in weight and heat content respectively are measured as a system is heated at a controlled rate. In common with any dynamic technique the results from TGA and DTA are often markedly affected by experimental conditions. These include sample size and packing, the nature and geometry of the sample holder, the heating rate, and the environmental atmosphere. Thus there is often difficulty in correlating TGA and DTA data for the same substance when these data are obtained respectively from the results of running two different samples in two different pieces of apparatus.

It is therefore advantageous to use simultaneous TGA-DTA, where both measurements are carried out at the same time on a single sample. In the following work this simultaneous TGA-DTA procedure was adopted.

The most significant source of error in TGA work is caused by buoyancy and aerodynamic effects and are much more serious in controlled atmosphere systems. As a source of error they can vary greatly in magnitude of effect and a considerable amount of work has been carried out in attempt to minimise them<sup>73,74,75,76</sup>. Many factors affect aerodynamic errors the most significant being turbulence at high temperatures, drag characteristics of gas flow, furnace pulsing effects, and so on but in the following studies these sources of error proved to be negligible, probably due to the fact that the temperatures required to cause complete dissociation

of the caesium trihalides were relatively low. As regards buoyancy effects this does not apply since the errors are more marked at low temperatures. To correct for this the thermo-balance was run under normal conditions, but without a sample, up to a furnace temperature of  $600^{\circ}$  and the apparent weight was plotted against the furnace temperature. The resultant graph showed that the apparent weight increase, due to buoyancy effects, over  $600^{\circ}$ , was less than 3 mg and up to the highest temperature required to completely dissociate the most stable of the compounds studied was less than 2 mg.

The original intention of the present work was to carry out thermogravimetric analyses on known weights of the caesium trihalides in order to check further their purity and to confirm, from the weight losses observed, that the mode of dissociation was the one expected (namely, the one in which the halogen or interhalogen molecules formed contain the heaviest halogen atoms). However, no previous attempt had been made using the technique of thermal analysis to obtain an order of stability for these compounds; thus DTA measurements were made simultaneously with the TGA measurements in an effort to do this.

TGA has been used previously to determine stabilities of complexes by noting the temperature at which weight loss begins. In this way, taking the start of weight loss as a measure of a complex's resistance to breakdown, Moedritzer and Miller<sup>77</sup> showed that for the series  $\text{NiCl}_2(\text{PPh}_3)_2$ ,  $\text{NiBr}_2(\text{PPh}_3)_2$ ,  $\text{NiI}_2(\text{PPh}_3)_2$ , the thermal stability increased in the order chloride < bromide <

iodide. It was, accordingly, thought worthwhile to make a similar examination of the caesium trihalides.

In DTA the peak (endotherm) area corresponding to a dissociation step is related to the enthalpy change in that step so that comparison of the areas of the decomposition peaks of the various caesium trihalides studied should provide a means of studying their relative enthalpies of decomposition. It must be borne in mind however that in the section describing the dissociation pressure studies  $\Delta H$  and  $\Delta G$  values for the dissociation of caesium trihalides did not run parallel so that comparison of  $\Delta H$  values does not give a true order for the thermodynamic stability of the solid trihalides.

The same experimental conditions were used for all the studies performed. The apparatus is fully described in the Experimental Section but the following significant details should be noted:

- (1) Furnace heating rate -  $4^{\circ}$  per minute
- (2) Chart speed (TGA and DTA)- 6" per hour
- (3) Sensitivity (DTA) - 100  $\mu$ V (FSD)
- (4) Atmosphere - air
- (5) Flow rate (air) - 100 ml per minute
- (6) Reference material - alumina

Table XXIII contains some relevant data obtained from the TGA and DTA studies.

Table XIII: Results From Simultaneous TGA and DTA Runs on Some Caesium Trihalides.

| Compound            | Melting Point (Sealed Tube) | % Weight Loss (From TGA) | Dissociation Products  | Temperature at which Decomposition Begins (From TGA) | DTA Peak Type  | DTA Peak Maxima (C°) |
|---------------------|-----------------------------|--------------------------|------------------------|--|----------------|----------------------|
| CsIBr <sub>2</sub>  | 245-247°                    | 48.33                    | CsBr + IBr             | 142°   | Composite      | 237°, 250°           |
| CsICl <sub>2</sub>  | 239-240°                    | 48.87                    | CsCl + ICl             | 152°   | "              | 248°, 254°           |
| CsI <sub>3</sub>    | 208-211°                    | 50.08                    | CsI + I <sub>2</sub>   | 77°  | "              | 206°, 213°           |
| CsI <sub>2</sub> Br | 198-202°                    | 53.08                    | CsBr + I <sub>2</sub>  | 51°  | simple (broad) | 183°                 |
| CsBr <sub>3</sub>   | 182-186°                    | 40.00                    | CsBr + Br <sub>2</sub> | 41°  | "              | 146°                 |

DTA Results.

(i) For  $\text{CsI}_3$ ,  $\text{CsIBr}_2$  and  $\text{CsICl}_2$ . The DTA trace was complex and consisted of the sharp melting point endotherm superimposed on the broad decomposition endotherm. (The decomposition endotherm itself was in these cases resolvable into two parts - the first being that due to decomposition of the solid caesium trihalide and the second due to decomposition of the halide after melting).

(ii) For  $\text{CsI}_2\text{Br}$  and  $\text{CsBr}_3$ . For these compounds the endotherm was a simple, unsymmetrical, broad peak. The peak area per mole of compound used gave values 72.31 and 59.62 for  $\text{CsI}_2\text{Br}$  and  $\text{CsBr}_3$  respectively, which is the reverse of the order found for the enthalpy changes occurring in the dissociation of these compounds. Although enthalpy is temperature dependent, this is not likely to be a significant factor. It must therefore be concluded from this that the dynamic, non-equilibrium conditions under which the DTA is carried out makes this an unreliable method for obtaining comparative figures which reflect the enthalpy of the dissociation process.

TGA Results.

Comparison of the temperatures at which dissociation of the compounds begins gives the sequence,



It is noteworthy that this coincides closely with the sequence obtained from the  $\Delta G^0$  data obtained from dissociation pressure measurements, except that caesium tribromide and caesium

diiodobromide are interchanged. The TGA method therefore does give a rough indication of the stability of these compounds to dissociation, and again the exception of  $\text{CsI}_2\text{Br}$  and  $\text{CsBr}_3$  must be attributed to the non-equilibrium conditions under which the TGA is carried out.

EXPERIMENTAL

## EXPERIMENTAL

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EXPERIMENTAL

I. General Techniques

(1) Ultra-violet Spectra, Infra-red Spectra and Analyses.

For details and descriptions of the above techniques consult the Experimental Section of Part I of this thesis.

(2) Vacuum System for Vapour Pressure Studies of Caesium Polyhalides.

For the vapour pressure studies of the caesium polyhalides the vacuum line, which had previously been used for the study of the  $\text{Br}_2-(\text{C}_6\text{H}_{11})_3\text{P}$  reaction, was modified so that the greased portion of the apparatus which would come into contact with halogen and high temperature was replaced by a system incorporating a new spiral gauge, greaseless joints and a large bore greaseless tap. Tap E, which was outwith the area that would come into contact with halogen vapour, was also replaced by a greaseless tap for finer control when evacuating the outer jacket. An oil bath was used to heat the sample and since it was essential that the whole area which would contain halogen vapour be at the same temperature, because the vapour pressure measured is the pressure at the coldest part, the following system was designed as shown in Figure XI:

The oil was heated using four 300 Watt Electrothermal Red-Rod Radiant Immersion Heaters, each having an independent connection to the mains voltage to enable any combination of the four possible, depending on the temperature required. Stirring was effected by

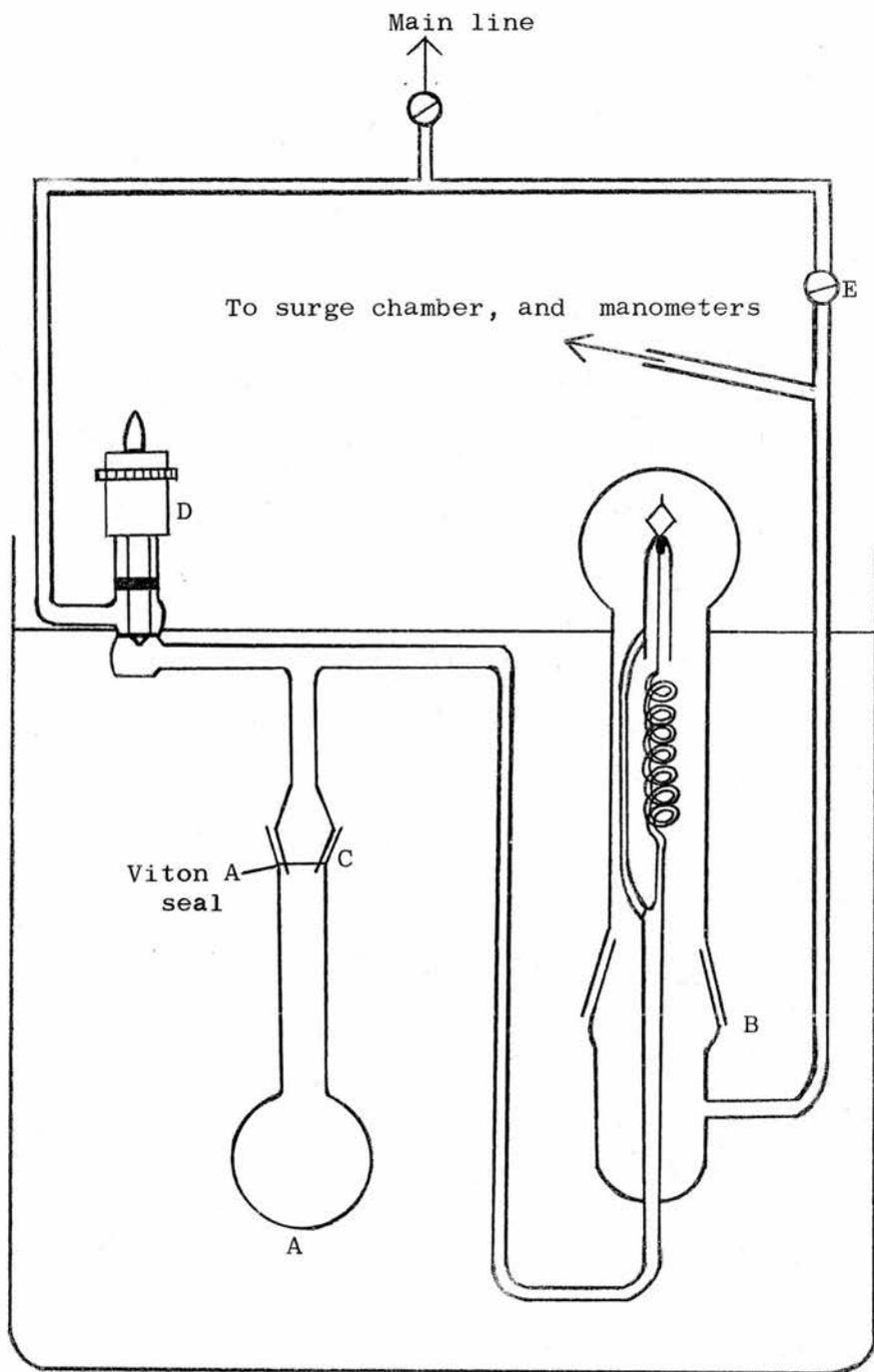


Figure XI: Vacuum System for Vapour Pressure Studies of Caesium Polyhalides.

means of a large paddle stirrer, 4 inches in diameter and driven by a Griffin-Citenco Stirring Motor, 300/50 r.p.m. at 240 volts. Normal vegetable cooking oil was used to heat the system, in preference to paraffin oil which gives off carcinogenic fumes at the relatively high temperatures demanded by these studies. A contact thermometer enabled the required temperature to be approximately pre-set, but accurate measurement of the temperature of the oil was made using a large scale calibrated mercury thermometer. The spiral gauge outer jacket was sealed to the spiral gauge, at joint B, with Araldite epoxy resin and left for one week to harden. The spiral gauge was, as before, used as a null instrument in which the deflection of the pointer was magnified by the optical lever principle, as described in the Experimental Section of Part I.

It was estimated that the volume of the system which would contain gaseous halogen was approximately 35 ml and so, basing the volume on 50 ml, the calculation of the weight of polyhalide sample required was made, thus ensuring an excess. The polyhalide to be studied was weighed into flask A, cooled in liquid nitrogen and attached to the vapour pressure system. P.T.F.E. tape was bound around the B.14 joint as a further precaution against oil seeping into the system, at higher temperatures. Keeping the flask and contents surrounded by liquid nitrogen the whole system was pumped out until the pressure was less than 0.005 mm Hg, when tap E was closed. Flask A was then allowed to attain room temperature before closing tap D; this ensures the absence of atmospheric moisture. The

vapour pressures of the polyhalides at room temperature were not high enough to cause any appreciable loss of halogen. Flask A was again surrounded by liquid nitrogen, the light spot adjusted to the zero point and the system checked for leaks. The liquid nitrogen Dewar flask was then removed and replaced by the oil bath before placing the rod heaters, thermometers and stirrer in position. Stirring was commenced and the system was now ready for the vapour pressure study to begin.

Readings of vapour pressure were taken at different temperatures determined by the setting of the contact thermometer and, as before, the vapour pressure was read as a difference in mercury levels between the manometers F and G, arranged close together and using a common mercury reservoir. Having closed tap  $T_4$  before the beginning of the experiment, with tube G fully evacuated, manometer G was employed as an ordinary barometer. The cathetometer was used to obtain accurate measurements of mercury levels. Before each reading of vapour pressure the system was always given sufficient time to stabilise. This varied, but the time required to attain stability increased with the rise in temperature.

On completion of the vapour pressure run, the oil bath was removed and, as the system cooled down, the reference side was slowly evacuated to maintain the light spot around the null point. Flask A was then cooled in liquid nitrogen, which condensed any halogen that had crystallised on other parts of the system, and the spiral gauge opened to the main pumping unit to check that no

leakage had occurred on the sample side of the system. The vapour pressure system was then isolated, both greaseless taps D and E opened, and air slowly let in through the air leak and surge chamber to the system. Finally, the sample flask A was removed and the original sample recovered.

### (3) Thermal Analysis.

A Stanton Thermobalance, Model TR-1, fitted with the Stanton Differential Thermal Analysis Attachment, Model STA 662, was used in the thermal studies. To the DTA attachment was fitted a Leeds and Northrup "Speedomax" W Recorder with a range of 10 mV. The complete set-up was located on an island site, away from sunlight and draughts.

Figure XII shows the DTA head and furnace as used in this work.

The thermobalance records the temperature of the furnace and the weight change of the sample material. As can be seen from the diagram the furnace contains a quartz sheath leading to a trap system consisting of two U-tubes immersed in Dewar flasks which contained acetone/solid carbon dioxide, and a flowmeter to record the volume of air displaced per minute. This volume was controlled by a needle valve situated between the flowmeter and a rotary pump. An inconel screen, A, was fitted inside the furnace tube and earthed. Its function was to minimise interaction between the furnace heating current and the  $\Delta T$  signal.

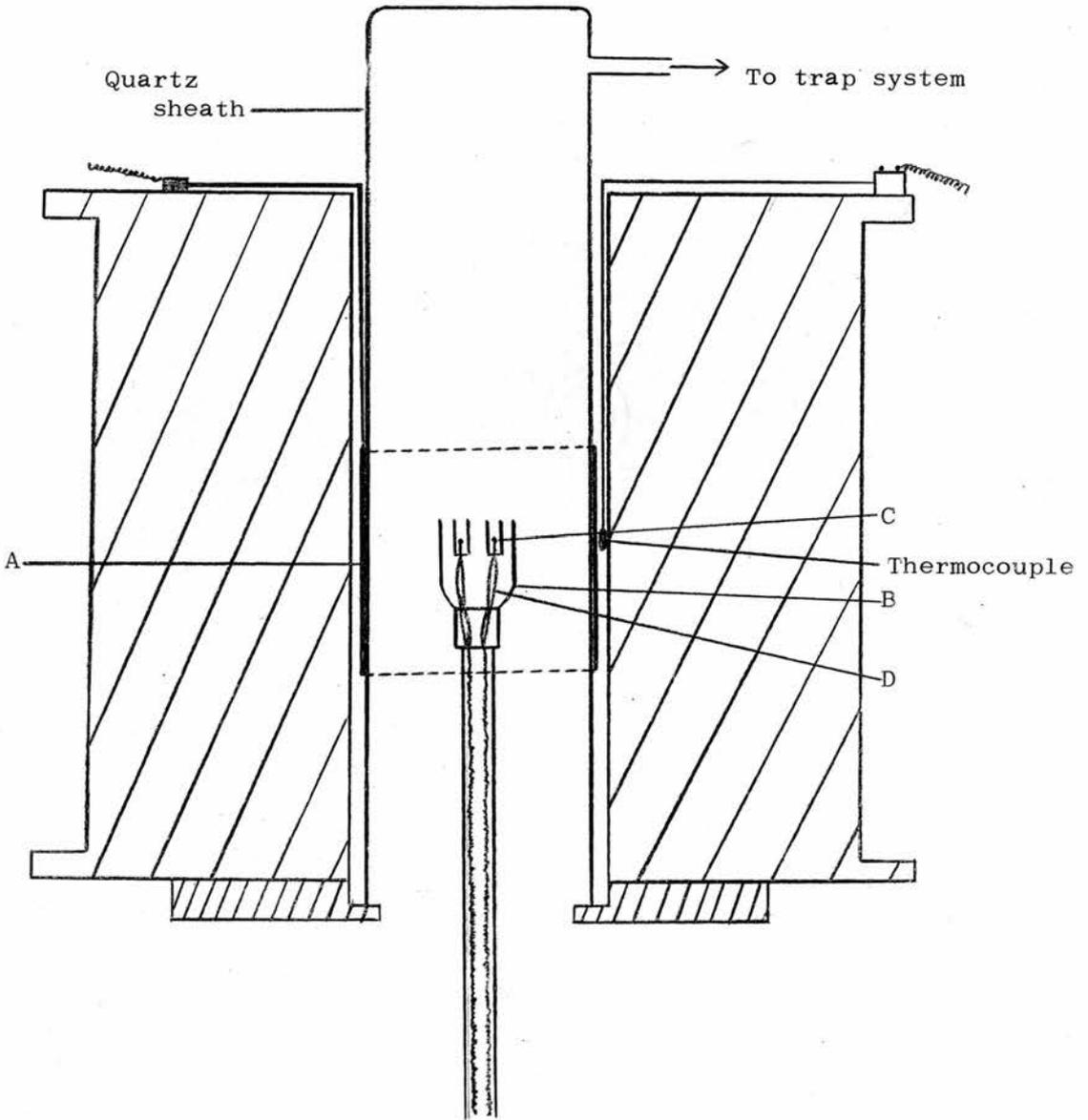


Figure XII: DTA Head and Furnace Assembly for Thermal Analysis Experiments.

The DTA head consisted of a high purity alumina block, B, attached to a rise arm of the same material. The rise arm, in turn, was coupled to the balance mechanism. Two wells were bored in the upper surface of the alumina block to take the dimped platinum-rhodium crucibles which contained the sample and reference materials. The block was placed on the rise rod such that the thermocouple beads, C, which were in the centre of their respective wells, were located in the top of the crucible dimp. The rise rod was drilled to take the thermocouple lead out wires, D, threaded through the rod. The leads were colour coded as follows,

Yellow: Common negative lead, platinum wire to sample well.

Red : Temperature positive lead, platinum-13% rhodium wires, one to each well.

Blue :  $\Delta T$  positive lead, platinum wire to reference well.

The lead out wires were connected to terminals on the balance mechanism. They were then coupled via 0.025 mm platinum and platinum-13% rhodium wires to the rear of the weighing chamber. From this point compensated cable is led to the cold junction formed by the precious metals being joined to copper wire and enclosed in a plastic tube which is then immersed in a Dewar vessel containing ice. The copper wires were now used as the lead to the DTA amplifier which amplifies the voltage caused by the temperature difference between the sample and reference materials during heating. This signal is displayed on the chart recorder. The amplifier also switched at five minute intervals, so that the

output from the sample thermocouple was displayed on the recorder, thus giving an accurate measure of the sample temperature. From this data, phase changes such as melting points, crystalline transitions, and decomposition can be observed.

The TGA and DTA systems thus described were run simultaneously. The balance was manually arrested at a point which coincided with a temperature readout on the DTA chart. These two points were clearly marked and this procedure was repeated at the end of each run. Although the chart speeds were the same this served as a check and so the two separate read-outs could be compared.

The sample and reference materials, namely the caesium polyhalide and alumina, were tamped down in their respective crucibles using a specially designed metal rod. This was done to ensure reproducibility of packing, thus eliminating one of the major sources of error in DTA.

The apparatus described above is based on a design by Charsley and Redfern<sup>78</sup> which has been used successfully for a number of years.

## II. Source and Purification of Materials.

### A. Solvents.

#### (1) Methyl Cyanide, Diethyl Ether and Carbon Tetrachloride.

The above mentioned solvents used in the following preparations were purified in the same manner as described in the Experimental Section of Part I.

For the ultra-violet spectroscopic studies careful screening of the Hopkins and Williams general purpose reagent was made before purification. It was found that the spectroscopic properties varied from batch to batch and the spectroscopic impurities could not be removed by the previously described method of purification. From its absorption characteristics the impurity was thought to be benzene or a benzene derivative which interfered with the polyhalide absorption spectra to a large degree. Therefore, once a batch of methyl cyanide was found to be free of this impurity, it was purified in the normal manner and used solely for ultra-violet spectroscopic work.

#### (2) Ethanol.

99.5% absolute ethanol was used without further purification.

#### (3) Methanol.

Analar methanol (Fisons) was used without further purification.

#### (4) Acetic Acid.

Analar glacial acetic acid (Fisons) was used without further purification.

B. Reagents.

(1) Bromine, Iodine and Iodine Monobromide.

Again, these reagents were purified or prepared according to the manner described in the Experimental Section of Part I.

(2) Iodine Monochloride.

Commercial iodine monochloride (B.D.H.) was purified by melting and allowing it to cool gradually until about 80% had solidified. The supernatant liquid was decanted off and the residue resublimed.

(3) Tetraethylammonium Chloride.

The commercial grade reagent (B.D.H.) existed as the monohydrate and was used as such without further purification.

(4) Tetraethylammonium Bromide.

The commercial grade reagent (B.D.H.) was supposed to be anhydrous but was found to be very wet. Before use it was dried in an oven at  $110^{\circ}$  for two hours and pumped in a vacuum desiccator for the same time.

(5) Tetraethylammonium Iodide.

The anhydrous commercial grade reagent (B.D.H.) was quite satisfactory and was used without further purification.

(6) Caesium Chloride, Caesium Bromide and Caesium Iodide.

The commercial grade caesium halides (B.D.H.) were used without further purification.

### III. Preparations of Polyhalides.

#### (1) Tetraethylammonium Polyhalides.

(i) Tetraethylammonium dibromiodide,  $(C_2H_5)_4NIBr_2$ . This is one of the most stable perhalides known and was prepared according to the method of Chattaway and Hoyle<sup>79</sup> by the addition of the equivalent amount of bromine dissolved in about twice its bulk of glacial acetic acid, to tetraethylammonium iodide, suspended in about ten times its weight of ethanol, and warming till the solid dissolved. On cooling tetraethylammonium dibromiodide was deposited. It was recrystallised from ethanol as shining, rhombic plates of a deep, somewhat reddish-orange colour. M.p. 123-124<sup>o</sup>. (Found: C, 22.95; H, 5.12; N, 3.43; I, 29.98; Br, 37.72.  $C_8H_{20}NIBr_2$  requires: C, 23.04; H, 4.83; N, 3.36; I, 30.46; Br, 38.32%).

(ii) Tetraethylammonium dichloriodide,  $(C_2H_5)_4NICl_2$ . Equimolar amounts of tetraethylammonium chloride and iodine monochloride were dissolved separately in the minimum of glacial acetic acid, and the interhalogen solution added dropwise to the halide solution. Addition of carbon tetrachloride to the resultant yellow solution precipitated pale yellow crystals, which were filtered and recrystallised from ethanol. It separated as shining, bright yellow plates. M.p. 101-102<sup>o</sup>. (Found: C, 28.25; H, 6.07; N, 4.03.  $C_8H_{20}NICl_2$  requires: C, 29.29; H, 6.14; N, 4.27%).

(iii) Tetraethylammonium diiodobromide,  $(C_2H_5)_4NI_2Br$ . Iodine, dissolved in the minimum volume of methyl cyanide, was added dropwise to a solution of tetraethylammonium bromide, dissolved in the minimum volume of the same solvent. Addition of anhydrous ether, almost to the point of precipitation, followed by cooling in the refrigerator for several days yielded deep red needles. The crystalline product was filtered and well washed with anhydrous ether. M.p.  $125^{\circ}$ . (Found: C, 20.71; H, 4.34; N, 3.02; I, 54.10; Br, 17.03.  $C_8H_{20}NI_2Br$  requires: C, 21.06; H, 4.67; N, 3.41; I, 54.70; Br, 17.22%).

(iv) Tetraethylammonium triiodide,  $(C_2H_5)_4NI_3$ . Iodine and tetraethylammonium iodide were dissolved, separately, in the minimum volume of methyl cyanide and the halogen solution added dropwise to the halide. The addition of a large volume of anhydrous ether to the dark solution, followed by cooling resulted in dark red needles slowly crystallising out. These were filtered and thoroughly washed with anhydrous ether. (Found: C, 19.04; H, 4.18; N, 2.99; I, 74.37.  $C_8H_{20}NI_3$  requires: C, 18.80; H, 3.94; N, 2.74; I, 74.51%).

(v) Tetraethylammonium tribromide,  $(C_2H_5)_4NBr_3$ . An excess of bromine, contained in a B.14 cone tube, was reacted with tetraethylammonium bromide on the vacuum line, by distilling it onto the halide which was contained in a B.19 socket tube. 'Kel-F' grease was used on all joints and taps because of its resistance to halogen attack. The bromine was solidified by cooling in liquid air, the system evacuated and the bromine warmed up to room temperature. The

tube containing the solid tetraethylammonium bromide was then slowly cooled down with liquid air causing the halogen to condense and thus the reaction to take place. After all the bromine had been condensed onto the halide, the reaction mixture was warmed to room temperature and left for thirty minutes before cooling again with liquid air. This process was repeated several times in an attempt to obtain homogeneous mixture of the reactants. A dark red product resulted and excess bromine was observed in the vapour phase. The empty tube, which had originally contained the bromine, was now cooled down and the excess bromine condensed over. The product gradually lightened until pale orange in colour, significant of the tribromide ion. This solid was then transferred to a desiccator and pumped for thirty minutes. M.p,  $81^{\circ}$  decomp. (Found: C, 26.20; H, 5.76; N, 3.93; Br, 65.96.  $C_8H_{20}NBr_3$  requires: C, 25.97; H, 5.44; N, 3.78; Br, 64.79%).

## (2) Caesium Polyhalides.

In a review of polyhalogen complex salts in Inorganic Synthesis<sup>80</sup> reference is made to fairly recent preparations of caesium polyhalides by Skelly<sup>81</sup>. However difficulty was found using the methods described which resulted in the isolation of impure products and, in some cases, no product at all. The methods of identification of these compounds were potentiometric titration, ultra-violet spectroscopy in methyl cyanide, and melting point determinations, carried out in sealed tubes. The following preparations were devised.

(i) Caesium dibromiodide, CsIBr<sub>2</sub>. Iodine monobromide (0.87 g), dissolved in ethanol (8 ml), was added dropwise to a hot solution of caesium bromide (0.90 g), dissolved in an ethanol/water mixture (7 ml). When addition was complete the resultant dark-orange solution was cooled in ice when orange-brown needles crystallised out. These were filtered and washed with a little ice-cold ethanol before pumping dry. M.p. 245-247° decomp. (Found: I, 30.46; Br, 37.23. CsIBr<sub>2</sub> requires: I, 30.24; Br, 38.09%).

(ii) Caesium dichloriodide, CsICl<sub>2</sub>. Caesium chloride (1.50 g) was suspended in methanol and warmed. Water was then added until almost all the halide had dissolved in the hot. To this was added, dropwise with shaking, an equi-molar amount of iodine monochloride (1.29 g), dissolved in a little methanol. The resultant dark solution was decanted from the trace of unreacted caesium chloride and cooled. Bright yellow plates gradually crystallised from solution. These were filtered, washed with a little cold methanol and pumped to dry. M.p. 240-241° (Found: I, 38.30; Cl, 21.54. CsICl<sub>2</sub> requires: I, 38.37; Cl, 21.44%).

(iii) Caesium diiodobromide, CsI<sub>2</sub>Br. Solid iodine (1.13 g) was added to a suspension of an excess of caesium bromide (1.01 g) in hot methanol (11 ml). Water was slowly added until complete solution was obtained in the hot. On cooling the dark solution in the refrigerator for several days, red-brown crystals were found to have separated out. These were filtered but not washed, since this

compound proved to be unstable. The sample was sucked dry on the water pump and stored in a sample tube, inside a black desiccator. M.p. 198-202<sup>o</sup> decomp. (Found: I, 52.35; Br, 18.09.  $\text{CsI}_2\text{Br}$  requires: I, 54.39; Br, 17.12%).

(iv) Caesium triiodide,  $\text{CsI}_3$ . Iodine (2.01 g) was suspended in ethanol (15 ml) to which was added an equi-molar amount of caesium iodide (1.87 g), dissolved in hot water (15 ml). The mixture was heated to obtain complete solution. However, on cooling the dark solution crystallisation did not occur, and so the alcohol was removed on a water bath. When the aqueous solution was now cooled in ice, dark plates crystallised out. These were filtered and pumped under vacuum to dry. M.p. 208-211<sup>o</sup> decomp. (Found: I, 74.84.  $\text{CsI}_3$  requires: I, 74.12%).

(v) Caesium tribromide,  $\text{CsBr}_3$ . Caesium bromide (2.00 g) was dissolved in an ethanol-water mixture and gently heated. To this was added dropwise, with care, an excess of bromine and on cooling in an ice bath orange crystals precipitated. This solid, which subsequently proved quite unstable, was filtered, quickly pressed dry on filter papers and stored in a well stoppered sample tube, out of direct light, in a black desiccator. However, the halogen analysis showed the compound to have a low bromine content and so it was placed on a watch glass in a desiccator, containing calcium chloride as desiccant, in contact with bromine vapour overnight.

By this time it had turned to a deep red very viscous semi-solid; probably a higher polyhalide. The excess bromine was removed on the vacuum line and a caked orange solid remained. This was scraped out into a mortar and powdered before returning to the sample tube and analysing. M.p. 182-186<sup>o</sup> decomp. (Found: Br, 62.18. CsBr<sub>3</sub> requires: Br, 64.32%).

Thermogravimetric analyses were carried out on all of the above compounds. Each run gave the calculated weight loss within two per cent and so was further proof of their purity.

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