A STUDY OF SOME ORGANOARSENIC AND ORGANOANTIMONY HALIDES

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TO MY PARENTS

A STUDY OF SOME ORGANOARSENIC AND ORGANOANTIMONY HALIDES

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DECLARATION

I Abdullah Khan hereby certify that this thesis which is approximately 52,000 words in length has been written by me, that it is the record of work carried out by me, and that it has not been submitted in any previous application for a higher degree

August 1985 signature

CERTIFICATE

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the degree of Doctor of Philosophy of the University of St. Andrews and he is qualified to submit this thesis in application for that degree.

August 1985 Research Supervisor

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The higher molar conductivity of R_3AsI_2 and R_3AsIBr results from their disproportionation

$$R_3AsX_2 \longrightarrow \tfrac{1}{2}R_3As + \tfrac{1}{2}R_3AsX^+ X_3^-$$

All of the 2:1 adducts, R_3AsX_4 are strong electrolytes in acetonitrile solution and are formulated $R_3AsX^+ X_3^-$. The mixed tetrahalides

R_3AsCl_3I and R_3AsBr_3I, were indicated from the reactions of R_3AsCl_2 with ICl and R_3AsBr_2 with IBr, and they can be obtained as solid adducts. These compounds ionise completely in acetonitrile and the halogen of lower atomic number resides, without exception, in the cation

$$R_3AsCl_3I \longrightarrow R_3AsCl^+ \ ICl_2^-$$

$$R_3AsBr_3I \longrightarrow R_3AsBr^+ \ IBr_2^-$$

Triarylstibine halides

The course of the reactions of tri(2-, 3-, 4-methylphenyl)-, tri(dimethylphenyl)-, tris(2-, and 4-trifluoromethylphenyl)stibine with bromine, iodine and iodine bromide in acetonitrile solution were investigated by conductometric titration in order to observe compounds formation in these systems. All of the 1:1 and 2:1 adducts (R_3SbX_2 and R_3SbX_4) whose existence was shown by the titrations were isolated. The electrolytic conductivity of acetonitrile solutions of the adducts were measured and values of molar conductivity were obtained; all of the compounds of general formula R_3SbX_2 (X = Cl or Br) are either non-electrolytes or very weak electrolytes in acetonitrile. The conductivity of the adducts R_3SbI_2 and R_3SbIBr are high and arise from their disproportionation in acetonitrile:

$$R_3SbI_2 \rightleftharpoons \tfrac{1}{2}R_3Sb + \tfrac{1}{2}R_3SbI^+I_3^-$$

$$R_3SbIBr \rightleftharpoons \tfrac{1}{3}R_3Sb + \tfrac{1}{3}R_3SbBr_2 + \tfrac{1}{3}R_3SbBr^+I_3^-$$

All of the tetrahalides except $(4\text{-}CF_3C_6H_4)_3SbI_4$ are strong electrolytes.

The conductometric titrations of R_3SbCl_2 with ICl and $SbCl_5$ and R_3SbBr_2 with IBr [R = $(CH_3)_2C_6H_3$, $2\text{-}CF_3C_6H_4$] have been studied in acetonitrile; there is no reaction between R_3SbCl_2 and ICl but with

$SbCl_5$ a highly conducting 2:1 adduct (R_3SbCl^+ $Sb_2Cl_{11}^-$) is formed. With the exception of $[(CH_3)_2C_6H_3]_3SbBr_2$, the reaction of R_3SbBr_2 with IBr does not go to completion, but produces an equilibrium mixture of reactants and product:

$$R_3AsBr_2 + IBr \longrightarrow R_3SbBr^+ \; IBr_2^-$$

No solid adduct was obtained. However the adduct $[(CH_3)_2C_6H_3]_3SbBr_3I$, suggested from the titration graph, was isolated as a solid. It is a strong electrolyte in acetonitrile solution.

Tetraphenylstibonium halides

All of the compounds Ph_4SbX (X = F, Cl, Br, I) and Ph_4SbX_3 (X_3 = Br_3, IBr_2, ICl_2) were isolated as crystalline solids. Their electrolytic conductivity was measured in acetonitrile and the molar conductivity was calculated for each compound; Ph_4SbF is a very weak electrolyte. Ph_4SbCl and Ph_4SbBr are weak electrolytes but Ph_4SbI is a strong electrolyte as are all of the trihalides, Ph_4SbX_3.

The conductometric titrations of Ph_4SbCl with ICl and Ph_4SbBr with Br_2 and IBr indicate that the trihalides Ph_4SbX_3 are formed readily in acetonitrile solution.

INTRODUCTION

Group VB Halides

The elements of Group VB (N, P, As, Sb, and Bi) with the exception of nitrogen, form numerous pentahalogeno compounds since they possess low energy d-orbitals which may be used for bonding. Nitrogen, which does not have low-lying d-orbitals, differs considerably in its chemistry from the other group members. The extent of utilisation of d-orbitals by these atoms depends both on the particular Group VB element and on the nature of the atom, or the group involved in the bond formation; it is most obvious in phosphorus and least obvious in bismuth.

Among the halides of this group the trihalides, EX_3[*], and the pentahalides, EX_5, (E = P, As, Sb, and Bi; X = halogen) are the most numerous and most important. Some of the halides of arsenic, antimony and bismuth have been known for more than 300 years. Arsenic trichloride was described by Glauber[1] in 1648. He also prepared antimony trichloride by distillation from a mixture of antimony sulphide with mercuric chloride, salt and clay or hydrochloric acid, and identified it in the same year. R. Boyle[2] made bismuth trichloride in 1664 by sublimation from a mixture of bismuth and mercuric chloride. Gay Lussac and L.J. Thenard[3] in about 1808

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[*] From time to time in this thesis the letter E is used to represent Group VB element and the letters X, Y represent halogens.

prepared liquid phosphorus trichoride by the action of chlorine on phosphorus. These were among the first non-metallic halides to be studied.

The five co-ordinated compounds of Group VB are unique and interesting. Structural studies have shown that they display a continuous range of conformations extending from the ideal trigonal bipyramid to the square or rectangular pyramid. For example, for pentaphenylantimony[4] square pyramidal is the stable form although most of the molecular species of type EX_5 have the trigonal bipyramid configuration.

A brief survey of the chemistry of the Group VB element halides and their derivatives is given in the sections that follow.

Group VB Trihalides

(a) TYPE EX_3

All of the trihalides, except PF_3, are best prepared by direct halogenation, keeping the element in excess. PF_3 is best made by fluorination of PCl_3[5]. All of the simple trihalogeno derivatives of this group have been isolated and characterised. With the exception of PF_3 which is a gas, the compounds are either liquid or solid at room temperature and their volatility decreases with increasing molecular weight. All of the trihalides are rapidly hydrolysed by water.

The gaseous molecules have pyramidal structures. The bonds are simple sigma bonds and do not apparently involve π bonding[6]. In the solid state these compounds generally crystallise with molecular lattices. Exceptions are the iodides of As, Sb, and Bi which crystallise with layer lattices with no discrete molecules, BiF_3 which has an ionic lattice, and SbF_3 which has an intermediate structure.

(b) TYPE EX_nY_{3-n}

In addition to the simple trihalides which contain one kind of halogen, compounds are known in which two different halogens are present. Although the possible number of these mixed halides of Group VB elements is large, relatively few have been prepared and characterised. The phosphorus compounds are best known and those halides which contain fluorine are the most stable. Phosphorus mixed trihalides are formed by rearrangement of a mixture of the simple trihalides, for example

$$PBr_3 + PCl_3 \rightleftharpoons PClBr_2 + PCl_2Br^{7,8}$$

The fluorine-containing mixed halides (e.g. PF_2Cl, PF_2Br, and PF_2I) are conveniently prepared by the following method [9]

$$(CH_3)_2NPF_2 + HX \longrightarrow PF_2X + (CH_3)_2NH.HX$$

All of these compounds tend to undergo decomposition (randomisation) reactions e.g.

$$5PClBr_2 \longrightarrow PCl_2Br + 3PBr_3 + PCl_3$$

Fluorine-containing compounds randomise more slowly but all of these compounds have to be stored at low temperature (-196^0C) to avoid decomposition. The chloride-bromides and chloride-iodides have not been isolated as pure compounds[10] although their existence may be detected by NMR, Raman, and Infra-red studies. There is Raman spectral evidence[8] for the formation of PFClBr, containing three different halogens, obtained from the mixture of $PFCl_2$ and $PFBr_2$.

Mixed trihalides of As and Sb are much less easily isolated but they can be detected in mixtures. ^{19}F NMR has shown the possible existence of AsF_2Cl and $AsFCl_2$[11] from the mixture of $AsCl_3$ and AsF_3. The Raman spectrum of the mixture of $AsCl_3$ and $AsBr_3$ showed the presence of $AsCl_2Br$ and $AsClBr_2$. SbI_2Br[12] is obtained by the elimination of ethylbromide from the organometallic compound, $EtSbI_2Br_2$[13]. The mixed trihalides for bismuth have not been reported yet. The gaseous molecules in these mixed trihalides have pyramidal structures and in the solid state they form molecular lattices[5].

Group VB Pentahalides

Pentahalides of Group VB elements have long been known. For example PF_5 was first prepared in 1876, well before the discovery of elemental fluorine. These compounds are generally prepared by one of three methods.

(a) treatment of the element with an excess of the appropriate halogen

e.g. $2P + 5Cl_2 \longrightarrow 2PCl_5$

(b) addition of halogen to a trihalide

e.g. $PF_3 + Cl_2 \longrightarrow 2PF_3Cl_2$

(c) halogenation (usually fluorination) of another pentahalide

e.g. $3PCl_5 + 5AsF_3 \longrightarrow 3PF_5 + 5AsCl_3$

TYPE EX_5

Phosphorus pentahalides of this type, with exception of PI_5, are all known. PF_5, is molecular (trigonal bipyramidal)[14] and is a non-electrolyte in liquid HF[5]. PCl_5 is a solid at room temperature and its structure is built from ions. Normal solid PCl_5 is $[PCl_4]^+$ $[PCl_6]^-$ [5] but recently it has been shown that other (metastable) forms of the compound exist:

(a) $[PCl_4]^+ [Cl]^-$ [15] (b) $[PCl_4]_2^+[PCl_6]^-Cl^-$[16]

(c) PCl_5 (molecular: trigonal bipyramidal)[5].

In the gas phase, trigonal bipyramidal PCl_5 molecules are present[17]. In polar ionising solvents (e.g. acetonitrile and nitrobenzene) PCl_5 is a weak electrolyte and the ions PCl_4^+ PCl_6^- have been shown to be present[5]

$$2PCl_5 \rightleftharpoons [PCl_4]^+ [PCl_6]^- \rightleftharpoons [PCl_4]^+ + [PCl_6]^-$$

In non polar solvents, however PCl_5 is molecular: in CCl_4 it may be dimeric, but in benzene it is monomeric[5]. Raman spectroscopy shows that in the liquid phase PCl_5 is trigonal bipyramidal[10].

In the solid state PBr_5 is ionic consisting of the ions $[PBr_4]^+$ $[Br]^-$ [5]. These ions are also present in acetonitrile solution[18]. A vapour pressure study of the compound has shown that it is completely dissociated in the vapour phase[18]

$$PBr_5 \longrightarrow PBr_3 + Br_2$$

The only arsenic pentahalide stable at room temperature is AsF_5[19] which is a gas like PF_5. In liquid HF, AsF_5 (and SbF_5) gives conducting solutions, probably because of the reaction[5]

$$2HF + 2AsF_5 \longrightarrow H_2F^+ + As_2F_{11}^-$$

$$(2HF + SbF_5 \longrightarrow H_2F^+ + SbF_6^-).$$

Arsenic pentachloride ($AsCl_5$), which is unstable above -50°C, has recently been prepared by photochlorination of $AsCl_3$ at -105°C[20], its structure is not known.

Antimony pentafluoride is a viscous liquid and it is not certain whether it is dimeric Sb_2F_{10} or whether polymers $(SbF_5)_n$ are present. An ^{19}F NMR study of the liquid suggests that each antimony atom is surrounded octahedrally by six fluorine atoms, two cis fluorine atoms, being shared with adjacent octahedra. In the solid it contains tetramers[19] in which each SbF_6 unit shares two adjacent corners, its structure is similar to that of $(RhF_4)_4$[21]. Its vapour from 140°C to 350°C consists of polymers plus a small amount of monomer and the proportion of the latter appears to have a trigonal bipyramidal structure[22]. Antimony pentachloride loses chlorine readily and is a powerful chlorinating agent. It is dimeric[5], $Cl_4Sb(\mu\text{-}Cl_2)SbCl_4$, Both solid and liquid $SbCl_5$, contain individual trigonal bipyramidal molecules[19].

Bismuth pentafluoride was synthesised by Fisher and Rudzitis[23] from bismuth and fluorine at 500°C. It has also been prepared by fluorination[24] of BiF_3 at 550°C, it is a white solid and an extremely powerful fluorinating agent. The solid appears to have the uranium pentafluoride structure with infinite chain of trans-briged BiF_6 octahedra. Raman data has confirmed that the bridges linking the octahedrally co-ordinated bismuth atoms are trans[25]. $BiCl_5$ is not known the pentabromides and pentaiodides of As, Sb, and Bi have not been reported in the literature.

Mixed pentahalides of Group VB elements (EX_nY_{5-n})

In spite of there being a large number of possible mixed halides of group VB elements, relatively few have been isolated and characterised Those containing fluorine and chlorine have received more attention [26] than the rest of the mixed pentahalides, although compounds containing fluorine and bromine have received some study[35].

Table 1. Mixed pentahalides.

Phosphorus	Arsenic	Antimony
PF_4Cl[27]		SbF_3Cl_2[37]
PF_3Cl_2[28 29]	AsF_3Cl_2[36]	SbF_2Cl_3[38]
PF_2Cl_3[30 31]		$SbFCl_4$[39]
$PFCl_4$		
PF_3Br_2[32]		SbF_3Br_2[37]
PF_2Br_3[33]		
$PFBr_4$[34 35]		

These compounds are prepared by the addition of halogen to the EX_3 compound

e.g. $PF_3 + Cl_2 \longrightarrow PF_3Cl_2$[40].

Table 2 lists those compounds which have been well characterised. The mixed pentahalides (e.g. PF_2Cl_3 and PBr_4F) on preparation usually form molecular liquids[41], which on standing for some time transform into ionic solids[42]. A summary of their behaviour is given in table 2.

Table 2. The nature of phosphorus mixed pentahalides

Imperical formula	Form (s) observed	Ref
$PFCl_4$	molecular + ionic (PCl_4^+ F^-)	43
PF_2Cl_3	molecular	31
PF_3Cl_2	molecular + ionic (PCl_4^+ PF_6^-)	44
PBr_4F	molecular + ionic (PBr_4^+ F^-)	45
PBr_2F_3	ionic (PBr_4^+ PF_6^-)	46
AsF_3Cl_2	ionic ($AsCl_4^+$ AsF_6^-)	47
$SbCl_4F$	ionic ($SbCl_4^+$ F^-)	48
SbF_3Cl_2	molecular ± ionic ($SbCl_4^+$ SbF_6^-)	49

Sometime a solid ionic product is obtained directly, for example fluorination of PCl_5 by AsF_3 gives a product of imperical formula PF_3Cl_2, which is solid at room temperature and contains PCl_4^+ PF_6^- $[(PF_3Cl_2)_2]$, whereas PF_3Cl_2 prepared from $PF_3 + Cl_2$ is liquid (b.p. 8°C) with a molecular structure containing trigonal bipyramidal molecules.

Thus a significant feature of these compounds is their existence in molecular and ionic forms. This can be regarded as covalent-ionic isomerism and as can be seen from Table 2, mixed halides of this group behave likewise. No mixed pentahalides of bismuth are known.

Higher Halides of Group VB elements (P, As, Sb, Bi)

Phosphorus is the only element in this group which exhibits an apparent oxidation number more than five in its halides. No work has been reported on higher halides of As, Sb and Bi, but a number of higher phosphorus halides both from single halogen and mixed halogens have been investigated. Biltz and K. Jeep[50] observed in the system PCl_5-Cl_2 that a phase richer in chlorine than phosphorus pentachloride may exist, but this has never been investigated.

There is evidence for PBr_7, PBr_9 and PBr_{17}[10, 51] in the phosphorus tribromide-bromine system. Because electrical conductivity is high in these systems, the results cannot be interpreted in terms of simple molecular equilibria, but undoubtedly electrolytic dissociation involving polybromide ionic species occurs[52]. PBr_7 has been shown by X-ray analysis to be $PBr_4^+ Br_3^-$[53].

The viscosity, density and electrical conductivity of the system phosphorus triiodide-iodine suggest the possible existence[10, 54] of higher iodides of phosphorus, but this has never been confirmed. The mixed halides, PCl_2Br_7[10], and PCl_3Br_n[55] ($n = 4$-10) are obtained from the phosphorus trichloride-bromine reaction. PCl_3Br_{18} and PCl_3Br_4[56] have been shown to exist from the evidence of thermal analysis. When a mixture of PBr_5 and PCl_3 in the ratio 2:3 is heated to 40-50°C, orange crystals of PCl_3Br_4[57] are obtained. Viscosity-composition studies also suggest a compound PCl_3Br_8[56] but there is no further evidence in support of this. PCl_6I[58, 59] is obtained by the reaction of PCl_5 and iodine in CCl_4 and has been shown by X-ray diffraction to be $[PCl_4]^+$ $[ICl_2]^-$[60].

The system PBr_5-IBr yields the compound PBr_6I which is formulated as $[PBr_4]^+$ $[IBr_2]^-$[61] but no compound has been isolated[10]. The mixed halides PBr_5ICl[62] (cherry red needles m.p. 112°C) and PCl_5IBr[63] (yellow m.p. 140°C) have been prepared from the mixture of PCl_5, PBr_5, IBr and ICl in carbon tetrachloride.

In general bromine containing compounds with a high halogen to phosphorus ratio are unstable and tend to lose bromine readily[64].

Lower halides of Group VB elements

All of the elements of group VB form compounds in which the formal oxidation state of the element is less than three. The monohalides, PCl, PBr, and PI are unstable under normal condition and are detected only in spectral bands[60]. Phosphorus dihalides , PX_2 are in fact dimeric, P_2X_4, and are represented by the known compounds P_2F_4, P_2Cl_4 and P_2I_4.

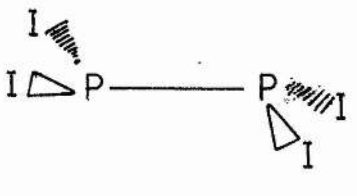
For the other group VB elements only As_2I_4[5], Sb_2I_4[65] and Bi_2I_4[66] are known. These compounds may be prepared either by direct reaction of the elements

e.g. $2As + 2I_2 \xrightarrow[\text{sealed tube}]{260^{\circ}C} As_2I_4$

or by a coupling reaction

e.g. $2PF_2I + 2Hg \xrightarrow{\text{reduced pressure}} P_2F_4 + Hg_2I_2$.

In the solid state it has been shown that these compounds contain an E-E bond. For example P_2I_4 has the trans structure[10]



Organo Substituted Group VB Halides

The preparation of the compounds R_nEX_{5-n} (R = alkyl or aryl), in which halogen atom in EX_5 has been replaced by organic groups can be readily achieved by standared procedures. It is usual for the organic group to be introduced at first to an E (III) compound, which is then further reacted with halogen, for example,

$$EX_3 + RMgX \longrightarrow REX_2 + MgX_2$$

followed by

$$REX_2 + X_2 \longrightarrow REX_4$$

Similarly,

$$R_2MX + X_2 \longrightarrow R_2MX_3$$

$$R_3M + X_2 \longrightarrow R_3MX_2.$$

The R_4EX compounds are prepared by a quaternization reaction

e.g. $R_3E + RX \longrightarrow R_4EX$

or by the reaction of halogen or hydrochloric acid on pentaalkyl or pentaaryl compounds, for example

$$Ph_5Sb + X_2 \longrightarrow Ph_4SbX + RX$$

and

$$Ph_5Bi + HCl \longrightarrow Ph_4BiCl + C_6H_6$$

Specific examples of compounds prepared thus are $(C_6H_5)PCl_4$[67], $(C_6H_5)_2PCl_3$[68], $(C_6H_5)_3PCl_2$[69], $(C_6H_5)_3PI_2$[70], and $(C_6H_5)_5P$[71]. Thus compounds in the series REX_4, R_2EX_3, R_3EX_2, R_4EX can be readily obtained and the number of such compounds known is large. A brief survey of the chemistry of each compound type follows.

REX_4

The phosphorus compounds RPX_4 have been described as molecular in non polar solvents by Rochow et al[72], but Van Wazer[63] and Kosolopoff[73] have both suggested that the structure is ionic, $[RPX_3]^+$ $[X]^-$. The formation of RPX_6[74, 75] ($RPX_3^+ X_3^-$) from $PhPBr_4$, $PhPBr_2Cl_2$ and halogen supports the ionic structure. There is now firm evidence for both ionic and molecular compounds of type REX_4. The ^{19}F NMR of the fluorine compounds, RPF_4 ($R = CH_3$, C_2H_5, $n\text{-}C_4H_9$, C_6H_5) and some arsenic and antimony analogues suggests that they are covalent molecular with trigonal bipyramidal structures[33, 76]. An electron diffraction study of CH_3PF_4[77] also showed that this has the trigonal bipyramidal structure.

Mc Pherson[78] determined the conductivity of $PhPCl_4$ in acetonitrile and his results ($\Lambda_m = 16.88$ S cm^2 mol^{-1}; $C_m = 0.02884$ mol dm^{-3}) indicate that this compound is a weak electrolyte,

$$PhPCl_4 \rightleftharpoons PhPCl_3^+ + Cl^-$$

and therefore probably covalent molecular in the solid. Recently[79] NQR spectroscopy and ^{31}P NMR spectroscopy have played an important role in determining the solid state structure of these compounds. Whitehead and coworkers[80, 81] from their ^{35}Cl NQR spectra concluded that $PhPCl_4$ possess the ionic structure $[PhPCl_3]^+ [Cl]^-$, but in contrast Svergun et al[82] from NQR measurements found for $PhPCl_4$ a trigonal bipyramidal structure. Waddington et al[79] re-examined the ^{35}Cl NQR spectra of $PhPCl_4$ and their conclusions were in complete agreement with those of Svergun et al[82] and Mc Pherson[78]. Waddington et al[79] also studied the ^{31}P NMR and ^{35}Cl NQR spectra of $PMeCl_4$ and found it to have an ionic structure of the type $[PMeCl_3]^+ [Cl]^-$ in the solid state. These results are in complete agreement with the previous vibrational spectroscopic studies of $PMeCl_4$ [83, 84], which showed that these compounds have ionic structures in the solid state although a molecular structure for $PMeCl_4$ is possible in solution[84]. ^{35}Cl NQR spectra confirmed trigonal bipyramidal structure for $C_6F_5PCl_4$[85].

Arsenic compounds of this type are rare and only a few have been isolated CH_3AsCl_4[86], CH_3AsI_4[87], $(2\text{-}CH_3C_6H_4)AsCl_4$[88], $(C_6H_5)AsCl_4$[89]. The structure of these compounds is not known with certainty. Smith[90] was unable to draw definite conclusions from the infra-red and NMR spectra of phenylarsenic tetrafluoride, but Muetterties [33] suggested five coordinate stereochemistry for this compound on the basis of its ^{19}F NMR spectrum. The vibrational spectrum of $PhAsCl_4$ suggests that it has a trigonal bipyramidal structure with an equatorial phenyl group[79]. The ^{35}Cl NQR spectrum of $PhAsCl_4$ is very similar to that of the analogous phosphorus compound[91, 79], which suggests that these compounds may be isostructural with strong similarities in bonding.

No alkylantimony tetrachlorides, tetrabromides or tetraiodides have been described, although several alkylantimony tetrafluorides[92] have been reported. Arylantimony tetrachlorides have been obtained[93, 94], but nothing is known about their structure. There is no report in the literature concerning the existence of bismuth compounds of type $RBiX_4$.

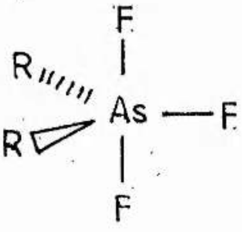
R_2EX_3

There has been fairly firm evidence produced for both ionic and covalent forms in the R_2EX_3 group of compounds. A trigonal bipyramidal structure has been determined for $(CH_3)_2PF_3$, by electron diffraction[77]. R_2PX_3 (R = C_2H_5, C_3H_7, and X = Br) reacts with halogen to form R_2PX_5 which gives conducting solutions in polar solvents indicating a structure ($R_2PX_2^+$ X_3^-) for these compounds[95].

The conductivity of Ph_2PCl_3[89] in acetonitrile ($\Lambda_m = 2.54$ S cm^2 mol^{-1}; $C_m = 0.02310$ mol dm^{-3}) suggests that Ph_2PCl_3 is a weak electrolyte in this solvent and hence probably molecular in the solid. The ionic structure for Ph_2PCl_3 reported by Whitehead and co-workers[80, 81] on the basis of ^{35}Cl NQR measurements is rejected by Svergun et al[82], who have shown that the compound has a molecular trigonal bipyramidal structure. Waddington et al[79] have studied ^{31}P NMR and ^{35}Cl NQR spectra for a number of compounds, PMe_nCl_{5-n} ($1 < n < 3$), PEt_2Cl_3 and PEt_3Cl_2 and have deduced that they have ionic structures of the type $[PR_nCl_{4-n}]^+ [Cl]^-$ in the solid state. The vibrational spectra of PMe_2Cl_3[83] and PMe_3Cl_2[96] are in agreement with this structure.

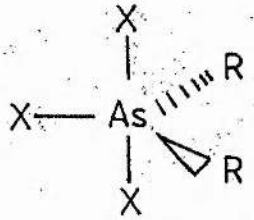
The number of arsenic compounds of type R_2AsX_3 is small and includes Me_2AsCl_3[86], Ph_2AsBr_3[97], Ph_2AsCl_3, $(CF_3)_2AsCl_3$[98] and dibenzylarsenic-trichloride[99]. Muetterties and co-workers[33, 76] have concluded from ^{19}F NMR spectra that diphenylarsine trifluoride has a slightly distorted trigonal bipyramidal structure in which two fluorine atoms occupy the axial position. Fig 1

Fig. 1.



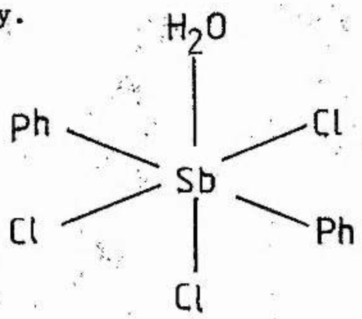
Vibrational spectral studies have also suggested that Me_2AsCl_3 and Ph_2AsCl_3 have trigonal bipyramidal structure[100] with the organic group in equatorial positions Fig. 2.

Fig. 2.



These results are in agreement with the results of ^{35}Cl NQR studies[79].

Few dialkyl- and diaryl-antimony trihalides are known. Dimethylantimony trichloride[101] and tribromide are unstable at room temperature. Dimethylantimony trifluoride[102] has also been prepared. These alkyl compounds are very unstable; in contrast the few known aryl derivatives appear to be much more stable e.g. $(C_6H_5)_2SbCl_3$[103, 104]. Very little is known about the structure of these compounds. Polynova and Porai-Koshit[105] on the basis of X-ray diffraction work described Ph_2SbCl_3 as trigonal bipyramidal, but later on, Polynova and Porai-Koshits[106] re-investigating its X-ray crystal structure formulated the compound as a monohydrate ($Ph_2SbCl_3.H_2O$) with octahedral geometry.



Kolditz and co-workers[107] have carried out conductivity studies on

Ph_2SbCl_3 and these showed that the compound is a weak electrolyte in acetonitrile. This is in keeping with the solid being molecular.

Dialkyl-or diaryl-bismuth trihalides have not been found in the literature.

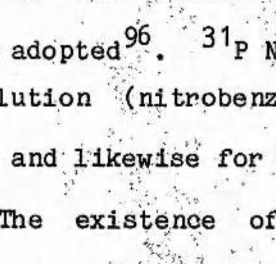
R_3EX_2

Of all the compounds of type R_nEX_{5-n} (n= 0,1,2,3,4), most work has been done on those of general formula R_3EX_2 and the structure of these compounds has been the subject of discussion by various authors[108, 72].

From spectroscopic studies of $(Me)_3PX_2$ (X= Cl, Br, I), it has been shown that in the solid state ionic structure of the type $[Me_3PX]^+$ $[X]^-$ are adopted[96]. ^{31}P NMR studies of Ph_3PBr_2[109] in the solid and in solution (nitrobenzene) have shown it to be ionic $[Ph_3PBr]^+$ $[Br]^-$, and likewise for solid Ph_3PI_2 the structure is $[Ph_3PI]^+$ $[I]^-$. The existence of the halogenotriorganylphosphonium cation, $[R_3PX]^+$ in the pentacovalent R_3PX_2 (R= Et, Pr, Bu, iso-amyl, Cyclohexyl or Ph) is now well established[110, 111].

A ^{35}Cl NQR study[112] indicates that R_3AsCl_2 (R= Me, Ph) like the phosphorus analogues have a trigonal bipyramidal structure in which all the R groups occupy equatorial positions and the two chlorine atoms are situated axially Fig. 3

Fig. 3



Infrared[113, 114, 115] and conductivity[116, 117] data indicate that compounds of type R_3AsX_2 (R= Me, Et, $PhCH_2$, 2-thienyl, Ph; X= F, Cl), also have trigonal bipyramidal structures. Brill and Long[112] have studied the NQR spectra of R_3EX_2 (R= Me, $PhCH_2$, Ph; X= F, Cl, Br, E= As, Sb, Bi) and concluded that with the exception of $(Me)_3AsBr_2$, the compounds have trigonal bipyramidal geometry in the solid state. Subsequently Hursthouse and Steer[118] have shown that $(CH_3)_3AsBr_2$ is ionic, $[(CH_3)_3AsBr]^+ [Br]^-$, by an X-ray crystal analysis.

Recently Ferguson and co-workers[119] have shown from an X-ray crystallographic study of Ph_3AsF_2 that the arsenic atom has near regular trigonal bipyramidal geometry with the two fluorine atom in the axial positions. The As-F bond is long (1.834 A^o) which is usual for axial E-X bonds in a trigonal bipyramidal structure. In arsenic pentafluoride[120], for example the As-F (axial) distance is 1.711 A^o [As-F (equatorial) = 1.656 A^o] and in $(CH_3)_3PF_2$[77], P-F (axial) is 1.643 A^o [P-F (equatorial) = 1.553 A^o.

Verdonck et al[121] reported both vibrational and ^1H and ^{19}F NMR spectra for the compounds $(PhCH_2)_3EX_2$ (E= As or Sb and X= F or Cl). The vibrational spectra (in solid and solution) have been interpreted in terms of a slightly distorted trigonal bipyramid. This is consistent with the ^{35}Cl NQR studies of Brill and Long[112].

From infrared data, molecular weights, and conductivity measurements[122] Ph_3BiX_2 (X= F, Cl) compounds were reported to be non-ionic molecular in constitution. The infrared and Raman spectra of Ph_3BiX_2[123] (X= F, Cl, Br, NCO) in the solid and in benzene have been recorded and the results are consistent with a trigonal bipyramidal skeleton for these compounds both in the solid and solution.

Wells[124] noted the abnormal length of the Sb-halogen bond in $(Me)_3SbX_2$ and he suggested that it is intermediate between ionic and covalent. Jensen[125] also concluded from the high atomic polarisability of the compounds that these Sb-X bonds were very polar. The As-F bonds in Ph_3AsF_2[119] [1.834 A°] are longer than As-F distance in AsF_3 (1.706 A°). The Bi-Cl bonds in Ph_3BiCl_2 are likewise longer than expected for a covalent Bi-Cl bonds (2.61 A°, compared with 2.48 A° for $BiCl_3$).

Harris and co-workers[116, 126] have made an extensive study of the compounds R_3EX_2 in ionising solvents (acetonitrile and nitrobenzene). They have shown by conductivity studies in methyl cyanide that the triphenylphosphorus dihalides (R_3PX_2) are strong electrolytes and that the triphenylantimony and -bismuth dihalides (R_3SbX_2 and R_3BiX_2) are non-electrolytes; and it is suggested that the solids are respectively ionic and covalent. These investigations also showed that triaryl-arsenic dihalides are weak electrolytes and therefore probably covalent in the solid state. From these results they concluded that covalent tendency increases down the group ie. $P < As < Sb < Bi$.

Harris et al[117] have studied the ionisation of Ph_3AsCl_2 and Ph_3AsBr_2 in acetonitrile and have concluded from quantitative electrolysis experiments that they ionise as follow.

$$2Ph_3AsCl_2 \rightleftharpoons Ph_3AsCl^+ + Ph_3AsCl_3^-$$

$$Ph_3AsBr_2 \rightleftharpoons Ph_3AsBr^+ + Br^-$$

This different mode of ionisation of the dichloride and dibromide is reminiscent of that of phosphorus pentachloride

$$2PCl_5 \longrightarrow PCl_4^+ + PCl_6^-$$

and phosphorus pentabromide

$$PBr_5 \longrightarrow PBr_4^+ + Br^-$$

in the same solvent[127, 128].

However, in contrast to these results the triphenylphosphorus dihalides have been shown from a ^{31}P NMR study[129] and from their reaction with a strong chloride ion donor (tetramethylammonium chloride)[130] to be ionised completely in acetonitrile in the sense;

$$Ph_3PX_2 \rightleftharpoons Ph_3PX^+ + X^-,$$

and there is no evidence for the alternative

$$2Ph_3PX_2 \rightleftharpoons Ph_3PX^+ + Ph_3PX_3^-$$

Nöth and Vetter[131] have shown by conductivity measurement in nitrobenzene that tris(dimethylamino)phosphine dichloride $(Me_2N)_3PX_2$ (X= Cl, Br, I) behave as strong electrolytes and have suggested the ionic structure $[(Me_2N)_3PX]^+ + [X]^-$ for these compounds. Harris et al[132] have also recently reported the conductivity of tris(dimethylamino)phosphine dihalides (X_2= Cl_2, Br_2, I_2, IBr and ICl) and of the corresponding tris(dimethylamino)arsine in acetonitrile and have concluded that the dihalides, with the exception of $(Me_2N)_3AsCl_2$ and $(Me_2N)_3PCl_2$, behave as strong electrolytes in acetonitrile. The molar conductivity values of the dichlorides are below the range expected for strong electrolytes. It is well established that the dichlorides are weaker electrolytes than the dibromides in other R_3EX_2 systems[117, 133].

R_4EX

Organic derivatives of the type $[R_4E]^+ X^-$ are well known for phosphines and arsines. Trialkyl and triarylphosphines and arsines, generally react fairly readily with alkyl or aryl halide to form quaternary salts.

$$R_3E + R'X \longrightarrow [R_3ER']^+ X^-$$

Quaternization becomes more difficult with antimony and bismuth, especially when organic group is electron withdrawing e.g, phenyl or CF_3.

These compounds (R_4EX) 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 and in solution. A crystal structure analysis of Ph_4PI[70] has confirmed that the structure is built from Ph_4P^+ and I^- ions. Recently Clark et al[134] have reported that Ph_4PF can exist in a molecular, covalent as well as normal ionic form. Harris and Mitchell[135], with a view to making a conductivity study of this compound, attempted to prepare Ph_4PF, but could not obtain it in any form.

Although the tetraphenylstibonium halides are also generally regarded as having an ionic structure $[R_4Sb]^+ X^-$, Schmidbaur and co-workers[136] suggested a covalent trigonal bipyramidal structure for Me_4SbF and Me_4SbOH[137]. Beauchamp et al[138] have determined the crystal structure of Ph_4SbOH[139] by X-ray diffraction and shown that the molecule of this compound is also a trigonal bipyramid with the hydroxide group occupying an axial position. The axial Sb-C distance (2.218 A^o) is longer than the equatorial Sb-C distance (2.116-2.140^{o}A). This result is consistent with the generally accepted rule that the more electronegative substituents groups occupy axial positions and that the axial bond lengths are greater than the equatorial ones.

The only known bismuth compounds of type R_4EX are the tetraphenyl compounds. They are obtained by the cleavage reactions involving pentaphenyl bismuth[140].

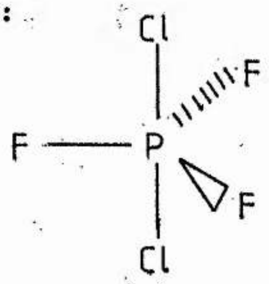
$$Ph_5Bi + Br_2 \xrightarrow[\text{ether}]{-70^{o}C} Ph_4BiBr + PhBr.$$

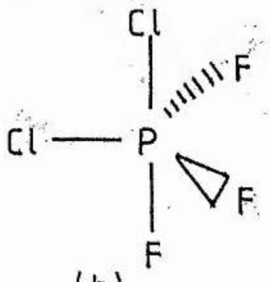
These compounds are very labile and decompose at room temperature. Their structure is not known.

Isomerism in Pentacovalent Molecule

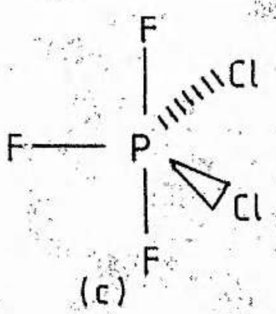
Because of the non-equivalence of axial and equatorial positions in the trigonal bipyramidal structure there is the possibility of geometrical isomerism occuring in the molecular form of the mixed pentahalides and organosubstituted pentahalides of the group VB elements (P, As, Sb, Bi). For example PF_3Cl_2 has three possible isomers:

(a)





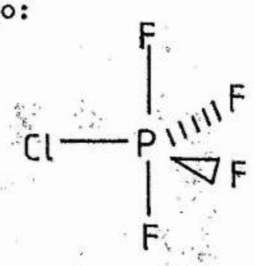
(b)



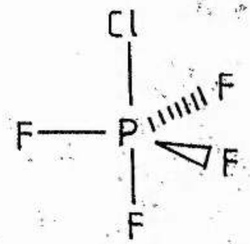
(c)

and $PClF_4$ has two:

(a)

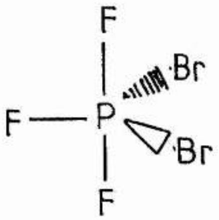


(b)

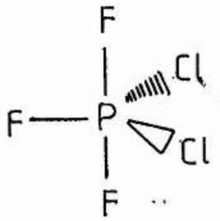


However, there is no example known of a compound being isolated in more than one of its forms.

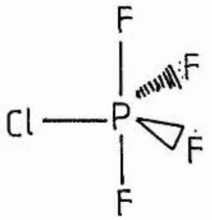
The molecules PF_3Br_2, PF_3Cl_2, and PF_4Cl have C_{2v} symmetry as indicated from their vibrational spectra[141, 142], and hence their structures are:



(a) PF_3Br_2

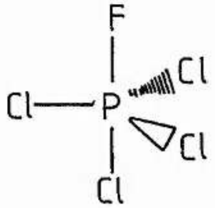


(b) PF_3Cl_2



(c) PF_4Cl

and $PFCl_4$ has C_{2V} symmetry indicating the structure



All of the structures of pentacovalent compounds of group VB elements so far determined lead to the empirical rule that the most electronegative ligands always occupy the axial positions[143, 144].

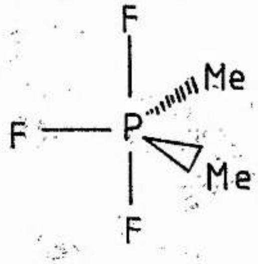
The mixed pentahalogeno derivatives PX_nY_{5-n} (n= 1-5) show also ionic-covalent isomerism of the type shown by the simple halides PCl_5 and PBr_5. For example molecular PF_3Cl_2 is a gas at room temperature and is formed in the vapour phase by the reaction

$$PF_3 + Cl_2 \longrightarrow PF_3Cl_2.$$

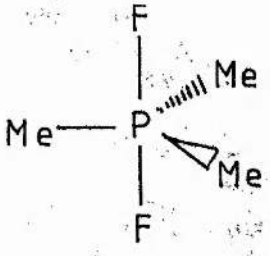
The isomeric salt-type compound has the structure $[PCl_4]^+[PF_6]^-$ and can be prepared quantitatively by the action of AsF_3 on PCl_5 in arsenic trichloride[145, 44]. Unlike the gaseous molecular compound, PF_3Cl_2, this isomer is a white solid which sublimes at 135°C, and is sparingly soluble in $AsCl_3$. The conductivity of $[PCl_4]^+[PF_6]^-$ in acetonitrile is high[44], whereas that of molecular PF_3Cl_2 in acetonitrile is low[27].

When the compound $[PCl_4]^+[PF_6]^-$ is sublimed, it changes to the gaseous covalent compounds, PF_5 and PCl_4F[27]. $PFCl_4$ is not stable on standing and is transformed to the isomeric $[PCl_4]^+ F^-$. The ionic nature of this isomer is shown by its solubility and conductivity in acetonitrile[27].

Organosubstituted pentacoordinated halogeno compounds R_nPX_{5-n} (n= 1-4) have similar structural features. The fluoromethylphosphoranes, Me_2PF_3 and Me_3PF_2, each have a trigonal bipyramidal framework and the spectra are best interpreted in terms of C_{2v} and D_{3h}[145] structures respectively.



(Me_2PF_3)
(a)



(Me_3PF_2)
(b)

Again, the general rule is followed that the fluorine atoms occupy the axial sites of the trigonal bipyramidal structure. In CH_3PF_4 the methyl group occupies an equatorial position. Infra-red and Raman spectra showed that in the compounds $(CF_3)_2PCl_3$ and CF_3PCl_4, the trifluoromethyl groups occupy axial sites[146], [147]. The electronegativity of the CF_3 group is greater than that of chlorine and lies between that of fluorine and chlorine.

Spectroscopic studies of the compounds, PMe_4Cl, PMe_3Cl_2, PMe_2Cl_3, $PMeCl_4$, PEt_2Cl_3, PEt_2Br_3, and Me_3PFCl suggest that the compounds exist as phosphonium salts of the type $[PR_nX_{4-n}]^+[X]^-$ [83]. However, the spectra of $PMeCl_4$ in non-ionising media show that the compound is molecular, possibly with C_{2v} symmetry[84].

Clark et al[134] have recently reported that tetraphenylfluorophosphorane can exist in three different forms the ionic form $Ph_4P^+F^-$, the molecular form Ph_4PF and a dimer.

Compounds of arsenic and antimony are expected to show similar stereochemical properties but compared with the phosphorus compounds relatively few experimental results are available[4].

Bonding in Penta-coordinated Compounds

In the pentacovalent molecular compounds of phosphorus, arsenic, and antimony the central atom has five bonding pairs of electrons in its valence shell and the usual trigonal bipyramidal arrangement is predicted. Structural analysis by ^{19}F, ^{31}P NMR, ^{35}Cl NQR, Raman and infra-red spectroscopy, electron diffraction, X-ray crystal structure analysis etc; have shown that the trigonal bipyramidal arrangement is in fact generally adopted by these compounds. In the trigonal bipyramidal structure different bond lengths are found for the axial and equatorial E-Halogen bonds. This variation in bond length inspired the development of theories to explain the nature of bonding in penta-coordinated compounds and to understand its influence on the type of geometry adopted.

One of these theories, the Valence Bond approach, describes the bonding of five coordinated molecules in terms of σ-bonds involving a set of five sp^3d hybrid orbitals on the central atom. This description requires the promotion of an s electron into an empty d-orbital, mixing of the orbitals, and pairing up of the valence shell electrons with those of the ligands.

Muetterties and co-workers[76] have proposed a slight variation of this approach and have suggested that in the trigonal bipyramidal structure the equatorial groups are bonded by sp^2 hybrids and the axial groups by pd hybrids, and the difference in energy level between these two sets should reflect the s electron promotion energy. As the electronegativity of the ligands (i.e halogens) increases the difference in energy of these hybrid orbitals becomes less and this is reflected in the relative bond distances e.g.

$P—Cl_{ax} = 2.19^{o}A$, $P—Cl_{eq} = 2.04^{o}A$ $\triangle = 0.15^{o}A$

and

$P—F_{ax} = 1.57^{o}A$ $P—F_{eq} = 1.53^{o}A$ $\triangle = 0.043^{o}A$ [77]

It has generally been thought that the high energy and diffuse nature of d-orbitals would not lead to effective hybridisation with s and p orbitals and that their diffuse nature would lead to a poor overlap with neighbouring atoms and hence would contribute only very slightly towards effective bonding. However D. P. Craig and co-workers[148] suggested that when electronegative groups are attached to the central atom, contraction of d-orbital occurs thus allowing more effective overlap and stronger bonding.

Attempts have been made to explain the bonding in compounds such as PX_5 (X= halogens) without recourse to d-orbitals. One such attempt is that of Rundle[149, 150], in his approach the X-P-X axial part of the molecule is regarded as being held together by a four electron three centre bond. The three centre bonding system arises from one atomic p-orbital from each atom giving rise to a bonding, a non-bonding and an antibonding molecular orbital. The bonding and non-bonding orbitals each contain a pair of electrons. The equatorial bonds are normal electron pair bonds and can be regarded as involving sp^2 hybrid orbitals on the central atom.

This scheme have two advantages:

(i) d-orbitals are not involved (it is still very much a controversial matter as to whether d-orbitals are involved in this type of molecule

(ii) The longer axial bonds follow as a natural consequence of the three-centre bond system.

Effect of the substituent Group R on the properties of R_3EX_2 Compounds

It has been shown that the molecular/ionic behaviour of the compounds R_3EX_2 is dependent on the nature of group R.

Harris and co-workers[151, 152, 153] have widely investigated the correlation between the nature of group R and the conductivity of R_3EX_2 in acetonitrile and nitrobenzene. They observed that R_3PX_2 compounds are not always strong electrolytes and R_3AsX_2 compounds are not always weak electrolytes. This is because the nature of the substituent group R plays a part in determining the behaviour of the compound. Changing the nature of R in R_nPX_{5-n} whilst keeping n and x the same can produce marked changes in conductivity e.g.

Table 3. Molar conductivity at $C_m = 0.01$ mol dm^{-3} in acetonitrile

Compound	Molar conductivity (S cm^2 mol^{-1})	Compound	Molar conductivity (S cm^2 mol^{-1})
$(C_6H_5)_3PCl_2$	78.1 [154]	$(C_6H_5)_3AsBr_2$	25.0 [152]
$(C_6F_5)_3PCl_2$	0.5 [154]	$(Me_2N)_3AsBr_2$	109.0[132]

They have concluded from these observations that there is a relationship between the electronegativity of group R in R_3EX_2 and the tendency of these compounds to adopt an ionic form. If R pulls electrons away from the central atom E the tendency to ionic behaviour is lessened [eg. $(C_6F_5)_3PCl_2$]: conversely if R pushes electrons on to E the tendency to ionic behaviour is increased. Or we can say that conductivity increases with a decrease in electronegativity of the substituent group R and vice versa.

Harris and Inglis[151] have made a preliminary study of some R_3AsX_2 compounds in which R is a para substituted phenyl group. Measurements of the conductivity of these compounds in methyl cyanide (Table 4) gave results which are consistent with the above conclusion.

Table 4. Molar conductivity of some R_3AsX_2 compounds in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Molar conductivity S cm^{-2} mol^{-1} X = Cl	Molar conductivity S cm^{2} mol^{-1} X = Br
$(4\text{-}ClC_6H_4)_3AsX_2$	3	12
$(C_6H_5)_3AsX_2$	12	25
$(4\text{-}CH_3C_6H_4)_3AsX_2$	13	54

It should be noted that the 4-chlorophenyl group is slightly more electronegative than the phenyl group and also that the 4-methylphenyl group is slightly less electronegative than the phenyl group. Thus these results support the idea that covalent character of these compounds increases with increasing electronegativity of the attached group. Decreasing the electronegativity would seem to weaken the As-X bond in the covalent molecule, making ionisation easier. It has been suggested[148] that the use of d-orbitals in trigonal bipyramidal structures is favoured by the attachment of electronegative groups to the central atom. Thus it may be regarded that the more electronegative the attached ligands, the more stable will be the covalent form of R_nEX_{5-n} compound relative to the ionic form.

The vibrational spectral results for the compounds Me_nPF_{5-n}, studied by Schmutzler and Downs[145] are closely correlated with these observations. On successive replacement of fluorine atoms in PF_5 molecule by methyl groups, a definite trend in stretching vibration frequencies of the axial P-F bonds is observed. These frequencies undergo a marked and regular decrease as fluorine atoms in PF_5 are replaced by methyl groups and this can be taken to indicate a weakening of the P-F bonds as the strongly electronegative fluorine atoms are replaced by the electron releasing methyl groups. For PF_5, CH_3PF_4 and $(CH_3)_2PF_3$ the electron diffraction results of Bartell and Hansen[77] confirmed that the trigonal bipyramidal skeletons are, at most, only slightly distorted. Moreover, the axial P-F bond distance increases significantly as the number of methyl groups increases eg. P-F bond length for PF_5 is $1.577^{\circ}A$, $CH_3PF_4 = 1.612^{\circ}A$, $(CH_3)_2PF_3 = 1.643^{\circ}A$.

From the vibrational spectral studies and calculation of bond order of axial P-F bonds in $(CH_3)_nPF_{5-n}$ molecules, Schmutzler and Downs[145] conclude that the replacement of four fluorine atoms by methyl groups would result in the formation, not of a five coordinate, but of an ionic system, viz $[(CH_3)_4P]^+ F^-$.

From the above observation one would expect molar conductivity to increase in the sequence $PF_4Me < PF_3Me_2 < PF_2Me_3$, due to the increasing weakening effect of the methyl groups on the P-F bond; weakening of the P-F bond should favour ionisation. G. S. Harris and F. Inglis[154] have studied the conductivity of some fluoromethylphosphoranes in acetonitrile and have shown that the results are entirely consistent with this.

Table 5. Molar conductivity of some $(CH_3)_nPF_{5-n}$ compounds in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	$\frac{\Lambda_m}{S\ cm^2\ mol^{-1}}$
CH_3PF_4	3.7
$(CH_3)_2PF_3$	6.2
$(CH_3)_3PF_2$	9.2

Mahomedy[153] has made a conductivity study of the R_3AsX_2 compounds in which $R = CH_3-C_6H_4$ and has studied the effect the position of the CH_3 group in the phenyl ring (2-, 3-, or 4-) has on the conductivity behaviour of these compounds in nitrobenzene. The results are summarised in Table 6.

Table 6. Molar conductivity of R_3AsX_2 in nitrobenzene at $C_m = 0.01$ mol dm^{-3}

Compound	$\frac{\Lambda_m}{S\ cm^2\ mol^{-1}}$	Compound	$\frac{\Lambda_m}{S\ cm^2\ mol^{-1}}$
$(2\text{-}CH_3C_6H_4)_3AsCl_2$	6.73	$(2\text{-}CH_3C_6H_4)_3AsBr_2$	14.30
$(3\text{-}CH_3C_6H_4)_3AsCl_2$	0.72	$(3\text{-}CH_3C_6H_4)_3AsBr_2$	5.57
$(4\text{-}CH_3C_6H_4)_3AsCl_2$	1.12	$(4\text{-}CH_3C_6H_4)_3Br_2$	5.02
$(C_6H_5)_3AsCl_2$	0.38	$(C_6H_5)_3AsBr_2$	2.67

It is noted that introduction of a CH_3 group in the phenyl ring enhances molar conductivity relative to the triphenylarsine compounds and that this enhancement is very much greater in the case of the 4-substituted compound. Mahomedy puts this down to a steric effect of the ortho position.

OBJECTIVES OF THE RESEARCH

The work described in this thesis is concerned with the reaction of triarylarsine and triarylstibine with halogens. The aryl groups are in the main monosubstituted phenyl (2-, 3-, and 4-) and were chosen to cover the range from electron releasing to electron withdrawing. It was thought to be of interest to examine the reactions of halogens with these arsines and stibines in order to determine the extent to which the course of the reactions, the adducts formed, and the electrolytic conductivity of the adducts were influenced by the substituent in the phenyl ring. It was of special interest to look at the effect on the conductivity properties of the dihalides (R_3EX_2) of

(a) the nature of the substituent (electron withdrawing or electron releasing)

and

(b) the position of the substituent in the ring (2-, 3-, 4-).

The research comprised three main parts:

I. A Study of some R_3As-Halogen Systems

This part is concerned with,

(a) A conductometric titration study of the $(YC_6H_4)_3$As-halogen systems to find out what adducts are formed in these systems and if the extent and ease of formation of adducts is affected by the nature of Y.

(b) Attempts to isolate adducts indicated by conductometric titration.

(c) An electrolytic conductivity study of the dihalides $(YC_6H_4)_3AsX_2$ in acetonitrile to determine the effect of group Y on the tendency of these compounds to ionise in solution.

II. A Study of some R_3Sb-Halogen systems

The object of this study is to gain information on the electrolytic conductivity of a series of ortho substituted phenyl compounds, $(YC_6H_4)_3SbX_2$. The parent phenyl compounds $(C_6H_5)_3SbX_2$ being non-electrolytes, it was thought that 2-substitution of the phenyl ring might favour partial ionisation in a suitable solvent. It was believed that a conductometric titration study along with molar conductivity measurements would throw light on this problem.

III. A Study of the Electrolytic Conductivity of Tetraphenylstibonium Halides, R_4SbX

In view of the observed covalent molecular nature of triphenylstibine dihalides (Ph_3SbCl_2 and Ph_3SbBr_2) and the fact that tetraphenylstibonium hydroxide (Ph_4SbOH) and tetramethylstibonium hydroxide and fluoride (Me_4SbOH, Me_4SbF) are also reported to be covalent molecular it was decided to carry out a preliminary conductivity study of the tetraphenylstibonium halides Ph_4SbX (X = F, Cl, Br) in acetonitrile solution to gain insight into the nature (ionic-covalent) of these compounds.

RESULT AND DISCUSSION

PART I

REACTIONS OF TRIARYL-ARSINES AND STIBINES WITH HALOGENS AND INTERHALOGEN

Conductometric titration in good ionising solvents proved to be a very useful technique for studying the reactions of triphenyl-phosphine, -arsine and stibine, with halogens and interhalogens. Information can be obtained on both the stoichiometry and electrolytic behaviour of the reaction products. The course of the reactions of other triaryl-arsines and -stibines has now been studied by this technique using acetonitrile (dielectric constant = 38.8 at 20^{o}) as the solvent.

Strong 1:1 electrolytes have molar conductivity of about 100-150 S cm^2 mol^{-1} and weak electrolytes have a molar conductivity of about 5-25 S cm^2 mol^{-1} at concentration of about 0.01 mol dm^{-3} which is the concentration used in the present work.

A.

1. REACTIONS OF THE TRIMETHYLPHENYL-ARSINES WITH HALOGENS AND INTERHALOGEN

(a) Reactions with bromine

The results of the conductometric titrations of tri(2-methylphenyl)arsine, tri(3-methylphenyl)arsine, and tri(4-methylphenyl)arsine with bromine in acetonitrile are illustrated graphically in Fig. 4 (curves A, B, and C respectively).

In these three titrations, as bromine reacted with tri(methylphenyl)arsine the conductivity rose up to the 1:1 mole ratio after which a change in slope occurred but the conductivity continued

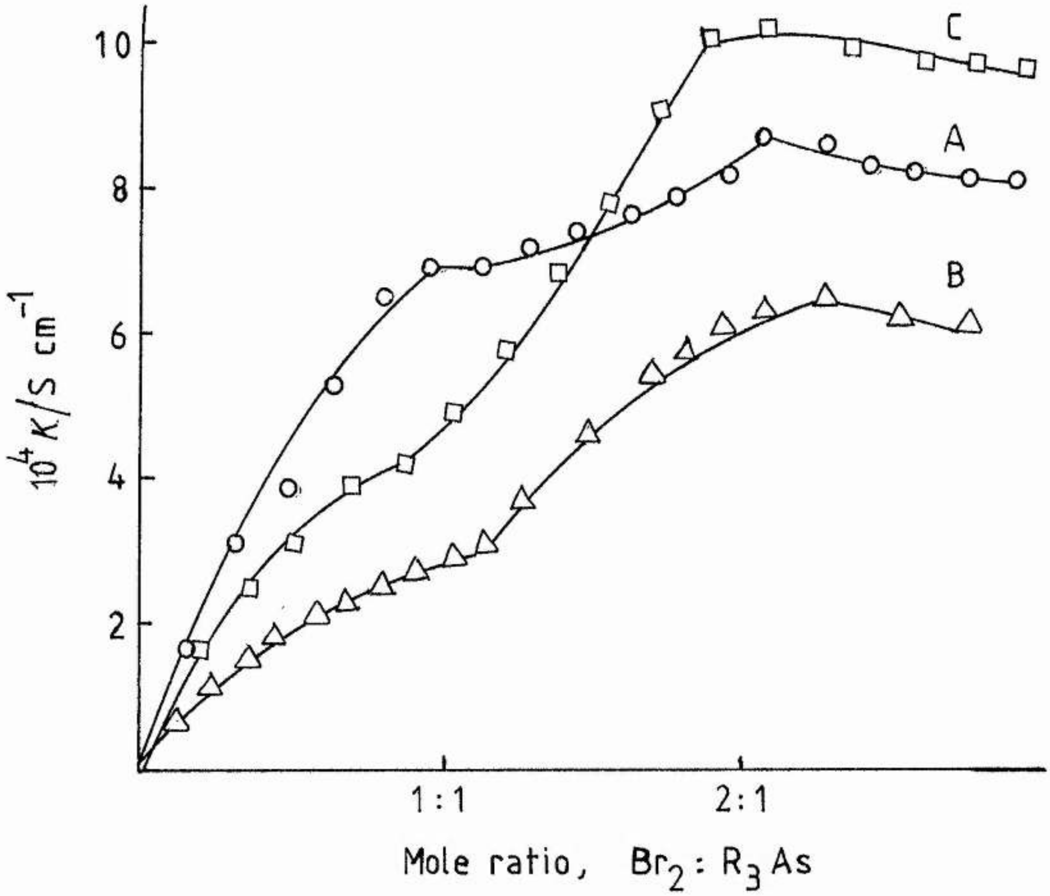


Fig. 4. Conductometric titration of R_3As with bromine

(A) $(2\text{-}CH_3C_6H_4)_3As\text{-}Br_2$

(B) $(3\text{-}CH_3C_6H_4)_3As\text{-}Br_2$

(C) $(4\text{-}CH_3C_6H_4)_3As\text{-}Br_2$

to rise until the 2:1* ratio was reached. Further addition of bromine resulted in a gentle decrease in conductivity. Thus distinct 1:1 and 2:1 breaks in the titration graphs occur in each case suggesting the formation in solution of 1:1 and 2:1 adducts (R_3AsBr_2 and R_3AsBr_4). In parallel with the conductivity changes during the titrations, distinct colour changes were observed; the solution remained colourless up to the 1:1 break but thereafter became yellow. Examination of the ultraviolet spectrum of the solution at selected points during the titration showed that tribromide ion (Br_3^-) was present after 1:1 ratio (strong broad peak with λ maximum at 269 mμ).

Molar conductivity values at 1:1 and 2:1 ratio are given in Table 7

Table 7

System	Λ_m (1:1)/S cm^2 mol^{-1}	Λ_m (2:1)/S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3As\text{-}Br_2$	96.6	137.7
	(C_m = 0.009006)*	(C_m = 0.0006234)
$(3\text{-}CH_3C_6H_4)_3As\text{-}Br_2$	51.5	131.7
	(C_m = 0.005626)	(C_m = 0.008265)
$(4\text{-}CH_3C_6H_4)_3As\text{-}Br_2$	51.5	121.0
	(C_m = 0.009708)	(C_m = 0.008265)

* units of molar concentration (C_m) are mol dm^{-3}

* All ratios refer to the halogen : triarylarsine ratios

These values suggest that all of the 2:1 adducts are strong electrolytes and that the 1:1 adducts are medium electrolytes (although it is noted that for $(2\text{-}CH_3C_6H_4)_3AsBr_2$ the value of Λ_m approaches that for a strong electrolyte). These dibromides are much more highly conducting than the parent triphenylarsine dibromide and-tetrabromide (Ph_3AsBr_2, $\Lambda_m = 16.6$ S cm^2 mol^{-1} at $C_m = 0.0250$ mol dm^{-3}, and Ph_3AsBr_4, $\Lambda_m = 104.2$ S cm^2 mol^{-1} at $C_m = 0.027$ mol dm^{-3}) and the unexpectedly high conductivity of $(2\text{-}CH_3C_6H_4)_3AsBr_2$ may indicate that an ortho steric effect may be operating.

From the foregoing evidence it is suggested that for each of the systems two consecutive reactions occur and these may be represented

$0:1 \longrightarrow 1:1$ ratio

$$R_3As + Br_2 \longrightarrow R_3AsBr_2 \; (\rightleftharpoons R_3AsBr^+ + Br^-)$$

colourless

$1:1 \longrightarrow 2:1$ ratio

$$R_3AsBr_2 + Br_2 \longrightarrow R_3AsBr_4 \; (\longrightarrow R_3AsBr^+ + Br_3^-)$$

Yellow

(b) Reactions of the tri(methylphenyl)arsine with iodine

The results of the conductometric titrations of tri(2-methylphenyl)arsine, tri(3-methylphenyl)arsine and tri(4-methylphenyl)arsine with iodine in acetonitrile are illustrated graphically in Fig. 5 (curves A, B and C respectively).

All these three graphs are similar and resemble that for the triphenylarsine-iodine system. In these systems the iodine reacted with the tri(methylphenyl)arsine and the conductivity rose steadily, without inflection to the 2:1 mole ratio. On further addition of

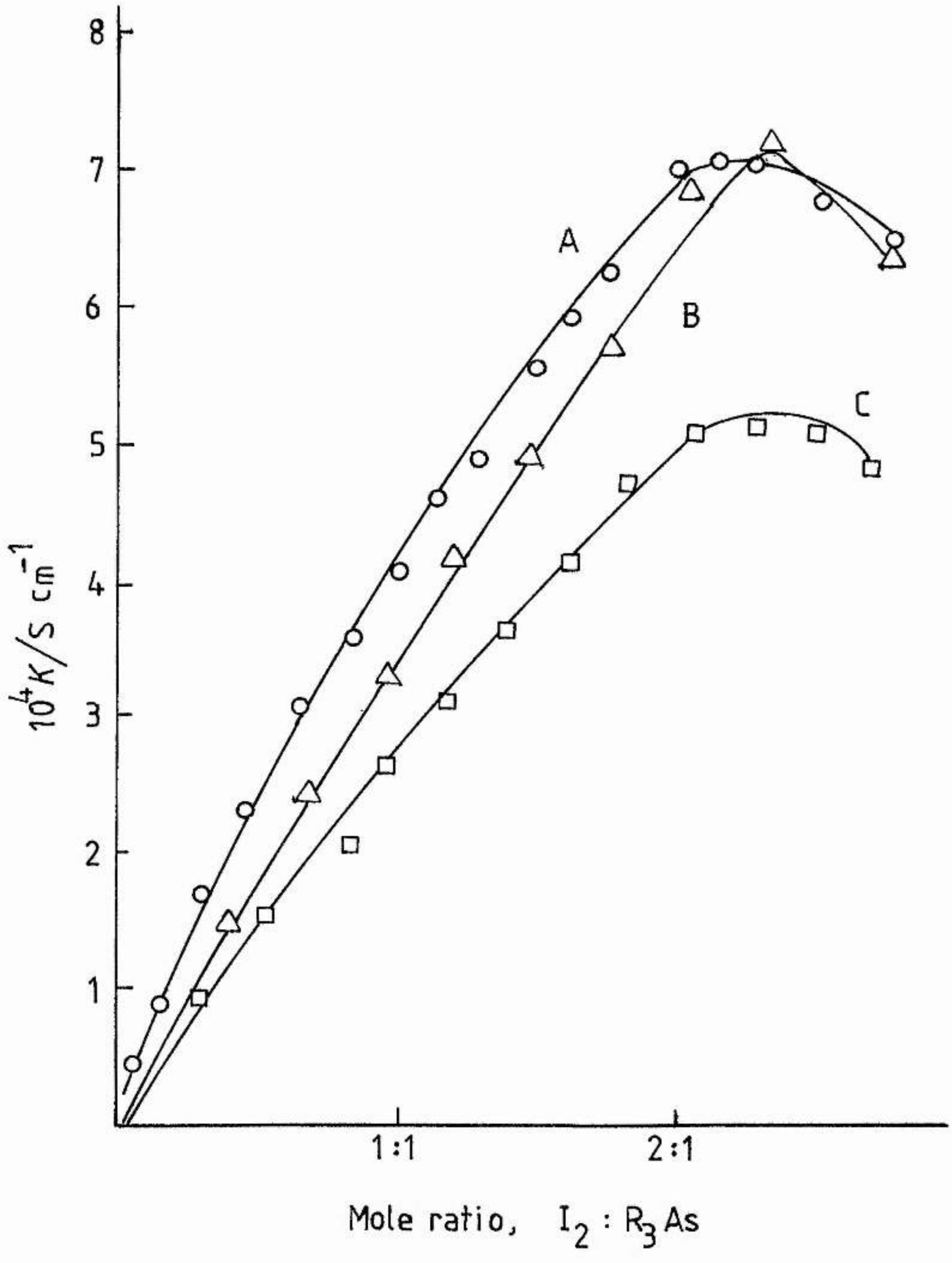


Fig. 5. Conductometric titration of R_3As with iodine

(A) $(2\text{-}CH_3C_6H_4)_3As\text{-}I_2$

(B) $(3\text{-}CH_3C_6H_4)_3As\text{-}I_2$

(C) $(4\text{-}CH_3C_6H_4)_3As\text{-}I_2$

iodine solution the conductivity gently decreased giving a 2:1 break in each titration graph, which suggests that the 2:1 adduct, R_3AsI_4, is the only reaction product present in acetonitrile solution. The strong colour (brown) of the trihalide ion appeared after the first addition of iodine solution to tri(methylphenyl)arsine and the ultraviolet spectrum of the solution showed that triiodide ion (I_3^-) (strong broad peak, λmaximum at 292 mµ) was present from the start of the reaction.

Molar conductivity values at the 2:1 ratios are given in Table 8.

Table 8

System	Λ_m (2:1)/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$(2\text{-}CH_3C_6H_4)_3As\text{-}I_2$	101.0	(C_m = 0.0063647
$(3\text{-}CH_3C_6H_4)_3As\text{-}I_2$	104.2	(C_m = 0.006188)
$(4\text{-}CH_3C_6H_4)_3As\text{-}I_2$	114.4	(C_m = 0.005357)

These values suggest that all of the 2:1 adducts are strong electrolytes in acetonitrile, therefore the reactions occurring may be regarded as follows

0:1 ⟶ 2:1 mole ratio

$$R_3As + 2I_2 \longrightarrow R_3AsI_4 \; (\longrightarrow R_3AsI^+ + I_3^-)$$

(c) Reactions of tri(methylphenyl)arsine with iodine bromide

The results of the conductometric titrations of tri(2-methylphenyl)arsine, tri(3-methylphenyl)arsine and tri(4-methylphenyl)arsine with iodine bromide in acetonitrile are illustrated graphically in Fig. 6 (curves A, B, and C respectively).

In these three titrations, as the iodine bromide solution was added to the tri(methylphenyl)arsine solution the conductivity rose

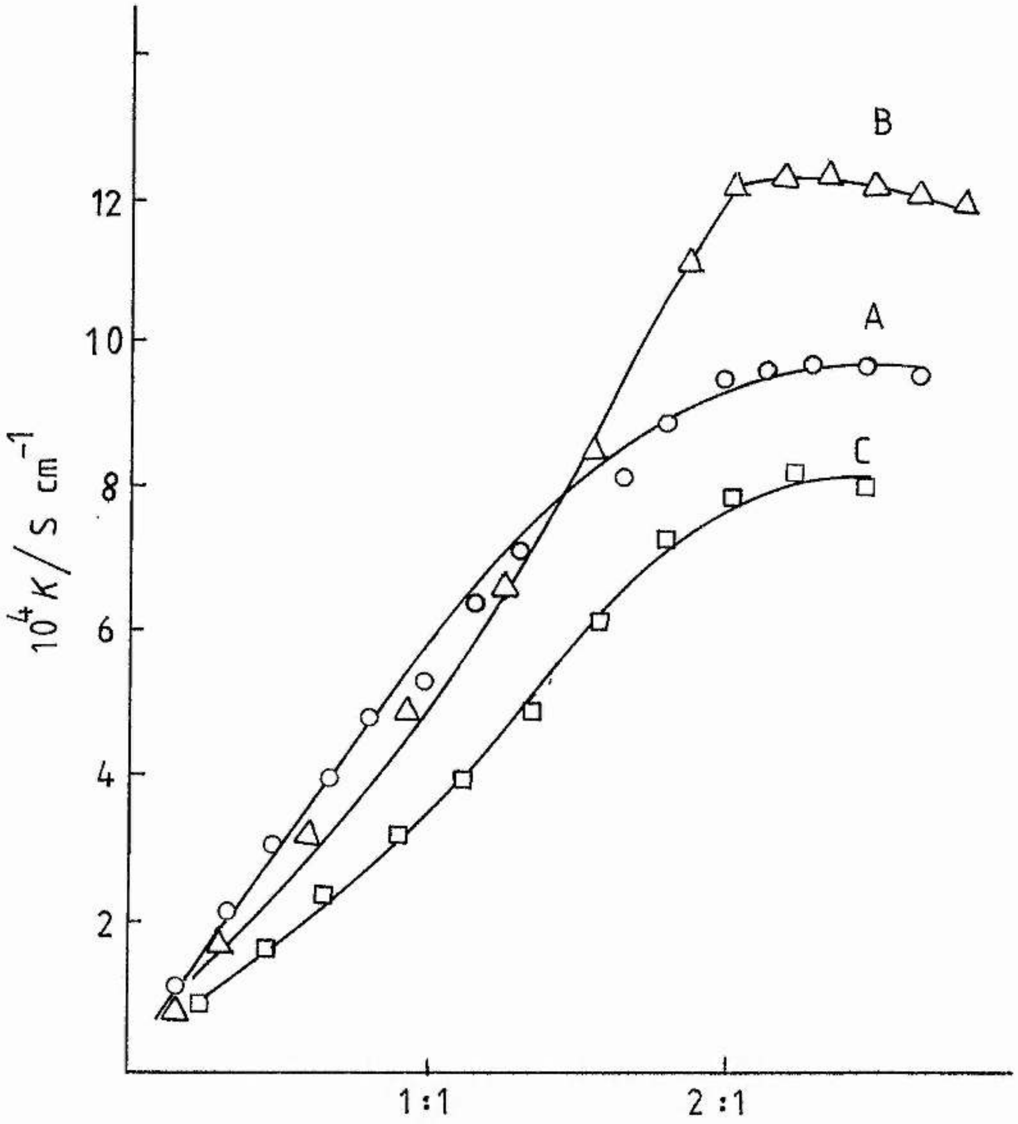


Fig. 6. Conductometric titration of R_3As with iodine bromide

(A) $(2\text{-}CH_3C_6H_4)_3As\text{-}IBr$ (B) $(3\text{-}CH_3C_6H_4)_3As\text{-}IBr$

(C) $(4\text{-}CH_3C_6H_4)_3As\text{-}IBr$

sharply up to the 2:1 mole ratio without any break at the 1:1 ratio. The conductivity decreased gently on further addition of IBr solution. Thus there was a distinct break at 2:1 ratio showing that $R_3AsBr_2I_2$ was the only compound in the solution in each case up to that point. During the titrations distinct colour changes were observed; the colour of the solution turned red on the first addition of iodine bromide and progressively darkened as the titration proceeded. Examination of the ultraviolet spectrum of the solution showed that trihalide ion (I_2Br^-) (medium broad peak with λmaximum at 275 mμ) was present from the start of the reaction.

Molar conductivity values at the 2:1 ratio are given in Table 9.

Table 9

System	Λ_m (2:1)/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$(2\text{-}CH_3C_6H_4)_3As\text{-}IBr$	124.1	(C_m = 0.007678)
$(3\text{-}CH_3C_6H_4)_3As\text{-}IBr$	115.6	(C_m = 0.01045)
$(4\text{-}CH_3C_6H_4)_3As\text{-}IBr$	113.0	(C_m = 0.006901)

These values suggest that all the 2:1 adducts are strong electrolytes and the evidence supports the idea that in these reactions the 2:1 adduct is formed from the beginning without the intermediate formation of a dihalide. The reaction occurring is

0:1 ⟶ 2:1 ratio

$$R_3As + 2IBr \longrightarrow R_3AsI_2Br_2 \ (R_3AsBr^+ + I_2Br^-).$$

It is evident therefore that the systems involving IBr are parallel to those involving iodine.

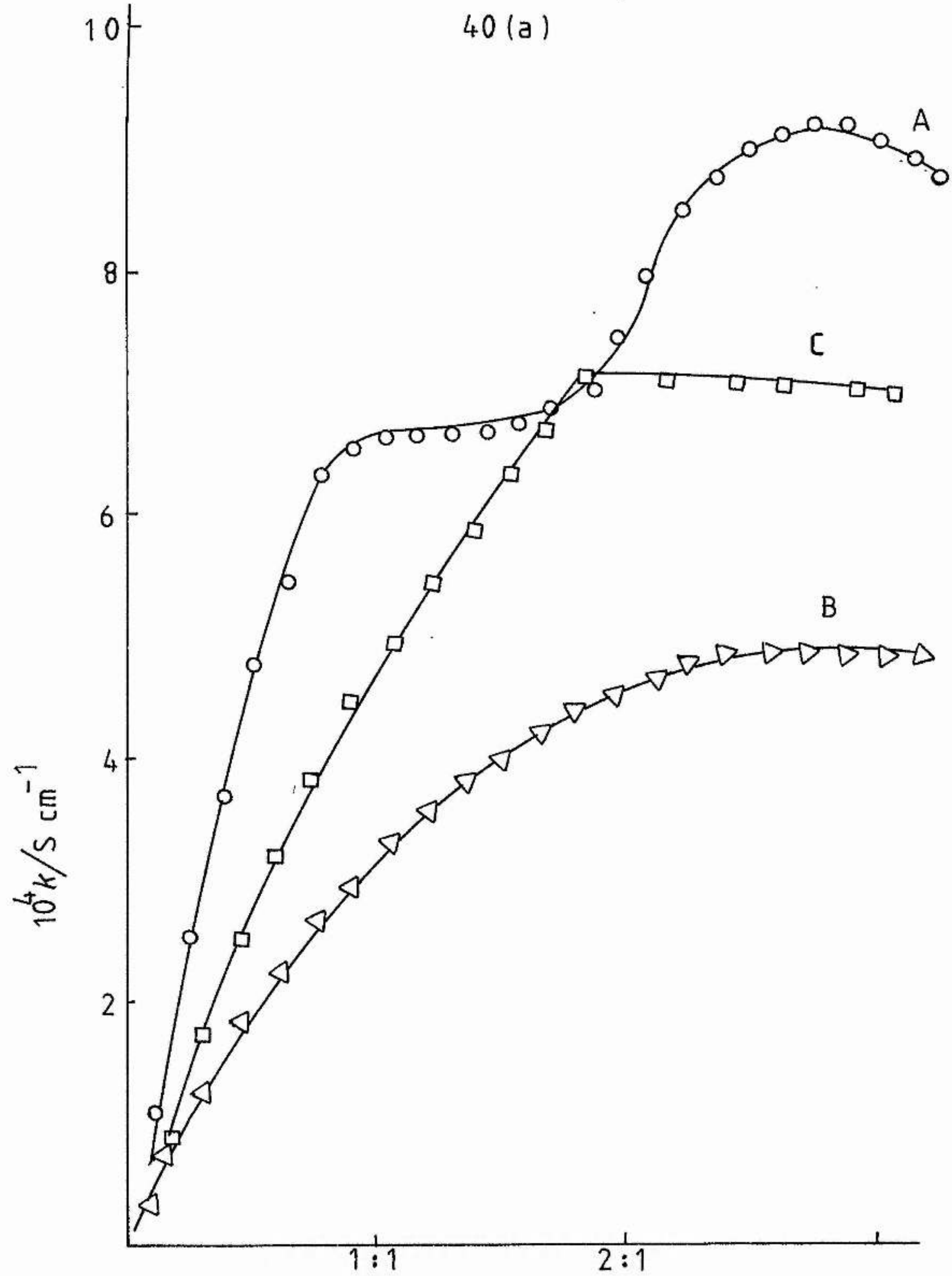
2. REACTIONS OF TRI(DIMETHYLPHENYL)ARSINE WITH HALOGENS AND INTERHALOGEN

Tri(dimethylphenyl)arsine was chosen for study to see if the anomalously high molar conductivity for the dihalides was sustained or even enhanced by the presence of two methyl groups in the ortho position thus lending strong evidence for a steric influence on the tendency of these compounds to ionise in solution.

(a) Reaction with bromine

The result of the conductometric titration of tri(2,6-dimethylphenyl)arsine with bromine in acetonitrile is illustrated graphically in Fig. 7 curve A.

During the titration, as bromine reacted with the tri(dimethylphenyl)arsine the conductivity rose sharply up to the 1:1 mole ratio; it then remained steady until the 2:1 ratio was reached. Further addition of bromine resulted in a sharp increase in conductivity (unlike other triarylarsine-bromine systems) until the 3:1 ratio was reached. After this ratio the conductivity dropped gently when more bromine solution was added. From these three distinct breaks in the titration graph (1:1, 2:1 and 3:1) the formation of adducts R_3AsBr_2, R_3AsBr_4, and R_3AsBr_6 is indicated. Colour changes were observed; the solution remained colourless up to the 1:1 ratio but thereafter became yellow. The ultraviolet spectrum of the solution during the titration showed that the tribromide ion (λmax = 269 mμ) was present from the 1:1 ratio onward.



mole ratio, X_2 : $[2,6\text{-}(CH_3)_2C_6H_3]_3As$

Fig. 7. Conductometric titration of 2,6-dimethyphenylarsine with bromine, iodine and iodine bromide

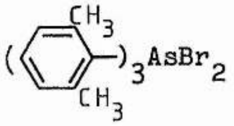
(A) $[(CH_3)_2C_6H_3]_3As\text{-}Br_2$ (B) $[(CH_3)_2C_6H_3]_3As\text{-}I_2$

(C) $[(CH_3)_2C_6H_3]_3As\text{-}IBr$

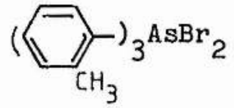
Molar conductivity values at different ratios are as follow

Mole ratio	Λ_m /S cm^2 mol^{-1}	C_m = mol dm^{-3}
1:1	94.5	0.0069608
2:1	130.5	0.0057443
3:1	186.0	0.0048917

These values suggest that the 1:1, 2:1 and 3:1 adducts are strong electrolytes, although the value for the 1:1 adduct is at the lower limit of the values expected for a strong (1:1) electrolytes and the value for 3:1 adduct is much higher than previously observed for any adduct. The dimethyl steric influence on ionisation can be clearly observed from the conductivity value of the following compounds in acetonitrile at C_m = 0.01 mol dm^{-3}



Λ_m = 124.5 S cm^2 mol^{-1}



Λ_m = 108.5 S cm^2 mol^{-1}

From the above evidence it is suggested that the reaction occurring in the first two stages of this system may be represented:

0:1 → 1:1 ratio

$$R_3As + Br_2 \longrightarrow R_3AsBr_2 \; (\rightleftharpoons R_3AsBr^+ + Br^-)$$

colourless

1:1 → 2:1 ratio

$$R_3AsBr_2 + Br_2 \longrightarrow R_3AsBr_4 \; (\rightleftharpoons R_3AsBr^+ + Br_3^-)$$

light yellow

An unexpected feature of this system and one that has not previously been observed in any R_3As-halogen system is the steep increase in conductivity after the 2:1 ratio leading to a break at the 3:1 ratio. A highly conducting adduct of composition R_3AsBr_6 is therefore indicated. Two modes of ionisation are possible for a compound of this composition

$$R_3AsBr_6 \longrightarrow R_3AsBr^+ + Br_5^- \text{ - - - - - - -I}$$

or

$$R_3AsBr_6 \longrightarrow R_3As^{2+} + 2Br_3^- \text{ - - - - - - - II}$$

If ionisation I was present it does not seem to be very likely that an increase in conductivity would occur on going from the 2:1 to 3:1 ratio in the conductometric titration. This is because the number of ions does not change and the ionic mobility of Br_5^- would almost certainly be less than that of the smaller Br_3^- ion (present at the 2:1 ratio). The very high molar conductivity at the 3:1 ratio lends support to ionisation II which regards R_3AsBr_6 as ionising as a (2:1) electrolyte. Further supporting evidence comes from a quantitative ultraviolet spectral study of solutions at the 3:1 mole ratio. The solutions absorb strongly at λ 269 mμ (Br_3^-)[117] and using the known value of extinction coefficient for the tribromide ion, it is concluded that there are two Br_3^- ions per mole of adduct present as in the following Table 10.

Table 10

C_m (R_3AsBr_6)	Log $\frac{I_o}{I}$	ε(Br_3^-, at λ269 mμ)	C_m (Br_3^-) mol dm^{-3}
0.00001878 7	1.01	53900	0.000037402
0.0000093936	0.56	53900	0.0000207377

The third stage of the reaction may therefore be described as follows

2:1 → 3:1 ratio

$$R_3AsBr_4 + Br_2 \longrightarrow R_3AsBr_6\ (\longrightarrow R_3As^{2+} + 2Br_3^-).$$

R_3As^{2+} has not been reported previously but R_3Sb^{2+} 157 is generally accepted.

(b) Reaction with iodine

The result of the conductometric titration of tri(2,6-dimethylphenyl)arsine with iodine in acetonitrile is illustrated graphically in Fig. 7 (curve B).

The graph is similar to other triaryl- (phenyl and tolyl) arsine-iodine systems, showing only one break, at the 2:1 mole ratio. The colour of the solution changed from colourless to light brown after the first addition of iodine solution and absorption due to I_3^- (λmax = 262, 362 mμ) in the ultraviolet spectrum of the solution was observed.

The molar conductivity at the 2:1 ratio (Λ_m = 84.7 S cm^2 mol^{-1} at C_m = 0.005309 mol dm^{-3}) suggests that this 2:1 adduct is a strong electrolyte like the other known tetrahalides of triarylarsines.

From the foregoing evidence it is suggested that for the above system the reaction occurring may be represented by the following equation

0:1 → 1:1 ratio

$$R_3As + 2I_2 \longrightarrow R_3AsI_4\ (\longrightarrow R_3AsI^+\ I_3^-).$$

(c) Reaction with iodine bromide

The result of the conductometric titration of tri(2,6-dimethylphenyl)arsine with iodine bromide in acetonitrile is illustrated graphically in Fig. 7 (curve C).

This titration follows exactly the same pattern as the tri(methylphenyl)arsine-iodine bromide system. The conductivity rose sharply as iodine bromide solution was added to the tri(2,6-dimethylphenyl)arsine solution giving only a 2:1 break in the titration graph. Further addition of iodine bromide solution resulted in a gentle decrease in conductivity. The adduct $R_3AsBr_2I_2$ is suggested by the distinct 2:1 break in the graph. The colour of the solution turned red at the beginning of the reaction and the ultraviolet spectrum of the solution showed absorption due to trihalide ion I_2Br^- (λmax = 257 mμ) from the start of the titration.

The molar conductivity value at the 2:1 ratio was $\Lambda_m = 117.5$ S cm^2 mol^{-1} at $C_m = 0.0060422$ mol dm^{-3}. The above Λ_m value showed that the adduct is a strong electrolyte in acetonitrile solution, thus the reaction may be written as

0:1 ⟶ 2:1 ratio

$$R_3As + 2IBr \longrightarrow R_3AsBr_2I_2\ (\longrightarrow R_3AsBr^+ + I_2Br^-).$$

3. REACTIONS OF THE TRI(FLUOROPHENYL)ARSINES WITH HALOGENS AND INTERHALOGEN

Having studied (in the previous two chapters) the effect of electron releasing substituents in the phenyl ring of the arsine $(YC_6H_4)_3As$ on the formation of halogen adducts it was decided to look into the effect of the presence of an electron withdrawing group on the phenyl ring. For this purpose the tri(fluorophenyl)arsines were chosen and the results are described below.

(a) Reaction with bromine

The result of the conductometric titrations of tri(2-fluorophenyl)arsine, tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine with bromine in acetonitrile are illustrated graphically in Fig. 8 (curves A, B, and C respectively).

Unlike the tri(methylphenyl)arsine-bromine titrations, the tri(fluorophenyl)arsine-bromine titrations do not give graphs of the same form. The reaction of tri(2-fluorophenyl)arsine with bromine gave only a slight increase in conductivity; this rose gently up to the 2:1 mole ratio after which the conductivity remained steady thus giving a rather indefinite 2:1 break in the graph. The solution assumed a light yellow colour from the start of the titration and the ultraviolet spectrum showed that tribromide ion λmax = 269 mμ) was present from the start of the titration.

In the titrations of tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine with bromine the conductivity increased only slightly up to the 1:1 mole ratio but thereafter the conductivity rose sharply and a distinct break was observed at the 2:1 ratio. Thus, in these two systems 1:1 and 2:1 breaks were observed suggesting the formation of 1:1 and 2:1 adducts (R_3AsBr_2 and R_3AsBr_4) in the solution. In conjunction with the conductivity changes, distinct colour changes were observed during the titrations; the solution remained colourless up to the 1:1 ratio but thereafter became yellow, and the ultraviolet spectrum of the solution at selected points during the titrations showed that Br_3^- ion was present after the 1:1 ratio (strong broad peak with λ_{max} = at 269 mμ).

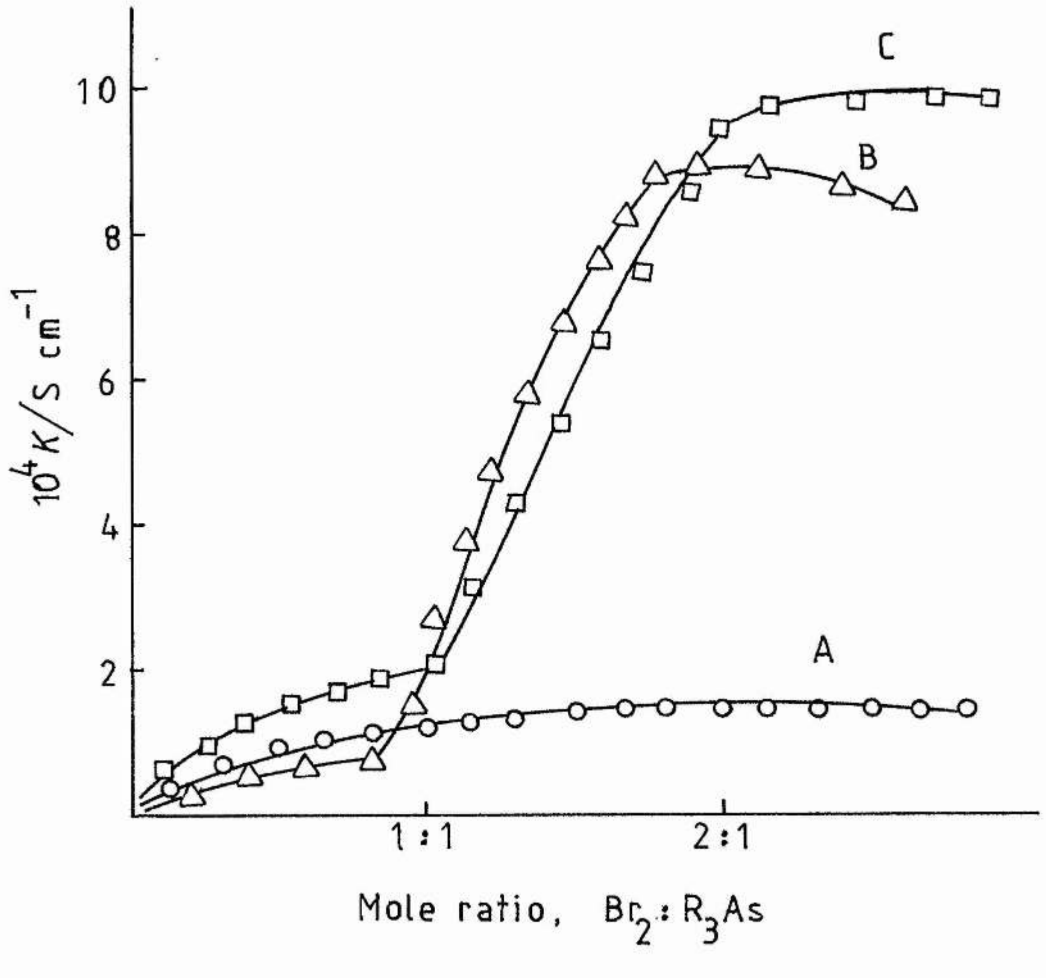


Fig. 8. Conductometric titration of R_3As with bromine

(A) $(2\text{-}FC_6H_4)_3As\text{-}Br_2$ (B) $(3\text{-}FC_6H_4)_3As\text{-}Br_2$

(C) $(4\text{-}FC_6H_4)_3As\text{-}Br_2$

Molar conductivity values at the 1:1 and 2:1 ratios are given in Table 11.

Table 11

System	Λ_m (1:1)/S cm^2 mol^{-1}	Λ_m (2:1)/S cm^2 mol^{-1}
$(2\text{-}FC_6H_4)_3As\text{-}Br_2$	—	66.2
		(C_m = 0.0022358)*
$(3\text{-}FC_6H_4)_3As\text{-}Br_2$	17.28	105.1
	(C_m = 0.0075014)	(C_m = 0.0066815)
$(4\text{-}FC_6H_4)_3As\text{-}Br_2$	16.8	112.1
	(C_m = 0.0098268)	(C_m = 0.0083853)

* C_m = mol dm^{-3}

These values suggest that all the 1:1 adducts are weak electrolytes and that the 2:1 adducts in the case of the 3-fluorophenyl and 4-fluorophenyl isomers are strong electrolytes. The molar conductivity and shape of the conductometric titration graph for the (2-fluorophenyl)arsine compound is suggesting an equilibrium.

From the above observation it is suggested that with tri(2-fluorophenyl)arsine the reaction proceeds directly to the tetrabromide adduct thus,

0:1 ⟶ 2:1 ratio

$$R_3As + 2Br_2 \rightleftarrows R_3AsBr_4 \; (\longrightarrow R_3AsBr^+Br_3^-).$$

With tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine the stepwise reaction may be represented by the following equations.

0:1 ⟶ 1:1 ratio

$$R_3As + Br_2 \longrightarrow R_3AsBr_2 \; (\rightleftarrows R_3AsBr^+ \; Br^-)$$

1:1 ⟶ 2:1 ratio

$$R_3AsBr_2 + Br_2 \longrightarrow R_3AsBr_4 \; (\longrightarrow R_3AsBr^+ \; Br_3^-).$$

(b) Reaction with iodine

The result of the conductometric titrations of tri(2-fluorophenyl)arsine, tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine with iodine in acetonitrile are illustrated in Fig. 9 (curves A, B, and C respectively).

The conductivity did not rise significantly when iodine was added to the tri(2-fluorophenyl)arsine, the colour of the solution changed to brown from the start of the iodine addition and a weak absorption due to I_3^- (λmax = 292, and 362 mμ) was observed in the ultraviolet spectrum of the solution. The presence mainly of molecular iodine is indicated and it is concluded from these results that no reaction occurs. In the other two titrations [tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine] the conductivity rose steeply giving a break at the 2:1 ratio. The solution, (originally the solution was colourless), assumed a brown colour after the first addition of iodine. The ultraviolet spectrum at selected points showed that triiodide ion (λmax = 292, 362 mμ) was present from the start of the reaction.

Molar conductivity values at the 2:1 mole ratio are given in Table 12.

Table 12

System	Λ_m (2:1)/S cm^2 mol^{-1}	c_m = mol dm^{-3}
$(3\text{-}FC_6H_4)_3\text{-}I_2$	68.8	0.0066815
$(4\text{-}FC_6H_4)_3\text{-}I_2$	74.2	0.0058585

These values show that the 2:1 adducts are medium electrolytes in acetonitrile. These molar conductivity values, considered in conjunction with the fact that the conductometric titration breaks are

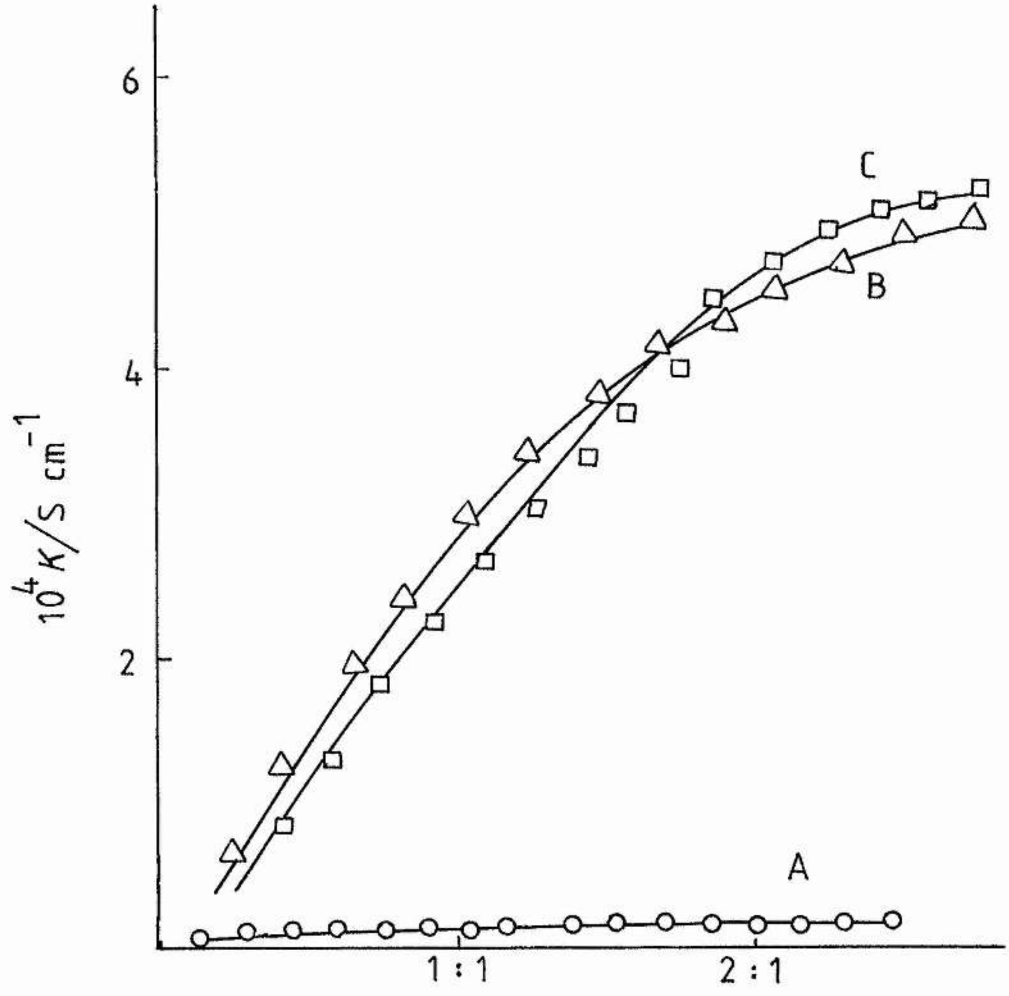


Fig. 9. Conductometric titration of R_3As with iodine

(A) $(2\text{-}FC_6H_4)_3As\text{-}I_2$ (B) $(3\text{-}FC_6H_4)_3As\text{-}I_2$

(C) $(4\text{-}FC_6H_4)_3As\text{-}I_2$

rather blunt, as in the case of the $(2\text{-}FC_6H_4)_3As\text{-}Br_2$ system, suggest that the reaction does not go to completion at the 2:1 ratio; or in other words the product of reaction is dissociating in acetonitrile solution. The reaction occurring is therefore represented as follows

$$R_3As + 2I_2 \rightleftharpoons R_3AsI_4 \; (\equiv R_3AsI^+ \; I_3^-).$$

(c) Reaction with iodine bromide

The result of the conductometric titrations of tri(2-fluorophenyl)arsine, tri(3-fluorophenyl)arsine and tri(4-fluorophenyl)arsine with iodine bromide in acetonitrile are illustrated in Fig. 10 (curves A, B, and C respectively).

All these titration graphs are similar to each other but different from other triarylarsine-iodine bromide systems. The conductivity rose steadily when the IBr solution was added to the tri(fluorophenyl)arsine solution, but no distinct breaks were displayed on the graphs although the conductivity rise tended to slow down near the 3:1 mole ratio. The colour of the solution turned light brown at the start of each titration and became progressively darker as the titration proceeded. The ultraviolet spectrum of the solution taken at selected ratios showed absorption due to the IBr_2^- ion $\lambda max = 257$ mμ. [This is different from what was expected in this system since other triarylarsine-iodine bromide systems previously studied gave a distinct 2:1 break and showed absorption due to I_2Br^- at $\lambda max = 275$ and 351 mμ]. The presence of IBr_2^- in solution suggests that a 3:1 reaction is occurring:

$$R_3As + 3IBr \rightleftharpoons R_3AsIBr_3 \; (\longrightarrow \underset{\substack{+\\ I_2}}{R_3AsBr^+} + IBr_2^-).$$

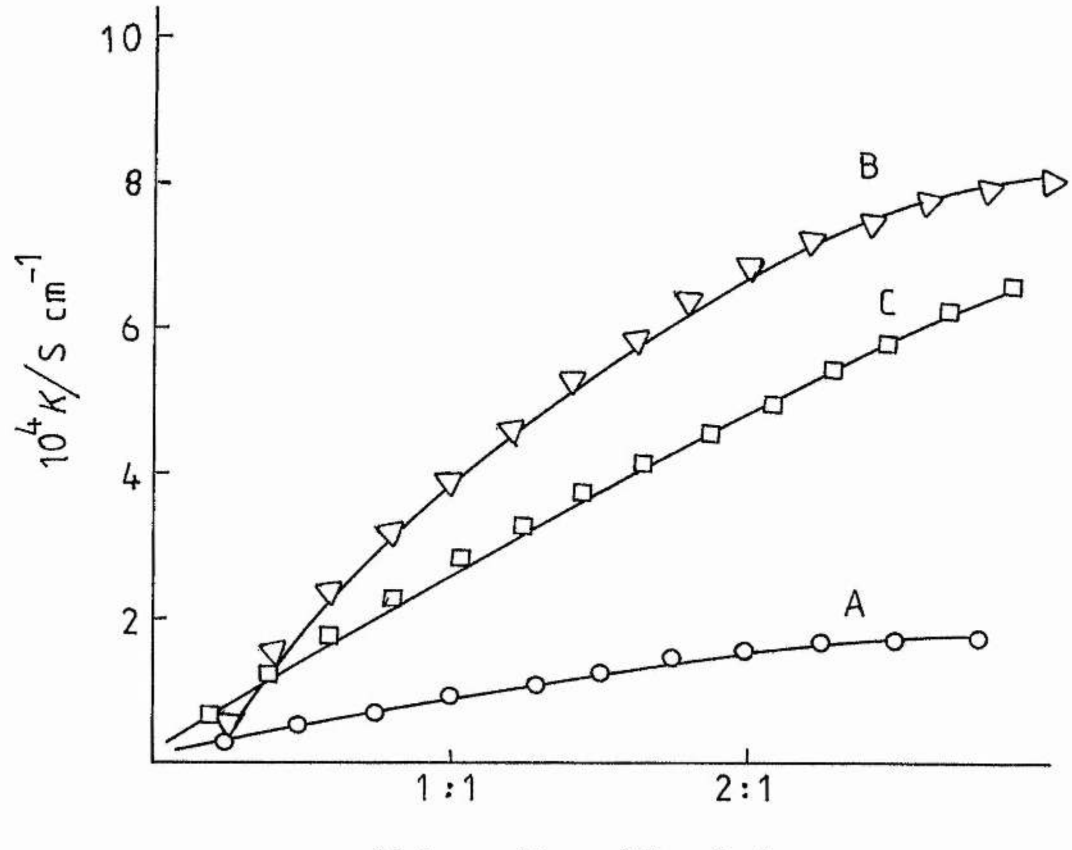


Fig. 10. Conductometric titration of R_3As with iodine bromide

(A) $(2\text{-}FC_6H_4)_3As\text{-}IBr$ (B) $(3\text{-}FC_6H_4)_3As\text{-}IBr$

(C) $(4\text{-}FC_6H_4)_3As\text{-}IBr$

However the absence of a sharp break at the 3:1 ratio implies that the reaction has not gone to completion at this point and must therefore be represented as an equilibrium.

Values of molar conductivity at the 3:1 ratio are given in Table 13.

Table 13

System	Λ_m (3:1)/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$(2\text{-}FC_6H_4)_3As\text{-}IBr$	93.8	0.0019275
$(3\text{-}FC_6H_4)_3As\text{-}IBr$	146.9	0.0054463
$(4\text{-}FC_6H_4)_3As\text{-}IBr$	79.2	0.0080753

It is worth noting that the reactions of iodine bromide with these arsines differ from the other arsines studied; the latter invariable give a sharp 2:1 titration break and show the presence of I_2Br^- ion indicating that in these cases the reaction is

$$R_3As + 2IBr \longrightarrow R_3AsI_2Br_2 \; (\longrightarrow R_3AsBr^+ + I_2Br^-).$$

4. REACTIONS OF TRIS(TRIFLUOROMETHYLPHENYL)ARSINES WITH HALOGENS AND INTERHALOGEN

To complete our study on the effect of different substituents (Y) in the aryl arsine $(YC_6H_4)_3As$ on halogen adduct formation by these compounds, it was thought of interest to look at the reactions of the tris(trifluoromethylphenyl)arsine. The CF_3 group is a strongly electron-withdrawing group and is also a much bigger group than the fluorine atom. Hence the combined effect of bulk and of electron-withdrawing power in the same group attached to the phenyl ring in $(YC_6H_4)_3As$ may be observed.

(a) Reactions with bromine

The result of the conductometric titrations of tris(2-trifluoromethylphenyl)arsine, tris(3-trifluoromethylphenyl)arsine, and tris(4-trifluoromethylphenyl)arsine with bromine in acetonitrile are illustrated graphically in Fig. 11 (curves A, B, and C respectively).

These three titrations give graphs similar to those of the tri(fluorophenyl)arsine-bromine systems except that in the tris(2-trifluoromethylphenyl)arsine-bromine titration, bromine reacted with the arsine and the conductivity rose sharply up to the 2:1 mole ratio without any break at the 1:1 ratio. Further addition of bromine resulted in a decrease in conductivity, giving a break in the graph at the 2:1 ratio suggesting the formation of R_3AsBr_4. The colour of the solution changed from colourless to yellow after the first addition of bromine solution, and the ultraviolet spectrum of the solution showed absorption for Br_3^- (λmax = 269 mμ) from the start of the reaction.

In the titrations of tris(3-trifluoromethylphenyl)arsine and tris(4-trifluoromethylphenyl)arsine with bromine the conductivity increased only slightly up to the 1:1 mole ratio but thereafter it rose sharply to the 2:1 ratio thus, in these two systems 1:1 and 2:1 breaks were observed suggesting the formation of 1:1 and 2:1 adducts (R_3AsBr_2 and R_3AsBr_4). The solution remained colourless up to the 1:1 break but thereafter became yellow, and the ultraviolet spectrum of the solution showed that the trihalide ion Br_3^- (λmax = 269 mμ) was present from the start of the reaction.

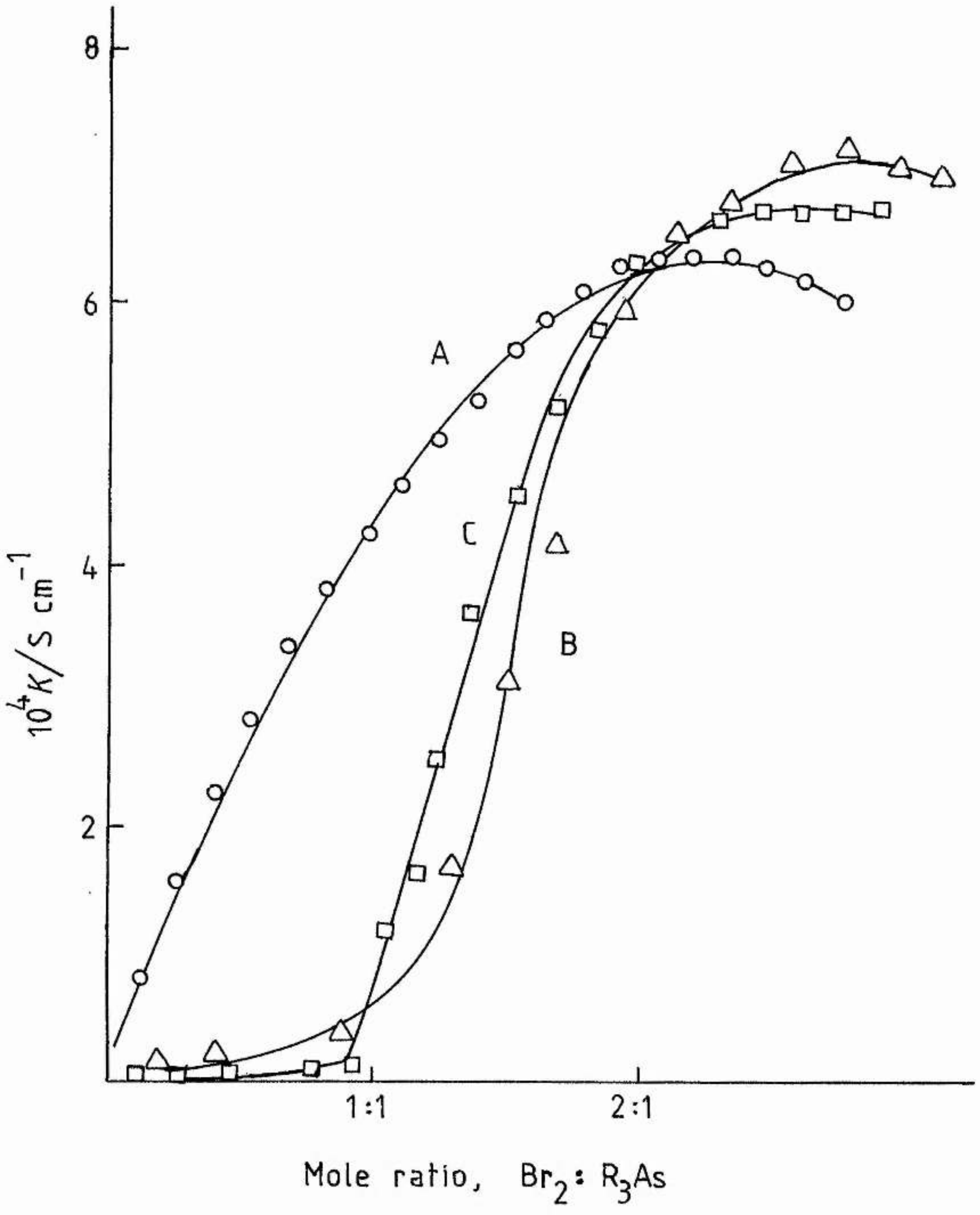


Fig. 11. Conductometric titration of R_3As with bromine

(A) $(2\text{-}CF_3C_6H_4)_3As\text{-}Br_2$

(B) $(3\text{-}CF_3C_6H_4)_3As\text{-}Br_2$

(C) $(4\text{-}CF_3C_6H_4)_3As\text{-}Br_2$

Molar conductivity values at 1:1 and 2:1 ratios are given in Table 14.

Table 14

System	Λ_m (1:1)/S cm^2 mol^{-1}	Λ_m (2:1)/S cm^2 mol^{-1}
$(2\text{-}CF_3C_6H_4)_3As\text{-}Br_2$		121.1 (C_m = 0.005282)*
$(3\text{-}CF_3C_6H_4)_3As\text{-}Br_2$	9.6 (C_m = 0.0062099)	109.1 (C_m = 0.0046956)
$(4\text{-}CF_3C_6H_4)_3As\text{-}Br_2$	3.9 (C_m = 0.0062677)	118.9 (C_m = 0.0051715)

* mol dm^{-3}

These conductivity values suggest that all of the 2:1 adducts are strong electrolytes in acetonitrile. It is of interest to note that for the 1:1 adducts the molar conductivity values are very much lower than those of the corresponding 1:1 adducts of tri(methylphenyl)arsine. This point will be discussed in chapter D).

From the foregoing evidence it is suggested that for $(2\text{-}CF_3C_6H_4)_3As\text{-}Br_2$ the reaction leads straight away to 2:1 ratio and is represented:

0:1 → 2:1 ratio

$$R_3As + 2Br_2 \longrightarrow R_3AsBr_4 \; (\longrightarrow R_3AsBr^+ + Br_3^-).$$

and in the case of $(3\text{-}CF_3C_6H_4)_3As\text{-}Br_2$ and $(4\text{-}CF_3C_6H_4)_3As\text{-}Br_2$ systems the reaction is in two stages

0:1 → 1:1 ratio

$$R_3As + Br_2 \longrightarrow R_3AsBr_2 (\rightleftharpoons R_3AsBr^+ + Br^-)$$

1:1 → 2:1 ratio

$$R_3AsBr_2 + Br_2 \longrightarrow R_3AsBr_4 \; (\longrightarrow R_3AsBr^+ + Br_3^-).$$

(b) Reactions with iodine

The result of the conductometric titrations of tris(2-trifluoromethylphenyl)arsine, tris(3-trifluoromethylphenyl)arsine and tris(4-trifluoromethylphenyl)arsine with iodine in acetonitrile are illustrated in Fig. 12 (curves A, B, and C respectively).

The titration graph of tris(2-trifluoromethylphenyl)arsine-iodine is different from the other two graphs; the conductivity did not rise significantly when iodine was added to the tris(2-trifluoromethylphenyl)arsine. The solution turned brown in colour from the start of the titration (due to iodine) and a very weak absorption due to the triiodide ion was present in the ultraviolet spectrum of the titration mixture (a solution of iodine itself in acetonitrile contains a small amount of tri-iodide ion). The above observations imply that there is no reaction occurring between iodine and $(2\text{-}CF_3C_6H_4)_3As$ in acetonitrile. No adduct was obtained as a solid crystalline compound.

The titration graphs of tris(3-trifluoromethylphenyl)arsine, and tris(4-trifluoromethlphenyl)arsine with iodine are similar with each other and resemble those of the tri(3-, and 4-fluorophenyl)arsine-iodine-systems. The conductivity rose gently as iodine was added but there was no break at any mole ratio in the range 0:1-4:1. The colour of the solution became brown after the first addition of iodine solution and the ultraviolet spectrum of the solution showed absorption due to triiodide ion (λmax = 292 and 362 mμ). The rise in conductivity during titration to fairly high values is indicative of a reaction occurring to provide ionic species. The

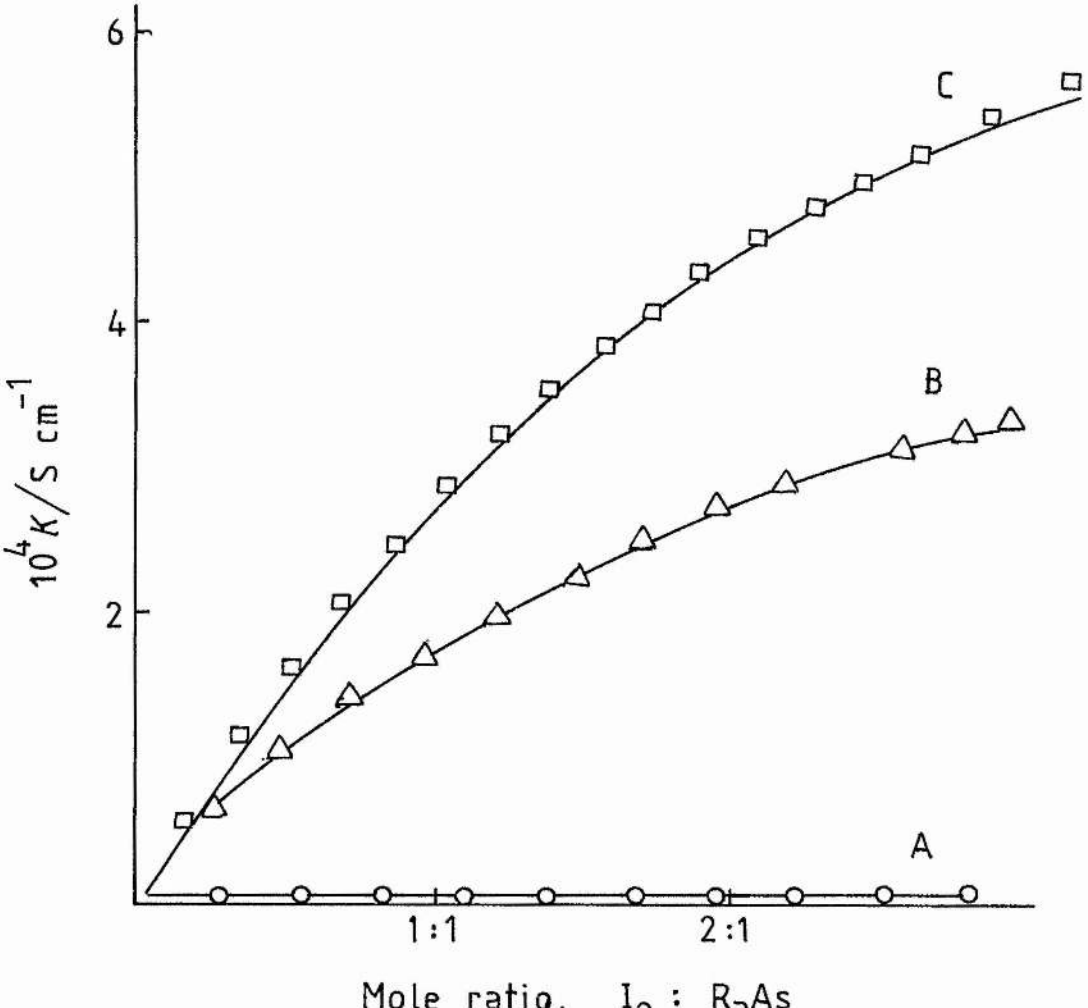


Fig. 12. Conductometric titration of R_3As with iodine

(A) $(2\text{-}CF_3C_6H_4)_3As\text{-}I_2$ (B) $(3\text{-}CF_3C_6H_4)_3As\text{-}I_2$

(C) $(4\text{-}CF_3C_6H_4)_3As\text{-}I_2$

presence of I_3^- from the start of the titration suggests that the reaction is

$$R_3As + 2I_2 \longrightarrow R_3AsI_4 \; (\longrightarrow R_3AsI^+ + I_3^-).$$

but the lack of sharp break at 2:1 points to this being essentially an equilibrium system,

$$R_3As + 2I_2 \rightleftharpoons R_3AsI_4$$

or alternatively one could say that the 2:1 adduct is strongly dissociated to the starting compounds. The 2:1 adduct R_3AsI_4 was isolated as a crystalline solid (chapter C) and, surprisingly, the 1:1 adduct R_3AsI_2 was also obtained. This emphasises the complexity of this system and shows that the equilibrium

$$R_3As + I_2 \rightleftharpoons R_3AsI_2$$

must be present to a small extent.

(c) Reactions with iodine bromide

The results of the conductometric titrations of tris(2-trifluoromethylphenyl)arsine, tris(3-trifluoromethylphenyl)arsine and tris(4-trifluoromethylphenyl)arsine with iodine bromide in acetonitrile are illustrated in Fig. 13 (curves A, B, and C respectively).

These three titrations follow the same course of reaction as the tri(fluorophenyl)arsine-iodine bromide reactions described in the previous section. The conductivity rises as iodine bromide is added to the arsine solution but no distinct break is observed in the graphs. The colour of the solution turned light brown from the beginning of the titrations, and the ultraviolet spectrum of the solution showed that IBr_2^- ion (λmax = 257 mμ) was present from the start of each titration.

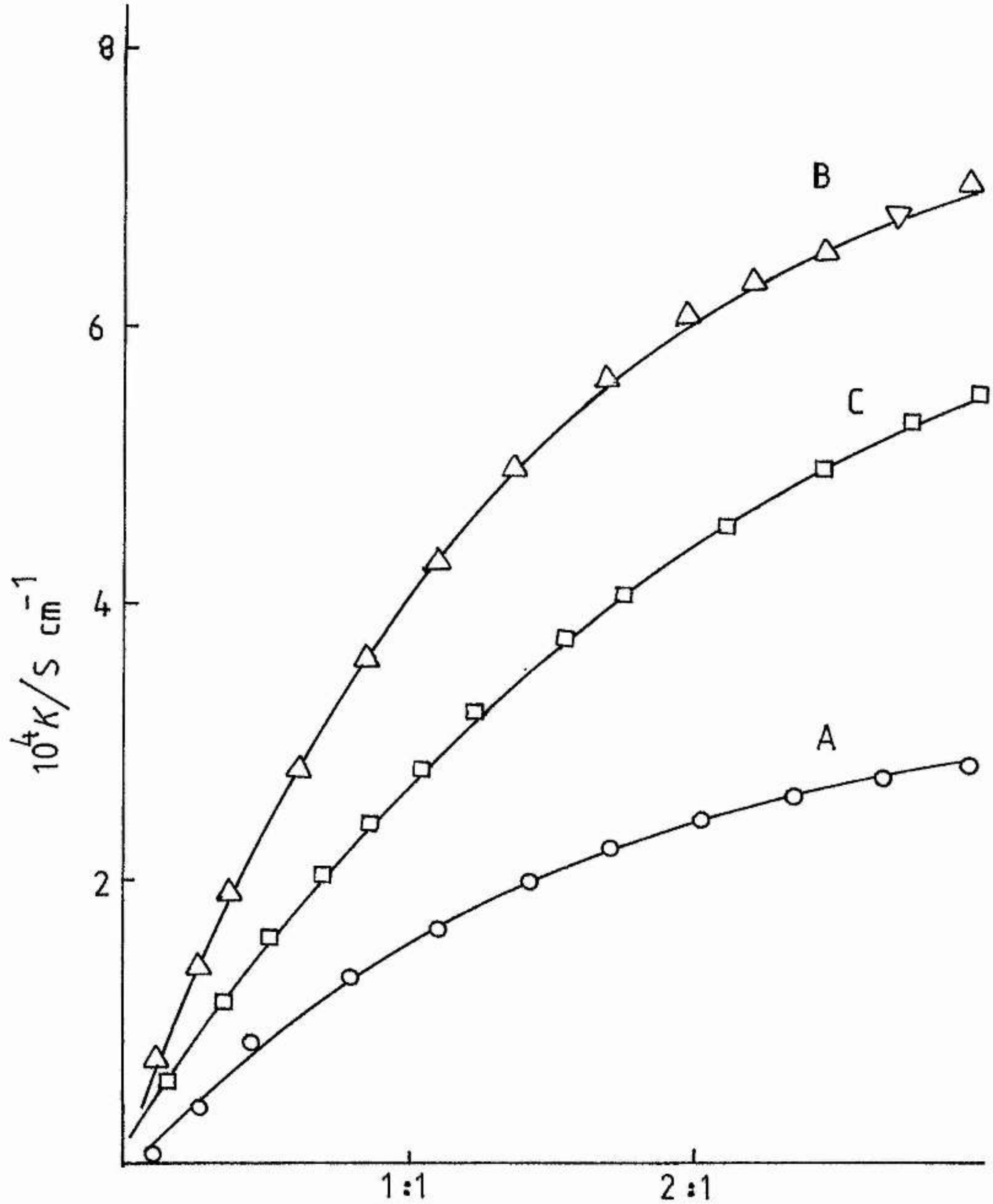


Fig. 13. Conductometric titration of R_3As with iodine bromide

(A) $(2\text{-}CF_3C_6H_4)_3As\text{-}IBr$ (B) $(3\text{-}CF_3C_6H_4)_3As\text{-}IBr$

(C) $(4\text{-}CF_3C_6H_4)_3As\text{-}IBr$

The molar conductivity values are given in the following Table.

Table 15

System	Λ_m (3:1)/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$(2\text{-}CF_3C_6H_4)_3As\text{-}IBr$	85.6	0.0036505
$(3\text{-}CF_3C_6H_4)_3As\text{-}IBr$	171.2	0.0041474
$(4\text{-}CF_3C_6H_4)_3As\text{-}IBr$	159.0	0.003488

The above observations suggest that the reactions may be represented by the following equation:

$$R_3As + 3IBr \rightleftharpoons \underset{\displaystyle I_2}{\underset{+}{R_3AsIBr_3}} \; (\longrightarrow R_3AsBr^+ + IBr)$$

SUMMARY OF RESULTS

(1) R_3As-Br_2

(a) The conductometric titrations of tri(2-, 3-, and 4-methylphenyl)arsine with bromine are identical with each other and similar to the triphenylarsine-bromine titration. In all the systems breaks were observed at the 1:1 and 2:1 mole ratios which suggests the formation of the adducts R_3AsBr_2 and R_4AsBr_4. These adducts are weak and strong electrolytes respectively in acetonitrile, with the exception of $(2\text{-}CH_3C_6H_4)_3AsBr_2$ which behaves as a strong electrolyte. Its high electrolytic conductivity is attributed to the presence of the ortho CH_3 group. The reactions are

0:1 ⟶ 1:1 mole ratio

$$R_3As + Br_2 \longrightarrow R_3AsBr_2 \quad (\rightleftharpoons R_3AsBr^+ + Br^-)$$

and

1:1 ⟶ 2:1 mole ratio

$$R_3AsBr_2 + Br_2 \longrightarrow R_3AsBr_4 \quad (\equiv R_3AsBr^+ Br_3^-)$$

(b) A 3:1 mole ratio break was observed in the reaction of tri(dimethylphenyl)arsine with bromine which suggests the formation of an adduct of formula R_3AsBr_6; this is a strong electrolyte in acetonitrile and quantitative measurements indicated that the ionisation is

$$[(CH_3)_2C_6H_3]_3AsBr_6 \longrightarrow [(CH_3)_2C_6H_3]_3As^{2+} + 2Br_3^-.$$

(c) The substitution of strongly electron withdrawing groups such as F or CF_3 on the phenyl ring of the arsines R_3As has two effects on the behaviour of the systems R_3As-Br_2

(i) If these groups are present in the ortho position, reaction between R_3As and Br_2 tends to give a break only at the 2:1 mole ratio in the conductometric titration suggesting that a 1:1 adduct is not forming in the solution. Thus the reaction occurring is

$$R_3As + 2Br_2 \longrightarrow R_3AsBr_4 \quad (R_3AsBr^+ + Br_3^-)$$

(ii) If these groups are present in the meta or para position then the reactions are similar to Ph_3As-Br_2 system.

(2) <u>R_3As-I_2 system</u>

(a) The reactions of tri(methylphenyl)arsine and tri(dimethylphenyl)arsine with iodine are similar to the triphenylarsine-iodine system; a sharp increase in the conductivity up to the 2:1 mole ratio and a distinct break at this ratio suggest the formation of a 2:1 addduct only which is a strong electrolyte [$R_3AsI_4 \equiv R_3AsI^+ I_3^-$].

(b) There is no conductivity rise in the systems $(2\text{-}FC_6H_4)_3As$-I_2 and $(2\text{-}CF_3C_6H_4)_3As$-$I_2$. It appears that no reaction occurs in these cases.

(c) The reactions of (3-, and 4-$FC_6H_4)_3As$ and (3-, 4-$CF_3C_6H_4)_3As$ with iodine are similar but different from other triarylarsine-iodine systems; a rise in conductivity occurs but there is no distinct break at any mole ratio. It is suggested that the reaction product is dissociating in the solution.

$$R_3As + 2I_2 \rightleftharpoons R_3AsI_4$$

(3) <u>R_3As-IBr</u>

(a) The reactions of tri(methylphenyl)arsines and tri(dimethylphenyl)arsine with iodine bromide are similar with the triphenylarsine-iodine bromide system; a 2:1 break was observed in each case suggesting the formation of $R_3AsI_2Br_2$ ($\equiv R_3AsBr^+ \; I_2Br^-$). The reaction occurring is

$$R_3As + 2IBr \longrightarrow R_3AsI_2Br_2 \quad (\longrightarrow R_3AsBr^+ + I_2Br^-)$$

(b) The reactions of tri(fluorophenyl)arsines and tris(trifluoromethylphenyl)arsines with iodine bromide resemble one another but are different from the previously studied triarylarsine-iodinebromide systems. There was no break in the conductometric titration graph at the 2:1 mole ratio but the observed rise in conductivity slowed down at the 3:1 mole ratio. The ion IBr_2^- was detected from the beginning of the titrations and it is suggested that the reaction occurring is

$$R_3As + 3IBr \rightleftharpoons \underset{\substack{+\\ I_2}}{R_3AsIBr_3} \quad (\longrightarrow R_3AsBr^+ + IBr_2^-)$$

B. AN ALTERNATIVE METHOD FOR PREPARING 2:1 ADDUCTS BY THE REACTION OF A TRIARYLARSINE DIHALIDES WITH HALOGEN OR INTERHALOGENS

The 2:1 adducts obtained from the reactions of triarylarsine with bromine, iodine, or iodine bromide have been shown to be ionic and the cation present is a halotriarylarsonium ion either R_3AsBr^+ or R_3AsI^+. To investigate the possibility of preparing 2:1 adducts containing the chlorotriaryl cation, R_3AsCl^+, the reactions of triarylarsine dichlorides and iodine chloride have been studied These reactions would be expected to lead to 2:1 adducts of composition R_3AsICl_3 which are likely to exist as $R_3AsCl^+ICl_2^-$.

Another reason for studying this type of reaction concerns the fact that the adducts of type R_3AsIBr_3 has been shown to be formed in certain R_3As-IBr systems [eg $(FC_6H_4)_3As$-IBr and $(CF_3C_6H_4)_3As$-IBr]. Adducts of this stoichiometry should arise directly from the reaction

$$R_3AsBr_2 + IBr \longrightarrow R_3AsIBr_3$$

(a) The reactions of triarylarsine dichlorides with iodine chloride

The results of the conductometric titrations of tri(2-methylphenyl)arsine dichloride, tri(3-methylphenyl)arsine dichloride, tri(4-methylphenyl)arsine dichloride and tris(dimethylphenyl)arsine dichloride with iodine chloride in acetonitrile are illustrated in Fig. 14 (curves A, B, C, and D respectively).

All these four titrations yield graphs of the same general shape and they are similar to the graphs for the reaction of triphenylarsine dichloride with iodine chloride[159]. When iodine chloride was added to the triarylarsine dichloride solution the conductivity rose sharply

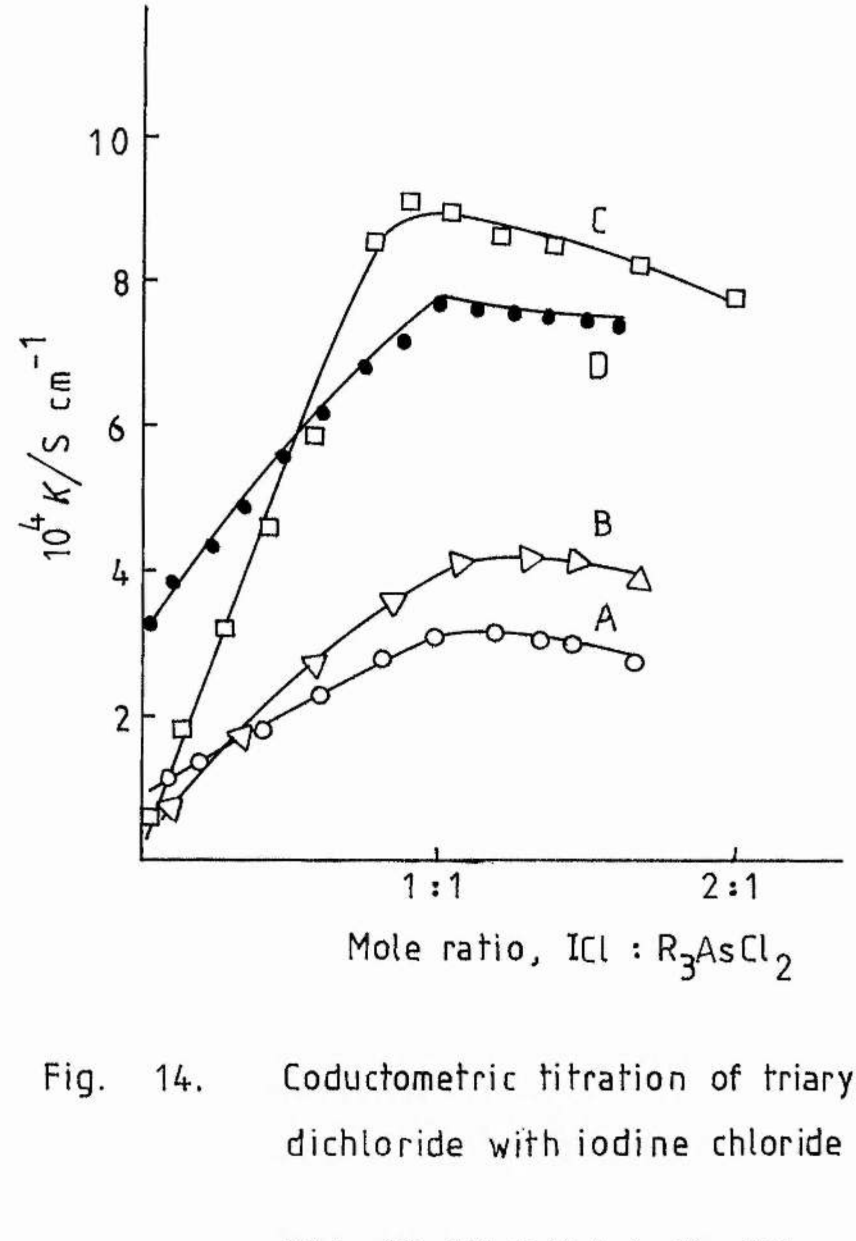


Fig. 14. Coductometric titration of triarylarsine—dichloride with iodine chloride

(A) $(2-CH_3C_6H_4)_3AsCl_2-ICl$

(B) $(3-CH_3C_6H_4)_3AsCl_2-ICl$

(C) $(4-CH_3C_6H_4)_3AsCl_2-ICl$

(D) $[2,6-(CH_3)_2C_6H_3]_3AsCl_2-ICl$

until the 1:1 mole ratio was reached. Addition of ICl solution beyond this ratio resulted in a gradual decrease in conductivity. Thus a distinct 1:1 break was obtained in each titration confirming the formation of the tetrahalide adduct (R_3AsICl_3) in the solution in each case. The colour of the solution turned yellow (the original solution was colourless) when ICl was added to the arsine solution and the ultraviolet spectrum of the solution taken at different points showed that the ICl_2^- ion (λmax = 227 mμ) was present from the beginning of each reaction.

molar conductivity values at the 1:1 mole ratio are given in the Table 16.

Table 16.

System	Λ_m (1:1)/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$(2\text{-}CH_3C_6H_4)_3AsCl_2\text{-}ICl$	131.5	0.002326
$(3\text{-}CH_3C_6H_4)_3AsCl_2\text{-}ICl$	123.8	0.0031903
$(4\text{-}CH_3C_6H_4)_3AsCl_2\text{-}ICl$	122.7	0.0074166
$[(CH_3)_2C_6H_3)_3AsCl_2\text{-}ICl$	125.6	0.00604787

These conductivity values indicate that all of these adducts are strong electrolytes in acetonitrile.

The above evidence confirms that the reaction occurring is

0:1 ⟶ 1:1 ratio

$$R_3AsCl_2 + ICl \longrightarrow R_3AsICl_3 \; (\longrightarrow R_3AsCl^+ + ICl_2^-).$$

That is ionic adducts containing chlorotriarylarsonium ion, R_3AsCl^+, are found in solution, and they have also been obtained (see Experimental section) as unstable crystalline solids.

(b) The reaction of tri(dimethylphenyl)arsine dibromide with iodine bromide

The result of the conductometric titration of tri(dimethylphenyl)arsine dibromide with iodine bromide in acetonitrile is illustrated in Fig. 15 curve A.
The conductivity rose uniformly from the start of the titration and gave a sharp break at the 1:1 mole ratio; it decreased on the further addition of iodine bromide. The colour of the solution (which was originally colourless) turned light brown when IBr was added and the ultraviolet spectrum of the solution showed absorption due to the IBr_2^- ion (strong broad peak with λ maximum at 257 mμ). The 1:1 ratio break in the titration graph indicates the formation of the tetrahalide R_3AsBr_3I and the molar conductivity value at this ratio corresponded with a strong electrolyte in acetonitrile (Λ_m (1:1) = 140.00 S cm^2 mol^{-1} at C_m = 0.0027489 mol dm^{-3}).

From the above observations we may represent the reaction by the equation

0:1 ⟶ 1:1 ratio

$$R_3AsBr_2 + IBr \longrightarrow R_3AsBr_3I \; (\longrightarrow R_3AsBr^+ + IBr_2^-).$$

A conductometric titration of R_3AsIBr with Br_2 gave graph B in Fig. 15. The colour of the solution changed to light brown from the start of the titration and the ultraviolet spectrum showed absorption due to IBr_2^- ion suggesting that the reaction is

$$R_3AsIBr + Br_2 \longrightarrow R_3AsIBr_3 \; (\longrightarrow R_3AsBr^+ + IBr_2^-).$$

Thus by both of the above conductometric titrations R_3AsIBr_3 has been shown to exist as a stable adduct in acetonitrile and it has been obtained solid from the stoichiometric quantities of R_3AsBr_2 and IBr

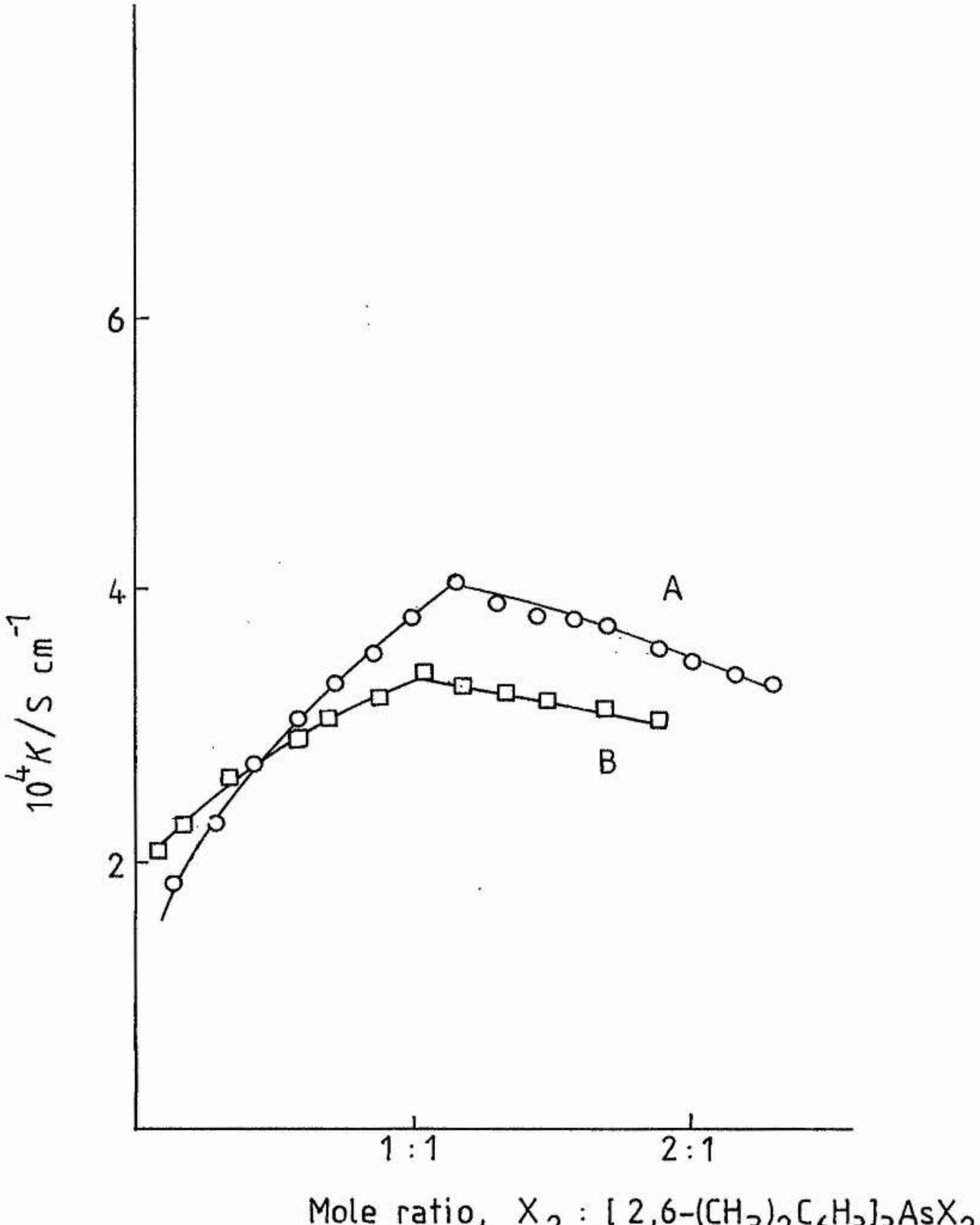


Fig. 15. Conductometric titration of tri(dimethylphenyl)arsine dihalides with iodine bromide and bromine

(A) $[(CH_3)_2C_6H_3]_3AsBr_2$ -IBr

(B) $[(CH_3)_2C_6H_3]_3AsIBr-Br_2$

in acetonitrile.

Summary of results

(a) Both R_3AsCl_3I and R_3AsBr_3I have been shown to exist in acetonitrile solution and these adducts can be obtained as solids from R_3AsCl_2 + ICl and R_3AsBr_2 + IBr respectively. They have high electrolytic conductivity in methyl cyanide solution.

(b) In adducts containing two different halogens the halogen of lower atomic number always resides in the cation ($R_3AsCl_3I \equiv R_3AsCl^+\ ICl_2^-$ and $R_3AsBr_3I \equiv R_3AsBr^+\ IBr_2^-$).

C. PREPARATION OF ADDUCTS

Triarylarsine dihalides (1:1 adducts)

Conductometric titrations were not carried out for the reaction of the triarylarsines with chlorine. Hence direct evidence for chlorine adducts of the arsine studied has not been obtained. However, 1:1 chlorine adducts, R_3AsCl_2, are well known for other triarylarsines and trialkylarsines. Attempts were therefore made to prepare these dichlorides for the conductivity studies described in chapter D.

In the triarylarsine-bomine, -iodine, and -iodine bromide systems the conductometric titration studies provide evidence for numerous adducts formed in solution. Attempts were made to prepare these as solid crystalline compounds, by mixing the constituents in the correct molar ratio in acetonitrile. Isolation of the solids was generally achieved by one of the following:

(i) direct precipitation on mixing the reagents
(ii) by addition of ether to the mixture
(iii) by freeze drying of the mixture.

In most, but not all, cases a solid adduct was obtained corresponding in composition to a break in the appropriate conductometric titration graph.

In some cases attempts were made to prepare an adduct even though there was no conductometric titration evidence for its existence in acetonitrile. It is worth noting that this was possible in a few cases [eg. R_3AsI_2 where R = $CH_3C_6H_4$ or 4-$CF_3C_6H_4$ and R'_3AsIBr where R' = $CH_3C_6H_4$ or $(CH_3)_2C_6H_3$].

It was also possible in some instances to obtain unindicated (by conductometric titration) adducts by using another solvent (eg benzene, petroleum ether).

The results of these preparative studies are given in the following sections.

(a) Dichlorides

All of the triarylarsine dichlorides mentioned in this Thesis have been prepared by passing dry chlorine gas, diluted in a stream of dry nitrogen, through a cooled solution of triarylarsine in a suitable solvent until the solution assumed a green-yellow colour. The dichlorides were obtained either by freeze drying of the solution or by adding dry ether to the solution. All of these dichloride derivatives are moisture sensitive, white crystalline solids. Their detailed preparation has been given in the Experimental Part, and the properties of the adducts are given in the following table.

Table 17

Compound	Colour	M.p/^{o}C
$(2\text{-}CH_3C_6H_4)_3AsCl_2$	White	184–185
$(3\text{-}CH_3C_6H_4)_3AsCl_2$	White	174–177
$(4\text{-}CH_3C_6H_4)_3AsCl_2$	White	220–224
$[(CH_3)_2C_6H_3]_3AsCl_2.0.25\ CHCl_3$	White	210–220
$[(CH_3)_2C_6H_3]_3AsCl_2.0.25\ CCl_4$	White	214
$(2\text{-}FC_6H_4)_3AsCl_2$	Light yellow	190–200
$(3\text{-}FC_6H_4)_3AsCl_2$	White	156–160
$(4\text{-}FC_6H_4)_3AsCl_2$	White	206–208
$(2\text{-}CF_3C_6H_4)_3AsCl_2.0.5\ CHCl_3$	Pale yellow	214–216
$(3\text{-}CF_3C_6H_4)_3AsCl_2$	White	166–168
$(4\text{-}CF_3C_6H_4)_3AsCl_2$	White	214–216

The compounds $[(CH_3)_2C_6H_3]_3AsCl_2$ and $(2\text{-}CF_3C_6H_4)_3AsCl_2$ were obtained from chloroform in the solvated form. The presence of chloroform of solvation was confirmed from elemental analysis and from the infrared spectrum of the compound. Attempts were made to isolate $[(CH_3)_2C_6H_3]_3AsCl_2$ from carbon tetrachloride in an attempt to obtain the unsolvated, but again the solid isolated contained CCl_4 of solvation.

(b) Dibromides

The triarylarsine dibromides whose existence was shown by the conductometric titrations are given in the following Table.

Table 18. Triarylarsine-bromine adducts indicated by the conductometric titration of R_3As-Br_2 in acetonitrile

System	Mole ratio (break)	Indicated halide
$(2-CH_3C_6H_4)_3AsBr_2$	1:1 sh.	$(2-CH_3C_6H_4)_3AsBr_2$
	2:1 sh.	$(2-CH_3C_6H_4)_3AsBr_4$
$(3-CH_3C_6H_4)_3As-Br_2$	1:1 sh.	$(2-CH_3C_6H_4)_3AsBr_2$
	2:1 sh.	$(3-CH_3C_6H_4)_3AsBr_4$
$(4-CH_3C_6H_4)_3As-Br_2$	1:1 sh.	$(4-CH_3C_6H_4)_3AsBr_2$
	2:1 sh.	$(4-CH_3C_6H_4)_3AsBr_4$
$[(CH_3)_2C_6H_3]_3As-Br_2$	1:1 sh.	$[(CH_3)_2C_6H_3]_3AsBr_2$
	2:1 sh.	$[(CH_3)_2C_6H_3]_3AsBr_4$
	3:1 n.sh.	$[(CH_3)_2C_6H_3]_3AsBr_6$
$(2-FC_6H_4)_3As-Br_2$	No break	No compound indicated
$(3-FC_6H_4)_3As-Br_2$	1:1 sh.	$(3-FC_6H_4)_3AsBr_2$
	2:1 n.sh.	$(3-FC_6H_4)_3AsBr_4$
$(4-FC_6H_4)_3As-Br_2$	1:1 sh.	$(4-FC_6H_4)_3AsBr_2$
	2:1 sh.	$(4-FC_6H_4)_3AsBr_4$
$(2-CF_3C_6H_4)_3As-Br_2$	No break	No compound indicated
$(3-CF_3C_6H_4)_3As-Br_2$	1:1 sh.	$(3-CF_3C_6H_4)_3AsBr_2$
	2:1 n.sh.	$(3-CF_3C_6H_4)_3AsBr_4$
$(4-CF_3C_6H_4)_3As-Br_2$	1:1 sh.	$(4-CF_3C_6H_4)_3AsBr_2$
	2:1 n.sh.	$(4-CF_3C_6H_4)_3AsBr_4$

sh = Sharp n.sh = not sharp

All these dibromide adducts have been obtained as crystalline solids by freeze drying an acetonitrile solution containing a 1:1 molar ratio of bromine and triarylarsine. The compounds were characterised by elemental analysis (C, H and Br). (see Experimental Part). Their properties are given in Table 19.

Table 19 Properties of R_3AsBr_2

Compound	Colour	M.p/^oC
$(2\text{-}CH_3C_6H_4)_3AsBr_2$	Pale yellow	192-193
$(3\text{-}CH_3C_6H_4)_3AsBr_2$	White	186-188
$(4\text{-}CH_3C_6H_4)_3AsBr_2$	White	236-238
$[(CH_3)_2C_6H_3]_3AsBr_2$	Pale yellow	204-205 (decomposed)
$(3\text{-}FC_6H_4)_3AsBr_2$	White	169-171
$(4\text{-}FC_6H_4)_3AsBr_2$	White	224-246 (decomposed)
$(3\text{-}CF_3C_6H_4)_3AsBr_2$	Pale yellow	171-172
$(4\text{-}CF_3C_6H_4)_3AsBr_2$	White	210-212 (decomposed)

The existence of $(2\text{-}FC_6H_4)_3AsBr_2$ and of $(2\text{-}CF_3C_6H_4)_3AsBr_2$ was not suggested by the conductometric titrations of the arsine with bromine and attempts to isolate them as solids from acetonitrile containing the stoichiometric quantities of bromine and the arsine were not successful.

(c) Tetrabromides

It has been found that when the 2:1 conductometric titration break is sharp it is strong evidence that the tetrabromide is stable and readily obtained as a crystalline solid. Those of the arsines

$(2\text{-}CH_3C_6H_4)_3As$, $(3\text{-}CH_3C_6H_4)_3As$, and $(4\text{-}CH_3C_6H_4)_3As$ have already been isolated by A. Y. Mahomedy[153] and their properties are shown in Table 20.

Table 20. Properties of R_3AsBr_4 adducts

Compound	Colour	M.p/°C
$(2\text{-}CH_3C_6H_4)_3AsBr_4$	bright yellow	154
$(3\text{-}CH_3C_6H_4)_3AsBr_4$	bright yellow	65
$(4\text{-}CH_3C_6H_4)_3AsBr_4$	dark orange	120–121
$[(CH_3)_2C_6H_3]_3AsBr_4$	yellow	194–198 (decomposed)

In addition to these attempts were made to prepare only a selected number of 2:1 bromine adducts- those of $[(CH_3)_2C_6H_3]_3As$, $(2\text{-}FC_6H_4)_3As$, $(2\text{-}CF_3C_6H_4)_3As$, and $(4\text{-}CF_3C_6H_4)_3As$. The first of these was indicated by a sharp break in the conductometric titration graph of the $[(CH_3)_2C_6H_3]_3As\text{-}Br_2$ system and was obtained readily (Table 20). In the remaining systems the 2:1 break in the conductometric titration graph was not sharp and attempts to prepare the adducts were not successful. There is evidence to suggest that when the R groups are strongly electronegative adducts formation is more difficult[155, 156]

(d) A hexabromide

Although no 3:1 adducts of triarylarsine have been reported previously, $[(CH_3)_2C_6H_3]_3AsBr_6$, which was shown by the 3:1 mole ratio break in the graph of the conductometric titration bromine-tri(dimethylphenyl)arsine (Table 18), has been prepared by freeze drying the 3:1 molar (Br_2 : R_3As) mixture in acetonitrile. It is an unstable orange colour solid (losing bromine on standing), melting at 192-194°C (decomposed).

(e) Diiodides

The conductometric titrations of iodine with triarylarsines did not indicate the existence of any 1:1 adducts (R_3AsI_2) in acetonitrile (see Table 21).

Table 21. Adducts indicated by the conductometric titrations of R_3As-I_2 in acetonitrile

System	Mole ratio (break)	Indicated adduct
$(2-CH_3C_6H_4)_3As-I_2$	No 1:1 break	No compound indicated
	2:1	$(2-CH_3C_6H_4)_3AsI_4$
$(3-CH_3C_6H_4)_3As-I_2$	No 1:1 break	No compound indicated
	2:1 sh.	$(3-CH_3C_6H_4)_3AsI_4$
$(4-CH_3C_6H_4)_3As-I_2$	No 1:1 break	No compound indicated
	2:1 sh.	$(4-CH_3C_6H_4)_3AsI_4$
$[(CH_3)_2C_6H_3]_3As-I_2$	No 1:1 break	No compound indicated
	2:1 sh.	$[(CH_3)_2C_6H_3]_3AsI_4$
*$(FC_6H_4)_3As-I_2$	No break	No compound indicated
*$(CF_3C_6H_4)_3As-I_2$	No break	No compound indicated

sh. = sharp

* = all of the systems (2-, 3-, and 4- position)

It was possible however to obtain a number of these diiodide adducts as crystalline solids using petroleum ether as the solvent or by freeze drying the 1:1 mixture of I_2 and R_3As in acetonitrile. Their properties are given in Table 22.

Table 22. Properties of R_3AsI_2 compounds

Compound	Colour	M.p/°C
$(2\text{-}CH_3C_6H_4)_3AsI_2$	dark brown	163-168
$(3\text{-}CH_3C_6H_4)_3AsI_2$	light brown	185-186
$(4\text{-}CH_3C_6H_4)_3AsI_2$	rust	166-167
$(4\text{-}CF_3C_6H_4)_3AsI_2$	dark brown	116-118
		(decomposed)

Attempts to prepare $[(CH_3)_2C_6H_3]_3AsI_2$ and $(4\text{-}FC_6H_4)_3AsI_2$ gave dark coloured unstable solids which lost iodine readily.

(f) Tetraiodides

All the triarylarsine tetraiodides whose existence was shown (Table 21) were obtained by adding ether to the concentrated acetonitrile solution containing a 2:1 molar ratio of iodine and triarylarsine. Although there was no 2:1 distinct break in any of the $(CF_3C_6H_4)_3As\text{-}I_2$ systems the solid crystalline adduct $(4\text{-}CF_3C_6H_4)_3AsI_4$ was obtained by freeze drying the acetonitrile solution containing a 2:1 molar ratio of iodine and tris(4-trifluoromethylphenyl)arsine. It is an unstable compound and tends to lose iodine. The properties of these tetrahalide adducts are given in the following table.

Table 23. Properties of R_3AsI_4

Compound	Colour	M.p/^oC
$(2\text{-}CH_3C_6H_4)_3AsI_4$*	brown black	114
$(3\text{-}CH_3C_6H_4)_3AsI_4$*	dark brown	152-153
$(4\text{-}CH_3C_6H_4)_3AsI_4$*	dark violet	101-102
$[(CH_3)_2C_6H_3]_3AsI_4$	dark red	138-240
$(4\text{-}CF_3C_6H_4)_3AsI_4$	dark violet	118-119

* First described by A. Y. Mahomedy[153]

(g) Bromide iodides

As with the $R_3As\text{-}I_2$ titrations, there was no sign of the formation of 1:1 adducts (R_3AsIBr) in the conductometric titrations of $R_3As\text{-}IBr$ (Table 25 page 71). However crystalline solids of composition R_3AsIBr (R = 2-, 3-, or 4-methylphenyl or dimethylphenyl) were obtained from a 1:1 molar mixture of iodine bromide and triarylarsine in acetonitrile. Their properties are given in the Table 24.

Table 24. Properties of R_3AsIBr

Compound	Colour	M.p/^oC
$(2\text{-}CH_3C_6H_4)_3AsIBr$	rust	162-163
$(3\text{-}CH_3C_6H_4)_3AsIBr$	bright yellow	136
$(4\text{-}CH_3C_6H_4)_3AsIBr$	bright yellow	149-151
$[(CH_3)_2C_6H_3]_3AsIBr$	rust	169-170 (decomposed)

(h) Dibromide di-iodide adducts

The possible existence of $R_3AsBr_2I_2$ adducts is clear from the conductometric titrations of R_3As-IBr systems summarised in the following table 25.

Table 25. Indicated $R_3AsBr_2I_2$ adducts by the systems R_3As-IBr in acetonitrile

System	Mole ratio (break)	Indicated adducts
$(2\text{-}CH_3C_6H_4)_3As$-IBr	2:1	$(2\text{-}CH_3C_6H_4)_3AsBr_2I_2$
$(3\text{-}CH_3C_6H_4)_3As$-IBr	2:1	$(3\text{-}CH_3C_6H_4)_3AsBr_2I_2$
$(4\text{-}CH_3C_6H_4)_3As$-IBr	2:1	$(4\text{-}CH_3C_6H_4)_3AsBr_2I_2$
$[(CH_3)_2C_6H_3]_3As$-IBr	2:1	$[(CH_3)_2C_6H_4]_3AsBr_2I_2$
$(FC_6H_4)_3As$-IBr	No break	No compound indicated
$(CF_3C_6H_4)_3As$-IBr	No break	No compound indicated

All these adducts were obtained as stable crystalline solids by adding ether to the concentrated solution of iodine bromide and triarylarsine (2:1 molar ratio), or by freeze drying the solution. The properties of the compounds are given in Table 26.

Table 26. Properties of $R_3AsBr_2I_2$ adducts prepared in acetonitrile

Compound	Colour	M.p/^oC
$(2\text{-}CH_3C_6H_4)_3AsBr_2I_2^*$	rust	149-150
$(3\text{-}CH_3C_6H_4)_3AsBr_2I_2^*$	red brown	102
$(4\text{-}CH_3C_6H_4)_3AsBr_2I_2^*$	chocolate brown	132-133
$[(CH_3)_2C_6H_4]_3AsBr_2I_2$	orange	166-168

* first described by A. Y. Mahomedy[153]

(i) trichloride iodide

Although the existence of R_3AsCl_3I was shown by all conductometric titrations of the systems R_3AsCl_2-ICl, the preparation of the adducts as solids was successful only in cases where R was $CH_3C_6H_4$ or $(CH_3)_2C_6H_3$. These R_3AsCl_3I were obtained by freeze drying the acetonitrile solution containing R_3AsCl_2 and ICl in a 1:1 molar ratio. They are unstable compounds and lose ICl readily. Their properties are given in the following table:

Table 27. Properties of R_3AsCl_3

Compound	Colour	M.p./°C
$(2\text{-}CH_3C_6H_4)_3AsCl_3I$	yellow	40 (decomposed)
$(3\text{-}CH_3C_6H_4)_3AsCl_3I$	yellow	room temperature
$(4\text{-}CH_3C_6H_4)_3AsCl_3I$	yellow	low melting solid
$[(CH_3)_2C_6H_3]_3AsCl_3I$	yellow	215-218

Attempts to prepare $(2\text{-}CF_3C_6H_4)_3AsCl_3I$ and $(4\text{-}CF_3C_6H_4)_3AsCl_3I$ in acetonitrile yielded the dihalides R_3AsCl_2 instead. It would seem that the presence of the strongly electronegative substituent (CF_3) confers instability on the above tetrahalides.

D. CONDUCTIVITY STUDY

Conductivity study of the 1:1 adducts (R_3AsX_2)

Measurement of the conductivity of acetonitrile or nitrobenzene solutions of compounds of type Ph_3EX_2 (E = P, As, Sb and Bi) and calculation of molar conductivity values has been found previously[126, 117 130 133], to provide useful information on the nature and behaviour of these compounds. In particular the triphenylarsenic dihalides, Ph_3AsX_2 (X = Br, Cl), were shown to behave as weak electrolytes in acetonitrile

$$Ph_3AsX_2 \rightleftharpoons Ph_3AsX^+ + X^-$$

The arylarsenic compounds, R_3AsX_2, should therefore be particularly suitable for a study of the effect of small variations in R on the tendency of R_3EX_2 compounds to ionise since, in the weak electrolyte case, changes in the equilibrium system will lead to higher or lower values of molar conductivity (compared with triphenylarsine dihalides).

Values of conductivity were obtained for solutions of each compound at several concentrations (solubility permitting, in the range 0.0005-0.015 mol dm^{-3}). Concentrations less than about 0.0005 mol dm^{-3} were avoided because at these very low concentrations the values of conductivity of the hydrolytically unstable compounds under investigation were thought to be unreliable. The molar conductivity values are recorded in the Experimental section. For a given compound a plot of molar conductivity against square root of concentration gave a slightly concave curve of gentle slope as expected for a weak electrolyte at these concentrations. In illustration the graphs for $(C_6H_5)_3AsCl_2$, $(3\text{-}CH_3C_6H_4)_3AsCl_2$, and $(4\text{-}CH_3C_6H_4)_3AsCl_2$ are shown in

Figure 16. Since most of the conductivity studies of these compounds were carried out at concentrations round about 0.01 M, this represents a suitable concentration at which to compare molar conductivity values and hence to obtain some idea of the relative tendencies of the compounds to ionise in solution. The molar conductivity values for all of the dihalides studied are given in Tables 28, 29 and 30.

Table 28. Molar conductivity of the triarylarsine dichlorides in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m / S cm^2 mol^{-1}
$(C_6H_5)_3AsCl_2$	4.0
$(2\text{-}CH_3C_6H_4)_3AsCl_2$	39.5
$(3\text{-}CH_3C_6H_4)_3AsCl_2$	4.8
$(4\text{-}CH_3C_6H_4)_3AsCl_2$	5.3
$(2\text{-}FC_6H_4)_3AsCl_2$	not soluble in acetonitrile
$(3\text{-}FC_6H_4)_3AsCl_2$	1.2
$(4\text{-}FC_6H_4)_3AsCl_2$	2.6
$(2\text{-}CF_3C_6H_4)_3AsCl_2$ $0.5CHCl_3$	7.2
$(3\text{-}CF_3C_6H_4)_3AsCl_2$	0.9
$(4\text{-}CF_3C_6H_4)_3AsCl_2$	0.5
$(C_6F_5)_3AsCl_2$	0.7

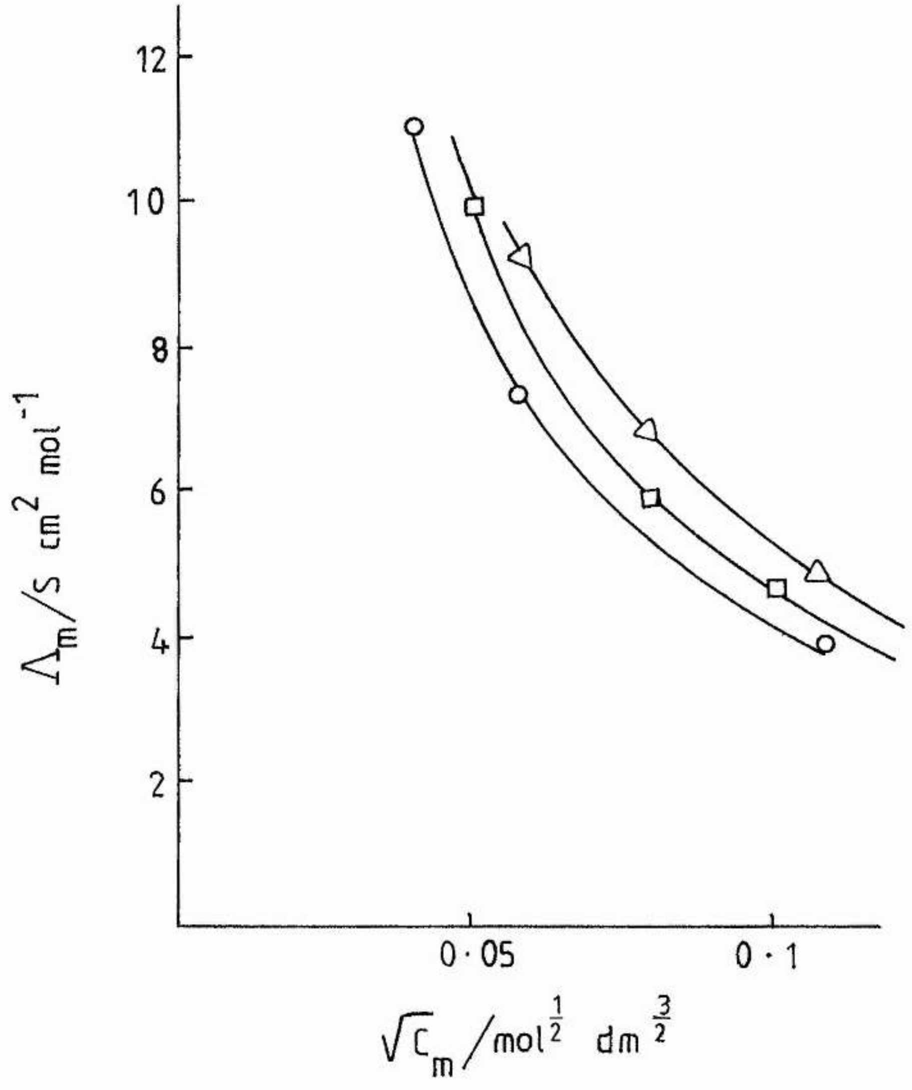


Fig. 16. Electrolytic Coductivity of R_3AsCl_2 in Acetonitrile at 25°C

$(C_6H_4)_3AsCl_2$ ○
$(3-CH_3C_6H_4)_3AsCl_2$ □
$(4-CH_3C_6H_4)_3AsCl_2$ △

Table 29. Molar conductivities of the triarylarsine dibromides in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m/S cm^2 mol^{-1}
$(C_6H_5)_3AsBr_2$	25.3
$(2\text{-}CH_3C_6H_4)_3AsBr_2$	108.5
$(3\text{-}CH_3C_6H_4)_3AsBr_2$	46.5
$(4\text{-}CH_3C_6H_4)_3AsBr_2$	58.5
$(3\text{-}FC_6H_4)_3AsBr_2$	9.5
$(4\text{-}FC_6H_4)_3AsBr_2$	20.5
$(3\text{-}CF_3C_6H_4)_3AsBr_2$	4.8
$(4\text{-}CF_3C_6H_4)_3AsBr_2$	2.8

Note: $(2\text{-}FC_6H_4)_3AsBr_2$ and $(2\text{-}CF_3C_6H_4)_3AsBr_2$ were not obtained as solids.

Table 30. Molar conductivities of other triarylarsine dihalides in acetonitrile at $C_m = 0.01$ mol dm^{-3}.

Compound	Λ_m/S cm^2 mol^{-1}
$[2,6\text{-}(CH_3)_2C_6H_3]_3AsIBr$	66.0
$(4\text{-}CF_3C_6H_4)_3AsI_2$	33.5

Comments on the Molar Conductivity Values

(a) The 3- and 4-substituted compounds

The molar conductivity values are low and with only two exceptions lie in the range 0-20 S cm^2 mol^{-1}. The compounds must therefore be regarded as weak electrolytes in acetonitrile solution

$$R_3AsX_2 \rightleftharpoons R_3AsX^+ + X^-$$

and from this it may be inferred that in the solid state these compounds are more than likely to possess covalent molecular structures.

It is clear from the data that monosubstitution of the phenyl ring influences the molar conductivity of the dihalides. Relative to the unsubstituted phenyl compounds, the introduction of an electron-releasing group raises the conductivity whereas an electron-withdrawing group lowers the conductivity. It is instructive to compare the molar conductivities of the dihalides $(YC_6H_4)_3AsX_2$, with the acid strengths of the corresponding substituted benzoic acids YC_6H_4COOH. In the latter it is well known that the nature of Y affects the equilibrium

$$YC_6H_4COOH \rightleftharpoons YC_6H_4COO^- + H^+$$

and hence the pK of the acid. The comparison is made, pictorially, in Figs. 17 and 18. The molar conductivity values at 0.01 M in acetonitrile for $[(4\text{-}YC_6H_4)_3AsCl_2$ and $(3\text{-}YC_6H_4)_3AsCl_2]$ and $[4\text{-}YC_6H_4)_3AsBr_2$ and $(3\text{-}YC_6H_4)_3AsBr_2]$ are given in Tables 31 and 32 respectively.

Explanation

pKa values in red

Λ_m values in blue

Y in 4-position - solid lines

Y in 3-position - broken lines

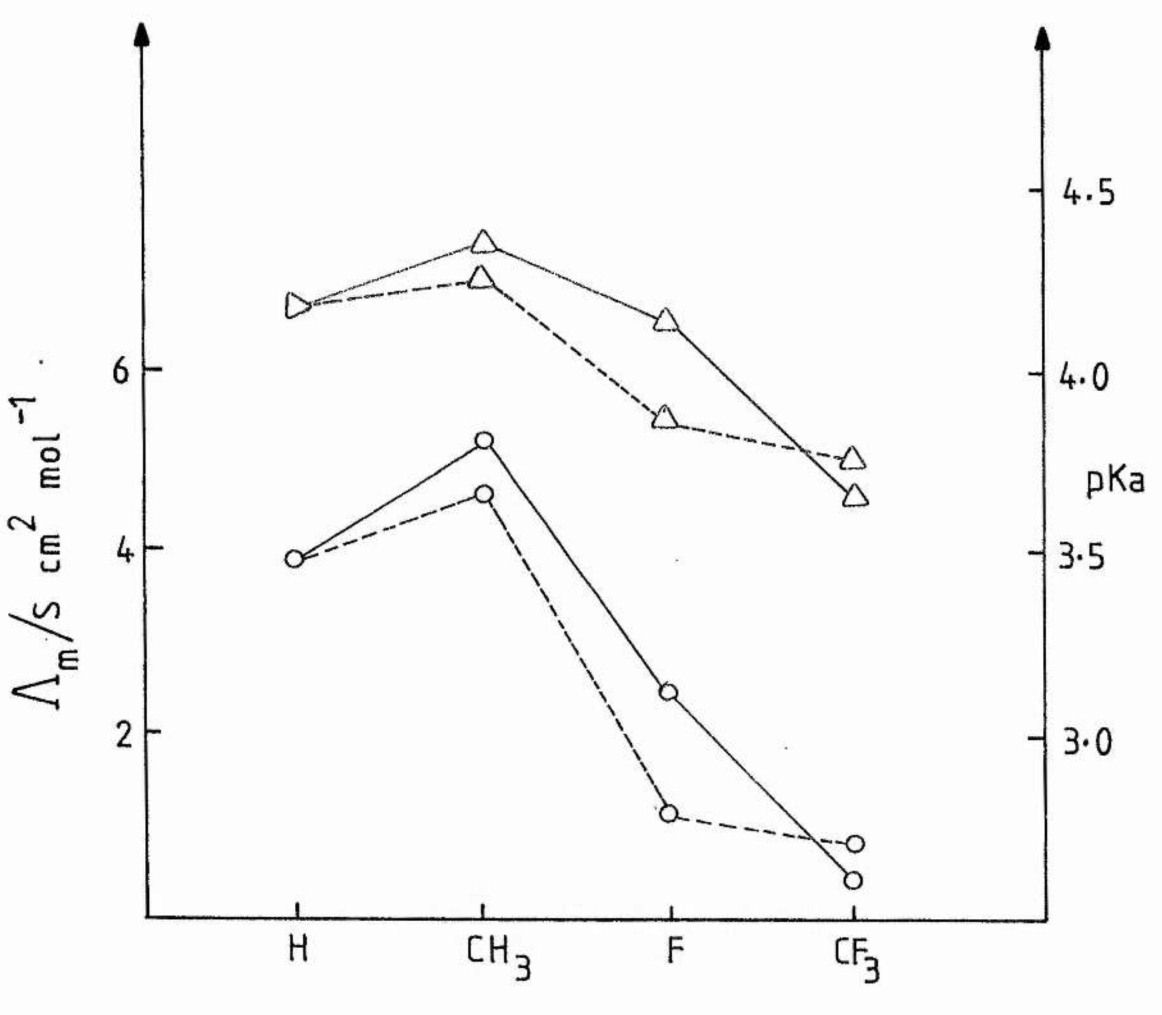


Fig. 17. Correlation of Λ_m values for $(3\text{-}YC_6H_4)_3AsCl_2$ [----○----] $(4\text{-}YC_6H_4)_3AsCl_2$ [——○——] with pKa for $3\text{-}YC_6H_4COOH$ [----△----] and $4\text{-}YC_6H_4COOH$ [——△——]

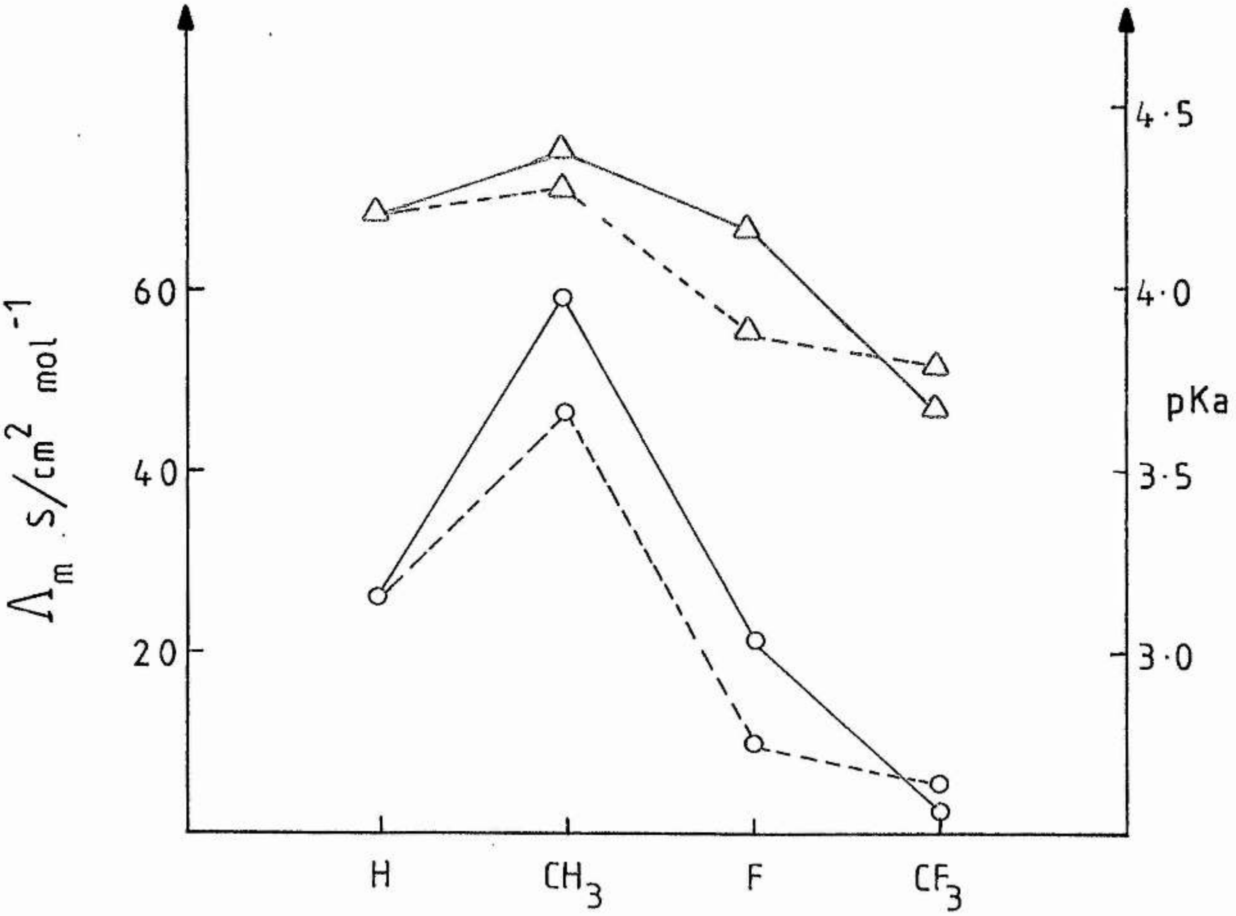


Fig. 18. Correlation of Λ_m values for $(3\text{-}YC_6H_4)_3AsBr_2$ [----○----] $(4\text{-}YC_6H_4)_3AsBr_2$ [——○——] with pKa for $3\text{-}YC_6H_4COOH$ [----△----] and $4\text{-}YC_6H_4COOH$ [——△——]

The pK values of substituted benzoic acids 4-YC_6H_4COOH and 3-YC_6H_4COOH are given in Table 33.

Table 31. Molar conductivity values (at C_m = 0.01 mol dm^{-3} for $(4\text{-}YC_6H_4)_3AsCl_2$ and $(3\text{-}YC_6H_4)_3AsCl_2$

Y	Λ_m (4-isomer)	Λ_m (3-isomer)
H	4.0	4.0
CH_3	5.3	4.8
F	2.6	1.2
CF_3	0.5	0.9

Table 32. Molar conductivity values (at C_m = 0.01 mol dm^{-3}) for $(4\text{-}YC_6H_4)_3AsBr_2$ and $(3\text{-}YC_6H_4)_3AsBr_2$

Y	Λ_m (4-isomer)	Λ_m (3-isomer)
H	25.3	25.3
CH_3	58.5	46.5
F	20.5	9.5
CF_3	2.8	4.8

Table 33. pK values of substituted benzoic acids 4-YC_6H_4COOH and 3-YC_6H_4COOH

Y	pK (4-isomer)	pK (3-isomer)
H	4.20	4.20
CH_3	4.37	4.27
F	4.14	3.87
CF_3	3.66	3.77

From these diagrams there is clearly a noticeable correlation between molar conductivity of $(YC_6H_4)_3AsX_2$ and pK of YC_6H_4COOH and from this it is deduced that the electron-withdrawing/releasing properties of group Y which are responsible for the variation in pK of benzoic acids are also responsible for the variation in molar conductivities of the compounds $(YC_6H_4)_3AsX_2$.

A useful measure of the electron-withdrawing/releasing power of an organic group is the Hammett Substituent Constant $(\sigma)^{158}$. This constant is derived from the dissociation constants of substituted benzoic acids and is numerically equal to the ratio $K(YC_6H_4COOH)/K(C_6H_5COOH)^{158}$. Properties (eg. rate constant of reactions) of organic molecules which depend on the electron-withdrawing/releasing properties of a group within the molecule are frequently found to vary systematically with σ and this is usually demonstrated by a correlation diagram in which the property or its logarithm is plotted against σ or $\log_{10}\sigma$. Figs. 19 and 20 shows a plot of molar conductivity (Λ_m) against σ and Figs. 21 and 22 shows a plot of $\log_{10}\Lambda_m$ against σ. In the latter case it can be seen that the points of the graphs lie approximately on straight lines hence the relationship between $\log_{10}\Lambda_m$ and σ would appear to be linear. The equations for the lines are

dichlorides : $\log_{10}\Lambda_m = 1.15\sigma + 0.78$

dibromides : $\log_{10}\Lambda_m = 2.26\sigma + 1.54$

These results establish the rule that for the 4-, and 3-, substituted compounds, $(YC_6H_4)_3AsX_2$, the greater the electron releasing properties of Y then the greater is the molar conductivity of the compound. That is, the nature of the substituent affects the tendency of $(YC_6H_4)_3AsX_2$ to ionise in acetonitrile solution. There are two possible ways in which this can happen

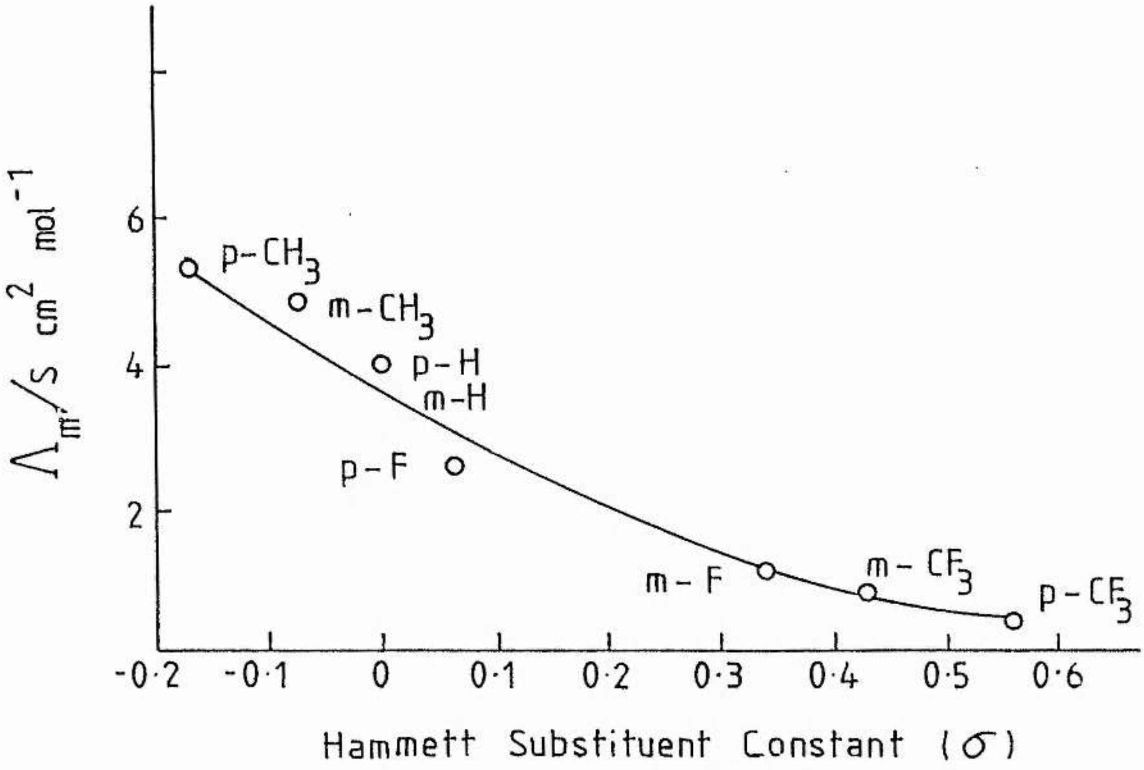


Fig. 19. Correlation of Λ_m values for (3- and 4-$YC_6H_4)_3AsCl_2$ with Hammett Substituent Constant (σ)

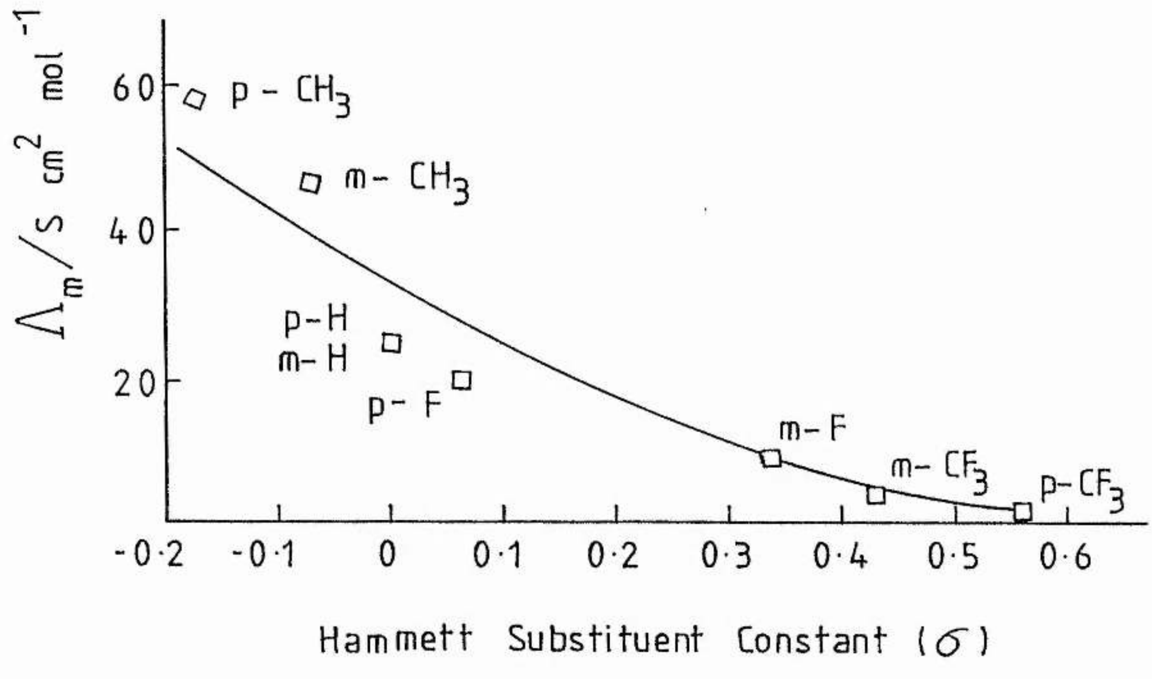


Fig. 20. Correlation of Λ_m values for (3- and 4-$YC_6H_4)_3AsBr_2$ with Hammett Substituent Constant (σ)

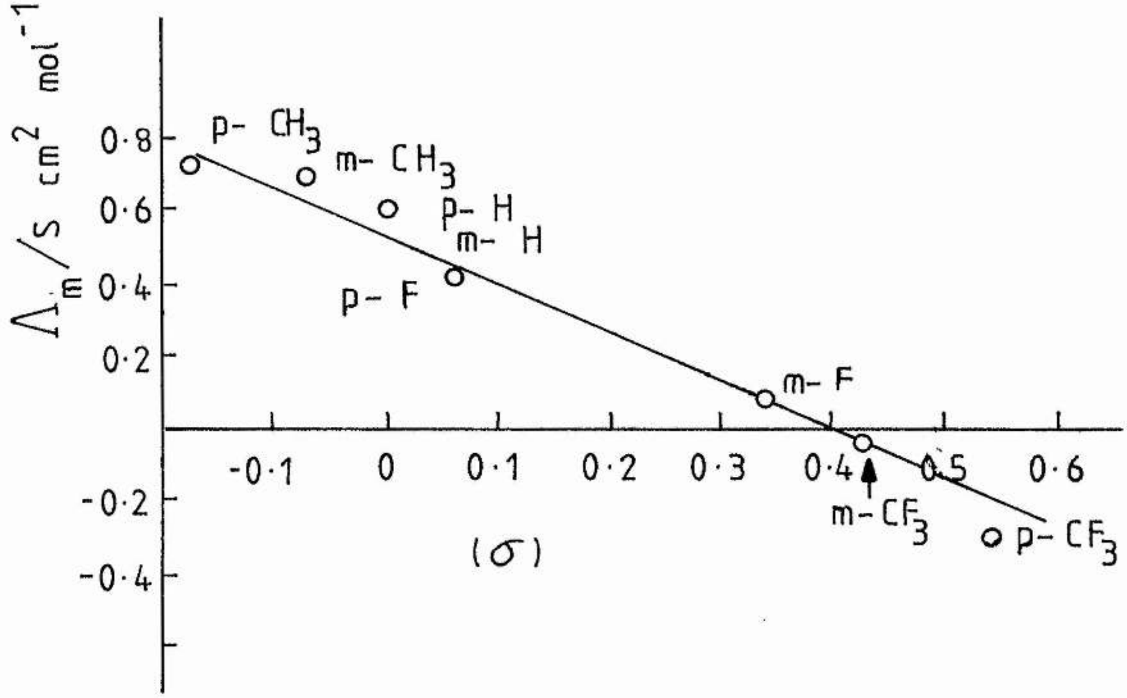


Fig. 21. Correlation of $\log_{10} \Lambda_m$ values for (3-, and 4-$YC_6H_4)_3AsCl_2$ with σ

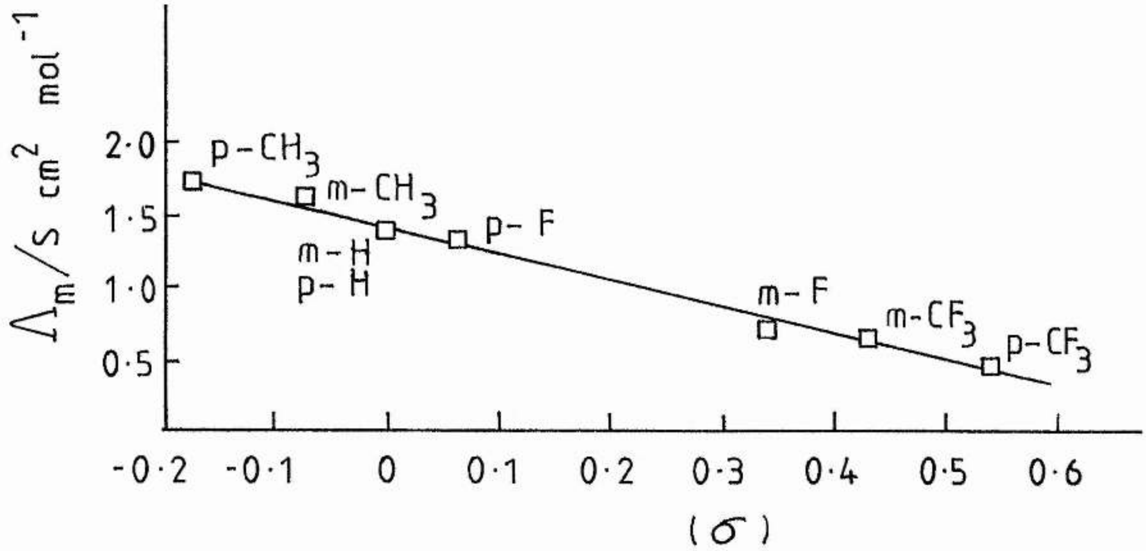


Fig. 22. Correlation of $\log_{10} \Lambda_m$ values for (3-, and 4-$YC_6H_4)_3AsBr_2$ with σ

(i) Electron release may weaken the As-X bond thus facilitating ionisation

$$(YC_6H_4)_3AsX_2 \rightleftharpoons (YC_6H_4)_3AsX^+ + X^-$$

Supporting evidence for this comes from the series of phosphorus compounds $(CH_3)_nPF_{5-n}$ in which it has been found that increasing n results in weakening of the axial P-F bonds[161]. That is, increasing electron release to the central atom of the trigonal bipyramidal molecule weakens the phosphorus halogen bonds.

(ii) In the ion $(YC_6H_4)_3AsX^+$ electron release from the organic group will help to spread the positive charge and hence enhance the stability of the cation.

(b) The 2-substituted compounds

The molar conductivity data for the 2-substituted compounds are limited because of the insolubility of $(2\text{-}FC_6H_4)_3AsCl_2$ and of the non-existence of the solid adducts $(2\text{-}FC_6H_4)_3AsBr_2$ and $(2\text{-}CF_3C_6H_4)_3AsBr_2$.

The tolyl compounds

Considering the tolyl compounds, the most significant feature is the much higher values for molar conductivity obtained for the 2-substituted compounds as compared with the 3-, and 4-substituted compounds (Table 28 and 29 page 74 and 75). The molar conductivity value for $(2\text{-}CH_3C_6H_4)_3AsCl_2$ is in the medium electrolyte range and that of $(2\text{-}CH_3C_6H_4)_3AsBr_2$ is in the strong electrolyte range. These enhanced values of molar conductivity cannot be attributed solely to an enhanced electronic (inductive) effect occurring when the substituent is in the 2-position. It would seem to be a clear example of the ortho effect.* It is well known that 2-substituted benzene derivatives often behave differently from the corresponding 3-, or 4-substituted compounds and this effect is often called the "ortho effect". An important structural factor which contributes to the "ortho effect" is the "steric hindrance" of the group in the 2-position. It is believed that this is in fact the reason for the anomalously high molar conductivity values of the tri(2-methylphenyl)arsine dihalides since steric crowding in the 5-coordinate trigonal bipyramidal neutral molecule $(2\text{-}CH_3C_6H_4)_3AsX_2$ will be greater than in 4-coordinate tetrahedral cation $(2\text{-}CH_3C_6H_4)_3AsX^+$. Consequently in the ionisation equilibrium

$$(2\text{-}CH_3C_6H_4)_3AsX_2 \rightleftharpoons (2\text{-}CH_3C_6H_4)_3AsX^+ + X^-$$

the right side will be favoured. Thus an enhanced presence of ions will lead to higher molar conductivity values.

Further support for this conclusion is given by the molar conductivity values of acetonitrile solutions of tri(2,6-dimethylphenyl)arsine dichloride and dibromide (Table 34).

Table 34. Molar conductivity values at $C_m = 0.01$ mol dm^{-3} for $[(CH_3)_2C_6H_3]_3AsX_2$

Compound	Λ_m/S cm^{2}mol^{-1}
$[(CH_3)_2C_6H_3]_3AsCl_2$ 0.25 $CHCl_3$	91.5
$[(CH_3)_2C_6H_3]_3AsBr_2$	124.5

---

* Older nomenclature

ortho = 2-substitution
meta = 3-substitution
para = 4-substitution

Because of the presence of two ortho methyl groups, the steric hindrance in these compounds would be expected to be greater than in the corresponding tri(2-methylphenyl)arsine dihalides. This is borne out by the molar conductivities which are in keeping with these dihalides behaving as strong electrolytes.

$(2\text{-}FC_6H_4)_3AsCl_2$

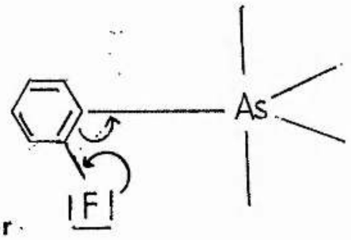
The relative insolubility of this isomer in acetonitrile made it impossible to obtain solutions of concentration around 0.01 mol dm^{-3}, nor was it possible to obtain solutions near enough to concentration 0.01 mol dm^{-3} for the molar conductivity of the compound at this concentration to be obtained by extrapolation.
All these isomers are however soluble in nitrobenzene and values of molar conductivity at C_m = 0.01 mol dm^{-3} have been obtained using this solvent. These are as follows:

Compound	Λ_m/S cm^2 mol^{-1}
$(2\text{-}FC_6H_4)_3AsCl_2$	2.3
$(3\text{-}FC_6H_4)_3AsCl_2$	0.1
$(4\text{-}FC_6H_4)_3AsCl_2$	0.4

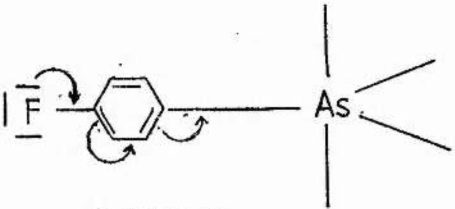
From these values it can be said that all three compounds are weak electrolytes in nitrobenzene (for a strong electrolyte in nitrobenzene molar conductivity for a solution of concentration 0.01 mol dm^{-3} lie in the range 20-25 S cm^2 mol^{-1}) but again it is noted that the 2-isomer has a much higher conductivity than the others.

If only the strong electron withdrawing inductive effect of the fluorine atom were considered then this would be greatest in the

2-position and hence should lead to a very low value of molar conductivity. However a mesomeric effect is possible in the 2-, and 4-substituted fluoro- compounds leading to electron release towards the central arsenic atom



2–isomer



4-isomer

This effect would be expected to be greatest in the 2-isomer but it is not thought likely that the large difference in conductivity between this isomer and the others can be accounted for by this effect alone. Thus it would seem that the steric effect of the fluorine atom in the 2-position must play an important role in determining the extent of ionisation and hence conductivity of this compound.

$(2\text{-}CF_3C_6H_4)_3AsCl_2$

The molar conductivity of this compound is considerably higher than that of the corresponding 3-, or 4- substituted compounds. It seems clear that a steric effect of the trifluoromethyl group is in action here, as in the case of the methyl compounds, thus offsetting the strong electron withdrawing effect of the trifluoromethyl group which would be expected to be at its maximum in the 2- position.

(c) Dichlorides and dibromides

It is noted from the values given in Table 28 and 29, pages 74 and 75 that for compounds of general formula R_3AsX_2, molar conductivity of the dibromides is always much higher than that of the dichlorides. This can be attributed to the relative magnitudes of the bond enthalpies of the As-X bond (As-Cl:$\triangle H$ = 317 kJ mol^{-1}; As-Br:$\triangle H$ = 243 kJ mol^{-1}).

It is also possible that a steric factor [as mentioned in (b)] plays a part since the bromine atom is larger than the chlorine atom.

(d) The molar conductivity of tri(2-methylphenyl)arsine dichloride and dibromide

The unexpected observation has been made that at very low concentrations in both acetonitrile and nitrobenzene (< ca. 5x10^{-3} mol dm^{-3}) the conductivity of the 2-substituted compounds $(2\text{-}CH_3C_6H_4)_3AsCl_2$ and $(2\text{-}CH_3C_6H_4)_3AsBr_2$ decreases with decreasing concentration Fig. 23 curve A and Fig. 24 curve A respectively. Thus the Λ_m versus $\sqrt{C_m}$ graph displays a maximum in the vicinity of $\sqrt{C_m}$ = 0.07 mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$. This contrasts with the behaviour of the corresponding 3-, and 4- substituted compounds which behave as expected for weak electrolytes over the whole concentration range studied.

At concentrations above the maximum in the graph the compounds display normal weak electrolyte behaviour. That is, molar conductivity increases with decreasing concentration, reflecting increasing ionisation [i.e. equilibrium (I) moves to the right as concentration decreases]

$$R_3AsX_2 \rightleftharpoons R_3AsX^+ + X^- \text{ -------------}(I)$$

At concentrations below the maximum the molar conductivity diminishes as the concentration decreases thus suggesting that the proportion of current carriers is becoming less. To explain this it is necessary to postulate a second equilibrium in addition to equilibrium (I), namely

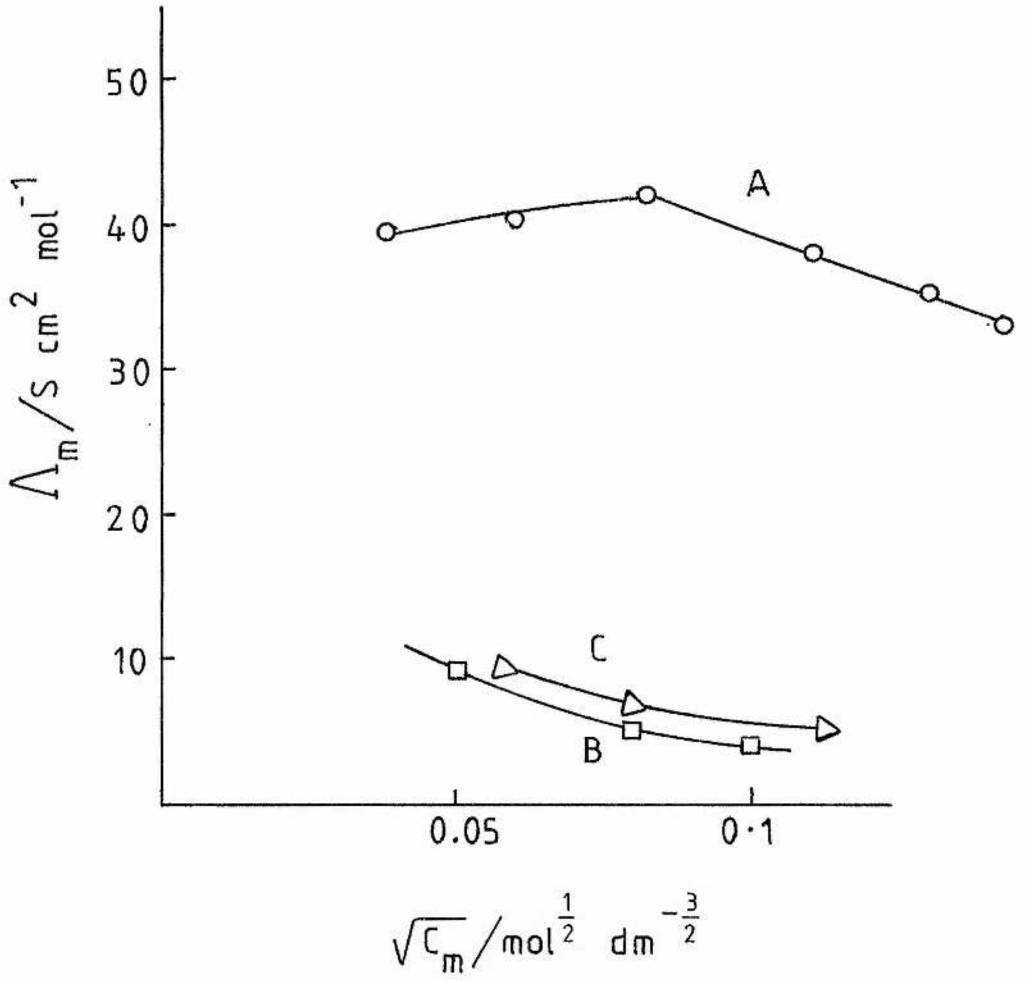


Fig. 23. Electrolytic Conductivity of R_3AsCl_2 in Acetonitrile at 25°C

(A) $(2\text{-}CH_3C_6H_4)_3AsCl_2$
(B) $(3\text{-}CH_3C_6H_4)_3AsCl_2$
(C) $(4\text{-}CH_3C_6H_4)_3AsCl_2$

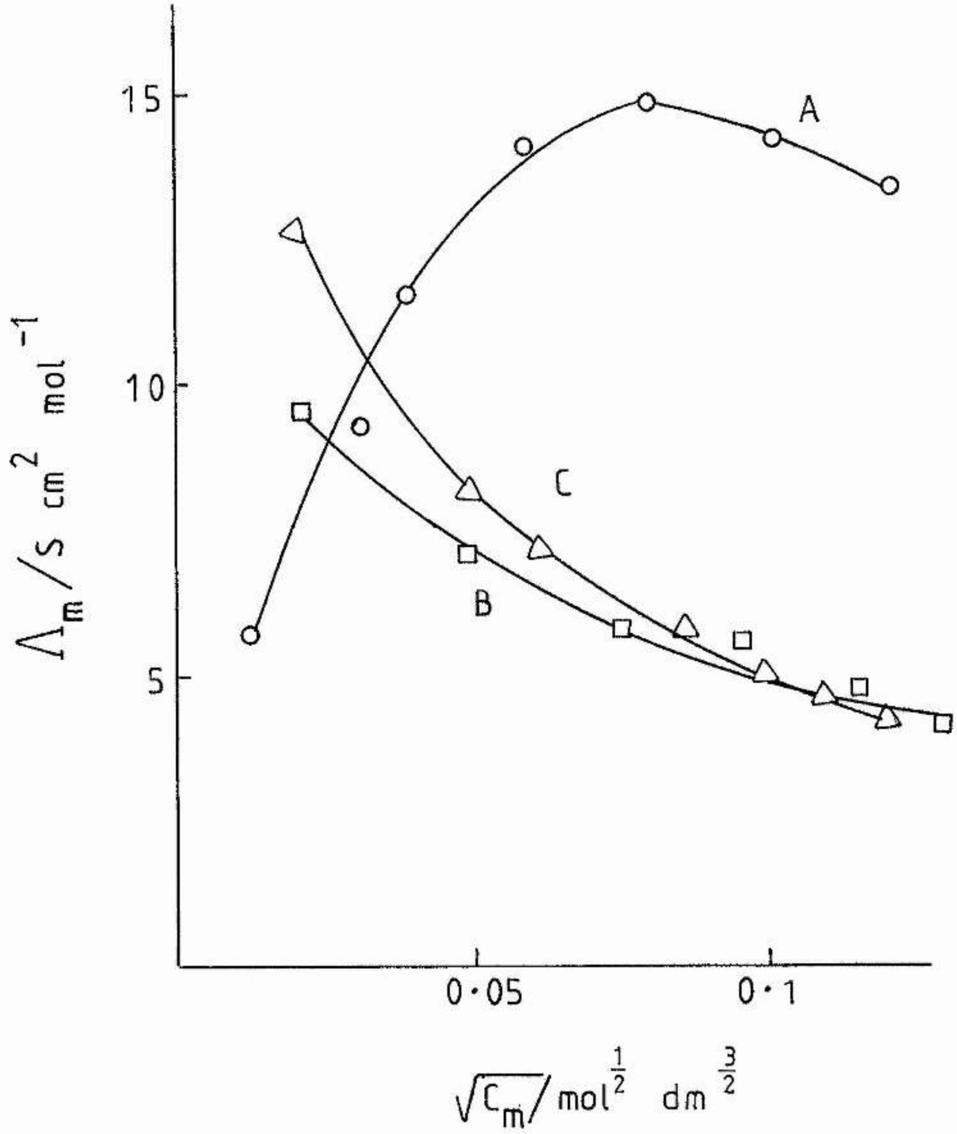


Fig. 24. Electolytic Conductivity of R_3AsBr_2 in Nitrobenzene at 25°C

(A) $(2-CH_3C_6H_4)_3AsBr_2$

(B) $(3-CH_3C_6H_4)_3AsBr_2$

(C) $(4-CH_3C_6H_4)_3AsBr_2$

$$R_3AsX^+ + X^- \rightleftharpoons R_3As + X_2 \text{———} (II)$$

and that this equilibrium becomes more predominant at the lower concentration. Because the products of equilibrium II are molecular and non-conducting then a fall in molar conductivity would result as this equilibrium comes more into play.

As molar concentration decreases the ionisation equilibrium I moves to the right. That is, there is an increasing concentration of ions ($R_3AsX^+ + X^-$) and this will have the effect of moving equilibrium II to the right which implies a higher concentration of non-conducting molecular species.

A piece of qualitative evidence in support of these two equilibria is the observation that a very small amount of tribromide ion is present in acetonitrile solutions of $(2\text{-}CH_3C_6H_4)_3AsBr_2$. This would be a natural consequence of the interaction of Br^- ions [produced in equilibrium (I)] and Br_2 molecules [produced in equilibrium II].

(e) Other Dihalides -di-iodides and bromide iodides

Although conductometric titration in acetonitrile shows that triarylarsine diiodides, R_3AsI_2, and bromide iodides R_3AsIBr do not exist in acetonitrile, some have been obtained as crystalline solids. Mahomedy [153] reported the tolyl compounds $(CH_3C_6H_4)_3AsI_2$ and $(CH_3C_6H_4)_3AsIBr$ and in the present work $[(2,6\text{-}(CH_3)_2C_6H_3]_3AsIBr$ and $(4\text{-}CF_3C_6H_4)_3AsI_2$ have been obtained as crystalline compounds.

The molar conductivity values of these compounds in acetonitrile (at $C_m = 0.01$ mol dm^{-3}) have been noted in Table 30 page 75. The values are high but are not real values for these compounds because the latter undergo disproportionation in the solvent. The solutions are strongly coloured and their ultraviolet spectra show the presence of a high concentration of trihalide ion, I_3^-, and I_2Br^- respectively. The disproportionation may be represented generally as

$$R_3AsX_2 \longrightarrow \tfrac{1}{2}R_3As + \tfrac{1}{2}R_3AsX^+ X_3^-.$$

Thus the observed high conductivities arise from the strong electrolytic 2:1 adducts $R_3AsX^+ X_3^-$ (at $C_m = 0.005$ mol dm^{-3} leading to $\Lambda_m = 132$ and 67 S cm^2 mol^{-1} respectively). Similar behaviour has been observed for the tolyl compounds mentioned above and for the corresponding phenyl compounds[117].

(f) Coductivity of 2:1 adducts (R_3AsX_4)

Previous workers[117, 153, 159] have concluded that all the tetrahalide adducts of triphenylarsine and trimethylphenylarsine are strong electrolytes both in acetonitrile and nitrobenzene.

The molar conductivity of R_3AsX_4 whose preparation is mentioned in this Thesis (Experimental Part) have been measured in acetonitrile at different concentrations. These values were plotted against the square root of molar concentrations $\sqrt{C_m}$ and the molar conductivities at $C_m = 0.01$ M were obtained by interpolation. These values are given in the following Table.

Table 35. Molar conductivity values of R_3AsX_4 in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m/S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3AsCl_3I$	134.0
$(3\text{-}CH_3C_6H_4)_3AsCl_3I$	139.0
$(4\text{-}CH_3C_6H_4)_3AsCl_3I$	141.0
$[(CH_3)_2C_6H_3]_3AsCl_3I$	141.5

Table 35. (cont)

$[(CH_3)_2C_6H_3]_3AsBr_4$	138.0
$[(CH_3)_2C_6H_3]_3AsBr_2I_2$	134.0
$[(CH_3)_2C_6H_3]_3AsBr_3I$	132.0
$[(CH_3)_2C_6H_3]_3AsI_4$	106.5
$(4\text{-}CF_3C_6H_4)_3AsI_4$	48.4

Conductivity values suggest that all these compounds, except $(4\text{-}CF_3C_6H_4)_3AsI_4$, are strong electrolytes like the previously studied R_3AsX_4 compounds.

$$R_3AsX_4 \longrightarrow R_3AsX^+ + X_3^-$$

The low value for the molar conductivity of $(4\text{-}CF_3C_6H_4)_3AsI_4$ coupled with the absence of a sharp break at the 2:1 mole ratio in the graph of the conductometric titration of I_2 versus $(4\text{-}CF_3C_6H_4)_3As$ suggests the following behaviour

$$(4\text{-}CF_3C_6H_4)_3As + 2I_2 \rightleftharpoons (4\text{-}CF_3C_6H_4)_3AsI_4 \rightleftharpoons (4\text{-}CF_3C_6H_4)_3AsI^+ + I_3^-$$

$$[(4\text{-}CF_3C_6H_4)_3AsI^+ I_3^-]$$

The nature of the trihalide ion (X_3^-) present in these compounds has been confirmed in each case from the ultraviolet spectrum of their solutions in acetonitrile. This shows that they ionise in the following way:

$$R_3AsCl_3I \equiv R_3AsCl^+ ICl_2^-$$
$$R_3AsBr_4 \equiv R_3AsBr^+ Br_3^-$$
$$R_3AsBr_3I \equiv R_3AsBr^+ IBr_2^-$$
$$R_3AsBr_2I_2 \equiv R_3AsBr^+ I_2Br^-$$
$$R_3AsI_4 \equiv R_3AsI^+ I_3^-$$

The above mode of ionisation is consistent with the other R_3AsX_4 compounds (R = Ph or $CH_3C_6H_4$); in the mixed halogen adducts the halogen in the halogenotriarylarsonium cation is always the one of lower atomic number.

(g) Conductivity study of $[(CH_3)_2C_6H_3]_3AsBr_6$

The xylyl compound $[(CH_3)_2C_6H_3]_3AsBr_6$, is the only compound of such stoichiometry obtained from triarylarsine-halogens or interhalogen systems. Its molar conductivity at $C_m = 0.01$ mol dm^{-3} (169.0 S cm^2 mol^{-1}) in acetonitrile is higher than that found for any other triarylarsine halogen adduct. The ultraviolet spectrum of a solution of this compound in acetonitrile shows the presence of tribromide ion and using the value 53900 cm^{-1} for the extinction coefficient for Br_3^- [117] it is estimated that there are two Br_3^- ions (see page 42) per mole of compound. This suggests for the ionisation of the compound

$$R_3AsBr_6 \longrightarrow R_3As^{2+} + 2Br_3^-$$

Although dipositive ions of the type R_3As^{2+} have not previously been reported, the analogous antimony containing ions, R_3Sb^{2+} are believed to be present in $R_3Sb(NO_3)_2$ [160] compounds.

PART II

A. REACTIONS OF THE TRIARYLSTIBINES WITH HALOGENS AND INTERHALOGEN

1. REACTIONS OF THE TRI(METHYLPHENYL)STIBINES WITH HALOGENS AND INTERHALOGEN

(a) Reaction with bromine

The results of the conductometric titrations of tri(2-methylphenylstibine, tri(3-methylphenyl)stibine and tri(4-methylphenyl)stibine were identical and are represented by one graph in Fig. 25.

All these three titrations are similar to each other and they resemble the triphenylstibine bromine system[126]. There was no significant rise in the conductivity when bromine was added to the tri(methylphenyl)stibine until the 1:1 mole ratio was reached, but thereafter the conductivity increased only slightly thus giving a break at the 1:1 ratio (see note* at the end of this section). There was no further break in the graph. The solution remained colourless to the 1:1 mole ratio but then it acquired a yellow colour as further bromine was added into it. The ultraviolet spectrum of the solution showed a weak absorption due to the Br_3^- ion (λmax = 269 mμ) after the 1:1 mole ratio.

Molar conductivity values are given in the Table 36.

Table 36

System	$\Lambda_m(1:1)/S\ cm^2\ mol^{-1}$	C_m = mol dm^{-3}
$(2\text{-}CH_3C_6H_4)_3Sb\text{-}Br_2$	1.5	0.00588
$(3\text{-}CH_3C_6H_4)_3Sb\text{-}Br_2$	0.4	0.0044416
$(4\text{-}CH_3C_6H_4)_3Sb\text{-}Br_2$	0.9	0.00499

The titration results indicate the formation of 1:1 adducts only

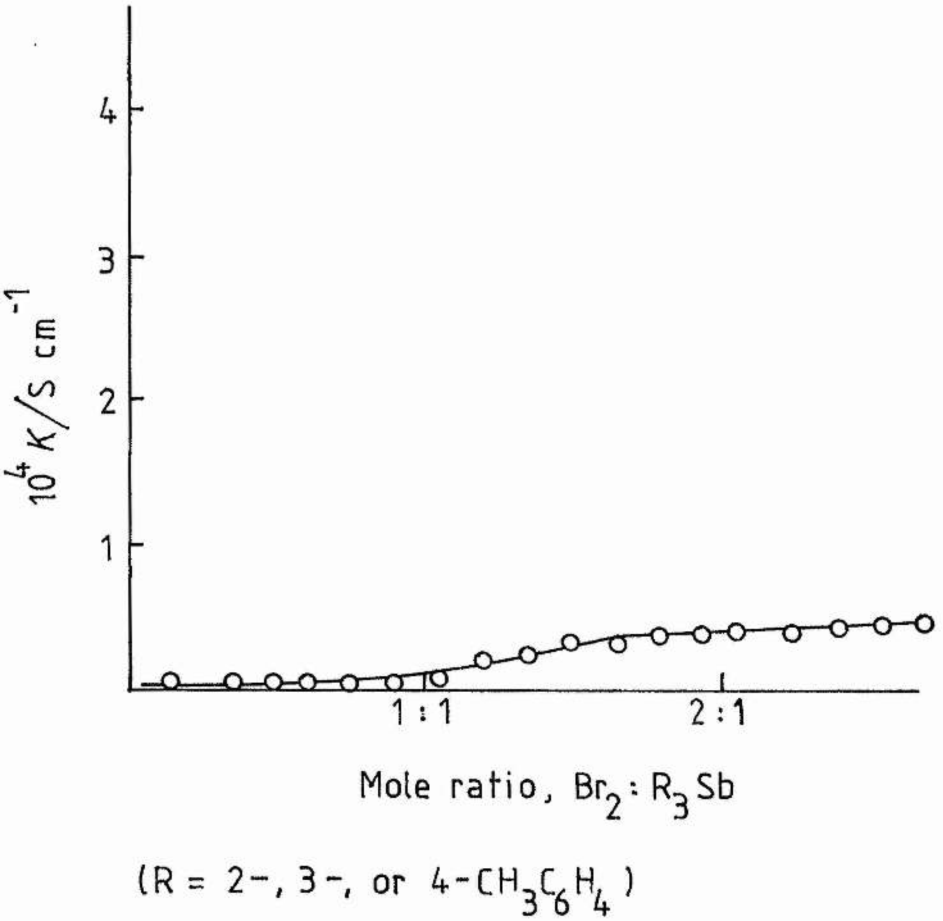


Fig. 25. Conductometric titration of tri(methylphenyl)stibine with bromine

and the molar conductivity values suggest that these 1:1 adducts (R_3SbBr_2) are probably molecular (or at most very weak electrolytes) in acetonitrile, like triphenyl stibine dibromide[126]. The reaction may be represented as

0:1 → 1:1 ratio

$$R_3Sb + Br_2 \longrightarrow R_3SbBr_2$$

* A blank conductometric titration (bromine in acetonitrile against pure acetonitrile) gave a graph in which conductivity rose at a very slow rate, comparable with that observed after the 1:1 ratio in the $(CH_3C_6H_4)_3Sb-Br_2$ systems. It is also noted that dilute solutions of bromine in acetonitrile show weak absorption at λ 269 mμ, attributable to a trace of tribromide ion. These observations indicate that bromine itself ionises to a small extent in acetonitrile:

$$2Br_2 + xCH_3CN \rightleftharpoons Br^+(CH_3CN)_x + Br_3^-$$

(b) Reaction with iodine

The results of the conductometric titrations of tri(2-methylphenyl)stibine, tri(3-methylphenyl)stibine and tri(4-methylphenyl)stibine with iodine in acetonitrile are illustrated in Fig. 26 (curves A, B, and C respectively).

It can be seen that these titration graphs are different from those observed in the titrations with bromine; also, the systems $(3-CH_3C_6H_4)_3Sb-I_2$ and $(4-CH_3C_6H_4)_3Sb-I_2$ have similar graphs but that of the $(2-CH_3C_6H_4)_3Sb-I_2$ system is different in pattern.

$(2-CH_3C_6H_4)_3Sb-I_2$ system. In this titration the conductivity rose sharply from the beginning and gave only one break, in the graph, at 2:1 ratio. The solution being titrated assumed a light brown colour

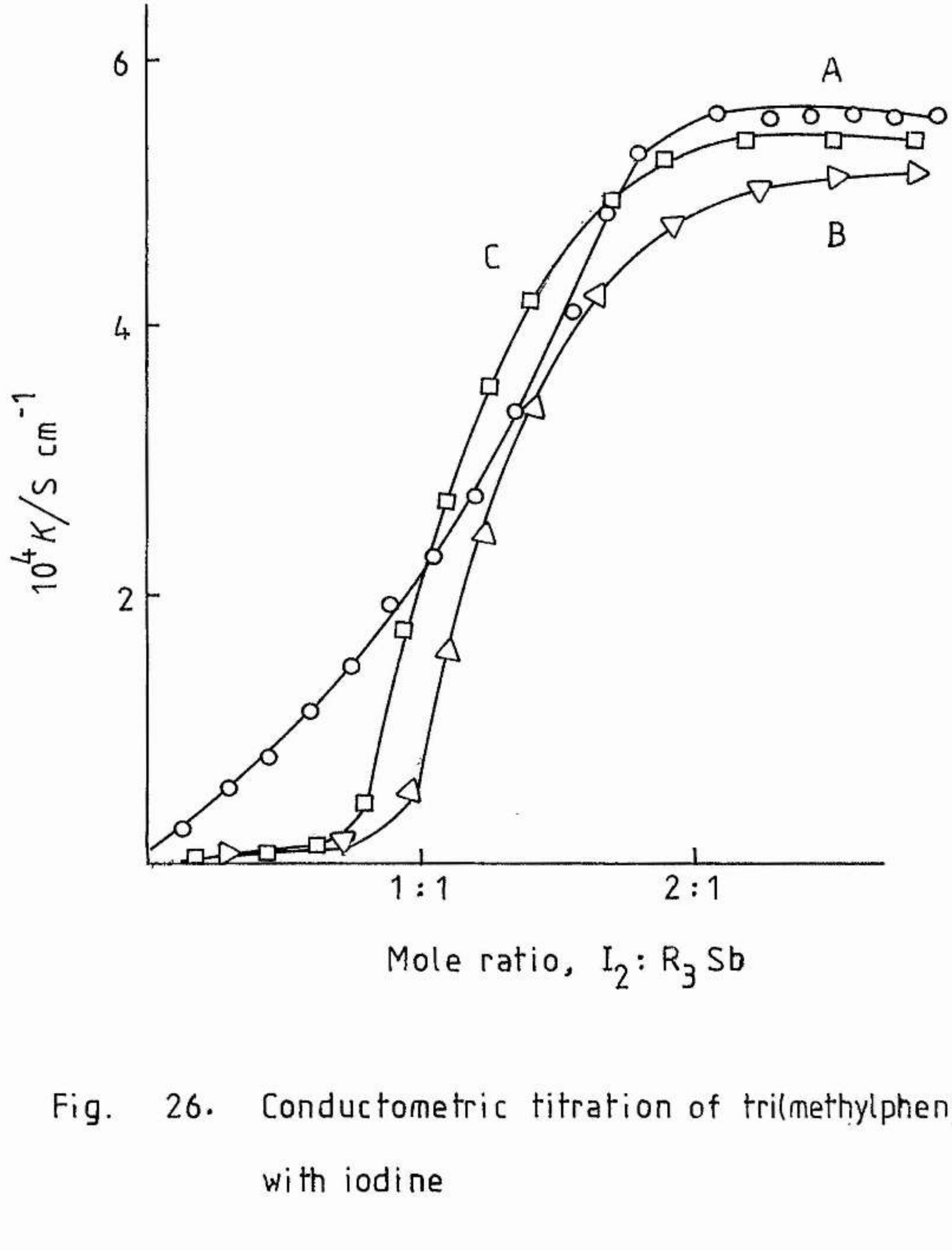


Fig. 26. Conductometric titration of tri(methylphenyl)stibine with iodine

(A) $(2\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$ (B) $(3\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$

(C) $(4\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$

from the beginning of the titration and the ultraviolet spectrum of the solution showed that I_3^- ion (λmax = 293, 362 mμ) was present from the start of the reaction. Thus, the evidence suggests the formation of R_3SbI_4 ($\equiv R_3SbI^+ I_3^-$) in the acetonitrile solution and there is no evidence for the formation of the diiodide R_3SbI_2.

$(3\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$ and $(4\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$ systems. The conductometric titration graphs for these systems are similar and resemble that of the triphenylstibine-iodine system. In both cases the conductivity did not increase significantly on the addition of iodine to the stibine solution until the 1:1 mole ratio was reached, but thereafter it increased sharply to the 2:1 mole ratio and then levelled off. Thus, two distinct breaks in the titration graphs indicate the formation of 1:1 and 2:1 adducts (R_3SbI_2 and R_3SbI_4) in solution. A pale yellow colour appeared in the solution just before the 1:1 ratio, coinciding with a slight rise in conductivity and as the titration progressed beyond the 1:1 ratio the colour of the solution became progressively darker (brown). The ultraviolet spectrum of the solution confirmed the presence of tri-iodide ion (λmax = 292, 362 mμ)

The molar conductivity values at different breaks in these systems are given in the following table.

Table 37.

System	Λ_m (1:1)/S cm^2 mol^{-1}	Λ_m (2:1)/S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	No break	101.3
		(C_m = 0.00525)*
$(3\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	7.4	82.5
	(C_m = 0.006389)	(C_m = 0.005759)
$(4\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	11.6	116.5
	(C_m = 0.005181)	(C_m = 0.004547)

* mol dm^{-3}

The reactions occurring in these three systems may be represented as follows

$\underline{(2\text{-}CH_3C_6H_4)_3Sb\text{-}I_2}$

0:1 ⟶ 2:1 ratio

$$R_3Sb + 2I_2 \longrightarrow R_3SbI_4 \quad (\longrightarrow R_3SbI^+ \, I_3^-)$$

$\underline{(3\text{-}CH_3C_6H_4)_3Sb\text{-}I_2 \text{ and } (4\text{-}CH_3C_6H_4)_3Sb\text{-}I_2}$

0:1 ⟶ 1:1 ratio

$$R_3Sb + I_2 \longrightarrow R_3SbI_2 \quad (\rightleftharpoons \tfrac{1}{2} R_3Sb + \tfrac{1}{2}R_3SbI^+ + \tfrac{1}{2}I_3^-)$$

1:1 ⟶ 2:1 ratio

$$R_3SbI_2 + I_2 \longrightarrow R_3SbI_4 \quad (\longrightarrow R_3SbI^+ \, I_3^-)$$

The appearance of triiodide ion in the solution slightly before the 1:1 ratio is interpreted as showing that the 1:1 compound is undergoing slight disproportionation. Further evidence for this will be given in the Conductivity study section.

(c) Reactions with iodine bromide

(i) (3-, and 4-$CH_3C_6H_4)_3Sb$-IBr systems

The results of the conductometric titrations of tri(3-methylphenyl)stibine and tri(4-methylphenyl)stibine with iodine bromide in acetonitrile are illustrated in Fig. 27 (curves B, and C respectively).

The graphs obtained are closely similar to each other and resemble the graph of the triphenylstibine-iodine bromide system. There was no significant rise in the conductivity when iodine bromide was added to the stibine solution until the 1:1 mole ratio was reached. Further addition of IBr increased the conductivity which reached a maximum at about the 1.5:1 ratio, then steadily dropped to the 2:1 mole ratio at which point it increased gently when more IBr was added to the solution and levelled off just after the 3:1 mole ratio. Thus three (at the 1:1, 1.5:1 and 2:1 ratios) distinct breaks were present in the conductometric titration graphs. The solution remained colourless to the 1:1 mole ratio but thereafter it became yellow and progressively darkened as further IBr was added to the solution. The ultraviolet spectrum of the solution showed absorption due to I_3^- ion (λmax = 293,363 mμ) between the 1:1 and 2:1 mole ratios and IBr_2^- ion (λmax = 256 mμ) was present after the 2:1 mole ratio.

The molar conductivity values at these breaks are given in Table 38.

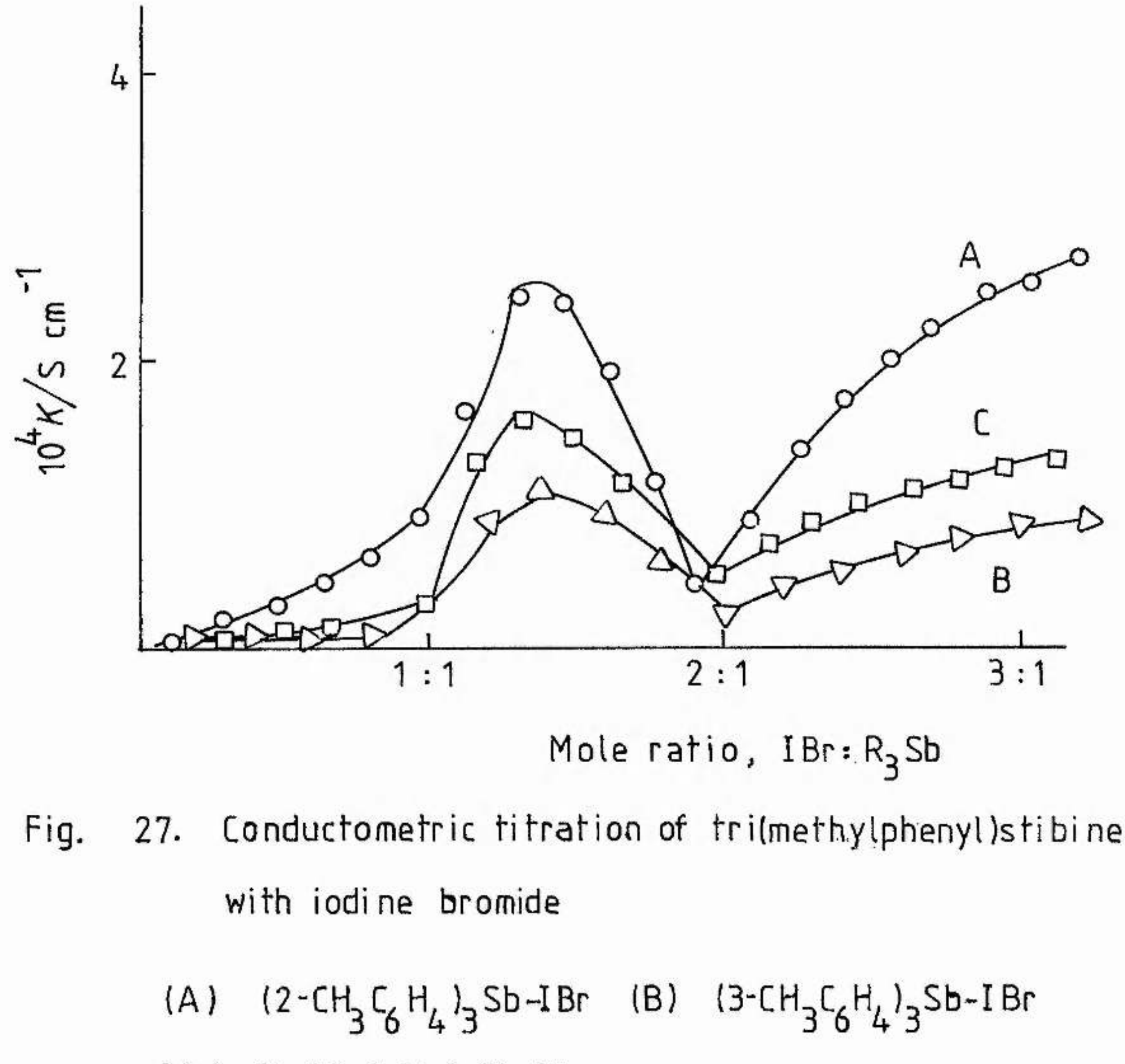


Fig. 27. Conductometric titration of tri(methylphenyl)stibine with iodine bromide

(A) $(2\text{-}CH_3C_6H_4)_3Sb\text{-}IBr$ (B) $(3\text{-}CH_3C_6H_4)_3Sb\text{-}IBr$

(C) $(4\text{-}CH_3C_6H_4)_3Sb\text{-}IBr$

Table 38. Molar conductivity values (Λ_m = S cm^2 mol^{-1}) at different breaks in the conductometric titration of the system ($R_3Sb-IBr$)

System	Λ_m (1:1)	Λ_m (1.5:1)	Λ_m (2:1)
$(3-CH_3C_6H_4)_3Sb-IBr$	2.3	27.2	4.9
	(0.004399*)	(0.004221)	(0.004056)
$(4-CH_3C_6H_4)_3Sb-IBr$	2.6	30.5	10.8
	(0.005798)	(0.0054148)	(0.005079)

* C_m = mol dm^{-3}

These values suggest that the adducts forming at the 1:1 and 2:1 mole ratios are weak electrolytes in acetonitrile and this suggests that they may be stibine dihalides: in support of this the adducts R_3SbIBr and R_3SbBr_2 have been recovered from solutions containing IBr and the stibine at these ratios. The adduct formed at the 1.5:1 mole ratio is thought to be R_3SbBrI_3 ($\equiv R_3SbBr^+I_3^-$). The evidence supporting this is the solutions strong brown colour, its high conductivity and the observed absorption due to I_3^- ion. However attempts to prepare R_3SbBrI_3 as a solid adduct were not successful. The reaction occurring in solution is believed to be the following

0:1 ⟶ 1:1 ratio

$$R_3Sb + IBr \longrightarrow R_3SbIBr$$

1:1 ⟶ 1.5:1 ratio

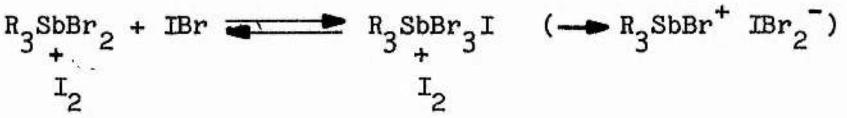
$$R_3SbIBr + \tfrac{1}{2}IBr \longrightarrow \tfrac{1}{2} R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+I_3^-$$

1.5:1 ⟶ 2:1 ratio

$$\tfrac{1}{2} R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+I_3^- + \tfrac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2$$

Although a sharp break was not seen in the conductometric titration graph at the 3:1 ratio it is suggested, in view of the presence of IBr_2^- ion at this ratio and the increase in conductivity between the 2:1 and 3:1 ratios, that the following reaction occurs

2:1 ⟶ 3:1 ratio



$$\underset{\displaystyle + I_2}{R_3SbBr_2} + IBr \rightleftharpoons \underset{\displaystyle + I_2}{R_3SbBr_3I} \quad (\longrightarrow R_3SbBr^+\ IBr_2^-)$$

(ii) $(2\text{-}CH_3C_6H_4)_3Sb$-IBr system

The result of the conductometric titration of tri(2-methylphenyl)-stibine with iodine bromide in acetonitrile is illustrated in Fig. 27 curve A. It differs from the previous two graphs in that at the 1:1 break the conductivity of the solution is higher compared with the 3-, and 4- isomers. The graph displayed three breaks - at the 1:1, 1.5:1 and 2:1 mole ratios.

The colour of the solution was pale yellow between the 0:1 and 1:1 ratio at which point it turned brown. The ultraviolet spectrum of the solution showed trace of I_3^- ion between 0:1 and 1:1 ratio but after the 1:1 ratio absorption due to I_3^- (λmax = 292, and 363 mμ) became strong. IBr_2^- ion (λmax = 257 mμ) was observed in the ultraviolet spectrum of the solution after the 2:1 mole ratio. The above observation supports the formation of R_3SbIBr, R_3SbBrI_3 ($\equiv R_3SbBr^+I_3^-$) and R_3SbBr_2 at mole ratio 1:1, 1.5:1 and 2:1 respectively.

The molar conductivity of the solution at these ratios is:

R_3SbIBr (Λ_m (1:1) = 13.9 S cm^2 mol^{-1} at C_m = 0.0075316 mol dm^{-3}

R_3SbBrI_3 (Λ_m (1.5:1) = 42.3 S cm^2 mol^{-1} at C_m = 0.005976 mol dm^{-3} and

R_3SbBr_2 (Λ_m (2:1) = 10.9 S cm^2 mol^{-1} at C_m = 0.005976 mol dm^{-3}.

The reactions occurring in this system appear to be similar to those in the other $(CH_3C_6H_4)_3Sb$-IBr systems, i.e.

0:1 ⟶ 1:1 ratio

$$R_3Sb + IBr \longrightarrow R_3SbIBr$$

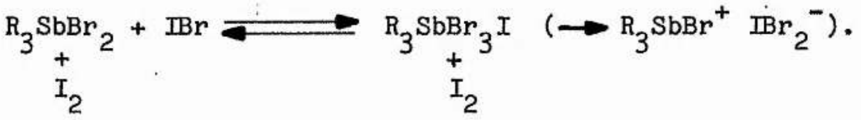
1:1 ⟶ 1.5:1 ratio

$$R_3SbIBr + \tfrac{1}{2}IBr \longrightarrow \tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ \ I_3^-$$

1.5:1 ⟶ 2:1 ratio

$$\tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ \ I_3^- + \tfrac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2$$

and 2:1 ⟶ 3:1 ratio



$$\underset{\underset{I_2}{+}}{R_3SbBr_2} + IBr \rightleftharpoons \underset{\underset{I_2}{+}}{R_3SbBr_3I} \ (\rightarrow R_3SbBr^+ \ IBr_2^-).$$

2. REACTION OF THE TRI(DIMETHYLPHENYL)STIBINE WITH HALOGENS AND INTERHALOGEN

(a) Reaction with bromine

The result of the conductometric titration of tri(dimethylphenyl)stibine with bromine in acetonitrile is illustrated in Fig. 28 curve A.

There was no significant rise in conductivity when bromine was added to the stibine solution until the 1:1 mole ratio was reached, but thereafter the conductivity increased steadily up to the 2:1 ratio after which it levelled off thus, giving a broad break at the 2:1 ratio (this kind of behaviour has not been observed in any other triarylstibine-bromine system; in these there is no significant conductivity rise during the titration). The solution turned yellow after the 1:1 mole ratio and the ultraviolet spectrum of the yellow solution showed absorption due to Br_3^- ion (λmax = 269mμ).

The molar conductivity at 1:1 and 2:1 mole ratio was (Λ_m 1:1 = 1.6 S cm^2 mol^{-1} at C_m = 0.008506 mol dm^{-3} and Λ_m 2:1 = 42.6 S cm^2 dm^{-3} respectively) suggesting that the 1:1 adduct (R_3SbBr_2) is a weak

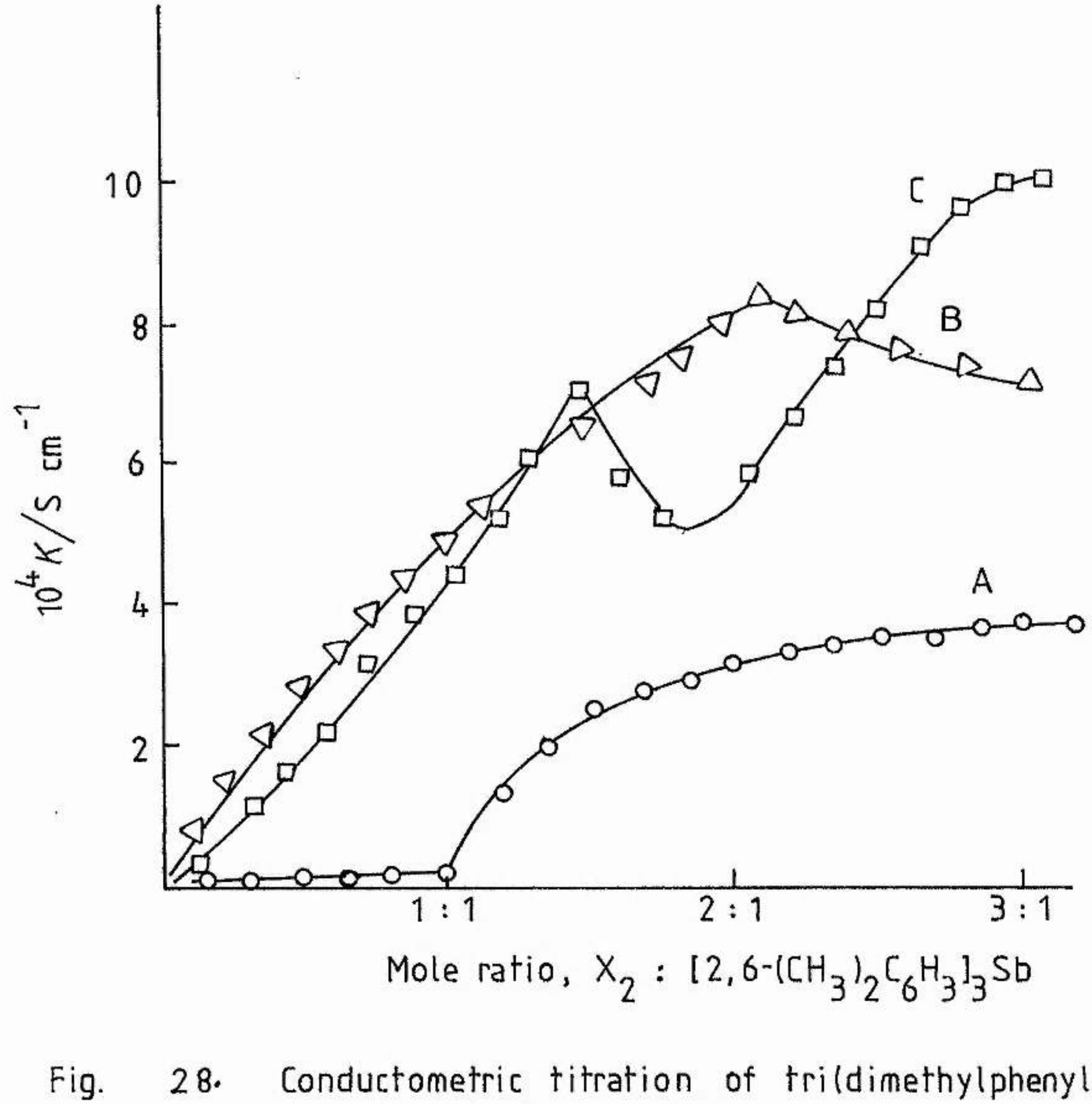


Fig. 28. Conductometric titration of tri(dimethylphenyl)-stibine with bromine, iodine and iodine bromide

(A) $[(CH_3)_2C_6H_3]_3Sb - Br_2$

(B) $[(CH_3)_2C_6H_3]_3Sb - I_2$

(C) $[(CH_3)_2C_6H_3]_3Sb - IBr$

electrolyte and the 2:1 adduct (R_3SbBr_4) is a medium electrolyte. In fact no compound of the latter composition (R_3SbBr_4) has been obtained from the 2:1 molar mixture of bromine and tri(2,6-dimethylphenyl)stibine. This may explain the absence of a distinct break at 2:1 ratio in the titration graph. It is suggested that the product of the reaction is dissociating in acetonitrile solution. From the above observations the reactions appear to be:

0:1 ⟶ 1:1 ratio

$$R_3Sb + Br_2 \longrightarrow R_3SbBr_2$$

1:1 ⟶ 2:1 ratio

$$R_3SbBr_2 + Br_2 \longrightarrow R_3SbBr_4 \; (\rightleftharpoons R_3SbBr^+Br_3^-).$$

(b) Reaction with iodine

The result of the conductometric titration of tri(dimethylphenyl)stibine with iodine in acetonitrile is illustrated in Fig. 28 curve B.

This titration graph is similar to the conductometric titration graph of the tri(2-methylphenyl)stibine-iodine titration but different from other triarylstibine- iodine systems. When iodine was added to the tri(dimethylphenyl)stibine solution, the conductivity increased sharply until the 2:1 mole ratio was reached. Further addition of iodine resulted in a decrease in conductivity , thus giving a sharp 2:1 break in the titration graph; this suggests the formation of R_3SbI_4 at this point. The solution turned brown from the start of the titration and the ultraviolet spectrum showed absorption due to I_3^- ion (λmax = 292, 362 mμ) from the beginning of the reaction.

The molar conductivity at the 2:1 ratio (Λ_m = 116.2 S cm^2 mol^{-1}, at C_m = 0.006973 mol dm^{-3}) is in keeping with the presence of the triiodide which is a strong electrolyte.

Thus, the reaction may be represented by the following equation 0:1 ⟶ 2:1 ratio

$$R_3Sb + 2I_2 \longrightarrow R_3SbI_4 \ (\rightarrow R_3SbI^+ \ I_3^-).$$

The resemblance between this system and the tri(2-methylphenyl)-stibine-iodine system strongly suggest that the presence of the ortho CH_3 group affects the stability of R_3SbI_2 in these systems.

(c) Reaction with iodine bromide

The result of the conductometric titration of tri(dimethylphenyl)stibine with iodine bromide in acetonitrile is illustrated in Fig. 28 curve C.

This reaction is different from the previously studied triarylstibine-iodine brimide systems in the sense that the conductivity rose sharply when iodine bromide was added to the tri(dimethylphenyl)stibine solution giving the first break at the 1.5:1 ratio. [In other triarylstibine-iodine bromide systems the initial conductivity is either negligible or gentle and a break is obtained at the 1:1 ratio eg. tri(2-methylphenyl)stibine- iodine bromide]. The conductivity then dropped to the 2:1 mole ratio then it rose again to give a final sharp break at the 3:1 ratio. The solution became yellow after the first addition of IBr getting darker on further IBr addition. The I_3^- ion (λmax = 292, 364 mμ) was shown by its ultraviolet spectrum to be present in the solution between the ratios 0:1 to 2:1 but beyond the 2:1 ratio the ultraviolet spectrum showed that IBr_2^- (λmax = 257 mμ) was present.

The absence of a break at the 1:1 ratio indicated that R_3SbIBr is not forming in the solution (it was a not obtained as a solid adduct from the acetonitrile solution either).

The reactions occurring in this system are thought to be:

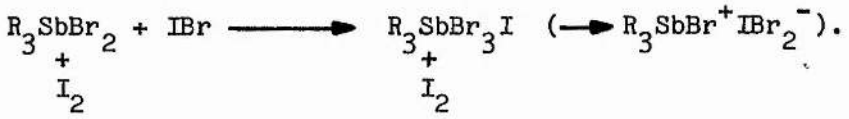
0:1 ——► 1.5:1 ratio

$$R_3Sb + \frac{3}{2}IBr \longrightarrow \frac{1}{2}R_3SbBr_2 + \frac{1}{2}R_3SbBr^+I_3^-$$

1.5:1 ——► 2:1 ratio

$$\frac{1}{2} R_3SbBr_2 + \frac{1}{2}R_3SbBr^+I_3^- + \frac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2$$

2:1 ——► 3:1 ratio



$$\underset{\underset{I_2}{+}}{R_3SbBr_2} + IBr \longrightarrow \underset{\underset{I_2}{+}}{R_3SbBr_3I} \quad (\longrightarrow R_3SbBr^+IBr_2^-).$$

{$[(CH_3)_2C_6H_3]_3SbBr_3I$ is the only solid adduct of stoichiometry R_3SbBr_3I obtained in such systems. It was prepared from a 1:1 mole ratio of R_3SbBr_2 and IBr in acetonitrile. (see Experimental section)}.

3. REACTIONS OF THE TRIS(TRIFLUOROMETHYLPHENYL)STIBINES WITH HALOGENS AND INTERHALOGEN

(a) Reactions with bromine

The results of the conductometric titrations of tris(2-trifluoromethylphenyl)stibine and tris(4-trifluoromethylphenyl)stibine with bromine in acetonitrile are illustrated in Fig. 29 (curves A and B respectively).

The titration graphs in these two systems are similar to that of the triphenylstibine-bromine system. The conductivity remained constant at a very low value until the 1:1 mole ratio was reached, and then increased only very slowly when further bromine was added. The solution remained colourless up to the 1:1 ratio at which point it turned light yellow thus confirming the occurrence of a 1:1 reaction. There was no absorption shown in the ultraviolet spectrum of the solution before the 1:1 ratio but after this ratio a trace of Br_3^- was

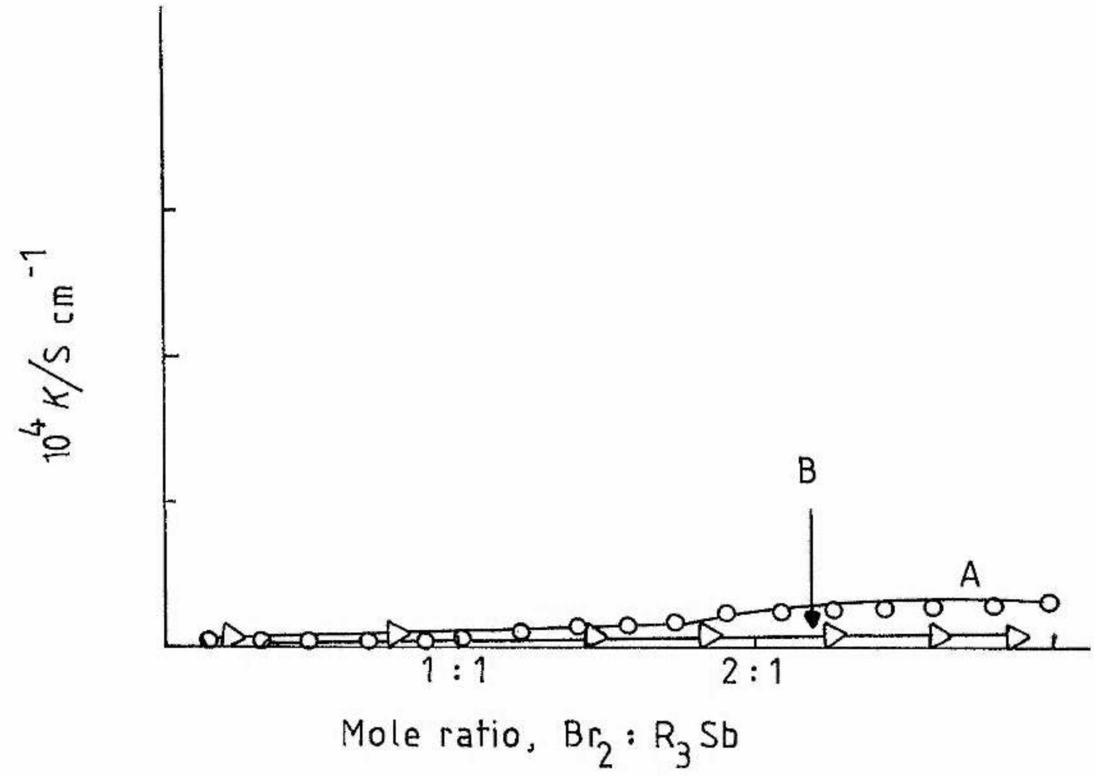


Fig. 29. Conductometric titration of tris(trifluoromethylphenyl)stibine with bromine

(A) $(2\text{-}CF_3C_6H_4)_3Sb\text{-}Br_2$

(B) $(4\text{-}CF_3C_6H_4)_3Sb\text{-}Br_2$

detected in the spectrum. This can be assumed to arise from the presence of free bromine in the solution. The above observations favour the formation of molecular 1:1 adducts, R_3SbBr_2, only in these systems in acetonitrile.

$$R_3Sb + Br_2 \longrightarrow R_3SbBr_2$$

(b) Reactions with iodine

The results of the conductometric titrations of tris(2-trifluoromethylphenyl)stibine and tris(4-trifluoromethylphenyl)stibine with iodine in acetonitrile are illustrated graphically in Fig. 30 (curves A and B respectively).

The graphs of these two titrations differ slightly from each other and from the triphenylstibine-iodine system.

$(2\text{-}CF_3C_6H_4)_3Sb\text{-}I_2$. The conductivity increased very slightly during the course of this titration and there was no break in the graph to suggest adduct formation at any ratio. The solution acquired a brown colour from the start of the titration, and the ultraviolet spectrum of the solution showed weak absorption due to I_3^- ion (λmax = 292, 363 mμ) after the first addition of I_2 to the solution. This and the low conductivity (Λ_m (1:1) = 2.4 S cm^2 mol^{-1} at C_m = 0.005925 mol dm^{-3} and Λ_m (2:1) = 4.4 S cm^2 mol^{-1} at C_m = 0.005218 mol dm^{-3}) can be attributed to the added iodine itself. These results are therefore consistent with there being no reaction occurring between iodine and tris(2-trifluoromethylphenyl)stibine. Additional evidence, recorded later, is the fact that neither a solid crystalline diiodide nor a tetraiodide adduct could be isolated from an acetonitrile or nitrobenzene solution containing the reagents in a 1:1 or 2:1 molar ratio.

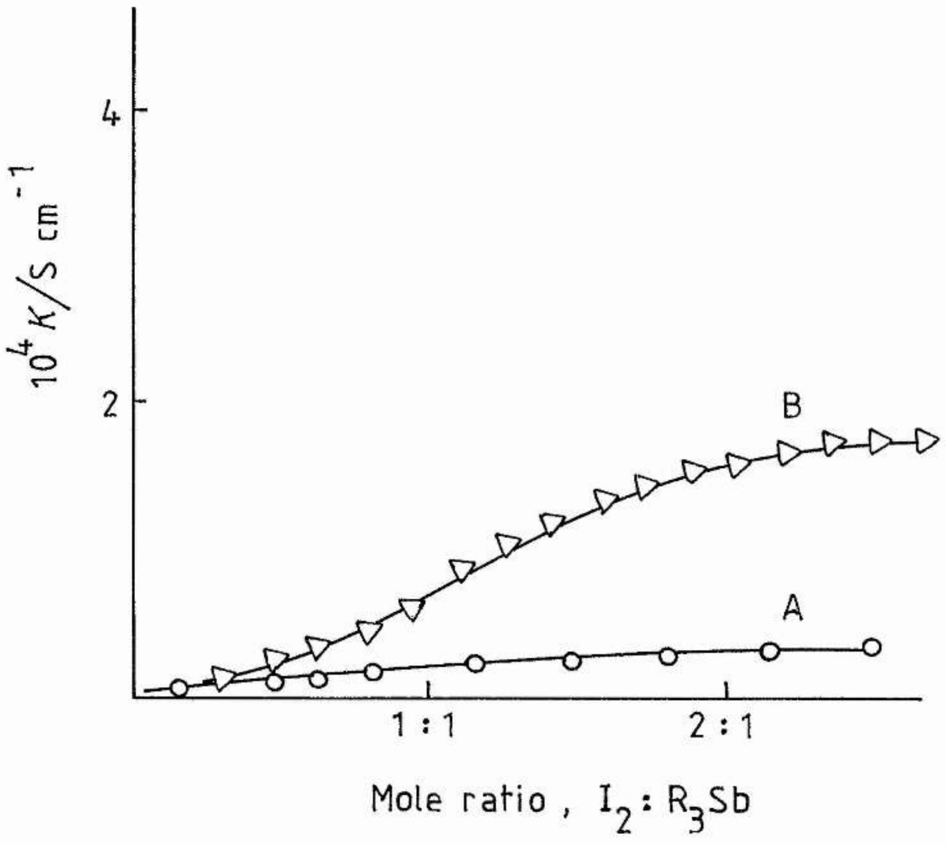


Fig. 30. Conductometric titration of tris(trifluoromethylphenyl)stibine with iodine

(A) $(2\text{-}CF_3C_6H_4)_3Sb - I_2$

(B) $(4\text{-}CF_3C_6H_4)_3Sb - I_2$

$\underline{(4\text{-}CF_3C_6H_4)_3Sb\text{-}I_2}$. In the tris(4-trifluoromethylphenyl)stibine-iodine system the conductivity rose gently up to the 2:1 mole ratio when iodine was added to the stibine solution and then levelled off near the 2:1 ratio. Thus there were no sharp breaks at any ratio although the graph may be interpreted as exhibiting very indistinct breaks at the 1:1 and 2:1 ratios. The solution acquired a brown colour from the beginning of the titration and the ultraviolet spectrum of the solution showed absorption due to I_3^- ion at λmax = 292, 362 mμ from the start of the reaction. The molar conductivity values at these ratios were (Λ_m (1:1) = 11.1 S cm^2 mol^{-1} at C_m = 0.005828 mol dm^{-3} and Λ_m (2:1) = 36.1 S cm^2 mol^{-1} at C_m = 0.004898 mol dm^{-3}). The rise in conductivity during titration indicates the occurrence of a reaction(s) but the lack of any distinct break suggests incomplete reaction(s) or alternatively that the reaction products are dissociating in acetonitrile solution (1:1 and 2:1 adducts, R_3SbI_2 and R_3SbI_4 were obtained as solid from the acetonitrile solution). The reactions may be represented by the following equations.

0:1 ⟶ 1:1 mole ratio

$$R_3Sb + I_2 \rightleftharpoons R_3SbI_2 (\rightarrow \tfrac{1}{2}R_3Sb + \tfrac{1}{2}R_3SbI^+ I_3^-)$$

1:1 ⟶ 2:1 ratio

$$R_3SbI_2 + I_2 \rightleftharpoons R_3SbI_4 \ (\rightarrow R_3SbI^+ I_3^-).$$

(c) Reactions with iodine bromide

The results of the conductometric titrations of tris(2-trifluoromethylphenyl)stibine and tris(4-trifluoromethylphenyl)stibine with iodine bromide in acetonitrile are illustrated graphically in Fig. 31 (curves A and B

Fig. 31. Conductometric titration of tris(trifluoromethylphenyl)stibine with iodine bromide

(A) $(2\text{-}CF_3C_6H_4)_3Sb\text{-}IBr$

(B) $(4\text{-}CF_3C_6H_4)_3Sb\text{-}IBr$

respectively).

<u>$(2\text{-}CF_3C_6H_4)_3Sb\text{-}IBr$</u> The reaction of tris(2-trifluoromethylphenyl)stibine is different from previously studied triarylstibine iodine bromide systems. The conductivity rose gradually and without inflection up to the 2:1 mole ratio at which point a break in the graph occurred and the conductivity of the solution increased more rapidly. The solution acquired a yellow-brown colour from the start of the reaction. Thus the titration graph displayed only one distinct break, at the 2:1 ratio, and unlike any other triarylstibine titration with iodine bromide, did not display a hump like feature with maximum at ratio 1.5:1. It would appear that the reaction leads straight away to the dibromide $(2\text{-}CF_3C_6H_4)_3SbBr_2$ without intermediate formation of the iodine bromide $(2\text{-}CF_3C_6H_4)_3SbIBr$:

$$(2\text{-}CF_3C_6H_4)_3Sb + 2IBr \longrightarrow (2\text{-}CF_3C_6H_4)_3SbBr_2 + I_2$$

This is supported by the relatively low molar conductivity at the 2:1 ratio

$$\Lambda_m\,(2{:}1) = 8.8\ S\ cm^2\ mol^{-1} \quad C_m = 0.003396\ mol\ dm^{-3}$$

$$\Lambda_m\,(3{:}1) = 48.4\ S\ cm^2\ mol^{-1} \quad C_m = 0.0030374\ mol\ dm^{-3}$$

and by the isolation of $(2\text{-}CF_3C_6H_4)_3SbBr_2$ as a solid from an acetonitrile solution containing IBr and $(CF_3C_6H_4)_3Sb$ in the 2:1 ratio. The increase in conductivity after the 2:1 ratio, coupled with the presence of IBr_2^- ion, suggests the reaction

$$(2\text{-}CF_3C_6H_4)_3SbBr_2 + IBr \rightleftharpoons (2\text{-}CF_3C_6H_4)_3SbBr^+ + IBr_2^-$$

but the lack of a sharp break at the 3:1 ratio indicates that this reaction is not complete at the stoichiometric point; also the observed presence of IBr_2^- ion slightly before the 2:1 end point would suggest that the second reaction begins slightly before the 2:1

ratio.

It is worth noting that the reaction of the ortho compound $(2\text{-}CF_3C_6H_4)_3Sb$ with iodine or iodine bromide does not give evidence of any 1:1 adducts involving iodine. i.e. $(2\text{-}CF_3C_6H_4)_3SbI_2$ and $(2\text{-}CF_3C_6H_4)_3SbIBr$ are not formed. This is presumably due either to a steric effect of the relatively large ortho or to the strong electron withdrawing effect of the ortho CF_3 group. In the latter connection it has been observed[161] that $(CF_3)_3Sb$ does not form the diiodide $(CF_3)_3SbI_2$.

<u>$(4\text{-}CF_3C_6H_4)_3Sb\text{-}IBr$</u> this system is different from the $(2\text{-}CF_3C_6H_4)_3Sb\text{-}IBr$ system but resembles the $(2\text{-}CH_3C_6H_4)_3Sb\text{-}IBr$ system (see page 94). The conductivity rose gently up to the 1.5:1 mole ratio when IBr was added to the stibine solution but then it decreased slowly to the 2:1 ratio and only a slight increase was observed beyond this ratio. The graph therefore has two breaks at 1.5:1 (maximum in the graph) and 2:1 mole ratios. The solution became light brown in colour from the start of the titration and its ultraviolet spectrum showed I_3^- ion (λmax = 292, 363 mμ) between the 1:1 and 2:1 ratios. A trace of this ion (I_3^-) was observed in the u.v. spectrum of the solution before the 1:1 ratio and of the IBr_2^- ion after the 2:1 ratio. The molar conductivity values at 1.5:1and 2:1 ratios were;

$$\Lambda_m\ (1.5:1) = 12.6\ \mathrm{S\ cm^2\ mol^{-1}}\quad C_m = 0.0049106\ \mathrm{mol\ dm^{-3}}$$

$$\text{and}\quad \Lambda_m\ (2:1) = 3.5\ \mathrm{S\ cm^2\ mol^{-1}}\quad C_m = 0.0045114\ \mathrm{mol\ dm^{-3}}.$$

The low value observed at the 2:1 ratio is suggestive of a dihalide adduct. The reactions occurring in this system are believed to be

0:1 ——➤ 1.5:1 ratio

$$R_3Sb + \tfrac{3}{2}IBr \longrightarrow \tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+I_3^-$$

1.5:1 ——➤ 2:1 ratio

$$\frac{1}{2}R_3SbBr_2 + \frac{1}{2}R_3SbBr^+I_3^- + \frac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2$$

2:1 → 3:1 ratio

$$\begin{array}{c}R_3SbBr_2\\+\\I_2\end{array} + IBr \rightleftharpoons \begin{array}{c}R_3SbBr^+IBr_2^-\\+\\I_2\end{array}$$

SUMMARY OF RESULTS

(1) R_3Sb-Br_2

(a) The reactions of tri(methylphenyl)stibine and tris(trifluoromethylphenyl)stibine with bromine are identical and similar to the triphenylstibine-bromine system. There is no sign of the formation of a 2:1 adduct but a 1:1 molecular adduct is indicated each time. The reaction is:

$$R_3Sb + Br_2 \longrightarrow R_3SbBr_2$$

(b) A 1:1 and 2:1 adduct is indicated in the conductometric titration of tri(2,6-dimethylphenyl)stibine with bromine.

(2) R_3Sb-I_2

(a) The reaction goes straight up to the 2:1 mole ratio (without any 1:1 break) in the systems $(2\text{-}CH_3C_6H_4)_3Sb-I_2$ and $[(CH_3)_2C_6H_3]_3Sb-I_2$. The reaction occurring is:

$$R_3Sb + 2I_2 \longrightarrow R_3SbI_4 \quad (\longrightarrow R_3SbI^+ \; I_3^-).$$

But with the tri(3-, and 4-methylphenyl)stibine the reaction is similar to the triphenylstibine-iodine system and gives 1:1 and 2:1 ratio breaks. The reactions occurring are:

$$R_3Sb + I_2 \longrightarrow R_3SbI_2 \quad (\rightleftharpoons \tfrac{1}{2}R_3Sb + \tfrac{1}{2}R_3SbI^+ + \tfrac{1}{2}I_3^-)$$
$$R_3SbI_2 + I_2 \longrightarrow R_3SbI_4 \quad (\longrightarrow R_3SbI^+ + I_3^-).$$

(b) When the CF_3 group is present in the ortho position on the phenyl ring then there is no reaction between the triarylstibine and iodine but when this group is present on the para position then the reaction does take place between the reactants.

(3). R_3Sb-IBr systems

(a) The reactions of (3-, and $4\text{-}CH_3C_6H_4)_3Sb$ with IBr are similar to that of the Ph_3Sb-IBr system; a hump-shaped curve with three breaks (1:1, 1.5:1 and 2:1) is observed suggesting the formation of R_3SbIBr, R_3SbBrI_3 ($\equiv R_3SbBr^+ I_3^-$) and R_3SbBr_2 respectively. The reaction may be represented as:

0:1 → 1:1

$$R_3Sb + IBr \longrightarrow R_3SbIBr$$

1:1 → 1.5:1

$$R_3SbIBr + \tfrac{1}{2}IBr \longrightarrow \tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ I_3^-$$

$$R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ I_3^- + \tfrac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2.$$

(b) In the conductometric titration of $[(CH_3)_2C_6H_3]_3Sb$ with IBr there is no 1:1 break but breaks occur at the 1.5:1, 2:1 and 3:1 ratios. The reactions occurring are believed to be

$$R_3Sb + \tfrac{3}{2}IBr \longrightarrow \tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ I_3^-$$

$$\tfrac{1}{2}R_3SbBr_2 + \tfrac{1}{2}R_3SbBr^+ I_3^- + \tfrac{1}{2}IBr \longrightarrow R_3SbBr_2 + I_2$$

$$\underset{\substack{+\\ I_2}}{R_3SbBr_2} + IBr \longrightarrow \underset{\substack{+\\ I_2}}{R_3SbIBr_3} \quad (\equiv R_3SbBr^+ IBr_2^-)$$

(c) The reaction of $(2\text{-}CF_3C_6H_4)_3Sb$ with IBr is different from the other R_3Sb-IBr reactions; there is no hump-like feature at the 1.5:1 mole ratio but only one break at the 2:1 mole ratio is indicated. Thus this system gives no evidence for the 1:1 adduct (R_3SbIBr). The reaction therefore is

$$R_3Sb + 2IBr \longrightarrow R_3SbBr_2 + I_2$$

The reaction of $(4\text{-}CF_3C_6H_4)_3Sb$ with IBr is similar to that of the $(2\text{-}CF_3C_6H_4)_3Sb$-IBr system.

B. PREPARATION OF ADDUCTS

Triarylstibine dihalides (1:1) adducts

The dichlorides R_3SbCl_2, were readily prepared by the direct reaction of chlorine and the appropriate stibine in a suitable solvent; all of the triarylstibine dibromides, diiodides, and iodides bromides whose existence was shown by the conductometric titrations of R_3Sb with Br_2, I_2 and IBr in acetonitrile were obtained as crystalline solids from acetonitrile containing the triarylstibine and the halogen in a 1:1 molar ratio. A few compounds [$(2\text{-}CH_3C_6H_4)_3SbI_2$, $(2\text{-}CH_3C_6H_4)_3SbIBr$, $[(CH_3)_2C_6H_3]_3SbI_2$ and $(4\text{-}CF_3C_6H_4)_3SbI_2$] whose existence was not predicted by conductometric titration were also obtained as unstable crystalline solids. Their preparations were carried out by the methods described above. Detailed descriptions of the preparations are given in the Experimental Part and the results are summarised in the following sections.

(a) Dichlorides

All of the R_3SbCl_2 compounds mentioned in Table 39, were obtained as crystalline solids by passing dry chlorine gas, diluted in a stream of dry nitrogen, through a cooled solution of triarylstibine in chloroform. The compounds were obtained as solids by freeze drying the solution or by adding ether to the solution. Their properties are given in Table 39.

Table 39. Properties of R_3SbCl_2

Compound	Colour	M.p / ^{o}C
$(2\text{-}CH_3C_6H_4)_3SbCl_2$	White	224-226
$(3\text{-}CH_3C_6H_4)_3SbCl_2$	White	137-138
$(4\text{-}CH_3C_6H_4)_3SbCl_2$	White	154-155
$[(CH_3)_2C_6H_3]_3SbCl_2$	White	250-252
$(2\text{-}CF_3C_6H_4)_3SbCl_2$	White	215-216
$(4\text{-}CF_3C_6H_4)_3SbCl_2$	White	118-119

(b) Dibromides

The existence of triarylstibine dibromides was shown by breaks at the 1:1 mole ratio in all the conductometric titrations graphs of the reactions carried out between R_3Sb and bromine. The adducts have been obtained as crystalline solids by freeze drying an acetonitrile solution containing a 1:1 molar ratio of bromine and triarylstibine. Their properties are shown in the Table 40.

Table 40. Properties of R_3SbBr_2

Compound	Colour	M.p / ^{o}C
$(2\text{-}CH_3C_6H_4)_3SbBr_2$	White	230-232
$(3\text{-}CH_3C_6H_4)_3SbBr_2$	White	106-107
$(4\text{-}CH_3C_6H_4)_3SbBr_2$	White	206
$[(CH_3)_2C_6H_3]_3SbBr_2$	White	192-194
$(2\text{-}CF_3C_6H_4)_3SbBr_2$	White	190-192
$(4\text{-}CF_3C_6H_4)_3SbBr_2$	White	140-142

(c) Di-iodides

Not all of the triarylstibine systems studied gave evidence of the existence of di-iodides. A summary of the predictions of the conductometric titrations is given in the following Table.

Table 41. Systems $R_3Sb\text{-}I_2$: Observations and conclusions regarding 1:1 adduct formation

System	Cond. Titn. Graph 1:1 break	Adducts indicated
$(2\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	absent	
$(3\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	present	$(3\text{-}CH_3C_6H_4)_3SbI_2$
$(4\text{-}CH_3C_6H_4)_3Sb\text{-}I_2$	present	$(4\text{-}CH_3C_6H_4)_3SbI_2$
$[(CH_3)_2C_6H_3]_3Sb\text{-}I_2$	absent	
$(2\text{-}CF_3C_6H_4)_3Sb\text{-}I_2$	absent	
$(4\text{-}CF_3C_6H_4)_3Sb\text{-}I_2$	absent	

All the R_3SbI_2 compounds which are indicated in the above table were obtained by freeze drying an acetonitrile solution of triarylstibine and iodine in a 1:1 molar ratio. Three more adducts [$(2\text{-}CH_3C_6H_4)_3SbI_2$, $[(CH_3)_2C_6H_3]_3SbI_2$ and $(4\text{-}CF_3C_6H_4)_3SbI_2$] were also obtained by the same method in spite of the fact that conductometric titrations did not give evidence for their existence in solution. The properties of the R_3SbI_2 adducts are given in the following Table 42.

Table 42. Properties of R_3SbI_2

Compound	Colour	M.p / °C
$(2\text{-}CH_3C_6H_4)_3SbI_2$	pale yellow	127–129
$(3\text{-}CH_3C_6H_4)_3SbI_2$	pale yellow	138–140
$(4\text{-}CH_3C_6H_4)_3SbI_2$	light brown	189
$[(CH_3)_2C_6H_3]_3SbI_2$	brown	133–136
$(4\text{-}CF_3C_6H_4)_3SbI_2$	brown	119–120

An attempt to prepare $(2\text{-}CF_3C_6H_4)_3SbI_2$ as a solid adduct was not successful; iodine was lost readily during the normal isolation procedure.

(d) Iodide bromides

Only two adducts of type R_3SbIBr were indicated by the conductometric titrations of R_3Sb with IBr (Table 43).

Table 43. Systems R_3Sb-IBr : Observations and conclusions regarding 1:1 adduct formation in acetonitrile

System	Con. Titn. Graph 1:1 break	Adduct indicated
$(2\text{-}CH_3C_6H_4)_3Sb$-IBr	absent	
$(3\text{-}CH_3C_6H_4)_3Sb$-IBr	present	$(3\text{-}CH_3C_6H_4)_3SbIBr$
$(4\text{-}CH_3C_6H_4)_3Sb$-IBr	present	$(4\text{-}CH_3C_6H_4)_3SbIBr$
$[(CH_3)_2C_6H_3]_3Sb$-IBr	absent	
$(2\text{-}CF_3C_6H_4)_3Sb$-IBr	absent	
$(4\text{-}CF_3C_6H_4)_3Sb$-IBr	absent	

The two adducts indicated were isolated as unstable (by loosing I_2 or IBr) crystalline solids by freeze drying an acetonitrile solution containing the stoichiometric quantities of the reagents (R_3Sb and IBr). Attempts to obtain the other R_3SbIBr adducts (i.e. those which were not indicated by conductometric titration (see Table 43) were successful only in the case of $(2\text{-}CH_3C_6H_4)_3SbIBr.CH_3CN$ which could only be obtained solvated. (it is also unstable and loses halogen). In all the other cases R_3SbBr_2 was obtained as the reaction product.

Their properties are given in Table 44.

Table 44. Properties of R_3SbIBr adducts

Compound	Colour	M.p / °C
$(2\text{-}CH_3C_6H_4)_3SbIBr.CH_3CN$	light yellow	163-165
$(3\text{-}CH_3C_6H_4)_3SbIBr$	yellow	120-122
$(4\text{-}CH_3C_6H_4)_3SbIBr$	yellow	206-208

Tetrahalides

Previous attempts to make triphenylstibine tetrahalides have been unsuccessful[126] in spite of their existence in acetonitrile solution being shown by conductometric titration of the appropriate R_3Sb-X_2 system. For the purpose of carring out a conductivity study of a series of tetrahalides R_3SbX_4, further attempts have been made to isolate such compounds from acetonitrile. The results are summarised in the following section and their preparative methods are given in detail in the Experimental Part.

(c) Tetra-iodides

The compounds of type R_3SbI_4, whose existence was shown by the conductometric titration of R_3Sb with iodine are given in the following Table 45.

Table 45. Systems R_3Sb-I_2 : Observations and conclusions regarding 2:1 adduct formation

System	Cond. Titn. Graph 2:1 break	Adduct indicated
$(C_6H_5)_3Sb-I_2$	present	$(C_6H_4)_3SbI_4$
$(2-CH_3C_6H_4)_3Sb-I_2$	present	$(2-CH_3C_6H_4)_3SbI_4$
$(3-CH_3C_6H_4)_3Sb-I_2$	present	$(3-CH_3C_6H_4)_3SbI_4$
$(4-CH_3C_6H_4)_3Sb-I_2$	present	$(4-CH_3C_6H_4)_3SbI_4$
$[(CH_3)_2C_6H_3]_3Sb-I_2$	present	$[(CH_3)_2C_6H_3]_3SbI_4$
$(2-CF_3C_6H_4)_3Sb-I_2$	absent	
$(4-CF_3C_6H_4)_3Sb-I_2$	absent	

Attempts were made to obtain all of the R_3SbI_4 compounds from I_2

and R_3Sb (2:1 mole ratio) in acetonitrile. Success was obtained only in few cases including $(4\text{-}CF_3C_6H_4)_3SbI_4$ (which was not indicated by the related system). The properties of the adducts prepared are given in the following Table.

Table 46. Properties of R_3SbI_4 adducts

Compound	Colour	M.p / °C
$(C_6H_5)_3SbI_4$	dark violet	sticky, wax-like
$(3\text{-}CH_3C_6H_4)_3SbI_4$	dark violet	130-132
$[(CH_3)_2C_6H_3]_3SbI_4$	dark brown	144-145
$(4\text{-}CF_3C_6H_4)_3SbI_4$	dark violet	118-120

All these tetrahalides decompose at their melting points and they are unstable, losing iodine during pumping to dryness. Attempts to make $(2\text{-}CH_3C_6H_4)_3SbI_4$ always gave a compound of composition R_3SbI_2 which is dark brown in colour and melts at 108-110 °C. Dialkylstibine trichloride[107] and trifluoride have been prepared previously, but no dialkyl- or diarylstibine triiodide has been reported to date.

(f) Iodide tribromides

Evidence was obtained for the formation in acetonitrile solution of compounds of formula R_3SbIBr_3 in each $R_3Sb\text{-}IBr$ system studied. Also, in the conductometric titration of the system $[(CH_3)_2C_6H_3]_3SbBr_2\text{-}IBr$ (graph 34 page 126) a very sharp break at the 1:1 mole ratio provided strong evidence for the adduct $[(CH_3)_2C_6H_3]_3SbIBr_3$. The solid adduct was in fact obtained by freeze drying the 1:1 mixture of $[(CH_3)_2C_6H_3]_3SbBr_2$ and IBr in acetonitrile. It is an unstable brown solid which melts at 181-182 °C. No other adduct of this composition (R_3SbIBr_3) has been obtained as a solid.

Other tetrahalides Attempts were made in some cases to make the remaining types of tetrahalide of triarylstibine. These were $[(CH_3)_2C_6H_3)_3SbBr_4$, $[(CH_3)_2C_6H_3]_3SbBr_2I_2$, $(4\text{-}CH_3C_6H_4)_3SbBr_2I_2$ and Ph_3SbBrI_3, but the attempts were not successful.

C. CONDUCTIVITY STUDY

(a) Conductivity study of the triarylstibine dihalides (R_3SbX_2)

(i) R_3SbCl_2 and R_3SbBr_2

It has been shown[126] that the molar conductivity of the compounds Ph_3EX_2 (E = P, As, Sb and X = Cl or Br) decreases with increasing the size of E. Also, it has been shown (Part I of this Thesis) that the monosubstitution of electron releasing groups on the phenyl ring in the R_3AsX_2 adducts, increases the molar conductivity of such adducts compared with that of the triphenyl compounds and the presence of electron withdrawing groups has the reverce effect. Also, it has been found that the position of the substituent (2-, 3-, or 4-) on the phenyl ring affects the conductivity behaviour of the compounds. A further observation is that the molar conductivity of R_3AsBr_2 is always much higher than the R_3AsCl_2 in acetonitrile.

Considering the above observations noted in the case of the arsenic compounds R_3AsX_2, a conductivity study has been made of analogous antimony halides, R_3SbX_2. Conductivity measurements in acetonitrile were made on solutions of concentrations in the range 0.0005-0.01 M. The value, of molar conductivity (Λ_m), all of which were very low, were plotted against the square root of molar concentration, $\sqrt{C_m}$, for each compound. The molar conductivity value, at 0.01 M were obtained by interpolation, and these are given in Table 47.

Table 47. Λ_m values of R_3SbCl_2 and R_3SbBr_2 at C_m = 0.01 mol dm^{-3} in acetonitrile

Compound	Λ_m*	Compound	Λ_m
$(2\text{-}CH_3C_6H_4)_3SbCl_2$	0.08	$(2\text{-}CH_3C_6H_4)_3SbBr_2$	0.10
$(3\text{-}CH_3C_6H_4)_3SbCl_2$	0.15	$(3\text{-}CH_3C_6H_4)_3SbBr_2$	0.14
$(4\text{-}CH_3C_6H_4)_3SbCl_2$	0.17	$(4\text{-}CH_3C_6H_4)_3SbBr_2$	0.23
$[(CH_3)_2C_6H_3]_3SbCl_2$	0.96	$[(CH_3)_2C_6H_3]_3SbBr_2$	0.77
$(2\text{-}CF_3C_6H_4)_3SbCl_2$	0.03	$(2\text{-}CF_3C_6H_4)_3SbBr_2$	0.20
$(4\text{-}CF_3C_6H_4)_3SbCl_2$	0.16	$(4\text{-}CF_3C_6H_4)_3SbBr_2$	0.12

* value is /S cm^2 mol^{-1}.

From the above table it is clear that the molar conductivity values for R_3SbCl_2 and R_3SbBr_2 are very low (<1 S cm^2 mol^{-1}) compared with the R_3AsCl_2 and R_3AsBr_2 analogues(see page 74 and 75). This suggests that these compounds are behaving as non-electrolytes in acetonitrile at this concentration; their behaviour thus parallels that of triphenylstibine dichloride and dibromide. Thus these compounds must be regarded as molecular in the solid and in acetonitrile solution.

The substitution of electron releasing/withdrawing groups on the phenyl ring in such compounds obviously does not have a sufficient effect to influence the molar conductivity. Also, the observed differences in molar conductivity, when these groups are substituted on different positions (2-, 3-, or 4-) on the phenyl ring are negligible. It is particularly significant that an "ortho effect" is not observed in the antimony compounds (compare the arsenic compounds -Part I of the Thesis) A further significant point is that values of molar conductivity for R_3SbCl_2 and R_3SbBr_2 are all <1 thus lending support for the suggestion that these compounds are non-electrolytes.

(ii) R_3SbI_2 and R_3SbIBr

During the conductivity measurement of these adducts in acetonitrile it was observed that the conductivity increased with time and the solution darkened in colour (yellow to brown). To standardise the molar conductivity measurements for these compounds a fresh solution was made for each concentration. On adding the solute to the solvent a stop clock was started and the conductivity measured (at 25°C) as soon as solution was complete. Values of conductivity were measured at 5 minutes intervals and a graph of conductivity versus time plotted. From this, by extrapolation, the value of conductivity at zero time was obtained and this value was used to calculate the molar conductivity of the compound. The values of molar conductivity are given in the following table 48.

Table 48. Molar conductivity values of R_3SbI_2 and R_3SbIBr in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m^*	Compound	Λ_m
$(2\text{-}CH_3C_6H_4)_3SbI_2$	47.0	$(2\text{-}CH_3C_6H_4)_3SbIBr$	10.4
$(3\text{-}CH_3C_6H_4)_3SbI_2$	3.0	$(3\text{-}CH_3C_6H_4)_3SbIBr$	1.0
$(4\text{-}CH_3C_6H_4)_3SbI_2$	8.0	$(4\text{-}CH_3C_6H_4)_3SbIBr$	4.0
$[(CH_3)_2C_6H_3]_3SbI_2$	70.0		
$(4\text{-}CF_3C_6H_4)_3SbI_2$	15.5		

* /S cm^2 mol^{-1}

These molar conductivity values are much higher than those obtained for the dibromides and dichlorides and are probably not "real" values for the compounds since solutions of these compounds in acetonitrile are complicated by the occurrence of a disproportionation reaction

$$R_3SbI_2 \rightleftharpoons \tfrac{1}{2}R_3Sb + \tfrac{1}{2}R_3SbI^+I_3^-$$

$$R_3SbIBr \rightleftharpoons \tfrac{1}{3}R_3Sb + \tfrac{1}{3}R_3SbBr_2 + \tfrac{1}{3}R_3SbBr^+I_3^-$$

The ultraviolet spectrum of acetonitrile solutions of both R_3SbI_2 and R_3SbIBr indicates the presence of I_3^- ion.

The extent [α] to which the above disproportionation takes place for each compound was determined spectroscopically after equilibrium had been reached (no further rise in conductivity). The concentration of tri-iodide present in solution was determined using the observed absorbance and the literature value of extinction coefficient for I_3^- [57,700; 31,000][117]. Values of α are given in table 49

Table 49. Degree of disproportionation for the 1:1 adducts of type R_3SbI_2 and R_3SbIBr in acetonitrile

Adducts	α = %	C_m = mol dm^{-3}	
$(2\text{-}CH_3C_6H_4)_3SbI_2$	80.0	0.000215	15671
$(3\text{-}CH_3C_6H_4)_3SbI_2$	32.5	0.000103	5039
$(4\text{-}CH_3C_6H_4)_3SbI_2$	16.0	0.000521	3437
$[(CH_3)_2C_6H_3]_3SbI_2$	88.9	0.000142	13775
$(4\text{-}CF_3C_6H_4)_3SbI_2$	65.0	0.000709	10154
$(2\text{-}CH_3C_6H_4)_3SbIBr$	48.2	0.0009078	4984
$(3\text{-}CH_3C_6H_4)_3SbIBr$	13.9	0.000375	1438
$(4\text{-}CH_3C_6H_4)_3SbIBr$	58.9	0.00008306	6085

It is seen that disproportionation as depicted above is extensive and the molar conductivity values obtained do not reflect simple ionisation of R_3SbI_2 and R_3SbIBr (which would be expected to be weak electrolytes) alone but arise mainly from the presence of the strong electrolytes R_3SbI_4 ($\equiv R_3SbI^+I_3^-$) and R_3SbBrI_3 ($\equiv R_3SbBr^+I_3^-$) respectively.

The fact that the Λ_m values at zero time for the compounds R_3SbI_2 and R_3SbIBr are higher than might have been expected and that there is a spread values 1-70 S cm^2 mol^{-1} suggests that the disproportionation may even be occurring at or close to zero time in certain cases. For example $(2-CH_3C_6H_4)_3SbI_2$ and $[(CH_3)_2C_6H_3]_3SbI_2$ have high Λ_m values 47.0 and 70.0 S cm^2 mol^{-1} respectively and these values parallel a high ultimate degree of disproportionation 80% and 88.9% respectively, in each case. It was noted that there was little variation in Λ_m with time for solutions of these two compounds. Thus the attempts to standardise Λ_m as described would not appear to be leading to "true values" of molar conductivity (representing simple ionisation $R_3SbX_2 \rightleftharpoons R_3SbX^+X^-$) for these compounds.

(b) Conductivity study of 2:1 adducts (R_3SbX_4)

The molar conductivity of the 2:1 adducts R_3SbX_4, whose preparation was mentioned in the previous section page 112 have been measured in acetonitrile at different concentrations. The molar conductivity values at C_m = 0.01 mol dm^{-3} were obtained by interpolation of the Λ_m versus $\sqrt{C_m}$. These values are given in the following table,

Table 50. Molar conductivity values of R_3SbX_4 in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m/S cm^2 mol^{-1}
$[(CH_3)_2C_6H_3]_3SbBr_3I$	106.0
$(C_6H_5)_3SbI_4$	82.0
$(3\text{-}CH_3C_6H_4)_3SbI_4$	78.0
$[(CH_3)_2C_6H_3]_3SbI_4$	141.0
$(4\text{-}CF_3C_6H_4)_3SbI_4$	29.0

These values suggest that with the exception of $(4\text{-}CF_3C_6H_4)_3SbI_4$ the compounds behave as strong electrolytes in acetonitrile. The low molar conductivity of $(4\text{-}CF_3C_6H_4)_3SbI_4$, coupled with the absence of a break at the 2:1 ratio in the conductometric titration of I_2 versus $(4\text{-}CF_3C_6H_4)_3Sb$, suggests that the solid when dissolved does not behave as $(4\text{-}CF_3C_6H_4)_3SbI^+\ I_3^-$. It may be that the solid is a simple molecular addition compound, $R_3Sb.2I_2$, which on solution sets up an equilibrium leading to partial production of ions:

$$R_3Sb.2I_2 \rightleftharpoons R_3SbI^+ + I_3^-$$

Alternatively, the compound may be behaving like its arsine analogue $(4\text{-}CF_3C_6H_4)_3AsI_4$ [$\equiv (4\text{-}CF_3C_6H_4)AsI^+\ I_3^-$] (see page 86) and becoming involved in molecular dissociation as well as partial ionisation

$$(4\text{-}CF_3C_6H_4)_3Sb + 2I_2 \rightleftharpoons (4\text{-}CF_3C_6H_4)_3SbI_4 \rightleftharpoons (4\text{-}CF_3C_6H_4)_3SbI^+ + I_3^-$$

$$[\equiv (4\text{-}CF_3C_6H_4)_3SbI^+I_3^-]$$

The ions (I_3^- or IBr_2^-) has been confirmed from the ultraviolet spectrum of acetonitrile solutions of the compounds which therefore ionise as follows:

$$R_3SbBr_3I \equiv R_3SbBr^+\ IBr_2^-$$

$$R_3SbI_4 \equiv R_3SbI^+I_3^-.$$

These modes of ionisation are similar to those observed in triarylarsenic tetrahalides where it is also found that the halogen with lower atomic weight resides in the cation.

(c) Conductivity of $(2\text{-}CH_3C_6H_4)_2SbI_3$ The molar conductivity of this compound was measured in acetonitrile and the value of Λ_m at 0.01 M was obtained by extrapolation as before. Λ_m (0.01M) was 97.0 S cm^2 mol^{-1} indicating that the adduct is a strong electrolyte. The only previous report of the conductivity of a compound of this stoichiometry refers to Ph_2SbCl_3[107] which is a weak electrolyte in acetonitrile. The ultraviolet spectrum of acetonitrile solutions of $(2\text{-}CH_3C_6H_4)_2SbI_3$ showed absorption due to I_3^- ion and the mode of ionisation

$$R_2SbI_3 \longrightarrow \tfrac{1}{2}R_2SbI + \tfrac{1}{2}R_2SbI_2^+ + \tfrac{1}{2}I_3^-$$

is suggested. This is analogous to the disproportionation proposed for the di-iodides, R_3SbI_2.

CONCLUSIONS

(1) The low conductivities of R_3SbCl_2 and R_3SbBr_2 (Λ_m<1), indicate that these compounds are non-electrolytes or very weak electrolytes in acetonitrile.

(2) The high molar conductivity values found for R_3SbI_2 and R_3SbIBr arise from disproportionation of these compounds in acetonitrile.

(3) All of the tetrahalides (R_3SbX_4) are strong electrolytes.

D. REACTIONS OF THE TRIARYLANTIMONY DIHALIDES WITH INTERHALOGENS AND ANTIMONY PENTACHLORIDE

The evidence provided by the conductometric titrations of various triarylantimony compounds, R_3Sb, with Br_2, I_2 and IBr suggests that ionic halogenotriarylantimony compounds ($R_3SbX^+ X^-$ and $R_3SbX^+ X^-_3$) are less readily formed than their phosphorus and arsenic counterparts.

To investigate further the possible formation of the halotriarylantimony cation, the reactions of triarylantimony dichlorides with the halide ion acceptors, iodine chloride and antimony pentachloride have been studied by conductometric titrations in acetonitrile. Antimony pentachloride was chosen because of its strong chloride ion acceptor properties[162]. Also, since the presence of the bromotriarylantimony cation, R_3SbBr^+, was indicated by the conductometric titrations of the R_3Sb-IBr systems, the direct reactions of some R_3SbBr_2 {R = $[2,6-(CH_3)_2C_6H_3]_3SbBr_2$ and $(2-CF_3C_6H_4)_3SbBr_2$} with IBr were studied with a view to confirming the existence of the bromotriarylantimony cation, R_3SbBr^+. The results are given in the following pages.

(a) Reactions with iodine chloride

The results of the conductometric titrations of R_3SbCl_2 (R = Ph, 2-, 3-, $4-CH_3C_6H_4$, $(CH_3)_2C_6H_3$, 2-, or $4-CF_3C_6H_4$] with ICl in acetonitrile are all very similar and they have been exemplified by curve A (ICl : Ph_3SbCl_2) and curve B (ICl : $(2-CH_3C_6H_4)SbCl_2$) in Fig. 32.

The main feature of all of these reactions is the small rise in conductivity and in this respect these systems are unlike the triarylarsine dichloride-iodine chloride systems. The slight increase

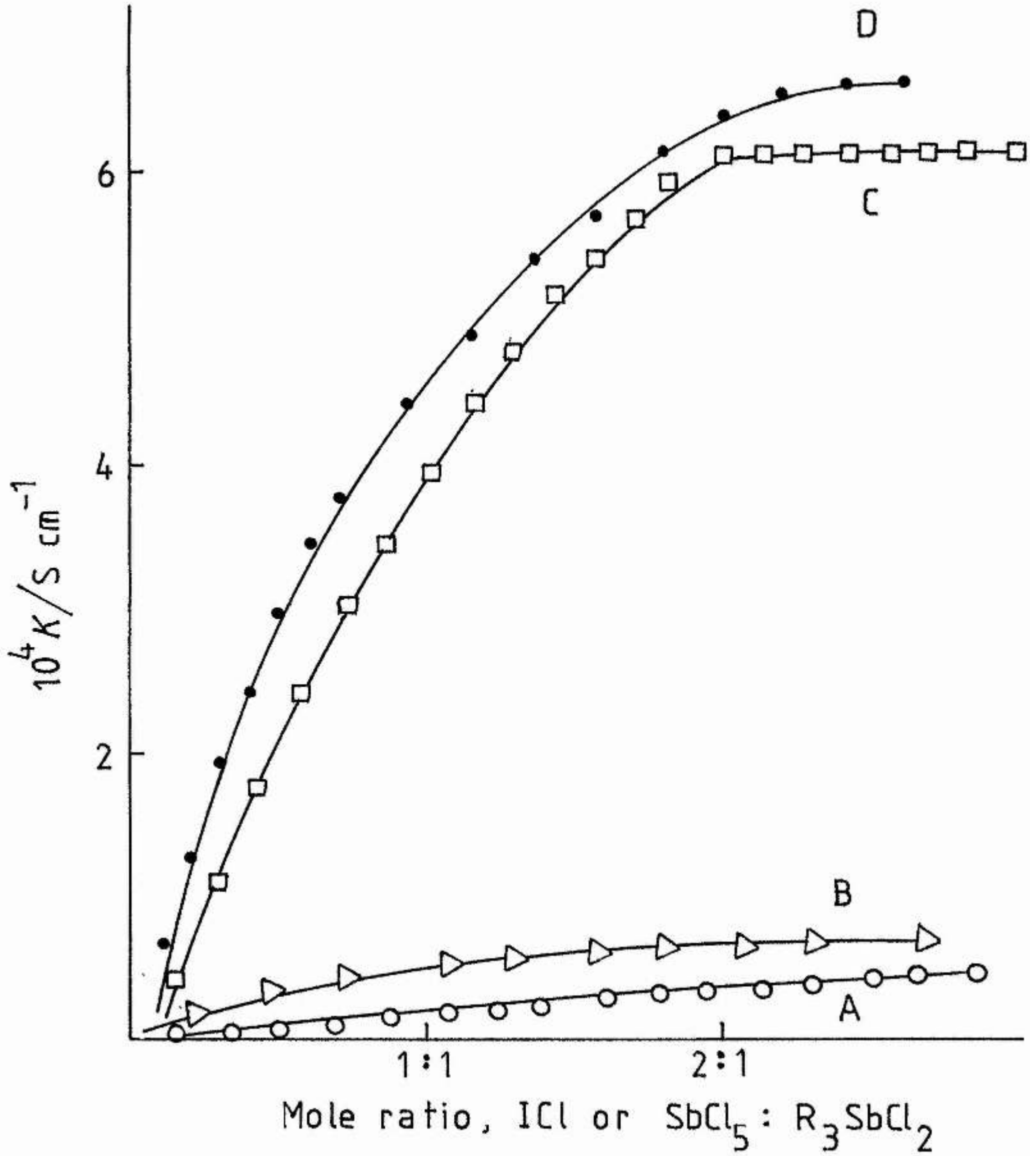


Fig. 32. Conductometric titration of triarylantimony dichloride with ICl or $SbCl_5$

(A) Ph_3SbCl_2 – ICl (B) $(2\text{-}CH_3C_6H_4)_3SbCl_2$ – ICl

(C) $(3\text{-}CH_3C_6H_4)_3SbCl_2$ – $SbCl_5$

(D) $(4\ CF_3C_6H_4)_3SbCl_2$ – $SbCl_5$

in conductivity observed when ICl was added to the R_3SbCl_2 is attributed to the added ICl itself. In each case the solution changed from colourless to light yellow from the start of the reaction (acetonitrile solutions of ICl are light yellow in colour) and the ICl_2^- ion was shown not to be present by the ultraviolet spectra of the solutions. It is concluded that there is no reaction between ICl and R_3SbCl_2 in acetonitrile.

(b) Reactions of antimony pentachloride with triarylantimony dichlorides

The results of the conductometric titrations of antimony pentachloride with triarylantimony dichlorides in acetonitrile give two types of graphs which are shown in Fig. 32. curve C and D.

Curve C $(3\text{-}CH_3C_6H_4)_3SbCl_2\text{-}SbCl_5$ system exemplifies the graphs obtained in the conductometric titrations of R_3SbCl_2 with $SbCl_5$ [R = Ph, 3-, $4\text{-}CH_3C_6H_4$ or $(CH_3)_2C_6H_3$]. All these titrations are similar with each other. The conductivity rose sharply up to the 2:1 mole ratio when antimony pentachloride was added to the triarylantimony dichloride. Further addition of $SbCl_5$ to the solution did not increase the conductivity, thus giving a distinct break in the graph at the 2:1 ratio.

Curve D [$(4\text{-}CF_3C_6H_4)_3SbCl_2\text{-}SbCl_5$system] is an example of the type of graph obtained in the conductometric titrations of R_3SbCl_2 (where R = $2\text{-}CH_3C_6H_4$, 2-, or $4\text{-}CF_3C_6H_4$) with $SbCl_5$ in acetonitrile. All the reactions are similar to each other but different from those mentioned above (curve C case), in the sense that there was no sharp break at the 2:1 mole ratio. Thus if there is a 2:1 reaction occurring in these cases it does not go to completion at the stoichiometric point.

None of the graphs show a break at the 1:1 mole ratio thus suggesting that no adduct of composition $R_3SbCl_2.SbCl_5$ ($\equiv R_3SbCl^+ SbCl_6^-$) is forming in the solution. However the breaks at 2:1 ratio suggest the formation of an adduct $R_3SbCl_2.2SbCl_5$.

The molar conductivity values at the 2:1 ratio are given in the following Table.

Table 51. Molar conductivity at the 2:1 breaks in the systems $R_3SbCl_2 - SbCl_5$

System	$\Lambda_m(2:1)/S\ cm^2\ mol^{-1}$	C_m = mol dm^{-3}
$Ph_3SbCl_2-SbCl_5$	192.1	0.003019
$(2-CH_3C_6H_4)_3SbCl_2-SbCl_5$	189.4	0.003378
$(3-CH_3C_6H_4)_3SbCl_2-SbCl_5$	196.4	0.003121
$(4-CH_3C_6H_4)_3SbCl_2-SbCl_5$	189.8	0.0041101
$[(CH_3)_2C_6H_3]_3SbCl_2-SbCl_5$	205.4	0.0030668
$(2-CF_3C_6H_4)_3SbCl_2-SbCl_5$	172.6	0.002925
$(4-CF_3C_6H_4)_3SbCl_2-SbCl_5$	192.8	0.003008

To confirm the absence of a 1:1 break in the systems $R_3SbCl_2-SbCl_5$ and to make sure that the presence of any break at this ratio is not being obscured by the high conductivity of the titrant, [$SbCl_5$ ($2SbCl_5 \equiv SbCl_4^+ SbCl_6^-$) is a strong conductor in acetonitrile and its conductivity increases with dilution] the above reactions were studied conductometrically the other way round using the non-conducting (or weakly conducting) R_3SbCl_2 solution as titrant (burette solution) and adding this to the $SbCl_5$ solution in the reaction vessel. The results are described in the following section (c).

(c) Reactions of triarylantimony dichlorides with antimony pentachloride

The conductometric titrations of the triarylantimony dichlorides with antimony pentachloride in acetonitrile are all similar (the only exception is the $SbCl_5$-$[(CH_3)_2C_6H_3]_3SbCl_2$ system which will be discussed later on in the section); the titration graphs are exemplified by curves A and B in Fig. 33.

The conductivity rose sharply up to the 0.5:1 mole ratio when R_3SbCl_2 was added to the $SbCl_5$ solution. On further addition of R_3SbCl_2 to the solution the conductivity dropped sharply (probably due to the dilution effect of the poorly conducting R_3SbCl_2 solution). Thus a distinct break at the 0.5:1 mole ratio was indicated in each titration graph.

$SbCl_5$-$[(CH_3)_2C_6H_3]_3SbCl_2$ system

Because of the low solubility of $[(CH_3)_2C_6H_3]_3SbCl_2$ in acetonitrile this titration was performed by adding small weighed quantities of the $[(CH_3)_2C_6H_3]_3SbCl_2$ to the $SbCl_5$ solution. As in the other $SbCl_5$-R_3SbCl_2 titrations the conductivity increased sharply up to the 2:1 mole ratio then stayed steady on the further addition of tri(2,6-dimethylphenyl)stibine dichloride to the solution. Thus again a distinct break at the 0.5:1 ratio* was observed in the graph.

Again there was no break observed at the 1:1 mole ratio in any of the systems graph, confirming the absence of the formation of a 1:1

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* the 0.5:1 ratio in the titrations is equivalent to the 2:1 break in the previous titration [section (b)] in which the $SbCl_5$ solution was added to the R_3SbCl_2 solution

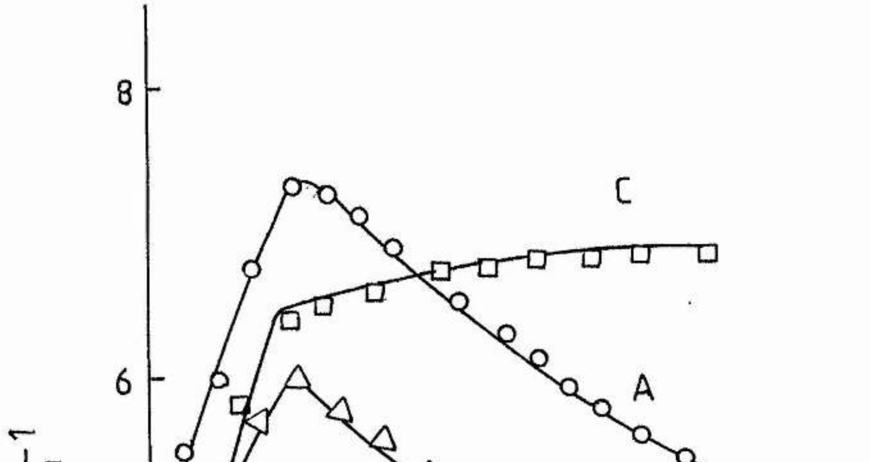


Fig. 33 Conductometric titration of $SbCl_5$ with triarylantimony dichloride

(A) $SbCl_5 - (2\text{-}CH_3C_6H_4)_3SbCl_2$ (B) $SbCl_5 - Ph_3SbCl_2$

(C) $SbCl_5 - [2,6\text{-}(CH_3)_2C_6H_3]_3SbCl_2$

adduct ($R_3SbCl_2.SbCl_5$) in solution: the 0.5:1 break represents the formation of adducts of stoichiometry $(SbCl_5)_2R_3SbCl_2$ and these titrations confirm the formation of these adducts by every system studied. Thus it is clear that in the previous titrations ($SbCl_5$ added to R_3SbCl_2) the 2:1 break was less sharp in some cases (graph D, Fig. 32) due to the highly conducting nature of the titrant solution.

The molar conductivity values at the 0.5:1 break are given in the following table

Table 52. Λ_m values at 0.5:1 ratio break in the system $SbCl_5$-R_3SbCl_2

System	Λ_m/S cm^2 mol^{-1}	C_m = mol dm^{-3}
$SbCl_5$-Ph_3SbCl_2	218.0	0.003366
$SbCl_5$-$(2\text{-}CH_3C_6H_4)_3SbCl_2$	211.9	0.002830
$SbCl_5$-$(3\text{-}CH_3C_6H_4)_3SbCl_2$	206.1	0.002847
$SbCl_5$-$(4\text{-}CH_3C_6H_4)_3SbCl_2$	198.7	0.003095
$SbCl_5$-$[(CH_3)_2C_6H_3]_3SbCl_2$	235.9	0.002754
$SbCl_5$-$(2\text{-}CF_3C_6H_4)_3SbCl_2$	203.5	0.002825
$SbCl_5$-$(4\text{-}CF_3C_6H_4)_3SbCl_2$	193.2	0.002147

Although 1:1 adducts $R_3SbCl_2.SbCl_5$ appear not to exist in acetonitrile solution, they have been prepared as solids from acetonitrile solutions containing stoichiometric quantities of the R_3SbCl_2 and $SbCl_5$.

The conductometric titrations and the conductivity values show that the adducts $R_3SbCl_2.(SbCl_5)_2$ form highly conducting solutions in acetonitrile and it is therefore clear that they are ionic adducts. Concerning the nature of the ions present, there would seem to be two possibilities,

$$R_3SbCl_2\ (SbCl_5)_2 \longrightarrow R_3Sb^{2+}(SbCl_6^{-})_2 \text{-----------}\ \mathrm{I}$$

$$\text{or}\quad R_3SbCl_2\ (SbCl_5)_2 \longrightarrow R_3SbCl^{+}Sb_2Cl_{11}^{-} \text{---------}\mathrm{II}$$

molar conductivity values for the adducts in acetonitrile, at concentration 0.01 mol dm^3, are in the range 100-140 S cm^2 mol $^{-1}$

$$[Ph_3SbCl_2(SbCl_5)_2 :\ \Lambda_m = 116\ S\ cm^2\ mol^{-1};$$

$$(2\text{-}CH_3C_6H_4)_3SbCl_2(SbCl_5)_2 :\ \Lambda_m = 168\ S\ cm^2\ mol^{-1}]$$

These values are more in keeping with strong 1:1 rather than 2:1 electrolyte behaviour and hence favour ionisation mode II. Also it is noted that Sowereby et al[162] from an infra-red spectral study of $Ph_3SbCl_2(SbCl_5)_2$ suggested that $Ph_3SbCl^{+}Sb_2Cl_{11}^{-}$ was more likely than $Ph_3Sb^{2+}(SbCl_6^{-})_2$.

There is in fact no previous report of any compound containing the Ph_3Sb^{2+} ion but it should be mentioned that the Raman spectrum of an aqueous trimethylstibine dinitrate $[Me_3Sb(NO_3)_2]$ has been interpreted in terms of the presence of either the solvated Me_3Sb^{2+} ion, $[Me_3Sb(OH_2)_2]^{2+}$, or the unipositive ion $[Me_3Sb(OH)OH_2)]^{+}$ [163].

(d) Reactions of triarylantimony dibromide with iodine bromide

The results of the conductometric titrations of tri(2,6-dimethylphenyl)antimony-dibromide and tris(2-trifluoromethylphenyl)antimony-dibromide with iodine bromide in acetonitrile are illustrated graphically in Fig. 34 (curves A and B respectively).

In the $[(CH_3)_2C_6H_3]_3SbBr_2$-IBr system the conductivity increased sharply up to the 1:1 mole ratio but thereafter it remained steady when further IBr was added to the solution. A definite 1:1 break in the titration graph was thus obtained. The solution became yellow in

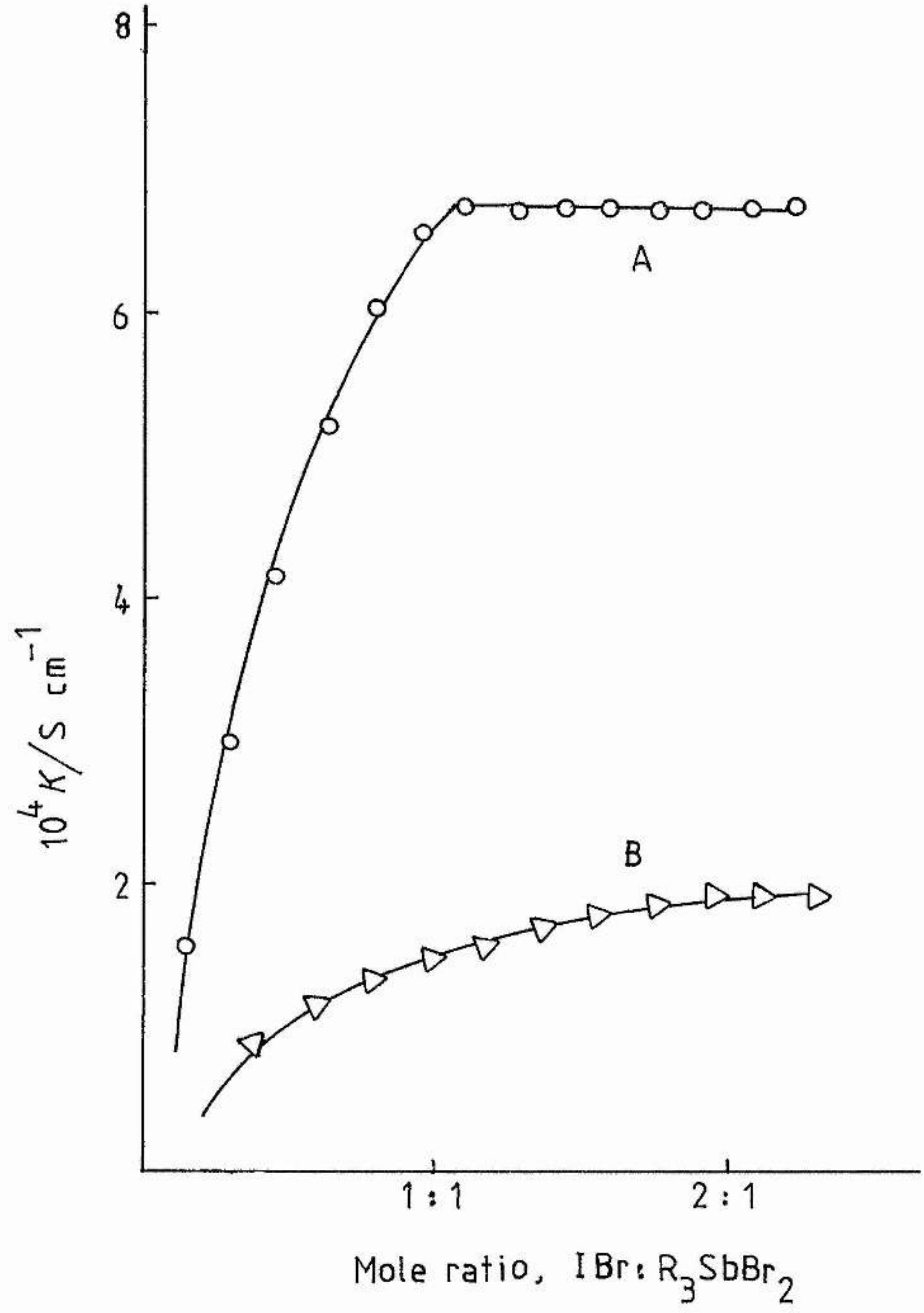


Fig. 34. Coductometric titration of triarylantimony dibromide with iodine bromide

(A) $[2,6-(CH_3)_2C_6H_3]_3SbBr_2-IBr$

(B) $(2-CF_3C_6H_4)_3SbBr_2-IBr$

colour from the start of the titration and the ultraviolet spectrum of the solution showed absorption due to the IBr_2^- ion (λmax = 257 mμ).

The molar conductivity value at the break ($\Lambda_m(1:1) = 106.2$ S cm^2 mol^{-1} at $C_m = 0.0063057$ mol dm^{-3}) suggests that the adduct is a strong electrolyte and the reaction may be represented as:

0:1 → 1:1 ratio

$$R_3SbBr_2 + IBr \longrightarrow R_3SbIBr_3 \quad (\longrightarrow R_3SbBr^+IBr_2^-)$$

The adduct R_3SbIBr_3 was obtained as a solid from acetonitrile solution.

The other R_3SbBr_2-IBr systems (R = 2-, 3-, 4-$CH_3C_6H_4$, 2-, and 4-$CF_3C_6H_4$) are similar with each other and they are exemplified by the reaction of $(2\text{-}CF_3C_6H_4)_3SbBr_2$-IBr. In the $(2\text{-}CF_3C_6H_4)_3SbBr_2$-IBr system (curve B Fig. 34) the conductivity rose as IBr was added to the $(2\text{-}CF_3C_6H_4)_3SbBr_2$ but the titration graph did not give a distinct break at any mole ratio. The reaction is obviously not complete at the 1:1 stoichiometric point. The solution was yellow from the start of the titration and its ultraviolet spectrum showed absorption due to the IBr_2^- ion. The Λ_m value at the 1:1 mole ratio was 42.2 S cm^2 mol^{-1} (C_m = 0.00003508 mol dm^{-3}). The reaction occurring may be represented as

$$R_3SbBr_2 + IBr \rightleftharpoons R_3SbBr^+ + IBr_2^-$$

The $[(CH_3)_2C_6H_3]_3SbIBr_3$ is the only solid adduct of such composition (R_3SbX_4) for the triarylstibine tetrahalides.

CONCLUSIONS

(1) Formation of cations of type R_3SbX^+ are not very common. R_3SbCl^+ can only be formed when halide acceptor is $SbCl_5$ and the complexes have composition $R_3SbCl_2.2SbCl_5$ ($\equiv R_3SbCl^+.Sb_2Cl_{11}^-$).

(2) Evidence for the R_3SbBr^+ cation is obtained from the conductometric titration of $[(CH_3)_2C_6H_3]_3SbBr_2$-IBr and from the formation of the solid adduct $[(CH_3)_2C_6H_3]_3SbBr_3I$ ($\equiv[(CH_3)_2C_6H_3]_3SbBr^+IBr_2^-$).

Adducts of composition, $R_3SbCl_2.SbCl_5$

The conductometric titrations of triarylstibine dichloride with antimony pentachloride do not give any indication of the formation of a 1:1 adduct, but the solvated adduct, $Ph_3SbCl_2.SbCl_5.CH_3CN$, was obtained as a crystalline solid from the mixture (1:1) of Ph_3SbCl_2 and $SbCl_5$ in acetonitrile. It is an off-white solid, extremely moisture sensitive, and melts at 40°C.

Adducts of composition, $R_3SbCl_2.2SbCl_5$

The existence of these 2:1 adducts was shown by the conductometric titrations of R_3SbCl_2 with $SbCl_5$ and vice versa. (see page 122 and 124).

The preparation of two adducts of this type was attempted. These were $Ph_3SbCl_2.2SbCl_5$ and $(2\text{-}CH_3C_6H_4)_3SbCl_2.2SbCl_5$ and they were obtained readily from the mixture of one moles of R_3SbCl_2 and two moles of $SbCl_5$ in acetonitrile. Their properties are given in the following Table.

Table 53. Properties of $R_3SbCl_2.2SbCl_5$

Compound	Colour	M.p / ^oC
$(C_6H_5)_3SbCl_2.2SbCl_5$	light yellow	~room temp.
$(2-CH_3C_6H_4)_3SbCl_2.2SbCl_5.2CH_3CN$	light yellow	84-86

Conductivity study of the 1:1 adduct $Ph_3SbCl_2.SbCl_5$

Sowerby et al[162] have suggested an ionic formulation $[Ph_3SbCl]^+[SbCl_6]^-$ for this compound on the basis of X-ray analysis. To gain information on the behaviour of this adduct in solution conductivity measurements were made on the acetonitrile solution of the compound at different concentrations. The molar conductivity Λ_m at $C_m = 0.01$ M was found to be 113.0 S cm^2 mol^{-1}. This high value suggest that the adduct is a strong electrolyte in acetonitrile. Its solution behaviour is therefore in keeping with its solid state structure.

Conductivity study of 2:1 adducts $R_3SbCl_2.2SbCl_5$
[R = Ph and $2-CH_3C_6H_4$]

The molar conductivity of the two compounds (R = Ph and $2-CH_3C_6H_4$) whose preparation was mentioned in Table 53 was measured in acetonitrile and values at $C_m = 0.01$ M were found to be
$Ph_3SbCl_2.SbCl_5$ ($\Lambda_m = 116.0$ S cm^2 mol^{-1}, $C_m = 0.01$ mol dm^{-3}
$(2-CH_3C_6H_4)_3SbCl_2.SbCl_5$ ($\Lambda_m = 168.0$ S cm^2 mol^{-1}, $C_m = 0.01$ mol dm^{-3}.

The Λ_m values suggest that the adducts are strong 1:1 electrolytes in acetonitrile and again this accords with Sowereby suggestion that compounds of this type are ionic in the solid state $[R_3SbCl^+.Sb_2Cl_{11}^-]$.

PART III

TETRAPHENYLSTIBONIUM HALIDES AND TRIHALIDES

A PREPARATION OF ADDUCTS

(a) Halides (Ph_4SbX)

Although a number of preparative methods have been described[163, 164, 165, 167, 168]; these stibonium halides have been conveniently prepared in good yield from the reaction of hydrogen halide with aqueous tetraphenylstibonium hydroxide (Ph_4SbOH), which was obtained by treating an aqueous solution of tetraphenylstibonium bromide with aqueous ammonia. A full description of the preparations is given in the Experimental Part.

All these stibonium halides are crystalline solids. Their properties are shown in the following table.

Table 54. Properties of the Ph_4SbX compounds

Compound	Colour	M.p /°C
$(C_6H_5)_4SbF$	White	153-155
$(C_6H_5)_4SbCl$	White	200-204
$(C_6H_5)_4SbBr$	White	202-208
$(C_6H_5)_4SbI$	Pale yellow	209-211

(b) Trihalides (Ph_4SbX_3) Tetraphenylstibonium trihalides whose existence was shown by the conductometric titrations of Ph_4SbX with halogen and interhalogens in acetonitrile are given in table 55.

Table 55.

System	Break in graph at mole ratio	Indicated adduct
$(C_6H_5)_4SbBr-Br_2$	1:1	$(C_6H_5)_4SbBr_3$
$(C_6H_5)_4SbBr-IBr$	1:1	$(C_6H_5)_4SbIBr_2$
$(C_6H_5)_4SbCl-ICl$	1:1	$(C_6H_5)_4SbICl_2$

For the purposes of carrying out conductivity studies on these trihalides to confirm their strong electrolyte nature $(C_6H_5)_4SbBr_3$, $(C_6H_5)_4SbICl_2$ and $(C_6H_5)_4SbIBr_2$ have been prepared by the reaction of one mole of stibonium halide with one mole of halogen or interhalogen in acetonitrile. The compounds were obtained as crystalline solids and their properties are:

$(C_6H_5)_4SbBr_3$	orange yellow	m.p. 112-114°C
$(C_6H_5)_4SbIBr_2$	orange yellow	m.p. 148-150°C
$(C_6H_5)_4SbICl_2$	pale yellow	m.p. 116-119°C

(B) Conductivity study of tetraphenylstibonium halides and -trihalides

Very little work has been reported on the structure of tetraphenylstibonium halides. $(C_6H_5)_4SbCl$[113] and $(C_6H_5)_4SbBr$[113] are thought to be ionic on the basis of their infra-red spectra. On the other hand X-ray diffraction has shown that the hydroxy derivative $(C_6H_5)_4SbOH$[138] is covalent and possesses a trigonal bipyramidal structure; the same molecular structure is suggested by Schidbaur et al[136] for $(CH_3)_4SbF$ and $(CH_3)_4SbOH$[137].

To investigate the nature of tetraphenylstibonium halides in solution, we have carried out a conductivity study of these compounds in acetonitrile. The results are reported in the following section.

(a) halides (Ph_3SbX) [X = F, Cl, Br or I]

The conductivity of the adducts in acetonitrile at 25°C was measured over a range of concentrations and the molar conductivity calculated. A plot of molar conductivity (Λ_m) against the square root of molar concentration ($\sqrt{C_m}$) was constructed for each compound (Fig. 35). For the purpose of comparison, values of Λ_m at C_m = 0.01 mol dm^{-3} were obtained from the graphs and these are given in the Table 56.

Table 56. Λ_m values at C_m = 0.01 mol dm^{-3} in acetonitrile

Compound	Λ_m/S cm^2 mol^{-1}
$(C_6H_5)_4SbF$	1.8
$(C_6H_5)_4SbCl$	15.0
$(C_6H_5)_4SbBr$	70.0
$(C_6H_5)_4SbI$	119.0

The molar conductivity of $(C_6H_5)_4SbF$ is very low indicating that the adduct is virtually a non-electrolyte in acetonitrile. This suggests that this compound is very likely to be covalent molecular in the solid state. The values of molar conductivity for $(C_6H_5)_4SbCl$ and $(C_6H_5)_4SbBr$ lie between those expected for a strong electrolyte and a weak-electrolyte in acetonitrile; thus they must be regarded as weak electrolytes:

$$(C_6H_5)_4SbX \rightleftharpoons (C_6H_5)_4Sb^+ + X^-$$

(X = Cl, Br)

It may therefore be deduced that the bromide and chloride like the flouride are covalent molecular in the solid and ionises only to a certain extent under the influence of the strongly ionising solvent.

The value for $(C_6H_5)_4SbI$ from the above table suggests that this

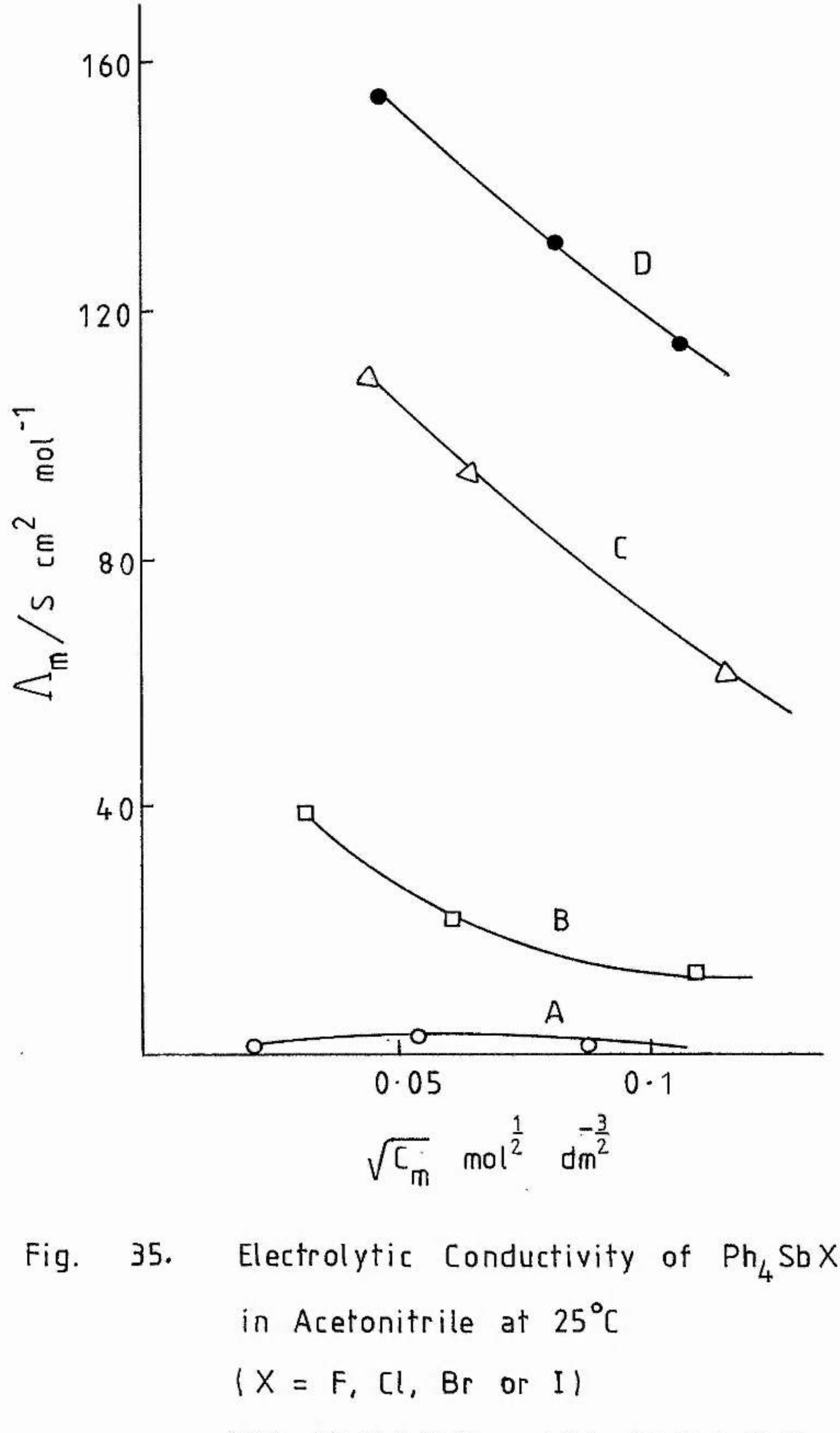


Fig. 35. Electrolytic Conductivity of Ph_4SbX in Acetonitrile at 25°C

(X = F, Cl, Br or I)

(A) $(C_6H_5)_4SbF$ (B) $(C_6H_5)_4SbCl$

(C) $(C_6H_5)_4SbBr$ (D) $(C_6H_5)_4SbI$

compound is a strong electrolyte in acetonitrile solution and the possibility of an ionic structure for this compound in the solid state is likely. The behaviour of this compound is thus analogous to $(C_6H_5)_4PI$[70]:

$$(C_6H_5)_4SbI \longrightarrow (C_6H_5)_4Sb^+ + I^-.$$

(b) trihalides (Ph_4SbX_3)

The molar conductivity values for tetraphenylstibonium trihalides in acetonitrile have been obtained by the same procedure as for tetraphenylstibonium halides (described previously). The values obtained are shown in the following table 57.

Table 57. Molar conductivity of $(C_6H_5)_4SbX_3$ in acetonitrile at $C_m = 0.01$ mol dm^{-3}

Compound	Λ_m/S cm^2 mol^{-1}
$(C_6H_5)_4SbBr_3$	131.0
$(C_6H_5)_4SbIBr_2$	110.0
$(C_6H_5)_4SbICl_2$	118.0

These high values are typical of strong electrolytes in acetonitrile.

$$(C_6H_5)_4SbBr_3 \longrightarrow (C_6H_5)_4Sb^+ + Br_3^-$$

$$(C_6H_5)_4SbIBr_2 \longrightarrow (C_6H_5)_4Sb^+ + IBr_2^-$$

$$(C_6H_5)_4SbICl_2 \longrightarrow (C_6H_5)_4Sb^+ + ICl_2^-$$

The trihalide ion has been confirmed from the ultraviolet spectrum of the solutions.

Conclusion

The molar conductivity of the tetraphenylstibonium halides follows the sequence $(C_6H_5)_4SbF$ < $(C_6H_5)_4SbCl$ < $(C_6H_5)_4SbBr$ < $(C_6H_5)_4SbI$. This follows a pattern observed in other systems such as R_3AsX_2. For example the molar conductivity of $(C_6H_5)_3AsF_2 < (C_6H_5)_3AsCl_2$ < $(C_6H_5)_3AsBr_2$. This trend is likely to be due to the bond strength variation Sb-F > Sb-Cl > Sb-Br > Sb-I and electronegativity effect.

(C) Conductometric titrations of the tetraphenylstibonium halide with Halogen, and Interhalogens

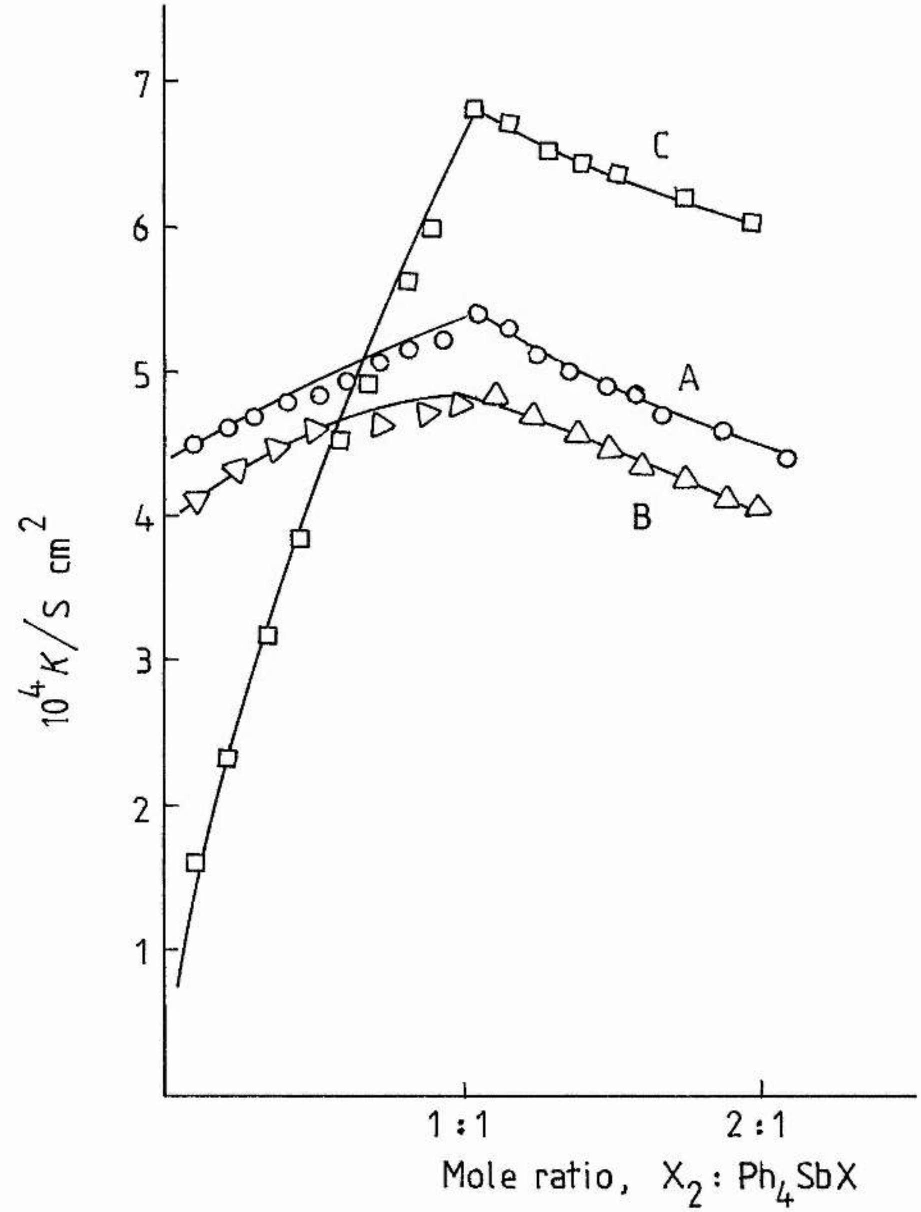
(a) Reaction of tetraphenylstibonium bromide with bromine

The result of the conductometric titration of Ph_4SbBr with Br_2 in acetonitrile is illustrated in Fig. 36 curve A.

The conductivity increased steadily up to the 1:1 mole ratio when bromine was added to the tetraphenylstibonium bromide. Further addition of bromine to the solution resulted in a decrease of the conductivity. Thus a distinct 1:1 mole ratio break was observed in the titration graph, indicating the formation of a 1:1 adduct (Ph_4SbBr_3) in solution. The colour of the solution went yellow from the start of the titration and its ultraviolet spectrum showed that tribromide ion (Br_3^- at λ max = 269 mμ) was present. The molar conductivity value at the 1:1 mole ratio was 125.9 S cm^2 mol^{-1} (C_m = 0.004293 mol dm^{-3}) indicating that the adduct is a strong electrolyte in acetonitrile. The reaction occurring is:

0:1 ⟶ 1:1 mole ratio

$$Ph_4SbBr + Br_2 \longrightarrow Ph_4SbBr_3 \quad (\equiv Ph_4Sb^+Br_3^-)$$



(X_2 = Br_2, IBr or ICl) (X = Br, or Cl)

Fig. 36. Conductometric titration of Ph_4SbX with bromine, iodine bromide and iodine chloride

(A) $Ph_4SbBr-Br_2$

(B) $Ph_4SbBr-IBr$

(C) $Ph_4SbCl-ICl$

(b) Reaction of tetraphenylstibonium bromide with iodine bromide

The result of the conductometric titration of Ph_4SbBr with IBr in acetonitrile is illustrated graphically in Fig. 36 curve B.

It is seen that the graph is very similar to that of the $Ph_4SbBr-Br_2$ system and displays a break at the 1:1 ratio. The originally colourless solution turned yellow after the first addition of IBr solution and the ultraviolet spectrum of the solution showed the presence of the IBr_2^- ion (λ max = 257 mμ). The molar conductivity value at the 1:1 mole ratio was 123.0 S cm^2 mol^{-1}, (C_m = 0.0039109 mol dm^{-3}) indicating that the adduct $Ph_4SbBr.IBr$ is a strong electrolyte. The reaction may be represented:

$$Ph_4SbBr + IBr \longrightarrow Ph_4SbIBr_2 \quad (\equiv Ph_4Sb^+ \ IBr_2^-)$$

(c) Reaction of tetraphenylstibonium chloride with iodine chloride

The result of the conductometric titration of Ph_4SbCl with ICl in acetonitrile is illustrated graphically in Fig. 36. Curve C.

Again a distinct 1:1 break was observed in the conductometric titration graph of this system showing that an adduct of stoichiometry $Ph_4SbCl.ICl$ is forming in solution. The solution acquired a light yellow colour from the beginning of the reaction and its ultraviolet spectrum showed absorption due to the ICl_2^- ion (λ max = 227 mμ). The molar conductivity [Λ_m (1:1) = 102.6 S cm^2 mol^{-1} at C_m = 0.005554 mol dm^{-3}] indicates that the adduct is a strong electrolyte in acetonitrile. The reaction occurring is

$0:1 \longrightarrow 1:1$ mole ratio

$$Ph_4SbCl + ICl \longrightarrow Ph_4SbCl_2I \quad (\equiv Ph_4Sb^+ \ ICl_2^-)$$

EXPERIMENTAL

EXPERIMENTAL

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III Preparations

General Remarks

Part I

Part II

Part III

I General Tehniques

(a) Handling of Materials

Because the compounds studied in this work were hydrolytically unstable, strict precautions were taken to ensure the absence of moisture at all times. This was made possible by the extensive use of a nitrogen-filled drybox kept dry by the passage of a stream of dry nitrogen through it. Commercial oxygen-free nitrogen, dried by passage through a column of molecular sieve (AE1-Birlec Ltd, absorber type AB 12.5) was used. The box also contained two trays of phosphorus pentoxide. Certain manipulations, chiefly removal of solvents, were carried out in a vacuum line, thus avoiding exposure of the sensitive halide to both atmospheric moisture and elevated temperature. Compounds so handled were stored in sample tubes with ground-glass joint stoppers and kept in a desiccator over silica gel.

(b) Vacuum System

The vacuum system used in this work was simple, made up of a pumping unit connected via protective sludge traps to a main line from which there were branches to various sub-sections designed for special operations (such as freeze-drying).

(c) Conductometric Titrations

conductometric titrations were carried out in acetonitrile which has been extensively employed as a solvent by Harris et al [151, 152] since it has a high dielectric constant (36.7 at 25 °). Acetonitrile is a good solvent for the type of compound under investigation and in it strong electrolyte exhibit high molar conductivity; Consequently it is easy to distinguish between non-electrolytes and weak electrolytes. The conductivity of purified acetonitrile was less than 10^{-7} **S** cm^{-1} at 25 °C. The resistance bridge used was the Philips(Type PR 9500). The apparatus used for the conductometric titrations was of special design allowing the titration to be carried out in a dry atmosphere[126].

(d) Conductivity Measurement

Conductivity measurements were made at 25 °C in a sealed cell. A standard pair of smooth platinum dipping electrodes were used. The cell constant was determined using standard potassium chloride solution and was checked from time to time. Solutions of known concentration were prepared in the dry box, by adding a weighed amount of the solid compound to the cell which contained a known weight of the solvent. When the solution was complete, the cell was placed in a thermostat bath at 25 °C and the conductivity was measured using a Philips PR 9500 resistance bridge. For higher concentrations, successive additions of known weights of compound were made to the solution in the cell; operations were carried out inside the dry-box. Molar conductivity values were then calculated and plotted against square-root of molar concentration.

(e) Ultra-Violet Spectra

Ultra-violet spectra were recorded on a Unicam SP 800 B UV/Visible recording spectrophotometer. Stoppered quartz cells of 0.5 cm or 0.01 cm path length were used, measurement being made at room temperature (ca. 20 °C).

(f) Infra-red Spectra

Infrared spectra were recorded on a Perkin-Elmer 1310 Infrared Spectrophotometer.

(g) Analyses

Microanalyses for carbon, hydrogen and nitrogen were performed in the chemistry department of St.Andrews University on a Perkin-Elmer Model 240 Elemental Analyser and a CARLO ERBA STRUMENTAZIONE MOD.1106. Halogen analysis was carried out Potentiometrically using an adoptation of the method described by Lingane[169]. A description of the method is as follows: Approximately 30 mg of sample was accurately weighed into a preweighed sample bottle and transferred into a Quickfit conical flask (100 ml) in the dry-box. The sample was then hydrolysed with 20 ml of 2 M sodium hydroxide solution. The resultant solution or suspension was left to stand for twenty minutes before boiling for a minimum of fifteen minutes in the case of the arsenic derivative and thirty minutes for the antimony compounds to ensure complete hydrolysis. It was then cooled and made just acidic with 6 M sulphuric acid before immediately bubbling sulphur dioxide gas through the solution, for two minutes to reduce any hypohalite ion present. Further boiling was necessary both to drive off excess sulphur dioxide and to 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 volumetric flask and made up to the mark. A 50 ml portion of this solution was pipetted into a 250 ml beaker and 2.5 g Analar barium nitrate added followed by 10 ml of Analar acetone and 3-5 dops of 6 M nitric acid, before titrating with

0.05 M silver nitrate. The solution was stirred throughout the titration using a magnetic stirrer. A silver wire was used as the indicator electrode and a saturated calomel electrode as reference electrode, with a salt bridge containing 3 M ammonium nitrate solution. The other half of the solution was treated in the same way and titrated to give duplicate analysis. 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 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 6 M 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 a point near the end-point. This was detected by a more rapid increase in the change in potential. When this was observed the burette additions were reduced to 0.02 ml. A graph of mV readings against ml of silver nitrate added was plotted, the point of inflection being taken as the end-point of the titration. Before each titration the silver wire indicator electrode was cleaned by immersing in 50% nitric acid for one minute, washing with distilled water, then immersing in concentrated ammonia for two minutes before a final thorough washing with distilled water.

(h) Column Chromatography

The compound was dissolved in benzene and applied to an alumina or silica gel column (36 inches in length 1 inch diameter) prepared with petroleum-ether (40-60 °C). It was eluted in turn with the following solvents: Petroleum-ether (40-60 °C) 5% benzene-95%petroleum-ether, 10% benzene-90%petroleum-ether, 20% benzene 80%petroleum-ether and benzene.

II Solvents and Purification of Materials

(a) Solvents

(i) Methyl cyanide

Pure anhydrous methyl cyanide suitable for conductivity studies was prepared by a modification of the method describe by Smith and Witten[170]. The commercial (BDH) material was allowed to stand for at least one week over potassium hydroxide pellets, with ocassional vigorous stirring to remove acid impurities. It was then filtered and distilled into a flask containing calcium chloride (14-20 mesh) and allowed to stand for one week to remove ammonia and water. It was filtered again and distilled on to phosphorus pentoxide. This procedure was repeated until the phosphorus pentoxide did not cake and turn yellow but formed a fine suspension in the liquid. Finally, before use it was refluxed and distilled using a nine inch column of glass helices (which had been oven dried), into another flask containing fresh phosphorus pentoxide. Then it was stored in a tightly stoppered round bottom flask kept in a large desiccator. The dry solvent was distilled on the vacuum line as required to remove any traces of phosphorus pentoxide. The conductivity of methyl cyanide purified by this method was always ca. 10^{-7}S cm^{-1} at 25°C. The boiling range was 81-82 °C.

(b) Chloroform[171 a]

The commercial grade solvent was washed with a large volume of water to remove ethanol, dried over anhydrous calcium chloride for at least 24 hours, then filtered and distilled on to fresh phosphorus pentoxide 2-3 times. This pure dry chloroform was stored in the dark to avoid photochemical formation of phosgene. Before use the pure chloroform was distilled on the vacuum line to remove traces of phosphorus pentoxide. The boiling range was 61-62 °C.

(iii) Diethyl ether[171 b]

Diethyl ether was first dried over anhydrous calcium chloride and filtered before sodium wire was added. After standing over the sodium wire for several days it was refluxed for one hour, distilled and fresh sodium wire added. The ether was distilled off before use; the boiling range was 34-35°C.

(b) Reagents

(i) Chlorine Chlorine, obtained from a cylinder, was dried by passage through two Drechsel bottles containing silica gel and one containing concentrated sulphuric acid. It was diluted with dry nitrogen for synthetic use.

(ii) Bromine

Analar bromine was first kept over anhydrous calcium bromide for 2-3 days. It was then filtered into a small round bottom flask under nitrogen. After brief direct pumping on the vacuum system to remove the more volatile impurities, it was distilled in vacuo.

(iii) Iodine

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

(iv) Iodine monobromide

Iodine monobromide was always freshly prepared from a 1:1 molar mixture of purified bromine and iodine.

(v) Iodine monochloride

Commercial iodine monochloride (BDH) was purified by distillation on the vacuum line.

STARTING MATERIALS

Preparation of Triarylarsines and Triarylstibines

(i) Tris(2,6-dimethylphenyl)arsine was prepared by reacting the Grignard reagent of 2-bromo-m-xylene with arsenic trichloride in diethyl ether. The mixture was refluxed for two hours and decomposed with dilute sulphuric acid (100 ml). The ether layer was separated and dried over sodium sulphate. After evaporation of the solvent a brown solid was obtained. This was recrystallised from ethanol to give a white crystalline solid. m.p. 130-132°C. Found: C, 73.39; H, 6.95% calculated for $C_{24}H_{27}As$: C, 73.84: H, 6.97%.

(ii) Tri(2-fluorophenyl)arsine was prepared by reacting the Grignard reagent of 2-bromofluorobenzene with arsenic trichloride in diethyl ether. The mixture was refluxed for two hours and decomposed with dilute sulphuric acid (100 ml). The ether layer was separated and dried over anhydrous sodium sulphate. After removing the solvent a brown solid was obtained, which was recrystallised from benzene/pet-ether (40-60°C). An off-white crystalline solid was obtained. m.p. 220-225°C (decomposed). Found: C, 60.37; H, 3.34% calculated for $C_{18}H_{12}F_3As$: C, 60.02; H, 3.35%.

(iii) Tri(3-fluorophenyl)arsine was prepared by exactly the same method as for tri(2-fluorophenyl)arsine. After the solvent was removed, an oily yellow liquid was obtained. Attempts were made to obtain crystals by treating the oil with benzene pet-ether (40-60°C). These were unsuccessful and a light yellow oily liquid was recovered.

This was found to crystallise slowly over a period of days giving pale yellow crystals of low m.p. 40-42°C. Found: C, 60.87; H, 3.43% calculated for $C_{18}H_{12}F_3As$ C, 60.02; H, 3.35%.

(iv) Tri(4-fluorophenyl)arsine was prepared by the same reaction as that used for tri(2-fluorophenyl)arsine. After removing the solvent on the rotary evaporator a yellow oily liquid was obtained, which was passed through a silica gel column using benzene 20% pet-ether (40-60°C) 80%. When the solvent was removed, a clear viscous liquid was obtained. This solidified on standing and gave a white powdery solid. m.p. 75-77°C. Found: C, 60.56; H, 3.41% calculated for $C_{18}H_{12}F_9As$ C, 60.02; H, 3.35%.

(v) Tris(2-trifluoromethylphenyl)arsine. The compound 2-$CF_3C_6H_4Li$ was made by the reaction of 2-bromobenzotrifluoride with n-butyl lithium in dry ether under a nitrogen atmosphere. A solution of arsenic trichloride in ether was then added dropwise with constant stirring, keeping the temperature of the reaction mixture at 0-5°C. After the arsenic trichloride solution was added the mixture was stirred for three hours and finally hydrolysed with dilute hydrochloric acid (100 ml). The mixture was allowed to warm up to room temperature and the ether layer was separated and dried over anhydrous sodium sulphate. The solvent was completely removed, and a crude product containing tris(2-trifluoromethylphenyl)arsine and some by-product was obtained. This was passed through a silica gel column using benzene 20%-pet ether 80% (40-60°C) as eluent. The product obtained was recrystallised from a water/ethanol mixture and dried on the vacuum line. m.p. 134-135°C. Found: C, 50.19% H, 2.45% calculated for

$C_{21}H_{12}F_9As$: C, 49.43: H, 2.37%.

(vi) Tris(3-trifluoromethylphenyl)arsine was prepared by exactly the same reaction as was used for tris(2-trifluoromethylphenyl)arsine. A dark brown oily liquid was obtained when the solvent was removed completely. This was passed through a silica gel column using benzene 10% pet-ether (40-60°C) 90%. The product was a light yellow liquid which did not solidify. Found: C, 50.86; H, 3.01% $C_{21}H_{12}F_9As$ requires C, 49.43; H, 2.37%.

(vii) Tris(4-trifluoromethylphenyl)arsine was made by an analogous reaction to that used for tris(2-trifluoromethylphenyl)arsine. The product was passed through a silica gel column using benzene 20% pet ether 80% (40-60°C) as eluent. The brown solid obtained was recrystallized from water/ethanol. This gave a pale yellow crystalline product which lost colour on exposure to light. m.p. 81-83°C. Found: C, 50.53; H, 2.60% calculated for $C_{21}H_{12}F_9As$: C, 49.43; H, 2.37%

(viii) Triphenylstibine Commercially available triphenylstibine (Fluka AG, chem, Fabric CH-9470 Buchs) was used as such.

(ix) Tri(2-methylphenyl)stibine was prepared by reacting the Grignard reagent of 1-bromo-2-methylbenzene with antimony trichloride in dry diethyl ether. The mixture was refluxed for two hours and hydrolysed with dilute sulphuric acid (100 ml). The ether was distilled off and the residue extracted with chloroform. After drying over anhydrous sodium sulphate, the solvent was completely removed on the rotary evaporator giving a brown product Recrystallization from ethanol gave a white crystalline solid. m.p. 100-102°C. Found: C, 63.19; H, 5.40% calculated for $C_{21}H_{21}Sb$: C, 63.83; H, 5.36%

(x) Tri(3-methylphenyl)stibine was prepared exactly as for tris(2-methylphenyl)stibine. After the chloroform was removed completely a yellow oily product was obtained, which after standing for two hours in the fridge gave white crystals of tris(3-methylphenyl)stibine. m.p. 62-64°C. Found: C, 63.69; H, 5.13% calculated for $C_{21}H_{21}Sb$: C, 63.83; H, 5.36%.

(xi) Tri(4-methylphenyl)stibine was prepared by reacting the Grignard reagent of 1-bromo-4-methylbenzene with antimony trichloride in diethyl ether. The product was hydrolysed with dilute sulphuric acid (100 ml). After removal of the ether by distillation the product was extracted with chloroform. The solvent was completely removed on a rotary evaporator leaving behind a brownish coloured product. Recrystallization of this solid from ethanol gave white crystals of the compound. m.p. 119-121°C. Found: C, 63.74; H, 5.35% calculated for $C_{21}H_{21}Sb$: C, 63.83; H, 5.36%.

(xii) Tri(2,6-dimethylphenyl)stibine was prepared by reacting the Grignard reagent of 2-bromo-m-xylene and antimony trichloride in diethyl ether. After the reaction was complete the mixture was refluxed for three hours, cooled, and hydrolysed with sulphuric acid (100 ml). The product was extracted with chloroform and dried over anhydrous sodium sulphate twice. The solvent was completely removed on the rotary evaporator leaving behind an oily brown product which solidified on standing in the fridge for 48 hours. It was recrystallised form ethanol giving a white product m.p. 99-102°C. Found: C, 65.24; H, 6.23% calculated for $C_{21}H_{24}Sb$: C, 65.93; H, 6.22%.

(xiii) Tris(2-trifluoromethylphenyl)stibine. The lithium derivative, $2\text{-}CF_3C_6H_4Li$, was prepared by the reaction of 2-bromobenzotrifluoride (10.90 ml)in dry ether with n-butyllithium (47.00 ml, 1.6 M) in the same solvent under a nitrogen atmosphere. The temperature was kept at 0-5°C during the reaction. The n-butyl lithium was added dropwise by syringing through a rubber septum and the mixture was stirred continuously. The colour of the solution changed from red to brown during the addition of the n—butyl lithium solution. The mixture was stirred for forty minutes. The $2\text{-}CF_3C_6H_4Li$ formed was then reacted with antimony trichloride (5.70 g in ether (50 ml) added dropwise, keeping the temperature below 5°C. The yellow turbid solution was stirred for three hours and finally hydrolysed with dilute hydrochloric acid (100 ml). The ether layer was separated and twice dried over anhydrous sodium sulphate, filtered and the solvent was removed on a rotary evaporator. A brown solid was obtained which after recrystallization from an ethanol/water mixture gave white crystalline tris(2-trifluoromethylphenyl)stibine. m.p. 134-135°C. Found: C, 45.30; H, 2.13% calculated for $C_{21}H_{12}F_9Sb$: C, 45.28; H, 2.17%.

(xiv) Tris(4-trifluoromethylphenyl)stibine was made by a similar method to that used for tris(2-trifluoromethylphenyl)stibine. The brown reaction product was recrystallised using ethanol/water. This gave a light-brown crystalline product. m.p. 125-126°C. Found: C, 44.72; H, 2.20% calculated for $C_{21}H_{12}F_9Sb$: C, 45.28; H, 2.17%. This was then passed through a silica gel column using benzene 20% pet-ether 80% (40-60°C) and finally recrystallized from an ethanol/water mixture. A buff coloured crystalline product was obtained. m.p. 125-127°C. Found: C, 44.34; H, 2.16%. calculated for $C_{21}H_{12}F_9Sb$: C, 45.28; H, 2.17%.

Attempted preparation of tris(2-trifluoromethylphenyl)stibine using a Grignard reaction

A solution of antimony trichloride (10.27 g) in dry ether (50 ml) was added dropwise with continuous stirring to the Grignard reagent of 2-bromobenzotrifluoride. No heat was evolved. The mixture was refluxed for three hours, cooled and then the ether was distilled off. The solid was decomposed by dilute sulphuric acid (100 ml). Chloroform (50 ml) was added to extract the product. The two layers were separated and the chloroform layer was dried over anhydrous sodium sulphate. The solvent was completely removed on a rotary evaporator leaving behind a black solid, which was passed through a silica gel column using benzene 50% pet-ether (40-60°C) 50%. After removing the solvent a dark brown solid was obtained which was soluble in chloroform, acetone, methylene chloride and benzene. It was recrystallised once from benzene /pet-ether(40-60°C) and twice with methylene chloride/pet-ether (40-60°C), but still the colour remained brown. m.p. 220-222°C (decomposed). Found: C, 52.37; H, 2.96% calculated for $C_{21}H_{12}F_9Sb$: C, 45.28; H, 2.17%. The reaction was repeated but no success was achieved in obtaining tris(2-trifluoromethylphenyl)stibine.

PART I

Halogen adducts of Tri(2-methylphenyl)arsine

(1) $(2\text{-}CH_3C_6H_4)_3AsCl_2$

Tri(2-methylphenyl)arsine (1.20 g, 3.44 mmol) was dissolved in chloroform (50 ml) and dry chlorine gas, diluted in a stream of dry nitrogen, was passed until the solvent assumed a yellow-green colour. Cooling was necessary during the reaction. The volume of the solvent was now reduced to the minimum on the vacuum line before adding ether to produce white crystals of tri(2-methylphenyl)arsine dichloride. The product was filtered, washed with ether, and dried in vacuo. m.p. 184-185°C (lit: 200-206°C)[153] Found: C, 59.62; H, 4.85; Cl, 16.70%. $C_{21}H_{21}AsCl_2$ requires: C, 60.15; H, 5.05; Cl, 16.90%.

(2) $(2\text{-}CH_3C_6H_4)_3AsBr_2$

Bromine (0.3287 g, 2.056 mmol) in acetonitrile (15 ml) was added dropwise with shaking to a solution of tri(2-methylphenyl)arsine (2.056 mmol) in acetonitrile (50 ml). The solvent was completely removed on the vacuum line, m.p. 192-193°C (lit: 92°C prepared in CCl_4). Found: C, 50.17; H, 4.33; Br, 31.73%.

$C_{21}H_{21}AsBr_2$ requires: C, 49.63; H, 4.17; Br, 31.45%

(3) $(2\text{-}CH_3C_6H_4)_3AsICl_3$

Iodine chloride (0.1160 g, 0.7144 mmol) dissolved in methyl cyanide (10 ml) was added dropwise to a solution of tri(2-methylphenyl)arsine dichloride (0.2990 g, 0.7144 mmol) in methyl cyanide (15 ml). A clear yellow coloured solution was obtained which did not give any solid adduct on the addition of ether. After freeze-drying a viscous yellow oil was obtained. This was pumped on the vacuum system to remove last traces of solvent but it was found that halogen (I_2 or ICl) was removed under these conditions. Found: C, 46.07; H, 4.10; I, 17.99; Cl, 19.47% $C_{21}H_{21}AsICl_3$ requires: C, 43.37; H, 3.64; I, 21.82; Cl, 18.28%

(b) Halogen adducts of Tri(3-methylphenyl)arsine

(1) $(3\text{-}CH_3C_6H_4)_3AsCl_2$

Tri(3-methylphenyl)arsine dichloride was prepared in exactly the same manner as tri(2-methylphenyl)arsine dichloride. White crystals were obtained. m.p. 174-177°C (Lit: 173-175°C). Found: C, 59.84; H, 5.47; Cl, 17.33%. $C_{21}H_{21}AsCl_2$ requires: C, 60.15; H, 5.05; Cl, 16.90%.

(2) $(3\text{-}CH_3C_6H_4)_3AsBr_2$

Bromine (0.2972 g, 1.8596 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(3-methylphenyl) arsine (0.6486 g, 1.8596 mmol) in acetonitrile (40 ml). The solvent was completely removed on the vacuum line leaving behind a white crystalline solid. This was dried under vacuum. m.p. 186-188°C (lit: 185-186°C). Found: C, 49.57; H, 4.23; Br, 30.80%. $C_{21}H_{21}AsBr_2$requires: C, 49.63; H, 4.17; Br, 31.45%.

(3) $(3\text{-}CH_3C_6H_4)_3AsICl_3$

Iodine chloride (0.1387 g, 0.8543 mmol) dissolved in methyl cyanide was added dropwise to a suspension of tri(3-methylphenyl)arsine dichloride (0.3581 g, 0.8542 mmol) in methyl cyanide (30 ml). Reaction occurred giving a clear yellow solution, which on freeze-drying gave a viscous yellow oil as in the case of the $(2\text{-}CH_3C_6H_4)_3AsCl_2$-ICl reaction. The oil was unstable losing halogen (I_2 or ICl) in the vacuum system. Found: C, 45.41; H, 4.07; I, 17.90; Cl, 17.29% $C_{21}H_{21}AsICl_3$ requires: C, 43.37; H, 3.64; I, 21.82; Cl, 18.28%.

(c) Halogen adducts of Tri(4-methylphenyl)arsine

(1) $(4\text{-}CH_3C_6H_4)_3AsCl_2$

Tri(4-methylphenyl)arsine dichloride was prepared in exactly the same manner as tri(2-methylphenyl)arsine dichloride. The product was a white crystalline solid. m.p. 220-224°C (lit: 240-242°C)[153]. Found: C, 59.76; H, 5.40; Cl, 17.04% $C_{21}H_{21}AsCl_2$ requires: C, 60.15; H, 5.05; Cl, 16.90%

(2) $(4\text{-}CH_3C_6H_4)_3AsBr_2$

Bromine (0.2510 g, 1.5705 mmol) dissolved in methyl cyanide (15 ml) was added dropwise to a suspension of tri(4-methylphenyl)arsine (0.5456 g, 1.5664 mmol) in the same solvent (20 ml). The arsine reacted with bromine, a clear and colourless solution resulted on complete addition of the bromine solution. Standing for 10 min. Gave white crystals of tri(4-methylphenyl)arsine dibromide. These were filtered, washed and dried on the vacuum line. m.p. 235-238°C (decomposed) (lit: 236-238°C). Found; C, 50.47; H, 4.03; Br, 31.06% $C_{21}H_{21}AsBr_2$ requires: C, 49.63; H, 4.17; Br, 31.45%.

(3) $(4\text{-}CH_3C_6H_4)_3AsICl_3$

Iodine chloride (0.1001 g, 0.0616 mmol) dissolved in methyl cyanide (15 ml) was added dropwise to a solution of tri(4-methylphenyl)arsine dichloride (0.2583 g, 0.0616 mmol) in the same solvent (30 ml). A clear yellow solution was formed, which after freeze-drying gave a yellow oil. The distillate from freeze-drying was slightly yellow indicating a slight loss of halogen. The oil was therefore not pumped further, Found: C, 44.32; H, 3.93; I, 20.31; Cl, 18.05% $C_{21}H_{21}AsICl_3$ requires: C, 43.37; H, 3.64; I, 21.82; Cl, 18.28%.

(d) Halogen adducts of Tri(2,6-dimethylphenyl)arsine

(1) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsCl_2.CHCl_3$

Chlorine gas, diluted in a stream of dry nitrogen was passed through a solution of tri(2,6-dimethylphenyl)arsine (1.000 g, 2.6616 mmol) in chloroform (30 ml) until the solution assumed a yellow-green colour. Cooling was necessary during the reaction. The solvent was removed on the vacuum line by the method of freeze-drying. A white crystalline solid was obtained. m.p. 210°C (decomposed). Found: C, 58.49; H, 5.72; Cl (hydrolysable) 14.00% $C_{24}H_{27}AsCl_2.CHCl_3$ requires: C, 58.67; H, 5.91; Cl, (hydrolysable) 13.85%. The compound was found to be in a solvated form and even after very long pumping it could not be obtained un-solvated. The presence of $CHCl_3$ was confirmed from the infra-red spectrum. Attempts to make the unsolvated compound in carbon tetrachloride were not successful.

(2) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsBr_2$

Bromine (0.232 g, 1.4516 mml) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.6667 g, 1.4616 mmol) in the same solvent (30 ml). Pale yellow crystals precipitated out during the addition of bromine solution. The crystals were filtered off and dried on the vacuum line. m.p. 204-205°C. Found: C, 52.77; H, 4.94; Br, 29.24% $C_{24}H_{27}AsBr_2$ requires: C, 52.39: H, 4.94; Br, 29.04%.

(3) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsIBr$

A solution of iodine bromide (I_2, 0.1206 g, 0.4751 mmol + Br_2, 0.0759 g, 0.4749 mmol) in acetonitrile was added with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.3710 g, 0.9503 mmol) in the same solvent (30 ml). After the addition of the iodine bromide solution was completed, the solution was freeze dried. A rust coloured solid was obtained and dried in vacuo. m.p. 169-170°C (decomposed). Found: C, 47.62; H, 4.76; Br, 13.32; I, 20.19% $C_{24}H_{27}AsIBr$ requires: C, 48.27; H, 4.55; Br, 13.38; I, 21.25%.

(4) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsBr_4$

Bromine (0.2716 g, 1.6994 mmol) dissolved in methyl cyanide (16 ml) was added dropwise with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.3316 g, 0.8494 mmol) in the same solvent (30 ml). After the bromine solution was added the solution was freeze-dried, and the light-yellow crystals were filtered off and dried on the vacuum line. m.p. 194-198°C (decomposed). Found: C, 41.32; H, 3.82; Br, 44.95% $C_{24}H_{27}AsBr_4$ requires: C, 40.59; H, 3.83;

Br, 45.01%.

(5) $[2,6-(CH_3)_2C_6H_3]_3AsBr_3I$

A 1:3 molar mixture of iodine and bromine (I_2, 0.1205 g, 0.4747 mmol + Br_2, 0.2277 g, 1.4247 mmol) in methyl cyanide (20 ml) was added dropwise with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.4038 g, 1.0343 mmol) in the same solvent (30 ml). The solvent was completely removed on the vacuum line. m.p. 198-200°C. Found: C, 39.02; H, 3.60; Br, 31.56; I, 16.70% $C_{24}H_{27}AsBr_3I$ requires: C, 38.07; H, 3.59; Br, 31.66; I, 16.76%.

(6) $[2,6-(CH_3)_2C_6H_3]_3AsBr_2I_2$

A 1:1 molar mixture of iodine and bromine (I_2, 0.2188 g, 0.8620 mmol + Br_2, 0.1378 g, 0.8622 mmol) in acetonitrile (20 ml) was added dropwise with continuous stirring to a solution of tri(2,6-dimethylphenyl)arsine (0.3367 g, 0.8623 mmol) in the same solvent (25 ml). The solvent was removed on the vacuum line leaving behind orange coloured crystals, which were pumped further on the vacuum line. m.p. 166-168°C. Found: C, 35.45; H, 3.42; I, 31.06; Br, 19.55% $C_{24}H_{27}AsBr_2I_2$ requires: C, 35.85, H, 3.38; Br, 19.88; I, 31.57%.

(7) $[2,6-(CH_3)_2C_6H_3]_3AsI_4$

Iodine (0.2962 g, 1.1670 mmol) dissolved in acetonitrile (15 ml) was added dropwise with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.2278 g, 0.5835 mmol) in the same solvent (20 ml). The bulk of the solvent was reduced on the vacuum line. No solid was obtained on adding ether, so the solvent was completely removed by freeze-drying leaving a black crystalline solid. This was pumped on the vacuum line m.p. 138-140°C (decomposed). Found: C, 31.55; H, 3.01; I, 56.71% $C_{24}H_{27}AsI_4$ requires: C, 32.10; H, 3.03; I, 56.52%.

(8) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsBr_6$

Bromine (0.3370 g, 2.1086 mmol) dissolved in acetonitrile (15 ml) was added dropwise with shaking to a solution of tri(2,6-dimethylphenyl)arsine (0.2744 g, 0.7028 mmol) in the same solvent (20 ml). During the addition of bromine solution the tri(2,6-dimethylphenyl)arsine dibromide started forming but redissolved on the further addition of bromine solution The solution after freeze-drying gave bright orange colour crystals of $[2,6\text{-}(CH_3)C_6H_3]_3AsBr_6$ During pumping to remove lost traces of solvent, bromine was last. m.p. 192-194°C (decomposed). Found: C, 31.69; H, 3.39; Br, 50.64, N, 0.65% $C_{24}H_{27}AsBr_6$ requires: C, 33.14; H, 3.13; Br, 55.12%.

(9) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsICl_3$

Iodine chloride (0.1219 g, 0.7508 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a suspension of tri(2,6-dimethylphenyl)arsine dichloride (0.3413 g, 0.7508 mmol) in the same solvent (20 ml). A clear yellow solution was obtained which afer freeze-drying gave yellow crystals. m.p. 215-218°C Found: C, 47.10; H, 4.54; Cl, 16.44; I, 19.61% $C_{24}H_{27}AsICl_3$ requires: C, 46.22; H, 4.36; Cl, 17.05; I, 20.35%.

Halogen adducts of Tri(fluorophenyl)arsines

(1) $(2\text{-}FC_6H_4)_3AsCl_2$

Dry chlorine gas, diluted in a stream of dry nitrogen, was passed through a solution of tri(2-fluorophenyl)arsine in chloroform (20 ml) until the solution assumed a yellow-green colour. The solution was freeze-dried. A yellow solid was obtained which was pumped dry. This solid slowly melt with decomposition at about 200°C. Found: C, 49.42; H, 2.89; Cl, 16.10% $C_{18}H_{12}F_3AsCl_2$ requires: C, 50.15; H, 2.80; Cl, 16.45%.

(2) $(3\text{-}FC_6H_4)_3AsCl_2$

Tri(3-fluorophenyl)arsine dichloride was prepared as a white crystalline solid by the same method as was used for tri(2-fluorophenyl)arsine dichloride. It melts at 156-160°C. Found: C, 49.99; H, 2.75; Cl, 16.33% $C_{18}H_{12}F_3AsCl_2$ requires: C, 50.15; H, 2.80; Cl, 16.45%.

(3) $(3\text{-}FC_6H_4)_3AsBr_2$

Bromine (0.5201 g, 3.2543 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(3-fluorophenyl)arsine (1.1723 g, 3.2544 mmol) in the same solvent (20 ml). The solution was freeze dried. A white crystalline solid was obtained which was dried on the vacuum line. m.p. 169-171°C. Found: C, 41.50; H, 2.24; Br, 30.26% $C_{18}H_{12}F_3AsBr_2$ requires: C, 41.57; H, 2.32; Br, 30.73%.

(4) $(4\text{-}FC_6H_4)_3Cl_2$ was prepared by the same method as was used for tri(2-fluorophenyl)arsine dichloride. It is a white solid, m.p. 206-208°C. Found: C, 49.23; H, 2.72; Cl, 17.04% $C_{18}H_{12}F_3AsCl_2$ requires: C, 50.15; H, 2.80; Cl, 16.45%.

(5) $(4\text{-}FC_6H_4)_3AsBr_2$ was made by the same method as for $(3\text{-}FC_6H_4)_3AsBr_2$. It is a white crystalline solid. m.p. 244-246°C (decomposed). Found: C, 42.45; H, 2.36; Br, 30.40% $C_{18}H_{12}F_3AsBr_2$ requires: C, 41.57; H, 2.32; Br, 30.73%.

(f) Halogen adducts of Tris(2-trifluoromethylphenyl)arsine

(1) $(2\text{-}CF_3C_6H_4)_3AsCl_2.CHCl_3$

Chlorine gas, diluted in a stream of dry nitrogen, was passed through a solution of tris(2-trifluoromethylphenyl)arsine (0.50 g, 0.9799 mmol) in chloroform (30 ml) until the solution assumed a yellow-green colour. On addition of ether a white crystalline solid was obtained. This was filtered off and dried on the vacuum line. m.p. 216-218°C. Found: C, 40.73; H, 2.13; Cl, (hydrolysable) 12.47% $C_{21}H_{12}F_9AsCl_2.CHCl_3$ requires: C, 41.83; H, 2.39; Cl, (hydrolyseable) 11.22%. The presence of chloroform of solvation was confirmed from the infra-red spectrum of the compound.

(g) Halogen adducts of Tris(3-trifluoromethylphenyl)arsine

(1) $(3\text{-}CF_3C_6H_4)_3AsCl_2$

Chlorine gas diluted in a stream of dry nitrogen, was passed through a solution of tris(3-trifluoromethylphenyl)arsine (1.5 g, 2.9397 mmol) in chloroform (20 ml) for 10 minutes. After freeze drying, the solution gave a light yellow solid. m.p. 166-168°C. Found: C, 43.66; H, 2.25; Cl, 11.57% $C_{21}H_{12}F_9AsCl_2$ requires: C, 43.40; H, 2.08; Cl, 12.20%.

(2) $(3\text{-}CF_3C_6H_4)_3AsBr_2$

Bromine (0.3227 g, 2.0192 mmol) in acetonitrile (10 ml) was added dropwise with shaking to a solution of tris(3-trifluoromethylphenyl)arsine (1.0304 g, 2.0194 mmol) in the same solvent (20 ml). The solution was freeze dried. A white crystalline solid was obtained and this was dried on the vacuum line. m.p. 172-174°C. Found: C, 38.64; H, 1.88; Br, 23.17% $C_{21}H_{12}F_9AsBr_2$ requires: C, 37.64; H, 1.80; Br, 23.85%.

(h) Halogen adducts of Tris(4-trifluoromethylphenyl)arsine

(1) $(4\text{-}CF_3C_6H_4)_3AsCl_2$

Chlorine gas, diluted in a stream of dry nitrogen, was passed through a solution of tris(4-trifluoromethylphenyl)arsine (0.70 g, 1.3719 mmol) in chloroform (30 ml) until the solution assumed a yellow-green colour. Cooling was necessary during the reaction. No solid was obtained when ether was added. The solvent was completely removed on the vacuum line giving a white crystalline solid which was dried under vacuum. m.p. 214-216°C. Found: C, 43.39; H, 2.14; Cl, 12.47% $C_{21}H_{12}F_9AsCl_2$ requires: C, 43.40; H, 2.08; Cl, 12.20%.

(2) $(4\text{-}CF_3C_6H_4)_3AsBr_2$

Bromine (0.1792 g, 1.1213 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tris(4-trifluoromethylphenyl)arsine (0.5722 g, 1.1214 mmol) in the same solvent (20 ml). After the addition of bromine solution was completed, the solvent was completely removed on the vacuum line. The white crystalline solid obtained was dried under vacuum. m.p. 210-212°C. Found: C, 38.20; H, 1.84; Br, 23.44% $C_{21}H_{12}F_9AsBr_2$ requires: C, 37.64; H, 1.80; Br, 23.85%.

(3) $(4\text{-}CF_3C_6H_4)_3AsI_2$

Iodine (0.2763 g, 1.0886 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tris(4-trifluoromethylphenyl)arsine (0.5555 g, 1.0886 mmol) in the same solvent (20 ml). The solution was freeze dried. A brown black solid was obtained. Last traces of solvent were removed by pumping on the vacuum system. During this process it was noted that a trace of iodine condensed in the cold trap. m.p. 116-118°C (decomposed). Found: C, 33.79; H, 1.67; I, 33.04% $C_{21}H_{12}F_9AsI_2$ requires: C, 33.01; H, 1.58; I, 33.21.

(4) $(4\text{-}CF_3C_6H_4)_3AsI_4$

Tris(4-trifluoromethylphenyl)arsine (0.4801 g, 0.9409 mmol) in acetonitrile (10 ml) was added dropwise with shaking to a solution of iodine (0.4776 g, 1.8817 mmol) in the same solvent. The solution was freeze dried. A black crystalline solid was obtained. (the solid lost some iodine during the pumping) m.p. 118-119°C (decomposed). Found: C, 25.93; H, 1.30; I, 50.76% $C_{21}H_{12}F_9AsI_4$ requires: C, 24.78; H, 1.19; I, 56.97%.

ATTEMPTED PREPARATIONS

(1) $[2,6\text{-}(CH_3)_2C_6H_3]_3AsI_2$

From a 1:1 mixture of iodine and tri(2,6-dimethylphenyl)arsine in acetonitrile, a dark brown solid was obtained; this was unstable and lost iodine during pumping. m.p. 134-136°C (decomposed). Found: C, 53.54; H, 4.81% $C_{24}H_{27}AsI_2$ requires: C, 44.74; H, 4.22%.

(2) $(2\text{-}FC_6H_4)_3AsBr_4$

Bromine (0.3209 g, 2.0079 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a suspension of tri(2-fluorophenyl)arsine (0.3617 g, 1.0040 mmol) in the same solvent. The solution was shaken for one hour, but some starting material $[(2\text{-}FC_6H_4)_3As]$ remained undissolved. Therefore the supernatant clear yellow solution was carefully decanted and freeze dried. A yellow solid was obtained which lost some bromine during pumping to dryness. m.p. 184-186° (decomposed). Found: C, 45.80; H, 2.50% $C_{18}H_{12}F_3AsBr_4$ requires: C, 31.80; H, 1.78%. On further pumping on the vacuum line it lost bromine and the analysis obtained was close to the starting material.

(3) $(4\text{-}FC_6H_4)_3AsI_2$ Iodine (0.2076 g, 0.8179 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(4-fluorophenyl)arsine (0.2924 g, 0.8117 mmol) in the same solvent. A brown solid was obtained which lost iodine readily. Found: C, 31.90; H, 1.75% $C_{18}H_{12}F_3AsI_2$ requires C, 35.21; H, 1.97%.

(4) $(2\text{-}CF_3C_6H_4)_3AsICl_3$

Iodine chloride (0.0670 g, 0.4126 mmol) dissolved in acetonitrile (10 ml) was added dropwise with continuous shaking to a solution of tris(2-trifluoromethylphenyl)arsine dichloride. A clear yellow solution was obtained which was freeze dried. The yellow solid obtained lost iodine during the pumping. m.p. 129-130°C. Found: C, 35.10; H, 1.79% $C_{21}H_{12}F_9AsICl_3$ requires: C, 33.90; H, 1.62%.

(5) $(2\text{-}CF_3C_6H_4)_3AsBr_2$

A 1:1 molar mixture of bromine and tris(2-trifluoromethylphenyl)arsine was prepared in acetonitrile. When the solution was freeze dried, it left behind an orange solid which was unstable and lost bromine readily during pumping. m.p. 147-149°C (decomposed). Found: C, 41.06; H, 2.09% $C_{21}H_{12}F_9AsBr_2$ requires: C, 37.64; H, 1.80%.

(6) $(2\text{-}CF_3C_6H_4)_3AsBr_4$

Bromine (0.2113 g, 1.3221 mmol) dissolved in acetonitrile (10 ml) was added dropwise to a solution of tris(2-trifluoromethylphenyl)arsine (0.3373 g, 0.6610 mmol) in the same solvent (20 ml). The solution was freeze dried. A dark brown sticky solid was obtained, which lost bromine during pumping. Found: C, 36.51; H, 2.05; N, 0.37% $C_{21}H_{12}F_9AsBr_4$ requires: C, 30.19; H, 1.45%. From the analytical data it was thought that the compound obtained was the dibromide contaminated with solvent $(2\text{-}CF_3C_6H_4)_3AsBr_2.CH_3CN$. To get rid of last traces of solvent the compound was pumped on the vacuum line, but this resulted in further loss of bromine. Found: C, 40.79; H, 2.06% N, 0.15% $C_{21}H_{12}F_9AsBr_2$ requires: C, 37.64; H, 1.80%.

(7) $(4\text{-}CF_3C_6H_4)_3AsICl_3$

When iodine chloride and tris(4-trifluoromethylphenyl)arsine dichloride (in a 1:1 molar mixture) were mixed in methyl cyanide, a brown crystalline solid was obtained after the solution was freeze dried. The product was unstable, losing iodine chloride during pumping to dryness. After long pumping the final product was white crystalline tris(4-trifluoromethylphenyl)arsine dichloride. m.p. 219-220°C. Found: C, 42.76; H, 2.04%. ($C_{21}H_{12}F_9AsCl_2$ m.p. 214-216°C. requires: C, 43.40; H, 2.08%). $C_{21}H_{12}F_9AsICl_3$ requires: C, 33.92; H, 1.62%.

PART II

(a) Halogen adducts of Triphenylstibine

(1) $(C_6H_5)_3SbCl_2$

Dry chlorine gas, diluted in a stream of dry nitrogen, was passed through the solution of triphenylstibine (2.900 g, 6.840 mmol) in (20 ml) chloroform until the solvent assumed a yellow-green colour . After freeze-drying a white crystalline adduct was obtained. The adduct was washed with dried ether and then pumped dry. m.p. 134-136°C (lit: 143°C.)[172] Found: C, 51.53; H, 3.58; Cl, 20.28% $C_{18}H_{15}SbCl_2$ requires: C, 50.99; H, 3.56; Cl, 21.20%.

(2) $(C_6H_5)_3SbBr_2$

Bromine (0.6819 g, 4.266 mmol) in acetonitrile (10 ml) was added dropwise, with shaking to a solution of triphenylstibine (1.5065 g, 4.266 mmol) in acetonitrile (20 ml), white crystals precipitated out during the addition of the bromine solution, these were filtered, washed with ether and dried on the vacuum line. m.p. 214-216°C (lit: 214-215°C)[172]. Found: C, 42.29; H, 2.83; Br, 30.70%. $C_{21}H_{15}SbBr_2$ requires: C, 42.15; H, 2.95; Br, 31.20%.

(3) $(C_6H_5)_3SbI_2$

Iodine (0.9864 g, 3.886, mmol) in acetonitrile (20 ml) was added dropwise with shaking to a solution of triphenylstibine (1.3722 g, 3.886, mmol) in acetonitrile (20 ml). This resulted in the formation of a pale yellow crystalline solid. The solid was filtered and pumped on the vacuum line. m.p. 168-170°C (decomposed). Found: C, 35.82; H, 2.41; I, 41.25%. $C_{18}H_{15}SbI_2$ requires: C, 35.62 ; H, 2.49; I, 41.82%.

(4) $(C_6H_5)_3SbI_4$

Triphenylstibine (0.8206 g, 2.324 mmol) in acetonitrile (10 ml) was added dropwise with continuous shaking to a solution of iodine (1.1799 g, 4.648,mmol) in acetonitrile (20 ml). A black coloured solution formed, which after freeze-drying gave a black, sticky solid. Loss of iodine was observed during the pumping to dryness. m.p. 138–140°C. Found: C, 26.73; H, 1.83; I, 57.45%. $C_{18}H_{15}SbI_4$ requires: C, 25.12; H, 1.75; I, 58.98%.

(5) $(C_6H_5)_3SbIBr$

Iodine bromide (0.7757 g, 3.750 mmol) in acetonitrile (15 ml) was added dropwise to a solution of triphenylstibine (1.3242 g, 3.750 mmol) in the same solvent (10 ml). After the complete addition of the iodine bromide solution a white solid precipitated out; this was filtered off, washed with ether and dried on the vacuum line. m.p. 194–196°C (decomposed). Found: C, 38.73; H, 2.66; Br, 14.30; I, 22.60%. $C_{18}H_{15}SbIBr$ requires: C, 38.61; H, 2.70; Br, 14.27; I, 22.66%.

(b) Halogen Adduct of Tri(2-methylphenyl)stibine

(1) $(2\text{-}CH_3C_6H_4)_3SbCl_2$

Tri(2-methylphenyl)stibine dichloride was prepared in exactly the same manner as triphenylstibine dichloride. The product was a white crystalline solid. m.p. 224–226°C. Found: C, 54.44; H, 4.61; Cl, 15.46; $C_{21}H_{21}SbCl_2$ requires: C, 54.12; H, 4.54; Cl, 15.21%.

(2) $(2\text{-}CH_3C_6H_4)_3SbBr_2$

Bromine (0.2770 g, 1.733 mmol) in acetonitrile (7 ml) was added dropwise with shaking to a solution of tri(2-methylphenyl)stibine (0.6850 g 1.733 mmol) in acetonitrile (25 ml). On reducing the volume of the solvent on the vacuum line, a white crystalline solid appeared. This was filtered off and dried on the vacuum line. m.p. 230-232°C. found: C, 45.21; H, 3.60; Br, 28.72; $C_{21}H_{21}SbBr_2$ requires: C, 45.45; H, 3.81; Br, 28.72%.

(3) $(2\text{-}CH_3C_6H_4)_3SbI_2$

Iodine (0.3952 g, 1.557 mmol) dissolved in acetonitrile (5 ml) was added dropwise to a suspension of tri(2-methylphenyl)stibine (0.6152 g, 1.577 mmol) in the same solvent (20 ml). The clear dark coloured solution was put in the fridge for one hour, after which pale yellow crystals appeared. These were filtered and dried under vacuum. m.p. 127-129°C. Found: C, 38.94; H, 3.26; I, 37.92% $C_{21}H_{21}SbI_2$ requires: C, 38.87; H, 3.26; I, 38.13%.

(4) $(2\text{-}CH_3C_6H_4)_2SbI_3$

Iodine (0.5676 g, 2.236 mmol) in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(2-methylphenyl)stibine (0.4402 g, 1.118 mmol) in acetonitrile (20 ml). This resulted in the formation of a dark coloured solution. The volume of the solution was reduced by freeze-drying. The black solid formed was removed by filtration, washed with dry ether and dried on the vacuum line. Found: C, 25.52; H, 2.13; I, 55.52; Sb, 17.38% $C_{14}H_{14}SbI_3$ requires: C, C, 24.55; H, 2.06; I, 55.59; Sb, 17.78%. Attempts to prepare $(2\text{-}CH_3C_6H_4)_3SbI_4$ using benzene as solvent gave the same compound.

(5) $(2\text{-}CH_3C_6H_4)_3SbIBr.CH_3CN$

Iodine bromide (0.311 g, 1.503 mmol) in acetonitrile (10 ml) was added dropwise to a solution of tri(2-methylphenyl)stibine (0.5939 g, 1.503 mmol) in the same solvent (10 ml), resulting in the formation of a clear yellow solution. The volume of the solution was reduced on the vacuum line producing a brown solid which was filtered off, washed with ether and pumped dry on the vacuum line. The elemental analysis showed that a monosolvated adduct had been formed. m.p. 163-165°C (decomposed). Found: C, 43.20; H, 3.76; Br, 12.79; I, 19.17; N, 2.17% $C_{21}H_{21}SbIBr.CH_3CN$ requires: C, 42.90; H, 3.76; Br, 12.42; I, 19.73; N, 2.17%. Attempts to prepare the unsolvated adduct were made using benzene as solvent, but this did not result in the formation of a pure compound; it appeared that a mixture of the iodide bromide and dibromide adduct crystallised from the benzene solution. (Found: C, 42.76; H, 3.50; I, 17.83; Br, 14.68% $C_{21}H_{21}SbIBr$ requires: C, 41.90; H, 3.52; I, 21.08; Br, 13.26%)

(c) Halogen Adducts of Tri(3-methylphenyl)stibine

(1) $(3\text{-}CH_3C_6H_4)_3SbCl_2$

Tri(3-methylphenyl)stibine dichloride was prepared in an identical manner to triphenylstibine dichloride. The product was a white crystalline solid. m.p. 137-138°C Found: C, 54.48; H, 4.57; Cl, 16.20% $C_{21}H_{21}SbCl_2$ requires: C, 54.12; H, 4.54; Cl, 15.21%.

(2) $(3\text{-}CH_3C_6H_4)_3SbBr_2$

Bromine (0.2894 g, 1.8100 mmol) in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(3-methylphenyl)stibine (0.7148 g, 1.810 mmol) in the same solvent (20 ml). The solution was freeze dried and a white crystalline adduct was obtained. m.p. 106-107°C. Found: C, 45.44; H, 3.74; Br, 28.80; $C_{21}H_{21}SbBr_2$ requires: C, 45.45; H, 3.81; Br, 28.72%.

(3) $(3\text{-}CH_3C_6H_4)_3SbI_2$

Iodine (0.3900 g, 1.536 mmol) dissolved in benzene (5 ml) was added to a solution of tri(3-methylphenyl)stibine (0.6073 g, 1.536 mmol) in benzene (20 ml). The solution was freeze dried and a light yellow coloured solid was obtained. m.p. 140-142°C. Found: C, 38.98; H, 3.24; I, 38.45% $C_{21}H_{21}SbI_2$ requires: C, 38.87; H, 3.26; I, 39.13%. This unsolvated compound could not be obtained from acetonitrile.

(4) $(3\text{-}CH_3C_6H_4)_3SbI_4$

Iodine (0.5780 g, 2.277 mmol) dissolved in acetonitrile (10 ml) was added dropwise to a solution of tri(3-methylphenyl)stibine (0.4499 g, 1.138 mmol) in acetonitrile (20 ml). A clear dark brown coloured solution was obtained. The dark violet solid obtained was pumped free of solvent on the vacuum line. During this process iodine was observed to condense in the cold trap. m.p. 130-132°C (decomp). Found: C, 29.27; H, 2.43; I, 53.18% $C_{21}H_{21}SbI_4$ requires: C, 27.93; H, 2.34; I, 56.23%. The observed low percentage of iodine and high percentage of carbon are in keeping with the loss of iodine during pumping.

(5) $(3\text{-}CH_3C_6H_4)_3SbIBr$

Iodine bromide (0.3427 g, 1.657 mmol) in acetonitrile (10 ml) was added dropwise to a solution of tri(3-methylphenyl)stibine (0.6548 g, 1.657 mmol) in acetonitrile (20 ml). A yellow crystalline solid was obtained after complete removal of solvent on the vacuum line m.p. 120-122°C. Found: C, 41.75; H, 3.54; Br, 12.51; I, 22.14% $C_{21}H_{21}SbIBr$ requires: C, 41.83; H, 3.51; Br, 13.25; I, 21.05%

(d) Halogen Adducts of Tri(4-methylphenyl)stibine

(1) $(4\text{-}CH_3C_6H_4)_3SbCl_2$

Tri(4-methylphenyl)stibine dichloride was prepared in exactly the same manner as triphenylstibine dichloride. The product was a white crystalline solid. m.p. 154-155°C. Found: C, 54.05; H, 4.52; Cl, 14.58%. $C_{21}H_{21}SbCl_2$ require: C, 54.12; H, 4.54; Cl, 15.21%

(2) $(4\text{-}CH_3C_6H_4)_3SbBr_2$

Bromine (0.2757 g, 1.725 mmol) dissolved in acetonitrile (7 ml) was added dropwise to a solution of tri(4-methylphenyl)stibine (0.6818 g, 1.725 mmol) in the same solvent (20 ml). A white crystalline solid formed readily during the bromine addition. This was filtered, washed with ether and dried on the vacuum line. m.p. 224-225°C. Found: C, 45.45; H, 3.78; Br, 29.51% $C_{21}H_{21}SbBr_2$ requires: C, 45.45; H, 3.81; Br, 28.72%.

(3) $(4\text{-}CH_3C_6H_4)_3SbI_2$

Iodine (0.3901 g, 1.537 mmol) dissolved in acetonitrile (10 ml) was added dropwise with shaking to a solution of tri(4-methylphenyl)stibine (0.6070 g, 1.536 mmol) in acetonitrile (20 ml). During the addition of the iodine solution a pale yellow solid was precipitated; this was filtered and washed with dry ether. m.p. 189°C (decomposed). Found: C, 39.34; H, 3.24; I, 38.91% $C_{21}H_{21}SbI_2$ requires: C, 38.87; H, 2.26; I, 39.13%.

(4) $(4\text{-}CH_3C_6H_4)_3SbIBr$

Iodine bromide (0.3685 g, 1.781 mmol) in benzene (15 ml) was added dropwise to a solution of tri(4-methylphenyl)stibine (0.7040 g, 1.781 mmol) in the same solvent (15 ml), a light yellow clear solution was formed, after freeze-drying a white crystalline compound was obtained. m.p 204-206°C (decomposed). Found: C, 41.48; H, 3.45; Br, 13.84; I, 20.74%. $C_{21}H_{21}SbIBr$ requires: C, 41.83; H, 3.51; Br, 13.25; I, 21.05%. An attempt to prepare this compound in acetonitrile gave a product with a low percentage of bromine and iodine.

Halogen Adducts Of Tri(2,6-dimethylphenyl)stibine

(1) $[(2,6\text{-}(CH_3)_2C_6H_4]_3SbCl_2$

Chlorine gas, diluted in a stream of dry nitrogen gas was passed through the solution of tri(2,6-dimethylphenyl)stibine (1.8 g, 4.1168 mmol) in chloroform (20ml) until the solution turned yellow. On freeze-drying a white crystalline adduct was obtained. The adduct was washed with ether and vacuum dried. m.p. 250-252°C (decomposed).

Found: C, 56.44; H, 5.32; Cl, 14.83%. $C_{24}H_{27}SbCl_2$ requires C, 56.73; H, 5.35; Cl, 15.95%.

(2) $[(2,6\text{-}(CH_3)_2C_6H_3]_3SbBr_2$

Bromine (0.2542 g, 1.5905 mmol) dissolved in acetonitrile (10 ml) was added dropwise, with shaking, to a solution of tri(2,6-dimethylphenyl)stibine (0.6954 g, 1.5905 mmol)in acetonitrile (20 ml). A white solid formed. This was filtered and vacuum dried. m.p. 192-194°C. Found: C, 48.27; H, 4.56; Br, 26.31%. $C_{24}H_{27}SbBr_2$ requires: C, 48.28; H, 4.56; Br, 26.77%.

(3)$[(2,6\text{-}(CH_3)_2C_6H_3]_3SbI_2$

Iodine (0.3773 g, 1.4865mmol) dissolved in acetonitrile (10 ml) was added dropwise, with shaking, to a solution of tri(2,6-dimethylphenyl)stibine (0.65 g, 1.4866 mmol) in the same solvent (20 ml). During the addition of the iodine solution a bright red solid formed. The solid was filtered and vacuum dried. m.p. 133-136°C (decomposed). Found C, 41.98; H, 3.93; I, 35.57%. $C_{24}H_{27}SbI_2$ requires: C, 41.21; H, 3.94; I,36.73%.

(4) $[(2,6\text{-}(CH_3)_2C_6H_3]_3SbI_3$

Tri(2,6-dimethylphenyl)stibine (0.5871 g, 1.3427 mmol) dissolved in acetonitrile (20 ml) was added dropwise, with shaking, to a solution of iodine (0.6816 g, 2.685 mmol) in the same solvent (10 ml). A black crystalline solid formed and this was filtered and dried on the vacuum line. m.p. 142-145°C Found: C, 30.49; H, 2.83; I, 53.11%. $C_{24}H_{27}SbI_4$ requires: C, 31.51; H, 2.88; I, 53.72%.

(5) $[(2,6\text{-}(CH_3)_2(C_6H_3)]_3SbIBr_3$

Iodine bromide (0.1941 g, 0.9384 mmol) dissolved in acetonitrile (10 ml) was added, with shaking, to a suspension of tri(2,6-dimethylphenyl)stibine dibromide (0.5604 g, 0.9386 mmol) in acetonitrile (30 ml) . A yellow solution formed which gave a brown compound after freeze-drying. A brown condensate (iodine or iodine bromide) appeared in the trap whilst drying in the vacuum system. This indicated that this adduct is not stable. m.p. 181-182°C (decomposed). Found: C, 37.10; H, 3.50; Br, 30.66; I, 15.24%. $C_{24}H_{27}SbIBr_3$ requires: C, 38.86; H, 3.38; Br, 29.82; I, 15.79%.

(f) Halogen Adducts Of Tris(2-trifluoromethylphenyl)stibine

(1) $(2\text{-}CF_3C_6H_4)_3SbCl_2$

Chlorine gas, diluted in a stream of dry nitrogen, was passed through a solution of tris(2-trifluoromethylphenyl)stibine (2.2 g, 3.9493 mmol) in chloroform (25 ml) until the solution became slightly yellow. After freeze-drying a white compound was obtained which was very soluble in ether. The compound was pumped dry. m.p. 215-216° C. Found: C, 40.50; H, 2.32; Cl, 12.23%. $C_{21}H_{12}F_9SbCl_2$ requires: C, 40.16; H, 1.93; Cl, 11.29%.

(2) $(2\text{-}CF_3C_6H_4)_3SbBr_2$

Bromine (0.2229 g, 1.3947 mmol) dissolved in acetonitrile (10 ml) was added to a solution of tris(2-trifluoromethylphenyl)stibine (0.7770 g, 1.3948 mmol) in acetonitrile (10 ml). A clear and colourless solution was obtained which gave a white crystalline adduct when freeze-dried. m.p. 190-192°C. Found: C, 35.03; H, 1.69; Br, 21.93%. $C_{21}H_{12}F_9SbBr_2$ requires: C, 35.18; H, 1.69; Br, 22.29%.

(g) Halogen Adducts Of Tris(4-trifluoromethylphenyl)stibine

(1) $(4\text{-}CF_3C_6H_4)_3SbCl_2$

Chlorine gas, diluted in a stream of dry nitrogen, was passed through the solution of tris(4-trifluoromethylphenyl)stibine (2.0 g, 3.5903 mmol) in chloroform (30 ml) until the solution became slightly yellow. After freeze-drying a white crystalline compound was obtained. m.p. 118-119°C. The compound was very soluble in ether. Found: C, 40.22; H, 2.01; Cl, 11.87%. $C_{21}H_{12}F_9SbCl_2$ requires: C, 40.16; H, 1.93; Cl, 12.29%.

(2) $(4\text{-}CF_3C_6H_4)_3SbBr_2$

Bromine (0.2167 g, 1.3597 mmol) dissolved in acetonitrile (5 ml) was added dropwise to a solution of tris(4-trifluoromethylphenyl)-stibine (0.7547 g, 1.3547 mmol) in the same solvent (15 ml). A slightly yellow solution was formed which gave a white crystalline adduct after freeze-drying. m.p. 140-142°C. Found: C, 34.77; H, 1.62; Br, 22.26%. $C_{21}H_{12}F_9SbBr_2$ requires: C, 35.03; H, 1.69; Br, 22.29%.

(3) $(4\text{-}CF_3\ C_6H_4)_3SbI_2$

Iodine (0.313 g, 1.2331 mmol) dissolved in acetonitrile (10 ml) was added dropwise to a solution of tris(4-trifluoromethylphenyl) stibine (0.6869 g, 1.2331 mmol) in acetonitrile (10 ml). A dark brown coloured solution was formed. On freeze-drying a pale yellow solid was obtained; the distillate was observed to be brown in colour, suggesting the presence of iodine. The solid was vacuum dried. Found; C, 30.44; H, 1.51; I, 29.48%. $C_{21}H_{12}F_9SbI_2$ requires: C, 31.10; H, 1.49; I, 31.30%. This adduct was found to decompose at 100°C.

ATTEMPTED PREPARATIONS

(1) $(2\text{-}CH_3C_6H_4)_3SbI_4$

Iodine (0.5582 g, 2.1993 mmol) dissolved in acetonitrile (15 ml) was added dropwise with shaking to a solution of tri(2-methylphenyl)stibine (0.4346 g, 1.0998 mmol) in the same solvent (10 ml). No solid was appeared when ether was added. The solution was freeze dried and it gave a dark brown solid which was washed with ether and dried on the vacuum line. m.p. 108-110°C. Found: C, 21.49; H, 2.01%. $C_{21}H_{21}SbI_4$ requires: C, 27.93; H, 2.34%. The analysis result suggests that the solid is $(2\text{-}CH_3C_6H_4)_2SbI_3$ ($C_{14}H_{14}SbI_3$ requires: C, 24.55; H, 2.06%). An attempt was made to obtain the adduct from benzene but again $(2\text{-}CH_3C_6H_4)_2SbI_3$ was recovered.

(2) $(4\text{-}CH_3C_6H_4)_3SbBr_2I_2$

A 2:1 molar mixture of iodine bromide and tri(4-methylphenyl)stibine in acetonitrile gave a pale yellow crystalline solid which was recognised as $(4\text{-}CH_3C_6H_4)_3SbIBr$. m.p. 204°C (decomposed). Found: C, 42.49; H, 33.58% $C_{21}H_{21}SbIBr$ requires: C, 41.90; H, 3.52%.

(3) $(4\text{-}CH_3C_6H_4)_3SbBrI_3$

When the correct stoichiometric quantities of tri(4-methylphenyl)stibine, bromine and iodine were mixed in acetonitrile, a dark coloured solution was obtained. After this solution was freeze dried, a light yellow solid was obtained. The analytical data suggested that the product was mainly $(4\text{-}CH_3C_6H_4)_3SbIBr$.

(4) $[(CH_3)_2C_6H_3]_3SbIBr$

Iodine bromide (I_2, 0.2447 g, 0.9641 mmol + Br_2 0.1540 g, 0.9636 mmol) dissolved in acetonitrile (10 ml) was added dropwise to a solution of tri(2,6-dimethylphenyl)stibine (0.8421 g, 1.9259 mmol) in the same solvent (30 ml). When the iodine bromide solution was added completely, light yellow crystals were obtained on standing for one hour. These were filtered and dried in vacuo. m.p. 138°C (decomposed). Found: C, 46.60; H, 4.33% $C_{24}H_{27}SbIBr$ requires: C, 44.76; H, 4.23%. The analysis is also close to $C_{24}H_{27}SbBr_2$ which requires: C, 48.28; H, 4.56% suggesting that the product is probably a mixture of $C_{24}H_{27}SbIBr$ and $C_{24}H_{27}SbBr_2$.

(5) $[(CH_3)_2C_6H_3]_3SbBr_2I_2$

A 2:1 molar mixture of iodine bromide and tri(2,6-dimethylphenyl)stibine in acetonitrile solution gave, after freeze drying, a dark brown solid which lost iodine during pumping to dryness. m.p. 186-188°C. Found: C, 48.04; H, 4.50% $C_{24}H_{27}SbBr_2I_2$ requires: C, 33.88; H, 3.20%. The analysis is close to that required for $C_{24}H_{27}SbBr_2$ but the colour of the product suggests the presence of iodine.

(6) $[(CH_3)_2C_6H_3]_3SbBr_4$

From a 2:1 molar mixture of bromine and tri(2,6-dimethylphenyl)stibine in acetonitrile, a pale yellow solid was obtained. m.p. 183-186°C. Found: C, 47.69; H, 4.45; Br, 27.28% $C_{24}H_{27}SbBr_4$ requires: C, 38.09; H, 3.59; Br, 42.23%. The analysis of the solid corresponds with the formula $C_{24}H_{27}SbBr_2$ but the colour of the solid suggests the presence of excess of bromine.

(7) $(2\text{-}CF_3C_6H_4)_3SbI_2$

An equimolar mixture of iodine and tris(2-trifluoromethylphenyl)stibine in acetonitrile gave a light yellow crystalline solid. The solid lost iodine during pumping to dryness and a white solid was left. m.p. 130-132°C. Analysis (found C, 45.01; H, 2.18%) suggests the solid is the starting material $C_{21}H_{12}Sb$ (requires: C, 45.30; H, 2.13%).

(8) $(2\text{-}CF_3C_6H_4)_3SbBr_2I_2$

A 1:1 molar mixture of bromine, iodine and tris(2-trifluoromethylphenyl)stibine in acetonitrile gave a dark coloured solid after it was freeze dried. The solid lost iodine during pumping leaving behind white crystalline product. m.p. 187-188°C. Found: C, 35.16; H, 1.70% $C_{21}H_{12}F_9AsBr_2I_2$ requires: C, 25.98; H, 1.25%. The compound was identified as $C_{21}H_{12}F_9SbBr_2$ which requires: C, 35.18; H, 1.69%.

(9) $(4\text{-}CF_3C_6H_4)_3SbIBr$

A 1:1 molar mixture of iodine bromide and tris(4-trifluoromethylphenyl)stibine in acetonitrile gave a dark brown solid. On freeze drying the solid lost iodine. m.p. 139-140°C. Found: C, 42.54; H, 2.04% $C_{21}H_{21}F_9SbIBr$ requires: C, 32.74; H, 1.61%. The solid is probably a mixture of the starting material and $C_{21}H_{12}F_9SbBr_2$.

PART III

Preparation of Tetraphenylstibonium Halides

(1) $(C_6H_5)_3SbF$ was prepared by adding an excess hydorfluoric acid (40%) to an aqueous solution of Ph_4SbOH. A white crystalline solid was formed. This was filtered, and dried in a desiccator. m.p. 153-155°C. (literature m.p. 145-160°C)[165]. Found: C, 64.07; H, 4.45% $C_{24}H_{20}SbF$ requires: C, 64.17; H, 4.49%.

(2) $(C_6H_5)_4SbCl$ was prepared by adding an excess of concentrated hydrochloric acid to a suspension of tetraphenylstibonium hydroxide in water. A clear solution was formed. The volume of the solution was reduced by boiling. On cooling it gave a white crystalline solid, this was filtered and pumped to dryness. m.p. 200-204°C (literature m.p. 200-206°C). Found: C, 61.75; H, 4.26% $C_{24}H_{20}SbCl$ requires: C, 61.91; H, 4.33%.

(3) $(C_6H_5)_4SbBr$ A mixture of triphenylstibine (10.00g, 28.323 mmol), bromobenzene (4.50 g, 28.659 mmol), and anhydrous aluminium trichloride (10.00 g, 74.985 mmol) was heated to 230°C. A black mixture was formed which was poured into water. The solution was boiled until a small black deposit remained, charcoal was added and the solution was filtered hot. Potassium bromide (20.00 g, 168.196 mmol)was added to the filtrate. White crystals of tetraphenylstibonium bromide were obtained when the solution was cooled. It was filtered and dried on the vacuum line (yield 85%).

m.p. 202-208°C (literature m.p. 200-213°C)[164]. Found: C, 56.46; H, 3.88% $C_{24}H_{20}SbBr$ requires: C, 56.51; H, 3.95%.

The compound was also prepared by adding excess HBr to a suspension of Ph_4SbOH in water. Found: C, 57.05; H, 3.93%.

(4) $\underline{(C_6H_5)_4SbI}$ was made by adding concentrated hydroiodic acid to an aqueous suspension of Ph_4SbOH until the solution was acidic. The solution was then heated and filtered. On cooling an-off white crystalline solid was formed. This was filtered off. After recrystallisation from water colourless needle-like crystals of Ph_4SbI were obtained. m.p. 209-211°C. Found: C, 51.88; H, 3.58% $C_{24}H_{20}SbI$ requires: C, 51.74; H, 3.62%.

(5) $\underline{(C_6H_5)_4SbOH}$ was obtained in excellent yield by adding ammonia solution to a hot solution of Ph_4SbBr in water. Upon cooling the solution gave a white solid. This was filtered and dried in a desiccator. m.p. 216-224°C Found: C, 64.23; H, 4.62% $C_{24}H_{21}SbO$ requires: C, 64.46; H, 4.73%.

(6) $\underline{(C_6H_5)_4SbCl_2I}$ Iodine chloride 0.1499 g, 0.9235 mmol) in acetonitrile (7.0 ml) was added dropwise with shaking to a solution of tetraphenylstibonium chloride (0.4300 g, 0.9235 mmol) in the same solvent (20 ml). A clear yellow solution was formed which gave a yellow powdery solid after freeze drying; this was pumped on the vacuum line. m.p. 116-119°C. Found: C, 46.85; H, 3.23; Cl, 11.14; I, 19.94% $C_{24}H_{20}SbCl_2I$ requires: C, 45.90; H, 3.21; Cl, 11.29; I, 20.21%.

(7) $(C_6H_5)_4SbBr_3$

Bromine (0.2775 g, 1.7363 mmol) in acetonitrile (10 ml) was added dropwise to a solution of Ph_4SbBr (0.8858 g, 1.7365 mmol) in 15 ml acetonitrile. After freeze drying the solution, an orange-yellow solid was obtained. m.p. 112-114°C. Found: C, 42.55; H, 2.93; Br, 35.65%. $C_{24}H_{20}SbBr_3$ requires: C, 43.03; H, 3.01; Br, 35.78%.

(8) $(C_6H_5)_4SbIBr_2$

Bromine (0.1300 g, 0.8134 mmol) in acetonitrile (15 ml) was added to the solid Ph_4SbI (0.45 g, 0.8100 mmol). A clear light yellow solution was formed. On freeze drying it gave an orange coloured crystalline solid. m.p. 148-150°C. Found: C, 40.16; H, 2.73; Br, 22.02; I, 17.10%. $C_{24}H_{20}SbIBr_2$ requires: C, 40.21; H, 2.81; Br, 22.29; I, 17.70%.

Experimental Data

Table 57. Conductivity of R_3AsCl_2 Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3AsCl_2$	0.001482	0.0385	0.5897	39.8
	0.01	0.10		39.8
	0.013683	0.1169	5.2272	38.2
	0.017559	0.1325	6.3013	35.9
	0.026517	0.1628	8.0701	30.4
$(3\text{-}CH_3C_6H_4)_3AsCl_2$	0.00260	0.0510	0.2570	9.9
	0.006840	0.0820	0.3964	5.9
	0.01	0.10		4.8
	0.01057	0.1028	0.4999	4.7
$(4\text{-}CH_3C_6H_4)_3AsCl_2$	0.003433	0.0586	0.3150	9.2
	0.0065205	0.0807	0.4423	6.8
	0.01	0.10		5.2
	0.01317	0.1148	0.6301	4.8
$[(CH_3)_2C_6H_3]_3AsCl_2$	0.000323	0.0180	0.3802	117.0
	0.001246	0.0353	1.2994	104.2
$.0.25CHCl_3$	0.002068	0.0469	2.2660	102.7
	0.01	0.10		91.5
$(3\text{-}FC_6H_4)_3AsCl_2$	0.000594	0.0243	0.0346	5.8
	0.004159	0.0645	0.0848	2.0
	0.010	0.10		1.2
	0.01424	0.1193	0.1484	1.0
$(4\text{-}FC_6H_4)_3AsCl_2$	0.0011284	0.0336	0.0855	7.6
	0.004867	0.0697	0.1885	3.9
	0.010	0.10		2.5
	0.020824	0.1443	0.4182	2.0
$(2\text{-}CF_3C_6H_4)_3AsCl_2$	0.0014559	0.0381	0.1790	12.3
	0.005035	0.0709	0.4259	4.8
$.0.5CHCl_3$	0.010	0.10		7.2
	0.010247	0.1012	0.6970	6.7
$(3\text{-}CF_3C_6H_4)_3AsCl_2$	0.0005431	0.0233	0.0220	4.0
	0.003234	0.0568	0.0504	1.6
	0.010	0.10		0.9
	0.01185	0.1088	0.1041	0.9
$(4\text{-}CF_3C_6H_4)_3AsCl_2$	0.00061118	0.0250	0.0151	2.4
	0.002619	0.0544	0.0270	0.9
	0.006884	0.0830	0.0400	0.6
	0.010	0.10		0.4

Table 58. Conductivity of $(FC_6H_4)_3AsCl_2$ Adducts in Nitrobenzene at 25 °C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(2\text{-}FC_6H_4)_3AsCl_2$	0.000596	0.0244	0.0139	2.3
	0.002609	0.0511	0.0584	2.2
	0.007709	0.0880	0.1811	2.3
	0.01	0.10		2.3
$(3\text{-}FC_6H_4)_3AsCl_2$	0.000848	0.0291	0.00407	0.5
	0.003818	0.0618	0.00684	0.2
	0.010	0.10		0.1
	0.015487	0.1244	0.0113	0.1
$(4\text{-}FC_6H_4)_3AsCl_2$	0.0008901	0.0298	0.0063	0.7
	0.005238	0.0724	0.0341	0.6
	0.010	0.10		0.4
	0.012196	0.1104	0.0328	0.4

Table 59. Conductivity of R_3AsBr_2 Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3AsBr_2$	0.002347	0.0484	2.8220	120.2
	0.005638	0.0751	6.3623	112.8
	0.008722	0.0934	9.5832	109.9
	0.010	0.10		108.5
$(3\text{-}CH_3C_6H_4)_3AsBr_2$	0.001281	0.0360	1.1616	90.7
	0.003805	0.0620	2.4865	65.3
	0.007238	0.0851	3.6800	50.8
	0.010	0.10		46.5
$(4\text{-}CH_3C_6H_4)_3AsBr_2$	0.003580	0.0598	2.8571	79.8
	0.006087	0.0780	4.1441	68.1
	0.006940	0.0833		61.0
	0.010	0.10		58.5
$[(CH_3)_2C_6H_3]_3AsBr_2$	0.0001795	0.0134	0.3651	203.3
	0.0004739	0.0217	0.6571	138.6
	0.0016085	0.0401	2.3834	148.0
	0.003324	0.0576	4.3809	131.8
	0.010	0.10		124.5
$(3\text{-}FC_6H_4)_3AsBr_2$	0.000829	0.0290	0.2350	28.3
	0.003190	0.0560	0.4730	14.8
	0.007370	0.0860	10.300	10.3

Table 59. (cont)

$(4\text{-}FC_6H_4)_3AsBr_2$	0.001290	0.0360	0.6060	47.0
	0.003210	0.0570	1.0630	33.1
	0.006350	0.0800	1.5610	24.6
	0.010	0.10		20.5
$(3\text{-}CF_3C_6H_4)_3AsBr_2$	0.0004247	0.0206	0.0886	20.9
	0.00338	0.0581	0.2659	7.9
	0.010	0.10		4.8
	0.01277	0.1130	0.5610	4.4
$(4\text{-}CF_3C_6H_4)_3AsBr_2$	0.0009063	0.0282	0.0630	7.8
	0.003226	0.0568	0.1377	4.3
	0.007658	0.0875	0.2160	2.8
	0.010	0.10		2.8

Table 60. Conductivity of R_3AsI_2 and R_3AsIBr Adducts in Acetonitrile at 25°C

Compound	Cm	$\sqrt{Cm}$	10^4K	Λ_m
	mol dm^{-3}	$mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$	S cm^{-1}	S cm^2 mol^{-1}
$(4\text{-}CF_3C_6H_4)_3AsI_2$	0.0003156	0.0180	0.1415	44.7
	0.001939	0.0440	0.7221	37.2
	0.009519	0.0975	3.2394	34.0
	0.010	0.10		33.5
$[(CH_3)_2C_6H_3]_3AsIBr$	0.000669	0.0191	0.3006	81.9
	0.001571	0.0396	1.2043	76.6
	0.005234	0.0723	3.6800	70.3
	0.010	0.10		66.0

Table 61. Conductivity of $R_3AsBr_nI_{6-n}$ (n = 6,5,4,3,2,1) Adducts in Acetonitrile at 25°C

Compound	Cm	$\sqrt{Cm}$	10^4K	Λ_m
	mol dm^{-3}	$mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$	S cm^{-1}	S cm^2 mol^{-1}
$[(CH_3)_2C_6H_3]_3AsBr_4$	0.000191	0.01382	0.4182	218.6
	0.000799	0.0282	1.9166	239.8
	0.001892	0.0435	3.7096	196.0
	0.010	0.10		138.0
$[(CH_3)_2C_6H_3]_3AsBr_6$	0.000307	0.0175	0.7088	230.2
	0.001414	0.0376	3.0463	215.3
	0.005088	0.0713	9.4650	186.0
	0.010	0.10		169.0

Table 61. (cont)

$[(CH_3)_2C_6H_3]_3AsBr_2I_2$	0.000252	0.0160	0.4182	165.7
	0.001578	0.0400	2.6136	165.6
	0.005299	0.0730	7.8365	147.9
	0.010	0.10		134.0
$[(CH_3)_2C_6H_3]_3AsBr_3I$	0.000413	0.0203	0.6970	168.7
	0.003334	0.0577	5.0550	151.6
	0.006516	0.0810	9.0900	139.5
	0.010	0.10		132.0
$[(CH_3)_2C_6H_3]_3AsI_4$	0.0002578	0.0112	0.0799	63.5
	0.0008175	0.0286	0.7395	90.4
	0.002662	0.0516	2.6136	98.1
	0.010	0.10		106.5
$(4\text{-}CF_3C_6H_4)_3AsI_4$	0.000779	0.0282	0.4381	56.4
	0.003466	0.0600	1.7490	50.4
	0.010551	0.1027	5.1110	48.4
	0.010	0.10		48.0

Table 62. Conductivity of R_3AsCl_3I Adducts in Acetonitrile at 25°C

Compound	Cm $mol\ dm^{-3}$	$\sqrt{Cm}$ $mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$	10^4K $S\ cm^{-1}$	Λ_m $S\ cm^2\ mol^{-1}$
$(2\text{-}CH_3C_6H_4)_3AsCl_3I$	0.001816	0.0426	2.7060	148.6
	0.006836	0.0520	3.8332	142.8
	0.003867	0.0622	5.8972	152.5
	0.010	0.10		134.0
$(3\text{-}CH_3C_6H_4)_3AsCl_3I$	0.001321	0.0363	2.3000	174.0
	0.008827	0.0940	12.6026	142.7
	0.009139	0.0956	12.7742	139.7
	0.010	0.10		139.0
$(4\text{-}CH_3C_6H_4)_3AsCl_3I$	0.002289	0.0478	3.6800	160.7
	0.00644	0.0802	10.4305	161.9
	0.01150	0.1072	16.1970	140.7
	0.010	0.10		141.0
$[(CH_3)_2C_6H_3]_3AsCl_3I$	0.0004569	0.0214	0.8646	188.2
	0.002904	0.0540	4.9997	171.8
	0.008272	0.0910	12.0736	145.9
	0.010	0.10		141.0

Table 63. Conductivity of R_3SbCl_2 Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ $mol^{\frac{1}{2}} dm^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3SbCl_2$	0.00292	0.0540	0.0044	0.15
	0.00706	0.0841	0.0058	0.08
	0.010	0.10		0.08
	0.01223	0.1106	0·0009	0.01
$(3\text{-}CH_3C_6H_4)_3SbCl_2$	0.001714	0.0414	0.0032	0.18
	0.00469	0.0685	0.00707	0.15
	0.00914	0.0956	0.0137	0.15
	0.010	0.10		0.15
$(4\text{-}CH_3C_6H_4)_3SbCl_2$	0.00211	0.0460	0.0034	0.16
	0.00468	0.0680	0.0074	0.16
	0.00755	0.0869	0.0130	0.17
	0.010	0.10		0.17
$[(CH_3)_2C_6H_3]_3SbCl_2$	0.00109	0.0331	0.0065	0.59
	0.00511	0.0715	0.0520	1.0
	0.010	0.10		0.96
	0.01035	0.1017	0.054	0.96
$(2\text{-}CF_3C_6H_4)_3SbCl_2$	0.001891	0.0435	0.0022	0.11
	0.00572	0.0756	0.0027	0.05
	0.010	0.10		0.03
	0.01092	0.1045	0.0034	0.03
$(4\text{-}CF_3C_6H_4)_3SbCl_2$	0.00205	0.0452	0.0044	0.21
	0.000559	0.0750	0.0096	0.17
	0.010	0.10		0.15
	0.01248	0.1120	0.0190	0.15

Table 64. Conductivity of R_3SbBr_2 Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ $mol^{\frac{1}{2}} dm^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3SbBr_2$	0.00279	0.0528	0.0079	0.28
	0.00539	0.0734	0.00974	0.18
	0.010	0.10		0.18
$(3\text{-}CH_3C_6H_4)_3SbBr_2$	0.00328	0.0573	0.0320	0.30
	0.00734	0.0856	0.04237	0.18
	0.010	0.10		0.15
	0.0112	0.1058	0.05025	0.14
$(4\text{-}CH_3C_6H_4)_3SbBr_2$	0.000965	0.0310	0.0135	1.39
	0.002375	0.0487	0.0144	0.60
	0.00503	0.0709	0.0209	0.41
	0.010	0.100		0.10

Table 64. (cont)

$[(CH_3)_2C_6H_3]_3SbBr_2$	0.00138	0.0371	0.0208	1.50
	0.003423	0.0585	0.0307	0.89
	0.006043	0.0777	0.0511	0.84
	0.010	0.10		0.50
$(2\text{-}CF_3C_6H_4)_3SbBr_2$	0.001198	0.0346	0.0460	0.38
	0.002682	0.0518	0.0575	0.21
	0.003702	0.0608	0.0793	0.21
	0.01	0.10		0.20
$(4\text{-}CF_3C_6H_4)_3SbBr_2$	0.001297	0.036	0.0059	0.46
	0.0034189	0.0584	0.0065	0.19
	0.0062282	0.0795	0.0075	0.12
	0.010	0.10		0.09

Table 65. Conductivity of R_3SbI_2 Adducts in Acetonitrile at 25°C

Compound	Cm	$\sqrt{Cm}$	10^4K	Λ_m
	mol dm^{-3}	$mol^{\frac{1}{2}}\,dm^{-\frac{3}{2}}$	S cm^{-1}	S cm^2 mol^{-1}
$(2\text{-}CH_3C_6H_4)_3SbI_2$	0.002675	0.0517	1.3731	51.32
	0.002812	0.0530	1.3731	48.82
	0.003676	0.0606	1.8032	49.04
	0.010	0.10		47.00
$(3\text{-}CH_3C_6H_4)_3SbI_2$	0.00330	0.0574	0.0979	2.96
	0.0057	0.0755	0.1714	3.00
	0.0103	0.1015	0.3152	3.06
	0.010	0.10		3.05
$(4\text{-}CH_3C_6H_4)_3SbI_2$	0.00083	0.0288	0.06003	7.23
	0.00234	0.0484	0.1990	8.5
	0.00383	0.0619	0.3172	8.28
	0.010	0.10		8.60
$[(CH_3)_2C_6H_3]_3SbI_2$	0.001261	0.0355	1.0042	79.63
	0.001597	0.0399	1.2920	80.90
	0.002996	0.0547	2.3000	76.77
	0.010	0.10		70.00
$(4\text{-}CF_3C_6H_4)_3SbI_2$	0.001543	0.0393	0.2555	16.56
	0.002631	0.0512	0.5050	19.20
	0.003538	0.0595	0.5860	16.53
	0.010	0.10		15.50

Table 66. Conductivity of R_3SbIBr Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(C_6H_5)_3SbIBr$	0.0049314	0.0702	0.1307	2.65
	0.010	0.10		2.20
	0.013606	0.1166	0.2893	2.13
	0.022384	0.1500	0.3108	1.39
$(2\text{-}CH_3C_6H_4)_3SbIBr$	0.0018829	0.0433	0.3710	19.70
	0.002504	0.0500	0.5225	20.84
	0.005017	0.0708	0.7682	15.30
	0.010	0.10		10.40
$(3\text{-}CH_3C_6H_4)_3SbIBr$	0.00375	0.0612	0.0514	1.37
	0.00731	0.0612	0.0811	1.00
	0.10	0.10		1.07
	0.0129	0.1136	0.1352	1.00
$(4\text{-}CH_3C_6H_4)_3SbIBr$	0.00141	0.0375	0.0531	3.76
	0.001934	0.0440	0.0684	3.53
	0.002253	0.0474	0.0920	4.08
	0.010	0.10		4.00

Table 67. Conductivity of $R_3SbBr_nI_{4-n}$ Adducts (n = 4,3,2,1and 0) in acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$(C_6H_5)_3SbI_4$	0.0023045	0.0480	1.8326	79.50
	0.0049367	0.0703	4.0350	81.70
	0.008559	0.0925	7.0334	82.17
	0.010	0.10		83.00
$(3\text{-}CH_3C_6H_4)_3SbI_4$	0.00443	0.0665	3.8560	87.04
	0.009515	0.0975	7.5280	79.12
	0.010	0.10		78.32
	0.0109	0.1044	8.5370	78.00
$[(CH_3)_2C_6H_3]_3SbI_4$	0.000704	0.0264	1.1330	161.76
	0.001428	0.0378	2.2330	156.37
	0.001849	0.0430	2.8750	155.49
	0.010	0.10		141.00
$[(CH_3)_2C_6H_3]_3SbBr_3I$	0.0005757	0.0239	0.7187	124.82
	0.0008197	0.0286	1.1057	134.88
	0.0012046	0.0347	1.5862	131.68
	0.010	0.10		106.00

Table 67. (cont)

$(4\text{-}CF_3C_6H_4)_3SbI_4$	0.001333	0.0365	0.3833	28.75
	0.0034316	0.0586	1.1300	32.93
	0.0034200	0.0585	1.0978	32.10
	0.010	0.10		29.0
$(2\text{-}CH_3C_6H_4)_2SbI_3$	0.00222	0.0471	2.3957	107.80
	0.004025	0.0634	4.2591	105.81
	0.00558	0.0747	5.6097	100.51
	0.010	0.10		97.00

Table 68. Conductivity of $Ph_3SbCl_2.SbCl_5$ and $R_3SbCl_2.2SbCl_5$ Adducts in Acetonitrile at 25°C

Compound	Cm mol dm^{-3}	$\sqrt{Cm}$ $mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$	10^4K S cm^{-1}	Λ_m S cm^2 mol^{-1}
$Ph_3SbCl_2.SbCl_5$	0.001693	0.0410	2.4340	143.80
	0.005254	0.0720	6.0680	115.50
	0.009466	0.0973	10.7980	114.10
	0.010	0.10		113.00
$(C_6H_5)_3SbCl_2.2SbCl_5$	0.001092	0.0300	2.4200	221.60
	0.0039126	0.0620	7.0600	180.40
	0.0119	0.109	11.50	96.64
	0.010	0.10		116.00
$(2\text{-}CH_3C_6H_4)_3SbCl_2.2SbCl_2$	0.00126	0.0350	2.3470	186.20
	0.001977	0.0440	5.5300	279.60
	0.004506	0.0670	8.0300	178.19
	0.010	0.10		168.00

Table 69. Conductivity of Ph_3SbX and Ph_3SbX_3 in acetonitrile at 25°C

Compound	Cm	$\sqrt{Cm}$	10^4K	Λ_m
	mol dm^{-3}	$mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$	S cm^{-1}	S cm^2 mol^{-1}
$(C_6H_5)_4SbF$	0.0005456	0.0230	0.0065	1.2
	0.002893	0.0540	0.0830	2.8
	0.007857	0.8800	1.0500	1.9
	0.010	0.10		1.8
$(C_6H_5)_4SbCl$	0.001108	0.0230	0.4340	39.2
	0.002875	0.0620	0.8720	22.5
	0.010	0.10		15.0
	0.011839	0.1080	1.5640	13.21
$(C_6H_5)_4SbBr$	0.002198	0.0460	2.4080	109.55
	0.00411	0.0640	3.8980	94.80
	0.010	0.10		70.00
	0.01346	0.1160	8.1970	60.9
$(C_6H_5)_4SbI$	0.002256	0.0470	3.4850	154.5
	0.006886	0.0830	8.9650	130.2
	0.010	0.10		119.0
	0.0113	0.1060	13.1050	115.9
$(C_6H_5)_4SbBr_3$	0.002717	0.0520	4.3390	159.6
	0.007947	0.0890	10.900	137.2
	0.010	0.10		131.0
	0.013687	0.1160	17.164	125.4
$(C_6H_5)_4SbBr_2I$	0.000927	0.0096	1.5430	166.5
	0.006756	0.0259	8.7119	128.9
	0.010	0.10		110.0
	0.01689	0.0411	20.4440	121.0
$(C_6H_5)_4SbCl_2I$	0.0009628	0.0310	1.5180	157.6
	0.002623	0.0510	3.8330	146.1
	0.007592	0.0870	9.3870	123.6
	0.010	0.10		118.0

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