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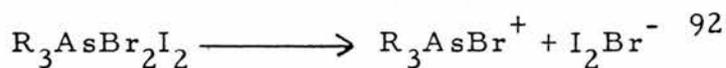
ABSTRACT

The course of the reaction of tris(2-methylphenyl)arsine $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$, tris(3-methylphenyl)arsine $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$, and tris(4-methylphenyl)arsine $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$ with the halogens bromine, iodine bromide and iodine in nitrobenzene solution were investigated by conductometric titration in order to investigate compound formation formed in these systems. 1:1 Adducts of tris(3-methylphenyl)arsine and tris(4-methylphenyl)arsine with Br_2 $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2, (4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2]$ were indicated, but with tris(2-methylphenyl)arsine there was no suggestion of a 1:1 compound. None of the three arsines gave a 1:1 adduct with IBr or I_2 . The conductometric titration results suggested that 2:1 adducts of these halogens with all three methylphenylarsines are formed in solution. All of these possible 1:1 adducts, R_3AsHal_2 ($\text{R}=2\text{-CH}_3\text{C}_6\text{H}_4, 3\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{Hal}_2=\text{Br}, \text{IBr}$ and I_2), were isolated as crystalline solids as were the 2:1 compounds, $\text{R}_3\text{AsBr}_n\text{I}_{4-n}$ ($n=4, 3, 2, 1$ and 0). The 1:1 adducts of the three methylphenylarsines with chlorine were prepared. 1:1 Adducts of fluorine with tris(4-methylphenyl)arsine and tris(2-methylphenyl)arsine were obtained by treating the corresponding arsine oxide with aqueous hydrofluoric acid.

The conductance of the 2:1 adducts ($\text{R}_3\text{AsBr}_n\text{I}_{4-n}$) and 1:1 adducts (R_3AsHal_2) have been studied in nitrobenzene solution at 25°C . All the 2:1 adducts behave as strong electrolytes. The 1:1 adducts with bromine (R_3AsBr_2) are weak electrolytes, with chlorine (R_3AsCl_2) are either very weak electrolytes or non-conducting and with fluorine (R_3AsF_2) are virtually non-conducting [with the

exception of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$]. The effect of (i) the position of the methyl group in the phenyl ring and (ii) the nature of the particular halogen in the R_3AsHal_2 compound, on the molar conductance of the molecules has been noted and is discussed in terms of possible steric effects.

The mode of ionisation of the 2:1 adducts, $\text{R}_3\text{AsBr}_n\text{I}_{4-n}$ ($n=3, 2,$ and 1), in nitrobenzene solution has been studied by a semiquantitative electrolysis technique and has been shown to parallel that found in tetrahalogeno adducts of triphenylarsine i.e. in these mixed halogen compounds the cation is always a bromoarsonium ion e.g.



The mode of ionisation of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ and $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ from a study of their reaction with the halide ion donor compound $(\text{C}_6\text{H}_5)_4\text{AsCl}$ was deduced to be

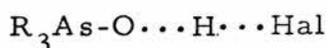


The hydrolysis products of R_3AsCl_2 and R_3AsBr_2 have been studied. Complete hydrolysis with aqueous alkali yielded the hydrated oxides, $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}\cdot\text{H}_2\text{O}$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}\cdot\text{H}_2\text{O}$. The anhydrous oxides were obtained by heating the hydrated oxides at 100°C for several hours. $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}$ was prepared by the oxidation of the corresponding arsine by potassium permanganate in acetone.

Partially hydrolysed derivatives $\text{R}_3\text{AsOHHal}$

($\text{R}=2\text{-CH}_3\text{C}_6\text{H}_4, 3\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{Hal}=\text{Cl}, \text{Br}$) were obtained by hydrolysis of R_3AsHal_2 with water. Their infrared spectra show strong broad absorption in the region $2750\text{-}2000\text{ cm}^{-1}$ which can be

assigned to the O-H group stretching vibration under conditions of strong hydrogen bonding. Their molar conductance values in nitrobenzene solution suggest that they are extremely weak electrolytes in nitrobenzene and their electrolytic conductance is independent of the nature of the aryl group. From these observations and by analogy with $\text{Ph}_3\text{AsOHHal}$ ^{121, 163} (Hal=Cl, Br) compounds it is concluded that they are simple hydrogen bonded 1:1 adduct of the tris(methylphenyl)arsine oxide with the appropriate hydrogen halide e.g.



The course of the reaction of $\text{R}_3\text{AsOHHal}$ with Br_2 , IBr and I_2 in nitrobenzene solution was investigated by conductometric titration. 1:1 Adducts of R_3AsOHBr with Br_2 and IBr and of R_3AsOHCl with ICl were indicated, thus showing formation of $[\text{R}_3\text{AsOH}]^+\text{Hal}_3^-$ ($\text{Hal}_3^- = \text{Br}_3^-, \text{IBr}_2^-$ and ICl_2^-) in nitrobenzene. Attempts to isolate all the $[\text{R}_3\text{AsOH}]^+\text{Hal}_3^-$ compounds indicated by conductometric titration gave only $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{IBr}_2^-$ and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$. In some cases compounds were obtained with mixed anions i.e. $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$, $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$, $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$, $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$. The reaction of R_3AsOHBr with mercuric bromide was studied to investigate the possibility of complex formation. This yielded $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ and $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$.

TO MY PARENTS

A STUDY OF
HALOGEN ADDUCTS OF SOME ARSINES

being a thesis

presented by

Amina Y. Mahomedy, B.Sc.(Hons), M.Sc.

to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews

April 1978



(ii)

DECLARATION

I declare that this thesis is a record of the results of my own experiments, that it is my own composition, and that it has not previously been presented in application for a higher degree.

The work was carried out in the Department of Chemistry of the University of St. Andrews under the direction of Dr. G.S. Harris.

Amina y. Mahomedy

CERTIFICATE

I hereby certify that Miss Amina Y. Mahomedy has spent eleven terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967, No. 1 and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

G. S. Harris.

Research Supervisor

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I sincerely thank Dr. G.S. Harris for providing this topic of research and for his guidance and constant encouragement throughout this work.

I am indebted to Professor Lord Tedder for providing me with an opportunity to work with Dr. Harris and the award of a maintenance grant from the University of St. Andrews.

I would like to thank Mr. J.S. McKechnie for his valuable help, Mr. James Bews and Mrs Syliva Smith for readily and efficiently performed analysis, Mr. N.G. West for making some special glass apparatus used in this work, the librarian Mrs. S. Johnson and other Departmental Colleagues for their friendly assistance, and Mrs. Wilma Pogorzelec for carefully typing this thesis.

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ABBREVIATIONS

Abbreviations used in this thesis are as follows:

\AA	=	Angstrom Unit, 10^{-8} cm
ϵ	=	dielectric constant
ir	=	infrared
ν	=	frequency cm^{-1}
K	=	specific conductance
C_m	=	molar concentration
Λ_m	=	molar conductance
nmr	=	nuclear magnetic resonance
nqr	=	nuclear quadrupole resonance
uv	=	ultraviolet
λ	=	wavelength
$m\mu$	=	millimicron = 10\AA

NOTE ON NOMENCLATURE

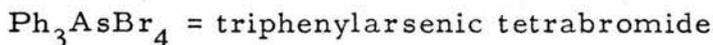
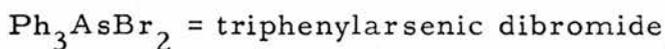
1:1 Adducts of type R_3AsHal_2 —

These are described as derivatives of the hypothetical compound arsorane (AsH_5) on the assumption that the compounds are covalent, molecular. Thus for example, $(2-CH_3C_6H_4)_3AsCl_2$ is named dichlorotris(2-methylphenyl)arsorane.

Similarly in the case of the analogous phosphorus compound the parent compound is phosphorane (PH_5). In keeping with the practice used in Chemical Abstracts the corresponding compounds of antimony and bismuth are described as derivatives of the metal eg. $(C_6H_5)_3SbCl_2$ as dichlorotriphenylantimony.

2:1 Adducts of type R_3AsHal_4 —

In general these are arsonium compounds and are so named. For example $(C_6H_5)_3AsBr_4$ is $(C_6H_5)_3AsBr^+Br_3^-$ and is called bromotriphenylarsonium tribromide. In some cases when the nature of the adduct is not known but only its stoichiometry, the older nomenclature is reverted to eg.



In these cases the names used merely indicates the analytical composition of the compound.

FOREWORD

Organometallic chemistry lies on the boundaries of organic and inorganic chemistry and thus serves both to fuse the subjects together and break down the traditional barriers between the two fields. It has become a very important part of the armoury of the industrial chemist and has received further recognition through the award in 1973 of the Nobel Prize for Chemistry to two of the leading organometallic chemists, namely G. Wilkinson and E.O. Fischer.

The study of the organic compounds of the Group VB elements phosphorus, arsenic, antimony and bismuth was started towards the end of the nineteenth century by Michaelis who set up three schools of chemistry at Karlsruhe, Aachen and Rostock to study these compounds. His synthetic contribution to this field was most extensive.

Whilst research into this field up to the beginning of this century was largely academic thereafter organoarsenic compounds drew more attention because of their possible value as chemotherapeutic agents. P. Ehrlich investigated the biological effect of over six hundred organoarsenic compounds and in 1909 was successful in synthesising two compounds which were effective remedies for syphilis. These compounds were salvarsan and its sodium methylene sulphinate derivative known as neosalvarsan. They were widely used in chemotherapy for many years before being superseded by antibiotics.

Organoarsenic compounds were introduced as chemical warfare agents during the 1914-18 war. They were directed towards the skin, eyes and respiratory organs. As a result of advances in the modern technique of war, the potential of organo-arsenicals as chemical warfare agents has been reduced, and the increasing use of antibiotics in medicine has shifted the value of organoarsenic compounds from the predominantly medicinal application as germicides to agricultural uses of pesticides.

PART I

REACTION OF TRIS(METHYLPHENYL)ARSINE WITH HALOGENS

INTRODUCTION

INTRODUCTION

The elements of the Phosphorus Group - phosphorus, arsenic, antimony and bismuth - react with halogens to give trihalogeno and pentahalogeno compounds. Nitrogen, whilst having a certain similarity to the Phosphorus Group elements, arising from their ability to form a simple octet leading to tervalency, has substantial differences because of its inability to make use of orbitals beyond the 2s and 2p levels. The extent to which elements of the Phosphorus Group utilise d orbitals for bonding varies markedly, both with the element and with the nature of the atom or group involved in bond formation; it is most marked in the case of the 3d orbitals of phosphorus and least obvious in the case of the 6d orbitals of bismuth.

The Trihalides MHal₃

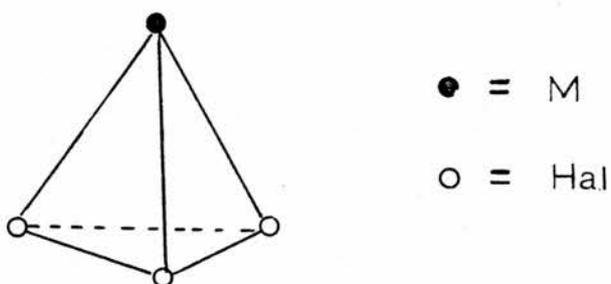
(M = P, As, Sb and Bi; Hal = F, Cl, Br and I)

All of the simple trihalogeno derivatives of the Phosphorus Group elements have been isolated and characterised. The number of possible mixed trihalides is large, but so far only a few have been prepared, some of which can be isolated, while others can be detected only by spectroscopic techniques; Raman, infrared and ³¹P nmr. The mixed trihalides which have been isolated and whose individual properties have been reorganised are PF₂Cl^{1, 2a}, PFCl₂^{1, 2a}, PF₂Br^{2b}, PFBr₂^{2b} and SbBrI₂³.

Other mixed trihalides have been identified in the course of nuclear magnetic resonance studies by Van Wazer and co-workers⁴. They identified PCl_2Br and PClBr_2 when mixtures of PBr_3 - PCl_3 were allowed to reorganise at room temperature. Similarly with the PBr_3 - PI_3 system there is evidence for the formation of PBr_2I and PBrI_2 in an equilibrium mixture⁵. There is also Raman spectral evidence for the formation of a chlorobromofluoride of phosphorus PFClBr , when PFCl_2 and PFBr_2 are mixed⁴. However none of these compounds have been isolated.

No mixed trihalides of arsenic have so far been prepared but like phosphorus there is physical evidence, using techniques such as nmr, for the formation of AsFCl_2 and AsF_2Cl in exchange equilibria set up by AsF_3 and AsCl_3 mixtures. Compared to phosphorus, little work has been done on mixed trihalides of As, Sb and Bi. The compound SbBrI_2 reported by Clark³ is the only mixed halide of trivalent antimony to be described. It exists as a yellow crystalline solid and is moderately stable in air. The trihalides of the Phosphorus Group elements are structurally simple, all being triangular pyramid molecules, similar to ammonia.

Figure 1. Triangular pyramid structure of MHal_3



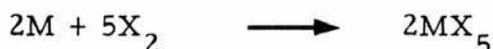
The Pentahalides MHA₅

While all the trihalides of P, As, Sb and Bi are known, the same cannot be said for simple pentahalides. Those which have been isolated and whose individual properties have been studied are shown in Table 1.

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

Phosphorus	Arsenic	Antimony	Bismuth
PF ₅	AsF ₅	SbF ₅	BiF ₅
PCl ₅	AsCl ₅	SbCl ₅	
PBr ₅			

The simple pentachloro and -bromo derivatives of the Phosphorus Group elements can be prepared by direct reaction of an excess of the halogen with the element e. g.

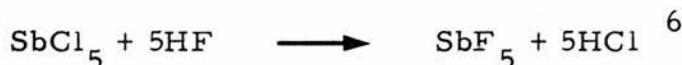


(M = P, As, Sb and Bi; X = Cl, Br)

The pentafluoro derivatives can be conveniently prepared by the fluorination of the pentachloro derivatives with arsenic trifluoride e. g.



Pentafluoroantimony has been obtained by the action of hydrogen fluoride on pentachloroantimony at 30°, e. g.



BiF₅ was prepared by Von Wartenberg⁷ by fluorination of bismuth trifluoride at 550°C. Fischer and Rudzitis⁸ prepared BiF₅ by synthesis from bismuth and fluorine at 500°C.

The phase diagram⁹ of the system arsenic trichloride-chlorine has shown no evidence for the formation of pentachloroarsorane.

However, this does not preclude the formation of metastable pentachloroarsorane in the solid state, or the formation of pentachloroarsorane in solution - for example as $\text{AsCl}_4^+ \text{AsCl}_6^-$ (both of these ions being well established)¹⁰. Condensation of arsenic trichloride and chlorine¹¹ after passage through a microwave discharge showed only the constituents to be present. The Raman spectra of solutions of arsenic chloride and chlorine at -50° in methyl cyanide did not show the presence of any new species¹¹.

Attempts¹² to prepare AsCl_5 by the interaction of AsCl_3 and chlorine in a sealed tube, at low temperature were not successful. The Raman spectrum of the solid is a superposition of the vibrational spectra of AsCl_3 and chlorine.

Recently, the preparation of pentachloroarsorane and determination of its molecular structure has been reported by K. Seppelt¹³. He isolated AsCl_5 by the irradiation of a solution of AsCl_3 in chlorine with uv light at -105° . The compound was characterised by chemical analysis and comparison of its Raman spectrum with those of PCl_5 and SbCl_5 . AsCl_5 is a soft yellow solid, which melts with partial decomposition at -50° . The Raman spectrum also indicates that AsCl_5 has a trigonal bipyramidal structure both in liquid and solid state. The difference in stability of PCl_5 and AsCl_5 lies not in As-Cl and P-Cl bond strengths but in the difference in ionisation energies in the 1st step of the chlorination reaction, which suffices to make the reaction of AsCl_3 with chlorine endothermic (the ionisation energy of AsCl_3 is $114.95 \text{ kJ mol}^{-1}$).

Pentaiodophosphorane has not been isolated nor is there evidence for its existence. This has been explained in terms of the incompatibility of the 3d orbitals of the phosphorus atom with the 7s, 7p and 7d-orbitals of the iodine atom^{14,31}. While pentafluoro and pentachloro derivatives of antimony are well known, measurement of vapour pressure in the system $\text{SbBr}_3\text{-Br}_2$ has given no evidence for the existence of SbBr_5 ¹⁵.

The possible number of pentahalides of Phosphorus Group elements which might be obtained allowing for simple and mixed fluorides, chlorides, bromides and iodides of phosphorus, arsenic, antimony and bismuth is well over 150, only about a tenth having so far been recognised. The mixed pentahalides of the Phosphorus Group elements which have been isolated and characterised are shown in Table 2.

Table 2. Mixed Pentahalides of Phosphorus Group Elements

Phosphorus	Arsenic	Antimony	Bismuth
PF_4Cl ¹⁶	AsF_3Cl_2 ²³	SbF_3Cl_2 ²⁴	
PF_3Cl_2 ^{17,18}		SbF_2Cl_3 ²⁵	
PF_2Cl_3 ^{19,20}		SbFCl_4 ²⁶	
PFCl_4 ^{19,20}		SbBr_2F_3 ²⁴	
PF_3Br_2 ²¹			
PF_2Br_3 ⁷⁸			
PFBr_4 ²²			

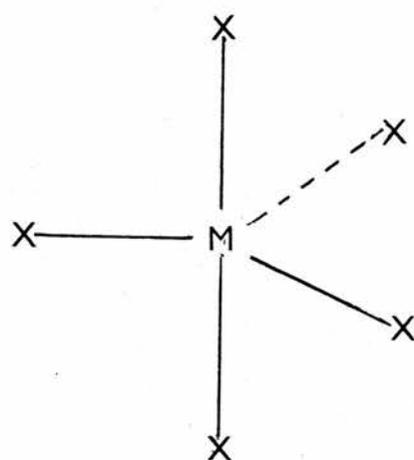
The mixed pentahalides are prepared by the addition of halogen to the appropriate trihalide, e.g.



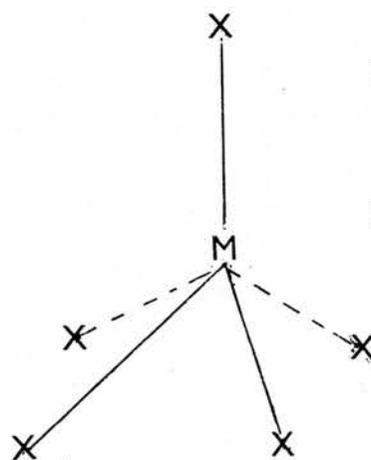
As one can see from Table 2 phosphorus dominates the series yet even here only the fluorochlorohalides can be said to be well known. In the case of arsenic AsF_3Cl_2 appears to be the only substantiated mixed pentahalide. In the case of antimony SbFCl_4 ²⁶ and SbF_3Cl_2 ²⁸ are well established. In an investigation by Van Wazer and Aubrey²⁹ found that in liquid phase mixture of SbCl_5 and SbF_5 simple mixed halogen species of type $\text{SbF}_n\text{Cl}_{5-n}$ were not present but it appears that these simple species polymerise and form ions (e. g. $\text{Cl}_4\text{SbFSbCl}_4^+$). No mixed pentahalides of bismuth have been reported.

The most favourable structure for a pentavalent molecule in which five atoms or groups are bonded to a central atom is either the trigonal bipyramidal (D_{3h}) involving Sp^3d_z^2 hybridisation, or the square pyramidal (C_{4v}) unit involving $\text{Sp}^3\text{d}_{x^2-y^2}$ hybridisation (figure 2).

Figure 2. The two possible configurations for MHal_5



(a) Trigonal bipyramidal



(b) Tetragonal pyramid

$\text{M} = \text{P}, \text{As},$
 $\text{Sb}, \text{Bi};$
 $\text{X} = \text{Hal}.$

The basic trigonal bipyramidal framework is now well established, as being the normal ground state configuration of five coordinated Phosphorus Group elements³⁰. All recent investigations, based on spectroscopy (nmr, ir, Raman, nqr), x-ray and electron diffraction methods, confirm this. There is no evidence for the adoption of the square pyramidal structure by any covalent $MHal_5$ compound.

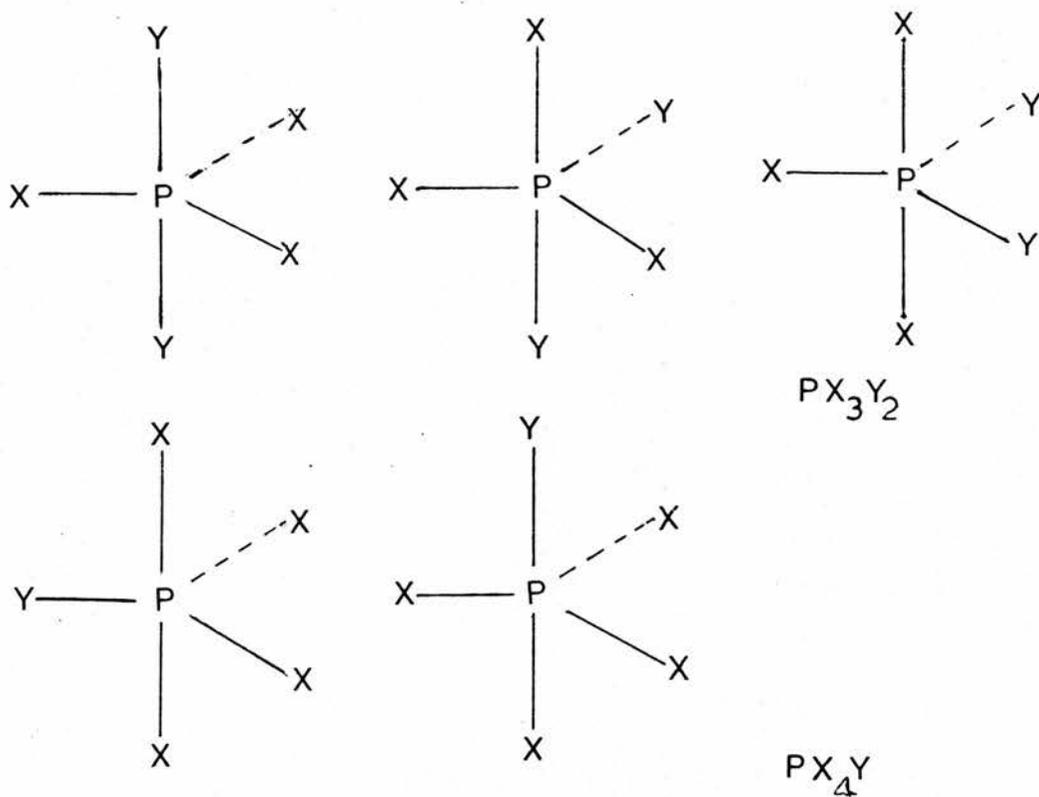
(M = P, As, Sb and Bi; Hal = F, Cl, Br and I).

Many of the pentahalides of the Phosphorus Group elements have phase dependent structures³¹ which illustrate the more characteristic coordination numbers 4 and 6 of M rather than 5 as suggested by their stoichiometry. In phases which favour ion formation they adopt ionic structures $[MHal_4^+][MHal_6^-]$ e.g. PCl_5 in the solid state³⁵. It is mostly in phases which do not favour ion formation that the simple trigonal bipyramidal molecules are found, e.g. $PF_{5(g),(l)}$ ³⁸; $PCl_{5(g),(l)}$ ³²⁻³⁴; $AsF_{5(g),(l)}$ ^{39,40}; $SbF_{5(g)}$; $SbCl_{5(g),(s)}$ ³². PBr_5 , in the solid state, has the ionic structure $[PBr_4^+][Br^-]$ ^{36,37}. X-Ray structure analysis of AsF_2Cl_3 ²³ has shown it to be isomorphous with PCl_5 and it consists of $[AsCl_4^+]$ cations and $[AsF_4Cl_2^-]$ anions. Pentachlorophosphorane is found to be ionic in polar solvents, the ions are $[PCl_4^+]$ and $[PCl_6^-]$ and is molecular in nonpolar solvents. Payne⁴¹ has shown, by transport number and electrolytic conductance measurements, that in methyl cyanide and nitrobenzene, ionised PCl_5 molecules are in equilibrium with PCl_4^+ and PCl_6^- ions. This equilibrium was further supported by the results obtained from conductance and spectral studies of PCl_5 in methyl cyanide⁴².

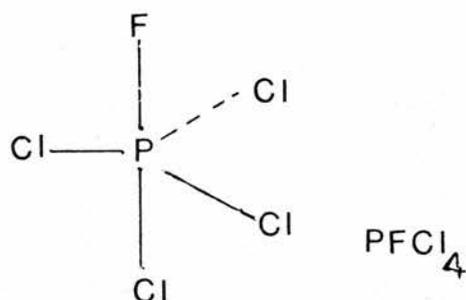
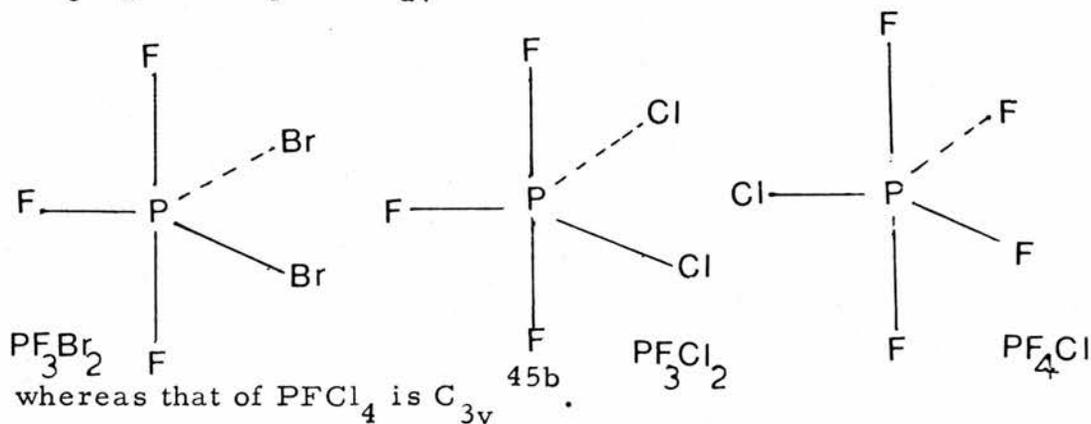
It can be seen that reference to a specific pentahalide of the Phosphorus Group elements is in many cases only a reference to its stoichiometric composition and in no way reflects the structural state of the compound concerned.

Isomerism in Pentacovalent Molecules

In the case of mixed pentahalogeno derivatives of the formula $\text{MX}_n\text{Y}_{5-n}$ ($M = \text{P, As, Sb and Bi}$; X and Y are different halogens F, Cl, Br and I) which are known, there is the possibility of geometrical isomerism in their covalent molecules because of the nonequivalence of axial and equatorial positions in the trigonal bipyramid. Pentahalogenophosphoranes⁴³, of the formula PX_3Y_2 have three possible geometrical isomers and there are two possible isomers for PX_4Y_1 compounds:

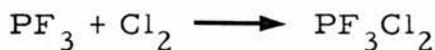


Vibrational spectra indicate that the symmetry of PF_3Br_2 , PF_3Cl_2 and PF_4Cl is C_{2v} ^{44, 45a} e. g.



Without exception all such structures so far determined lead to the empirical rule that the axial positions are occupied by the most electronegative ligands^{46a, 30}.

These mixed pentahalogeno derivatives $\text{PX}_n\text{Y}_{5-n}$ also show ionic-covalent isomerism of the type shown by simple 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 reaction

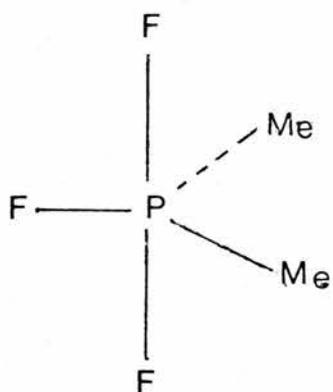
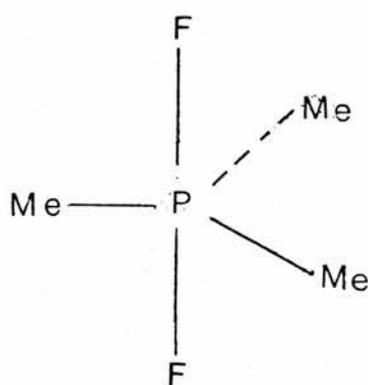


The isomeric salt type compound has the structure

$[\text{PCl}_4^+][\text{PF}_6^-]$ and can be prepared quantitatively by the action of arsenic trifluoride on pentachlorophosphorane in arsenic trichloride^{47, 48}. Unlike the gaseous molecular compound, PF_3Cl_2 , this isomer is a white solid which sublimes at 135° , and is sparingly soluble in arsenic trichloride. The conductivity of molecular PF_3Cl_2 in methyl cyanide is small¹⁶, whereas that of $[\text{PCl}_4^+][\text{PF}_6^-]$ is

relatively high⁴⁸. When sublimed the compound $[\text{PCl}_4^+][\text{PF}_6^-]$ changes to the gaseous covalent compounds PF_5 and PCl_4F ⁴⁹. PCl_4F is not stable over long periods and is transformed quantitatively into a white product of the same composition, $[\text{PCl}_4]^+\text{F}^-$. The ionic nature of this isomer is shown by its solubility and conductivity in methyl cyanide⁴⁹.

Organosubstituted pentahalogeno compounds $\text{R}_n\text{PX}_{5-n}$ (where $n = 1-4$) have similar structural problems and have been the subject of the same kinds of investigations. The fluoromethylphosphoranes, Me_2PF_3 and Me_3PF_2 , have a trigonal bipyramidal framework and the spectra according to Downs and Schmutzler⁴⁷, are best interpreted in terms of C_{2v} and D_{3h} structures respectively:

 Me_2PF_3  Me_3PF_2

In each of these, fluorine atoms occupy the axial sites of the trigonal bipyramidal molecule. In CH_3PF_4 the methyl group occupies an equatorial position of the trigonal bipyramid⁵⁰. Likewise, for $(\text{CF}_3)_2\text{PCl}_3$ and CF_3PCl_4 it is deduced from infrared and Raman data that CF_3 groups occupy axial sites^{51, 52}. The CF_3 group has an electronegativity between that of fluorine and chlorine.

Spectroscopic studies of the substituted compounds PMe_4Cl , PMe_3Cl_2 , PMe_2Cl_3 , PMeCl_4 , PEt_2Cl_3 , PEt_2Br_3 and PMe_3FCl , suggest that the compounds exist as phosphonium salts of the type $[\text{PR}_n\text{Hal}_{4-n}]^+\text{Hal}^-$ ⁵³. Solution spectra of PMeCl_4 show however that in nonionising media the compound is molecular, possibly with C_{2v} symmetry⁵⁴.

Organo-substituted Pentahalogeno Derivatives of Phosphorus Group

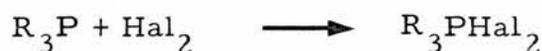
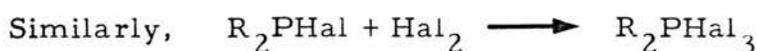
Elements $\text{R}_n\text{MHal}_{5-n}$ (where M = P, As, Sb and Bi;

R = alkyl, aryl;

Hal = F, Cl, Br, I;

n = 1-5).

Substitution of one or more halogen atom in MHal_5 by an organic group can be readily achieved by standard procedures. It is usual for an organic group to be introduced at first to a M(III) compound which is then further reacted with halogen,



Typical compounds which have been prepared in this way are $\text{C}_2\text{H}_5\text{PCl}_4$ ⁵⁵, $(\text{C}_6\text{H}_5)_2\text{PCl}_3$ ⁵⁶, and $(\text{C}_6\text{H}_5)_3\text{PCl}_2$ ⁵⁷. Thus the series RMHal_4 , R_2MHal_3 , R_3MHal_2 , R_4MHal , and R_5M can be obtained.

R_5M Compounds

Known compounds of the fully substituted type are pentaphenyl derivatives⁵⁸, and some pentaalkenyls⁵⁹.

Pentaphenylphosphorane is a molecular substance which like the pentahalogeno derivatives, adopts a trigonal bipyramidal structure in which the axial bonds are slightly longer than the equatorial (1.987 \AA and 1.8506 \AA respectively)⁶⁰. It is of considerable interest to note that although pentaphenylarsorane is isomorphous with Ph_5P ⁶¹, Wheatley has shown that the pentaphenyl-antimony molecule adopts the geometry of a tetragonal pyramid⁶², (figure 2b).

This seems to be the only well established example of this stereochemistry in a five coordinate compound of the Phosphorus Group elements, although theory predicts that the stability of the two geometries is comparable⁶³.

A study⁶⁴ of their vibrational spectra indicated that Ph_5Sb and Ph_5As are respectively square pyramidal and trigonal bipyramidal in solution in dichloromethane and dibromomethane respectively. Kok⁶⁵ reinvestigated the structures of Ph_5As and Ph_5Sb by laser-Raman and infrared spectra in the solid state and in solution. Structural conclusions for these molecules based on an analysis of the phenyl-metal vibrations, show that pentaphenyl-antimony and pentaphenylarsorane retain their solid state geometries in solution.

Recently, Brock and Ibers⁶⁶ investigated the structure of Ph_5Sb by x-ray crystal structure analysis. Calculations of intramolar forces have shown that square pyramidal is the favoured structure for Ph_5Sb but on taking intramolar interactions into account the calculations favoured the trigonal bipyramidal structure.

However in these latter calculations coulombic interactions were ignored and this may account for the discrepancy.

Spectroscopic studies of $(\text{CH}_3)_5\text{As}$ ⁶⁷ and $\text{R}_n\text{As}(\text{OMe})_{5-n}$ ⁶⁸ compounds are interpreted in terms of a trigonal bipyramidal structure.

The crystal structure of methoxytetraphenyl and dimethoxytriphenylantimony was studied by x-ray diffraction⁶⁹. The molecular structure of $(\text{OCH}_3)(\text{C}_6\text{H}_5)_4\text{Sb}$ is trigonal bipyramidal with the oxygen atom and a carbon atom of one benzene ring occupying the apical positions. The Sb-O bond distance is $2.061(7)\text{\AA}$. The apical Sb-C bond distance of $2.199(14)\text{\AA}$ is significantly larger than the equatorial Sb-C distances of $2.131(11)$, $2.128(13)$, and $2.097(15)\text{\AA}$. These results are in agreement with the generally accepted rule that the more electronegative substituents always occupy the apical position and that this bond distance is always greater than the equatorial one. The molecular structure of dimethoxytriphenylantimony is also trigonal bipyramidal with two oxygen atoms occupying the apical positions and the benzene ring carbon atoms in the basal plane. The bond distance Sb-O apical and Sb-C equatorial are in agreement with those expected for trigonal bipyramidal structure.

R_4MHal Compounds

A large number of quaternary substituted compounds R_4MHal are known for phosphorus, arsenic and antimony. They tend to be high melting, crystalline solids, soluble in polar solvents in which they give highly conducting solutions, suggesting therefore that they

are ionic both in the solid state and in solution. A crystal structure analysis of Ph_4PI ⁷⁰ has shown that the structure is built from Ph_4P^+ and I^- ions. Indeed, there is no evidence to be found in the literature of any R_4MHal type of compound exhibiting a covalent structure.

In sharp contrast to the R_4MHal type of compounds which are ionic, tetraphenylstibonium hydroxide Ph_4SbOH has been shown by means of x-ray diffraction analysis⁷¹ to be a covalent compound with trigonal bipyramidal geometry. The oxygen atom occupies the apical position, and the axial C-Sb distance is significantly longer than the mean equatorial C-Sb distance. The results are consistent with the generally accepted rule that the more electronegative substituents occupy apical positions and that the axial bond lengths are greater than the equatorial ones.

RMHal_4 and R_2MHal_3 Compounds

Discussion of the intermediate members of the series $\text{R}_n\text{MHal}_{5-n}$ ($n = 1$ and 2) is not clear cut and conflicting viewpoints have been put forward concerning their nature. For the RMHal_4 and R_2MHal_3 compounds, low melting points and ease of solubility in non-polar solvents led Rochow et al^{72a} to deduce that they are molecular. On the other hand, Van Wazer⁷³, by analogy with the pentahalogeno derivatives of P, suggests the ionic structure $[\text{RPHal}_3]^+\text{Hal}^-$, for the RPHal_4 type of compounds. Kosolapoff⁷⁴ agrees with Van Wazer's view that one of the halogen atoms is in

the ionic state. This view is further supported by the behaviour of certain $RPHal_4$ derivatives (e. g. $PhPBr_4$, $PhPBr_2Cl_2$) which add another molecule of halogen to form compounds of the type $RPHal_6$ ^{75,76}, analogous to those formed between the ionic quaternary salts and the halogens. Similarly R_2PHal_3 ($R = C_2H_5$, C_3H_7) reacts with halogens to form R_2PHal_5 , which have been shown to give conducting solutions in polar solvents indicating a dihalogenophosphonium salt type of structure $(R_2PHal_2^+Hal_3^-)$ for these compounds⁷⁷.

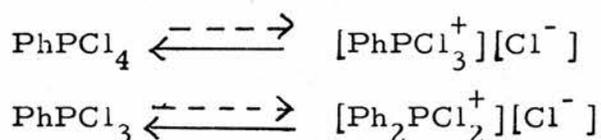
There now appears to be fairly firm evidence for both ionic and covalent forms in the $RMHal_4$ and R_2MHal_3 group of compounds. ¹⁹F nmr investigation of a considerable number of fluorophosphoranes (e. g. RPF_4 ; $R = CH_3$, C_2H_5 , $n-C_4H_9$, C_6H_5) and a few of the analogous arsenic and antimony compounds suggest trigonal bipyramidal structure for these compounds^{78,79}. The structures of gaseous CH_3PF_4 and $(CH_3)_2PF_3$ have been determined by electron diffraction⁸⁰ and that of crystalline Ph_2SbCl_3 by x-ray diffraction⁸¹ with the same results.

However, McPherson⁸² has carried out some careful conducting measurements on the systems $Ph_2PCl-Cl_2$ and $PhPCl_2-Cl_2$ in methyl cyanide, and has found that values of molar conductance are low at compositions corresponding to Ph_2PCl_3 and $PhPCl_4$:

$$PhPCl_4, \Lambda_m = 16.88 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; C_m = 0.02884 \text{ mol l}^{-1}.$$

$$Ph_2PCl_3, \Lambda_m = 2.54 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; C_m = 0.02310 \text{ mol l}^{-1}.$$

$PhPCl_4$ and Ph_2PCl_3 can therefore be regarded as weak electrolytes in methyl cyanide thus;

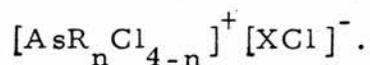


That is the covalent compound undergoes partial ionisation under the influence of the solvents of high dielectric constant.

Recently⁸³, ³⁵Cl nuclear quadrupole resonance spectroscopy and ³¹P nuclear magnetic resonance spectroscopy have played an important role in determining the solid state structure of $\text{PR}_n\text{X}_{5-n}$ compounds ($1 \leq n \leq 3$) ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$ or C_6H_5 ; $\text{X}=\text{Cl}$). Whitehead and co-workers^{84, 85} from their ³⁵Cl nqr results, concluded that (solid) PPhCl_4 and PPh_2Cl_3 possess ionic structures $[\text{PPh}_n\text{Cl}_{4-n}]^+\text{Cl}^-$. Svergun et al⁸⁶ further studied the ³⁵Cl nqr spectra of PPhCl_4 and PPh_2Cl_3 and in contrast found them to be molecular trigonal bipyramidal, with the phenyl groups occupying equatorial. Waddington et al⁸³ re-examined the ³⁵Cl nqr spectra of PPhCl_4 and PPh_2Cl_3 and their conclusions about the structures of these compounds are in complete accordance with those of Svergun et al⁸⁶ and McPherson⁸². Waddington et al⁸³ further studied ³¹P nmr and ³⁵Cl nqr spectra of a number of compounds $\text{PMe}_n\text{Cl}_{5-n}$ ($1 \leq n \leq 3$), PEt_2Cl_3 and PEt_3Cl_2 and PPh_3Cl_2 and deduced that they had ionic structures of the type $[\text{PR}_n\text{Cl}_{4-n}]^+\text{Cl}^-$ in the solid state and these conclusions were supported by spectral data for their 1:1 adducts with strong Lewis acids such as PCl_5 , SbCl_5 , BCl_3 , AlCl_3 or ICl , which have the structure $[\text{PR}_n\text{Cl}_{4-n}]^+[\text{XCl}]^-$ (where X = the Lewis acid molecule). These results are in agreement with the previous vibrational spectroscopic studies of PMeCl_4 ^{53, 54}, PMe_2Cl_3 ⁵³, and PMe_3Cl_2 ⁸⁷ which showed that these compounds

have ionic structures in the solid state, although a molecular structure for PMeCl_4 is possible in solution⁵⁴.

A ^{35}Cl nqr study⁸⁸ of the compounds AsPhCl_4 , AsPh_2Cl_3 and AsPh_3Cl_2 indicated that they have trigonal bipyramidal structure in the solid state, with the phenyl groups occupying equatorial positions. The ^{35}Cl nqr frequencies for AsPhCl_4 and AsPh_2Cl_3 are indeed directly proportional to those for PPhCl_4 and PPh_2Cl_3 suggesting that these compounds may be isostructural with strong similarities in bonding. Trichlorodimethylarsorane and dichlorotrimethylarsorane also have the trigonal bipyramidal form in the solid, with the methyl groups occupying equatorial sites. They thus differ from their phosphorus analogues, which are ionic. 1:1 adducts of the As (V) compounds with Lewis acids, X, such as BCl_3 , SbCl_5 or ICl have been prepared; these showed the expected structure

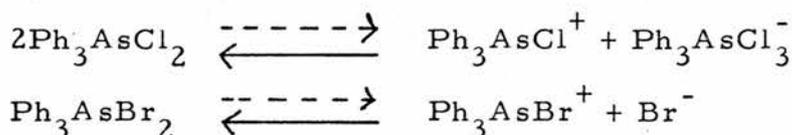


R_3MHal_2 compounds

The structure of the derivatives R_3MHal_2 has been discussed from time to time by various authors^{89, 90, 72a}. In particular, Harris and co-workers⁹¹⁻⁹³ have made an extensive study of halogen adducts of the triaryl derivatives of the Phosphorus Group elements. They have shown from their conductance studies in methyl cyanide solutions that the dihalogenotriphenylphosphoranes are strong electrolytes and the dihalogenotriphenylantimony and bismuth (V) are non-electrolytes and have suggested that the solids are respectively ionic and covalent. Dihalogenotriarylarso-

on the other hand, are weak electrolytes and therefore probably covalent in the solid state. From these results they have concluded that covalent tendency increases down the periodic group i.e. $P \rightarrow As \rightarrow Sb \rightarrow Bi$.

The ions present in these conducting solutions of Ph_3AsHal_2 and Ph_3PHal_2 have been the subject of some study. From the measurement of ion transport numbers of their solutions in methyl cyanide, Harris et al⁹² have concluded that Ph_3AsCl_2 and Ph_3AsBr_2 ionise as follows:



That is, different modes of ionisation are adopted by the chloride and bromide; this behaviour is reminiscent of that of pentachlorophosphorane



and pentabromophosphorane

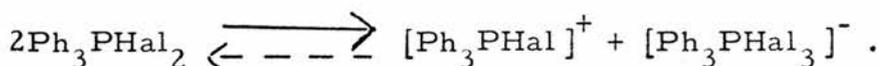


in the same solvent^{94, 41}.

However, in contrast to the results of the transport number experiments it has been shown by a ^{31}P nmr study⁹⁵ and from their reactions with the strong chlorine ion donor, tetraethylammonium chloride⁹⁶, that the dihalogenotriphenylphosphoranes ionise completely in methyl cyanide in the sense;

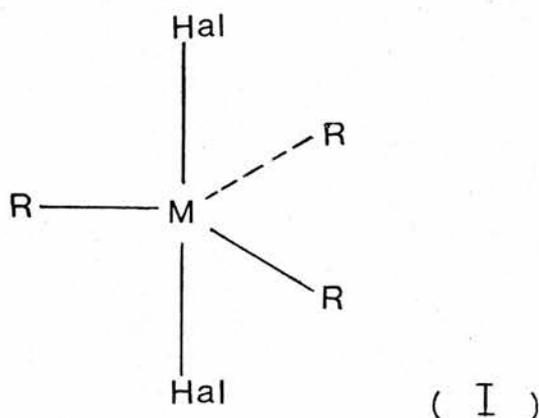


and there is no evidence for the alternative



The existence of the halogenotriorganophosphonium cation, $[R_3PHal]^+$, in the pentavalent R_3PHal_2 compounds (R=Et, Pr, Bu, iso-amyl, cyclohexyl or Ph) has also been inferred from their solubility behaviour, their high decomposition temperature and the electrical conductivities of their nitrobenzene solutions⁹⁷. Some addition compounds of R_3PHal_2 compounds with metal halides, $MHal_n$ [e.g. M = Sb (V), Sb (III), Hg (II)], have been prepared and they too would appear to be derived from a phosphonium-type structure, $[R_3PHal]^+ [MHal_{n+1}]^-$; they have high melting points, are insoluble in nonpolar solvents, and their nitrobenzene solutions are good electrolyte conductors.¹⁹⁴

The dihalogenotrimethylphosphoranes have been the subject of spectroscopic studies from which it has been shown that in the solid state ionic structure of the type $[Me_3PHal]^+ Hal^-$ are adopted⁸⁷. In contrast with this, dihalogeno derivatives of trimethyl-, triethyl-, and triphenylantimony would seem to have D_{3h} symmetry indicating the trigonal bipyramidal structure I⁹⁸⁻¹⁰⁰.



This latter geometry has in fact been established by x-ray crystal structure analysis for $(CH_3)_3SbHal_2$ (Hal=Cl, Br, I)¹⁰¹,

$(\text{ClCH:CH})_3\text{SbCl}_2$ ¹⁰², Ph_3SbCl_2 ¹⁰³ and Ph_3BiCl_2 ^{104, 105}.

Dichlorotriphenylarsorane may well have a similar structure as its dipole moment in benzene solution is zero¹⁰⁶. Recently, a ³⁵Cl nqr study⁸⁸ of Ph_3AsCl_2 has shown that it has trigonal bipyramidal structure in the solid state with the phenyl groups occupying equatorial positions.

Brill and Long¹⁰⁷ have studied the nuclear quadrupole resonance spectra of the compounds R_3MHal_2 ($\text{R}=\text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2, \text{C}_6\text{H}_5$; $\text{Hal}=\text{F}, \text{Cl}, \text{and Br}$; $\text{M}=\text{As}, \text{Sb and Bi}$). They have found all the compounds except one $(\text{CH}_3)_3\text{AsBr}_2$ to have trigonal bipyramidal geometry in the solid state with idealised D_{3h} symmetry. They suggested that $(\text{CH}_3)_3\text{AsBr}_2$ may be ionic - $[(\text{CH}_3)_3\text{AsBr}]^+\text{Br}^-$ - and this has been confirmed by an x-ray crystal study by Hursthouse and Steer¹⁰⁸.

From molecular weight, conductance measurement, and infrared data¹⁰⁹, dihalogenotriphenylbismuth compounds were reported to have nonionic molecular constitution. The ir and Raman spectra of Ph_3BiX_2 compounds¹¹⁰ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{NCO}$) in the solid and in benzene solution were recorded at $< 700 \text{ cm}^{-1}$. The results are consistent with a trigonal bipyramidal skeleton in both physical states. ³¹P nmr studies of Ph_3PBr_2 ¹¹¹ in the solid and in solution ($\text{C}_6\text{H}_5\text{NO}_2$) have shown it to be ionic $[\text{Ph}_3\text{PBr}]^+\text{Br}^-$, and for solid Ph_3PI_2 the structure is $[\text{Ph}_3\text{PI}]^+\text{I}^-$, with a 4-coordinated P atom.

Spectroscopic studies of $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{MX}_2$ ¹¹² ($\text{M}=\text{As}, \text{Sb and X}=\text{F}, \text{Cl}$) have given results in accordance with a slightly distorted

trigonal bipyramidal geometry in the solid state; this is consistent with the results of ^{35}Cl nqr spectroscopic studies by Brill and Long¹⁰⁷. Vibrational spectroscopic studies¹¹³ of R_3SbX_2 ($\text{R}=\text{CH}_3, \text{C}_6\text{H}_5; \text{X}=\text{F}$) have indicated a trigonal bipyramidal structure for these compounds.

Recently, an x-ray crystallographic study¹¹⁴ of Ph_3AsF_2 * has shown the arsenic atom has near regular trigonal bipyramidal geometry with apical fluorine atoms [$\text{As}-\text{F}$ 1.834(7) Å] and equatorial phenyl rings [mean $\text{As}-\text{C}$ 1.925(5) Å].

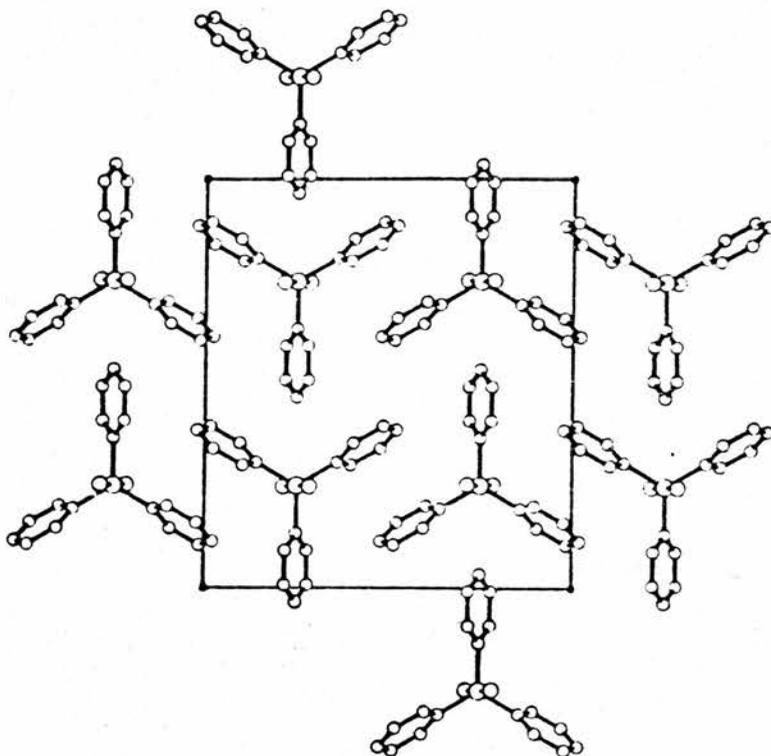


Figure 3. The crystal structure of Ph_3AsF_2 viewed down a .¹¹⁴

It is a characteristic of these pentacovalent compounds that axial M-Hal bonds are longer than normal M-Hal bonds and

* Ph_3AsF_2 crystals were provided by Dr. G.S. Harris, Department of Chemistry, University of St. Andrews.

in particular than equatorial M-Hal bonds. In pentafluoroarsorane⁴⁰ for instance, axial and equatorial As-F bonds are respectively $(1.711 \pm 0.005 \text{ \AA})$ and $(1.656 \pm 0.004 \text{ \AA})$. In $(\text{CH}_3)_2\text{PF}_3$ they are $(1.643 \text{ \AA}$ and $1.553 \text{ \AA}^{80a})$, compared to the average of $(1.53 \pm 0.02 \text{ \AA})$ for a variety of phosphorus fluorides^{115a}.

Wells⁹⁷ noted the abnormal length of the Sb-Hal bonds in dihalogenotrimethylantimony and they have therefore been described as intermediate between ionic and covalent and as resonance linkages. Jensen¹⁰⁶ also concluded, from the high atomic polarisability of the compounds, that these Sb-Hal bonds were very polar. The Bi-Cl bonds in dichlorotriphenylbismuth are likewise longer than expected for a covalent Bi-Cl bond $(2.61 \pm 0.01 \text{ \AA av.})$ compared with $(2.48 \pm 0.02 \text{ \AA}$ for BiCl_3). The As-F bonds in Ph_3AsF_2 ¹¹⁴ are $[1.834 (7) \text{ \AA}]$ longer than As-F distance in AsF_3 $(1.706 \pm 0.002 \text{ \AA})$.

Bonding in Penta-coordinated Compounds, MHal_5

The covalent forms of pentahalogenophosphoranes in which phosphorus, the central atom, (ground state $1s^2; 2s^2, 2p^6; 3s^2, 3p^3$) is surrounded by five ligand atoms are examples of five-coordinated compounds. In these compounds, structural analyses, by ^{19}F , ^{31}P nmr, ^{35}Cl nqr, Raman and ir spectroscopy, electron diffraction, x-ray, etc., have revealed the trigonal bipyramidal configuration to be the one generally adopted and in the structures so far studied different bond lengths are found for the axial and equatorial P-Halogen bonds. This variation in bond length prompted many chemists to

develop theories to explain the nature of bonding in penta-coordinated compounds, and to understand its influence on the type of the geometry adopted.

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. A slight variation of this has been proposed by Muetterties and coworkers⁷⁹ who suggested that in the trigonal bipyramidal structure the equatorial groups are bonded by sp^2 hybrids and the axial ligands by pd hybrids, and that the difference in energy levels between these two sets should reflect the s electron promotion energy. As the electronegativity of the ligands (ie. halogens) increases the differences in energy of these hybrid orbitals become less and this is reflected in the relative bond distances:

$$\begin{aligned} \text{e.g. } P-Cl_{ax} &= 2.19 \text{ \AA}, P-Cl_{eq} = 2.04 \text{ \AA} & \Delta &= 0.15 \text{ \AA} \text{ and} \\ P-F_{ax} &= 1.577 \text{ \AA}, P-F_{eq} = 1.534 \text{ \AA} & \Delta &= 0.043 \text{ \AA} \quad 80b. \end{aligned}$$

It has generally been thought that the high energy and diffuse nature of d-orbitals would not lead to effective hybridisation with s- and p-orbitals and that their diffuse nature would lead to poor overlap with neighbouring atoms and hence would contribute only very slightly towards effective bonding. In this connection it has been suggested that when electronegative groups are attached to the central atom contraction of the d-orbitals occurs thus allowing more effective overlap and stronger bonding¹¹⁶. For this reason attempts

have been made to explain the bonding in compounds such as PHal_5 without recourse to d-orbitals. One such attempt is that of Rundle^{117, 118}. In this approach the Hal-P-Hal axial part of the molecule is regarded as being held together by a four electron three centre bond. The three centre bonding system arises from one atomic p-orbital from each atom giving rise to a bonding, a non-bonding, and an antibonding molecular orbitals, the former two of which contain a pair of electrons. The equatorial bonds are normal electron pair bonds and involve sp^2 hybrid orbitals of the central atom.

Advantages of this scheme are (a) d-orbitals not involved (it is very much a controversial matter whether d-orbitals are involved in this type of molecule) and (b) 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_3MHal_2 -Compounds

It has been shown that the properties of the substituted pentahalogeno compounds R_3MHal_2 are dependent on the nature of the organic group R. Thus, Harris and coworkers^{120, 121} have drawn attention to a correlation between the nature of the group R and the molar conductance of R_3MHal_2 in methyl cyanide solution. It was observed that R_3PHal_2 compounds are not always strong electrolytes and R_3AsHal_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 compounds.

e. g.

$$(\text{C}_6\text{H}_5)_3\text{PCl}_2, \Lambda_m^{119} = 78.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; (\text{C}_m = 0.01 \text{ mol l}^{-1})$$

and

$$(\text{C}_6\text{F}_5)_3\text{PCl}_2, \Lambda_m^{119} = 0.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; (\text{C}_m = 0.01 \text{ mol l}^{-1})$$

Similarly,

$$(\text{C}_6\text{H}_5)_3\text{AsBr}_2, \Lambda_m^{120} = 25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; (\text{C}_m = 0.01 \text{ mol l}^{-1})$$

and

$$(\text{Me}_2\text{N})_3\text{AsBr}_2, \Lambda_m^{120} = 109 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; (\text{C}_m = 0.01 \text{ mol l}^{-1})$$

From these observations they concluded that there is a relation between the electronegativity of R and tendency of R_3MHal_2 to behave in an ionic form, i.e. a group which pulls electrons away from the atom M lessens the tendency to ionic behaviour i.e. $(\text{C}_6\text{F}_5)_3\text{PCl}_2$, and a group which pushes electrons on to M increases the tendency to ionic behaviour or we can say molar conductance increases with decrease in electronegativity of the substituent group R. Harris and Inglis¹²¹ have studied the conductance of dihalogenotriphenylarsorane, dihalogenotris(4-chlorophenyl)arsorane and dihalogenotris(4-methylphenyl)arsorane in methyl cyanide and have found that the results are consistent with the above conclusions.

Table 3 Λ_m Conductance at $\text{C}_m = 0.01 \text{ mol l}^{-1}$

Compound	$\Lambda_m \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\Lambda_m \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	dichloro	dibromo
$(4\text{-ClC}_6\text{H}_4)_3\text{AsHal}_2$	3	12
$(\text{C}_6\text{H}_5)_3\text{AsHal}_2$	12	25
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$	13	54

increase in electronegative group decreases the Λ_m

The 4-chlorophenyl group is slightly more electronegative than the phenyl group and also the 4-methylphenyl group is slightly less electronegative than the phenyl group. Again these results are in keeping with the idea that covalent character of these compounds increases with increasing electronegativity of the attached groups. Decreasing the electronegativity, would seem to weaken the As-Hal bond in the covalent molecules, making ionisation easier. It has been suggested¹¹⁶ that the use of d orbitals in trigonal bipyramidal structures is favoured by the attachment of electronegative ligands to the central atom. Thus it may be argued that the more electronegative the attached ligands then the more stable will be the covalent form of the $R_n MHal_{5-n}$ compound relative to the ionic form.

Closely correlated with these observations are the results of a vibrational spectral study of $Me_n PF_{5-n}$ made by Schmutzler and Downs⁴⁷. They replaced F atoms in PF_5 molecules by Me groups and observed a marked trend in the frequencies of the symmetric and asymmetric stretching vibrations of the axial P-F bonds. These frequencies suffer a marked and regular decrease as fluorine atoms in PF_5 are replaced by methyl groups. For PF_5 , CH_3PF_4 and $(CH_3)_2PF_3$ the electron diffraction results of Bartell and Hansen⁸⁰ confirm 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. The results contained in Table 4 shows the correlation of the lengthening of the axial P-F bond with the decrease in the mean P-F stretching frequency. The axial P-F

bond clearly suffers a marked weakening as the number of methyl substituents increases.

Table 4. Vibration of P-F (axial) stretching frequencies

Molecule	P-F stretching frequencies			P-F bond length Å
	Symmetric (cm ⁻¹)	Asymmetric (cm ⁻¹)	Mean (cm ⁻¹)	
PF ₅	640	945	793	1.577
CH ₃ PF ₄	596	843	720	1.612
(CH ₃) ₂ PF ₃	540	755	648	1.643
(CH ₃) ₃ PF ₂	500.5	670	585	-

From the vibrational spectral studies and calculation of bond order of axial P-F bonds in (CH₃)_nPF_{5-n} molecules Schmutzler and Downs⁴⁷ conclude that the replacement of a further fluorine atom by a methyl group would result in the formation, not of a 5-coordinate molecule, but of an ionic system, viz. [(CH₃)₄P]⁺F⁻.

From the electron diffraction and spectroscopy data one would expect molar conductivity to increase from PF₄Me → PF₂Me₃, due to the introduction of less electronegative group R (ie. methyl) weakens P-Hal bond and favours ionisation. Conductance measurements of these fluoromethylphosphoranes¹²² in methyl cyanide solutions are entirely consistent with this, e. g.

Table 5

Compound	Λ_m ohm ⁻¹ cm ² mol ⁻¹ at C _m 0.09 mol l ⁻¹
PF ₄ Me	4.00
PF ₃ Me ₂	6.5
PF ₂ Me ₃	8.5

Therefore we can say that pushing electrons on to P weakens the P-F bond thus making ionisation easier and consequently giving higher molar conductance.

In view of the observed sensitivity of the electrolytic conductance of R_3MHal_2 compounds to the nature of R it was thought to be of interest to study further this effect when R is the $(CH_3-C_6H_4)-$ (ie. tolyl group) and the substituent CH_3- is varied between 2-, 3-, and 4-position of the pheny ring (ie. ortho, meta, and para positions). This part, therefore, is concerned with a study of some tris(2-methylphenyl)arsine, tris(3-methylphenyl)-arsine and tris(4-methylphenyl)arsine-halogen ($Br_2, I_2,$ and IBr) systems. These systems have been studied by conductometric titration, and where this has indicated adduct formation, attempts have been made to isolate these. The properties of the isolated adducts have been examined.

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REACTION OF TRIS(METHYLPHENYL)ARSINES WITH HALOGENS

Introductory Note: Reaction of R_3M with Halogens

(R_3M , R = phenyl or substituted phenyl group and $M = P, As, Sb$ and Bi ; Halogens = F_2, Cl_2, Br_2 and I_2 .)

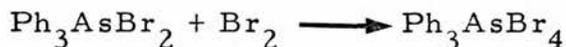
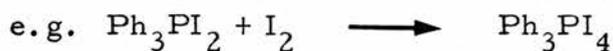
Triaryl derivatives of phosphorus, arsenic, antimony and bismuth (R_3M) react with halogens and interhalogens (IBr, ICl) giving products of composition R_3MHal_2 , and in some cases R_3MHal_4



The R_3MHal_4 compounds, have been obtained as crystalline solids by the addition of halogen to the dihalogeno compounds in methyl cyanide,



The reaction of R_3MHal_2 compounds with halogens has been shown to be dependent on the nature of the R_3MHal_2 compound. For example, diiodotriphenylphosphorane and dibromotriphenylarsorane take up an additional molecule of halogen readily,

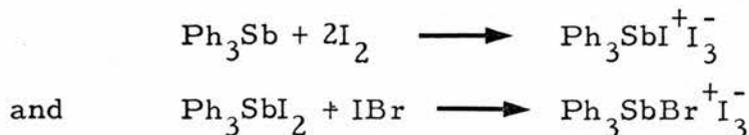


and it has been possible to prepare mixed tetrahalogeno derivatives,

$Ph_3PBr_nI_{4-n}$ ¹²³ and $Ph_3AsBr_nI_{4-n}$ ⁹² by reactions such as



On the other hand, tetrahalogeno derivatives of triphenyl-antimony and bismuth have not yet been obtained as crystalline solids, although Ph_3SbI_4 and Ph_3SbBrI_3 have been detected in solution by studying the reaction¹²³:

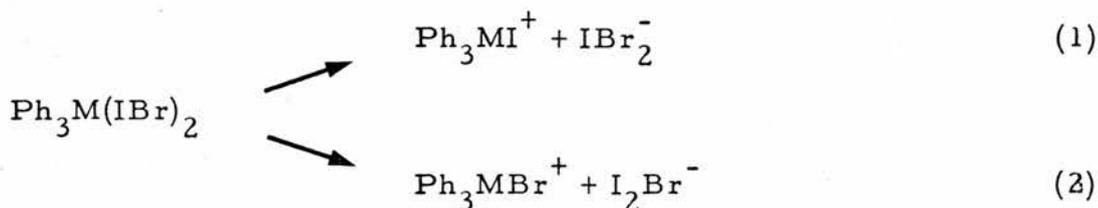


by conductometric titration.

In the tetrahalogeno compounds, containing only one kind of halogen it has been shown by conductance measurements and the ultraviolet spectra of their methyl cyanide solution, that trihalide $(\text{Hal}_3)^-$ ions are present, arising from the ionisation

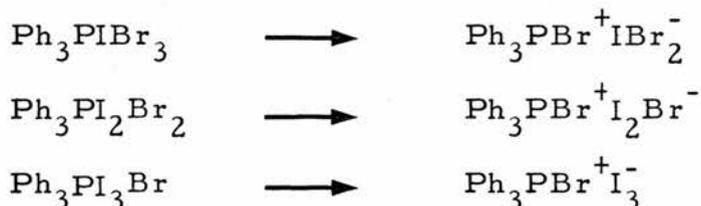


The case of mixed halogen tetrahalogeno compounds is of particular interest since two ionisation schemes are possible, e. g.



From a study of the ultraviolet spectra of methyl cyanide solution of compounds of this type it has been shown that the second ionisation takes place. Without exception, the evidence so far points to the empirical rule that in the mixed tetrahalogeno compounds; the cation contains the halogen of lower atomic number⁹².

For example, in $\text{Ph}_3\text{PBr}_n\text{I}_{4-n}$ ($n=1-3$), the ions are as follows:



The R_3AsHal_2 and R_3AsHal_4 compounds prepared and studied in this work are crystalline solids at room temperature, and on account of their susceptibility to hydrolysis, they must be handled in the absence of moisture: thus all reactions, isolation of products, and preparation of solutions for ultraviolet

spectra and conductance measurements were carried out in a nitrogen-filled drybox containing trays of phosphorus pentoxide. Solvents used were of high purity and thoroughly dry. Contact of solutions with tap grease and moisture was minimised by using specially designed apparatus, which was baked in an oven several hours before use.

RESULTS AND DISCUSSION

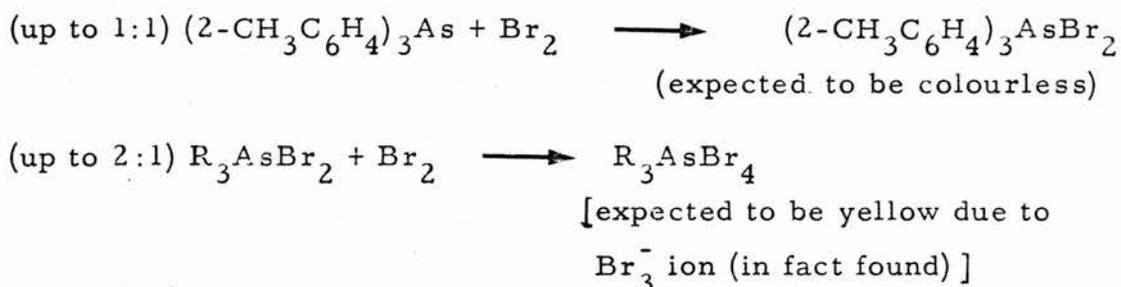
A. REACTION OF TRIS(2-METHYLPHENYL)ARSINE WITH HALOGENS

A convenient technique for studying the reactions of triarylsarsines, and their derivatives, with halogens has been shown to be the conductometric titration. Information may be obtained not only on the stoichiometry of the reaction products but also on their electrolytic behaviour. The course of the reaction of tris(methylphenyl)arsines with halogens was studied by conductometric titration and the solvent employed was nitrobenzene (dielectric constant $\epsilon = 34.8$ at 25°C). Strong 1:1 electrolytes have $\Lambda_m = \text{ca. } 20\text{-}26 \text{ }^{124} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and weak electrolytes have $\Lambda_m = \text{ca. } 1\text{-}5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in nitrobenzene. The apparatus and details of the technique has been described earlier by Harris and co-workers⁹³.

(a) Reaction of Tris(2-methylphenyl)arsine with Bromine

The results of the conductometric titration of tris(2-methylphenyl)arsine with bromine in nitrobenzene are recorded in Table 6 and illustrated graphically in figure 4. The graph does not show a break at the 1:1 $[\text{Br}_2 : (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$ mole ratio and the conductivity of the product formed in the solution increases uniformly up to the 2:1 $[\text{Br}_2 : (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$ mole ratio. It shows a sharp break at 2:1 mole ratio and the curve falls again immediately after the 2:1 ratio, the conductivity of the solution decreasing up to 3:1 mole ratio. The colour of the

solution remained pale yellow (as the pure solvent) up to 1:1 mole ratio, and thereafter had the bright yellow colour characteristic of the Br_3^- ion. The break in the graph at the 2:1 ratio shows the formation of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$ in the solution. The absence of a break in the conductometric titration graph at 1:1 ratio would tend to suggest the absence of the 1:1 compound [ie. $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$] in solution. The observed change in colour of the solution at 1:1 ratio would on the other hand tend to suggest that a dibromo adduct is being formed and that the following sequence of events is occurring



As will be seen later however considerable difficulty was experienced when attempts were made to isolate the dibromide, suggesting inherent instability of the dibromotris(2-methylphenyl)-arsorane. The molar conductance value at the 2:1 mole ratio was:

$$\Lambda_m = 29.17 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.007816 \text{ mol l}^{-1})$$

The high molar conductance value at the 2:1 mole ratio indicates that the tetrabromo compound is a strong 1:1 electrolyte:



(strong electrolytes have a molar conductance of ca. 20-26 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in nitrobenzene¹²⁴)

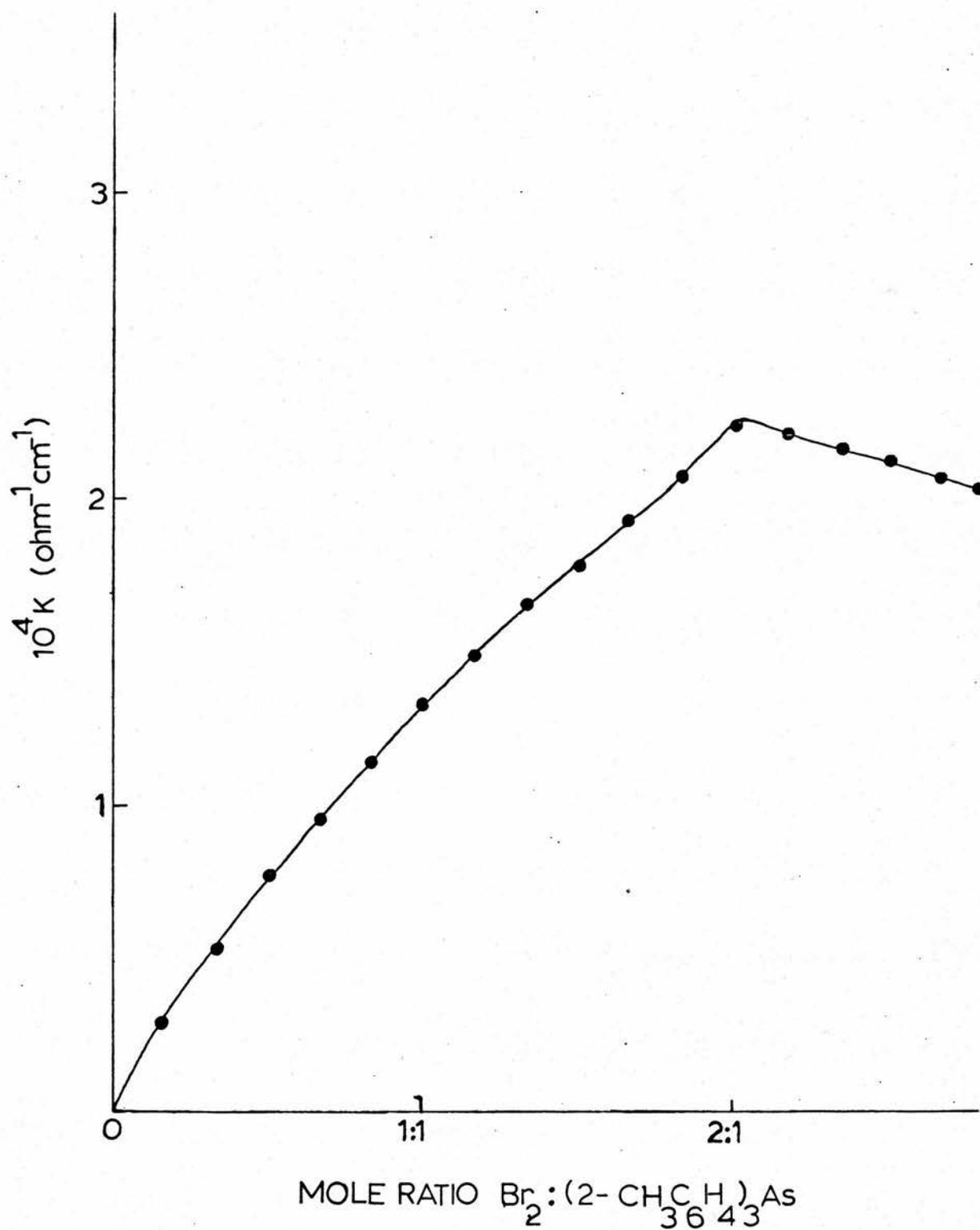


Figure 4. Conductometric Titration of $\text{Br}_2 : (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

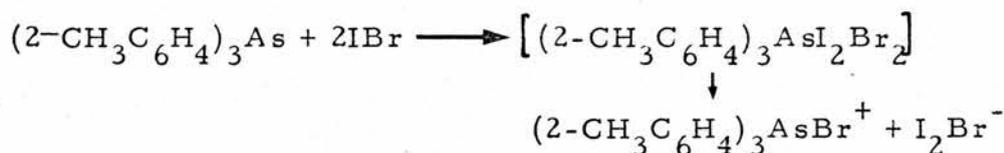
(b) Reaction of Tris(2-methylphenyl)arsine with Iodinebromide

The results of the conductometric titration of tris(2-methylphenyl)arsine with iodine bromide in nitrobenzene are recorded in Table 7 and illustrated graphically in figure 5.

The solution showed the characteristic colour of the trihalide ion (ie. I_2Br^- ion, by analogy with Ph_3As/IBr system)¹²³ from the first addition of halogen, the conductance rose uniformly up to the 2:1 [$I_2Br:(2-CH_3C_6H_4)_3As$] mole ratio, indicating that $(2-CH_3C_6H_4)_3AsI_2Br_2$ was the only compound formed in solution up to that point. The molar conductance value at the 2:1 mole ratio was:

$$\Lambda_m = 27.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.007761 \text{ mol l}^{-1})$$

$(2-CH_3C_6H_4)_3AsI_2Br_2$ is therefore a strong electrolyte and we can represent the reaction occurring in solution as:

(c) Reaction of Tris(2-methylphenyl)arsine with Iodine

The results of the conductometric titration of tris(2-methylphenyl)arsine with iodine in nitrobenzene are recorded in Table 8 and illustrated graphically in figure 6.

As in the titration with I_2Br the strong colour of the trihalide ion, this time I_3^- , appeared after the first addition of halogen, and the conductance rose uniformly up to the 2:1 [$I_2:(2-CH_3C_6H_4)_3As$] mole ratio. Thereafter the graph flattened out giving a rather rounded break at the 2:1 ratio. On further addition of I_2 solution the conductance began to fall

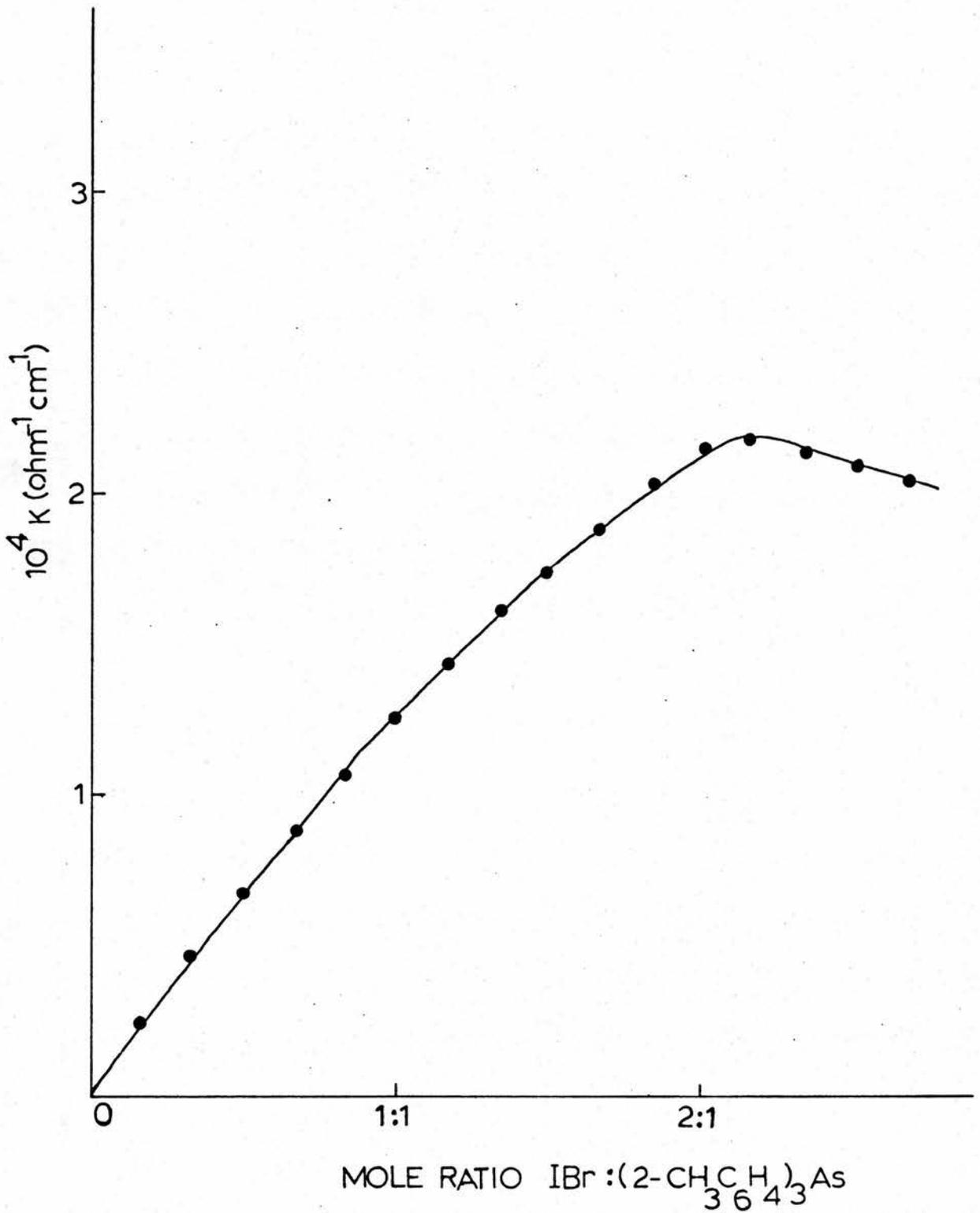


Figure 5. Conductometric Titration of $\text{IBr}:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

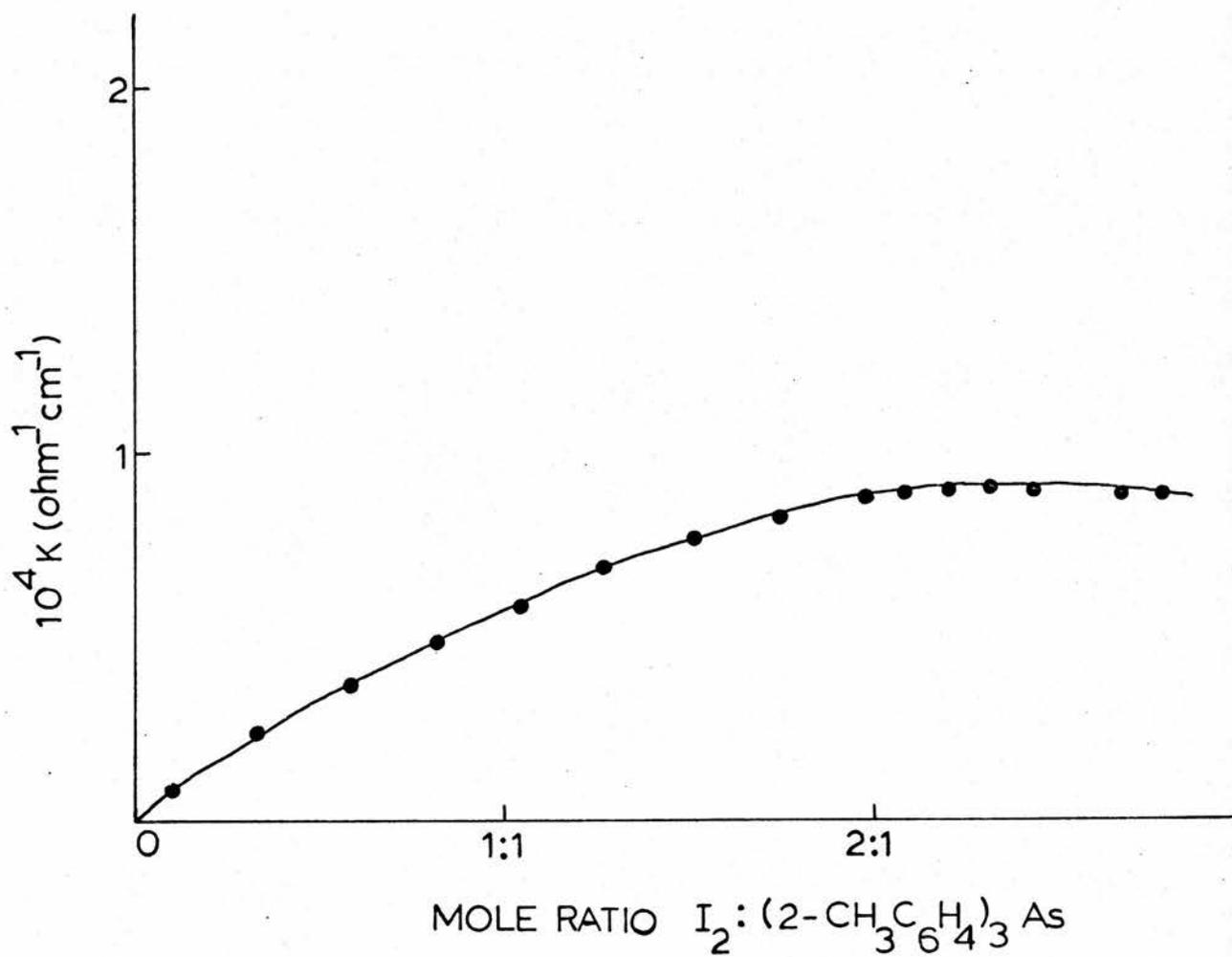


Figure 6. Conductometric Titration of $\text{I}_2 : (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

as the solution was diluted with the relatively poorly conducting iodine solution. Thus $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$ is the only reaction product present in nitrobenzene solution of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ and I_2 .



The molar conductance value at the 2:1 mole ratio was:

$$\Lambda_m = 24.49 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.003675 \text{ mol l}^{-1})$$

(d) Adducts Isolated

All the 2:1 adducts ie. $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$, $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$ and $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$ whose existence was suggested by conductometric titration were isolated as crystalline solids usually by the addition of ether to mixtures of the reactants in the appropriate ratio in methyl cyanide. In addition to these tetrahalogeno compounds, two more $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$ and $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ were isolated as crystalline solids from the appropriate mixtures of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ and $\text{I}_2 + \text{Br}_2$. All these tetrahalogeno compounds are the members of series $\text{R}_3\text{AsBr}_n\text{I}_{4-n}$ ($\text{R} = (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$; $n = 4, 3, 2, 1$ and 0).

Although the existence of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$ was not indicated in the conductometric titration the solid compound could be isolated by careful addition of IBr solution in methyl cyanide to a solution of tris(2-methylphenyl)arsine in the same solvent. Reducing the bulk of the solvent to a minimum and adding ether gave rust coloured crystals of stoichiometry

Table 9 Crystalline Adducts of $(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Halogens

compound	colour	mp(°C)	Hal ⁻ ion present ¹	$\lambda_{\text{max}} = m \mu$
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsF}_2$	white	178-180	-	-
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$	white	200-206	-	-
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$	pale yellow	92	-	-
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$	rust	162-163	I_2Br^-	271, 351
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$	dark brown	163-164	I_3^-	291, 361
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	bright yellow	154	Br_3^-	269
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	orange	171	IBr_2^-	257, 370
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	rust	149-150	I_2Br^-	265, 351
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	chocolate brown	132	I_3^-	285, 355
$(2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	brown black	114	I_3^-	291, 360

1. shown by uv spectrum of methyl cyanide solution of the adduct

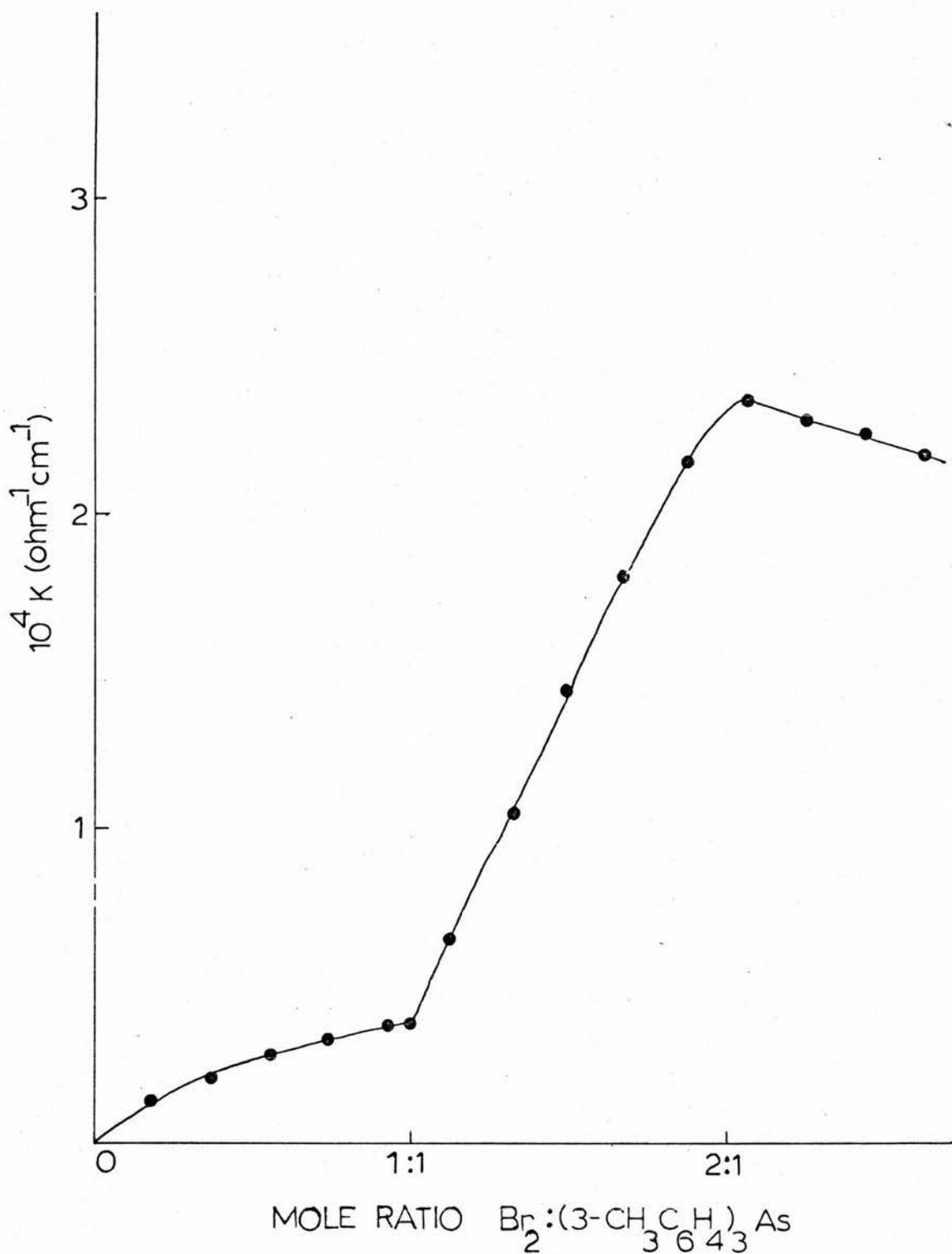


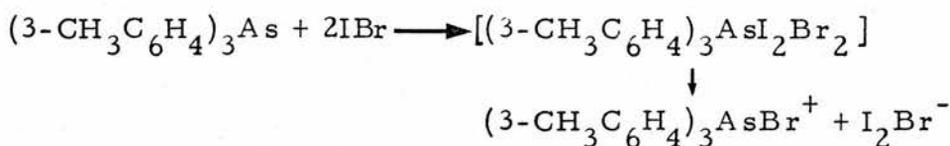
Figure 7. Conductometric Titration of $\text{Br}_2:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$
in Nitrobenzene

(b) Reaction of Tris(3-methylphenyl)arsine with Iodine Bromide

The results of the conductometric titration of tris(3-methylphenyl)arsine with iodine bromide in nitrobenzene are recorded in Table 11 and illustrated graphically in figure 8.

As expected, the conductance of the solution rose rapidly as IBr was added up to the 2:1 [IBr:(3-CH₃C₆H₄)₃As] mole ratio, without any discontinuity to indicate formation of a 1:1 adduct, and the solution showed bright yellow colour from the first addition of IBr solution. A distinct break occurred in the graph at the 2:1 ratio after which the conductance decreased slowly.

Thus it would appear that (3-CH₃C₆H₄)₃AsI₂Br₂ is the only product formed in this system. The reaction occurring is therefore,



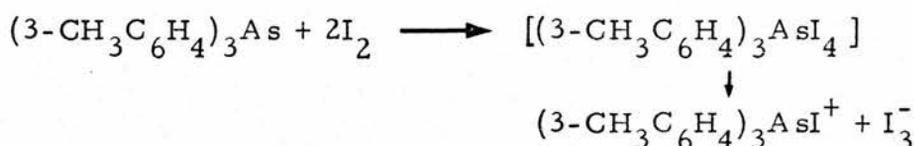
The molar conductance value at the 2:1 mole ratio was:

$$\Lambda_m = 28.18 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.005535 \text{ mol l}^{-1})$$

(c) Reaction of Tris(3-methylphenyl)arsine with Iodine

The results of the conductometric titration of tris(3-methylphenyl)arsine with iodine in nitrobenzene are recorded in Table 12 and illustrated graphically in figure 9.

This curve showed features similar to those of the IBr curve giving a distinct break at the 2:1 [I₂:(3-CH₃C₆H₄)₃As] mole ratio. As with IBr the reaction leads straight away to the 2:1 adduct



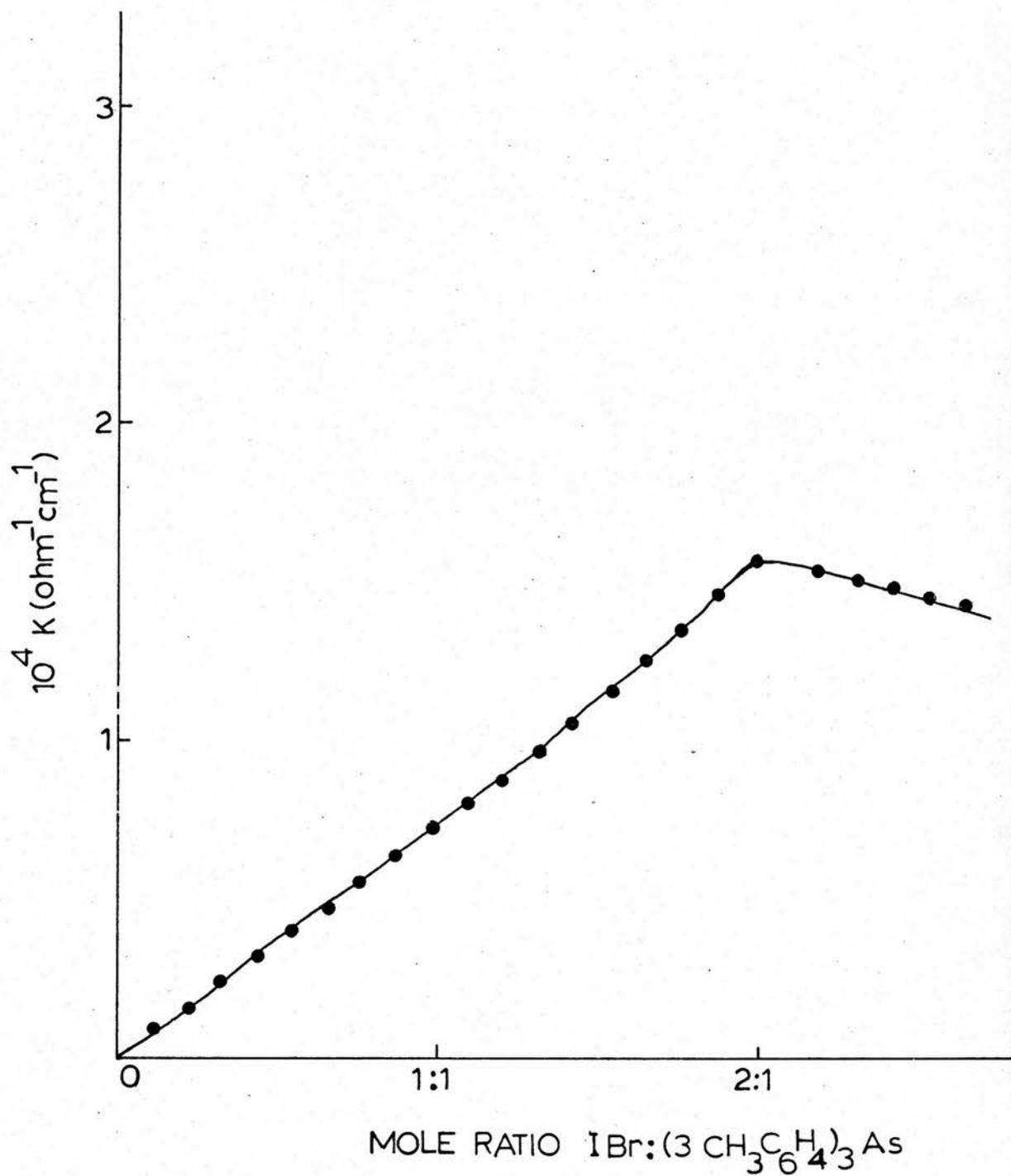


Figure 8. Conductometric Titration of $\text{IBr}:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

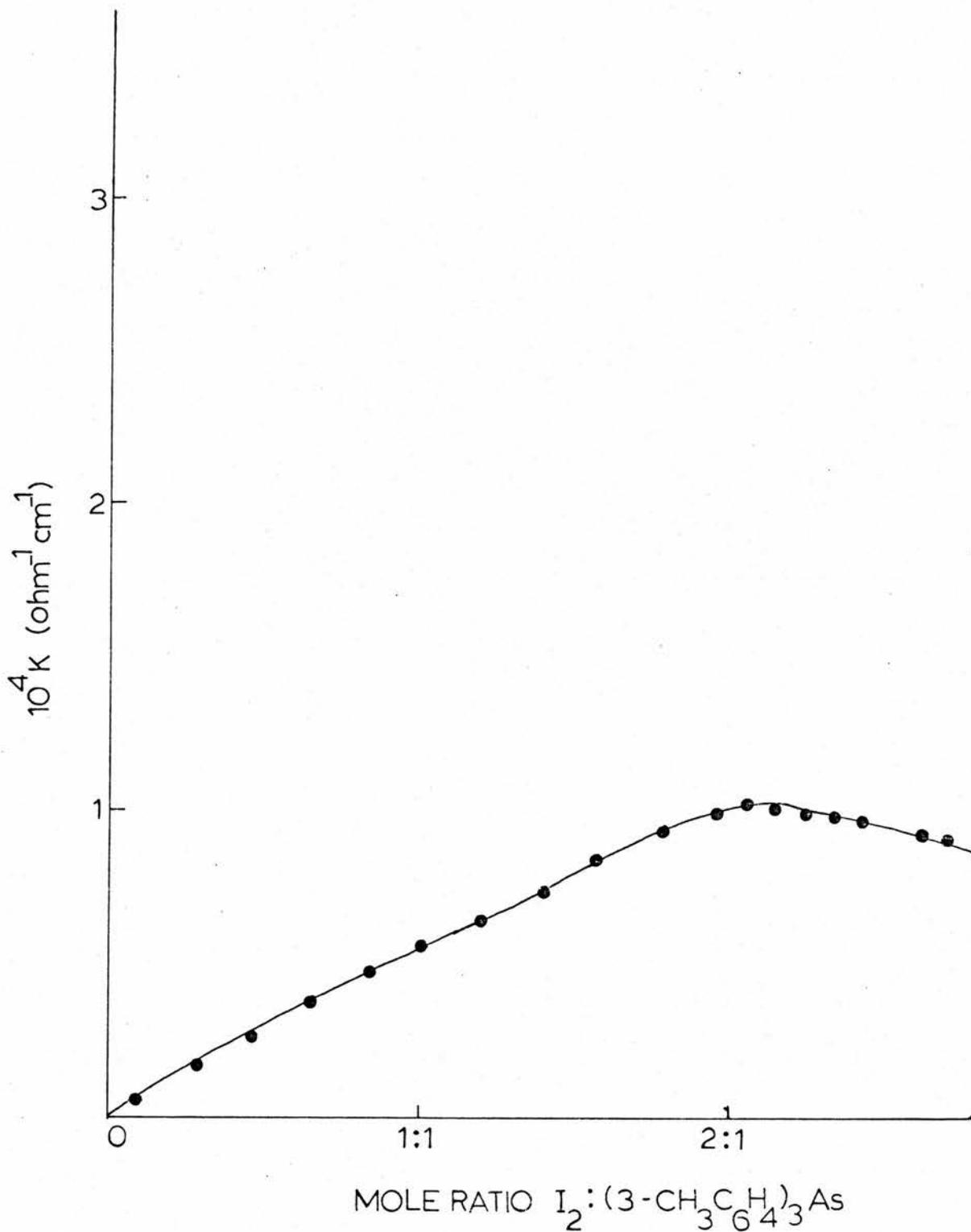


Figure 9 . Conductometric Titration of $\text{I}_2 : (3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

The molar conductance at the 2:1 mole ratio was:

$$\Lambda_m = 26.13 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.003979 \text{ mol l}^{-1})$$

Thus like all other tetrahalogeno adducts, $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$ is a strong electrolyte in nitrobenzene.

(d) Adducts Isolated

Dibromotris(3-methylphenyl)arsorane, the formation of which was indicated by conductometric titration, was isolated by reacting equimolar amounts of Br_2 and $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ from carbon tetrachloride. Analysis of the product obtained in this way showed it to be solvated $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2] \cdot \text{CCl}_4$. Carbon tetrachloride of solvation was removed by repeated trituration of the material with petroleum ether. $\left\{ \begin{array}{l} \text{C, H, analysis of } (3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2 \\ \text{isolated from methyl cyanide/ether, showed it to be partially} \\ \text{solvated } [(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2] \cdot \frac{1}{2}\text{CH}_3\text{CN} \end{array} \right\}$. $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$ and $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$ whilst not indicated in the conductometric titration studies were isolated as crystalline solids from equimolar mixtures of the halogen and arsine in methyl cyanide/ether and petroleum ether respectively. Dichlorotris(3-methylphenyl)arsorane was also obtained following the same procedure as that of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$.

All the 2:1 adducts ie. $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$, $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$, and $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$ whose existence was suggested by conductometric titration were isolated as crystalline solids from mixtures of the appropriate halogens and arsine in the ratio of 2:1 from methyl cyanide and ether.

$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$ and $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ compounds which also belong to this series ($\text{R}_3\text{AsBr}_n\text{I}_{4-n}$, $n=4, 3, 2, 1$ and 0) were also prepared as: $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$ was isolated by the addition of ether to the equimolar mixture of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}$, IBr and Br_2 in methyl cyanide. $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ was obtained in pure form by reacting $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}$ and I_2 (in 1:1 mole ratio) from carbon tetrachloride. (Material obtained from methyl cyanide/ether did not give correct C, H and halogen analysis.) The properties of these crystalline adducts are summarised in Table 13 on page 44.

C. REACTION OF TRIS(4-METHYLPHENYL)ARSINE WITH HALOGENS

(a) Reaction of Tris(4-methylphenyl)arsine with Bromine

The results of the conductometric titration of tris(4-methylphenyl)arsine with bromine in nitrobenzene are recorded in Table 14 and illustrated graphically in figure 10 .

Conductance rose slowly to a low value at the 1:1 mole ratio, during which the colour of the solution was pale yellow (as the pure solvent). From the 1:1 to 2:1 mole ratio it changed to bright yellow and the conductance rose rapidly. After the 2:1 mole ratio the conductance fell slowly with addition of the poorly conducting bromine solution. The graph thus showed distinct breaks at the 1:1 and 2:1 $[\text{Br}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}]$ mole ratios, indicating formation of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$ in solution. The reaction is therefore a

Table 13. Crystalline Adducts of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Halogens

Compound	colour	mp(°C)	Hal ⁻ ₃ ion present ¹	$\lambda_{\text{max}} =$ m μ
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$	white	173-175	-	-
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$	white	185-186	-	-
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$	bright yellow	136	I_2Br^-	279, 355
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$	light brown	185-186	I_3^-	292, 358
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	bright yellow	65	Br_3^-	269
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	rust	99-100	IBr_2^-	256, 370
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	red brown	102	I_2Br^-	276, 351
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	brown	103-104	I_3^-	287, 355
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	dark violet	101-102	I_3^-	291, 360

1. shown by uv spectrum of methyl cyanide solution of the adduct¹²⁵

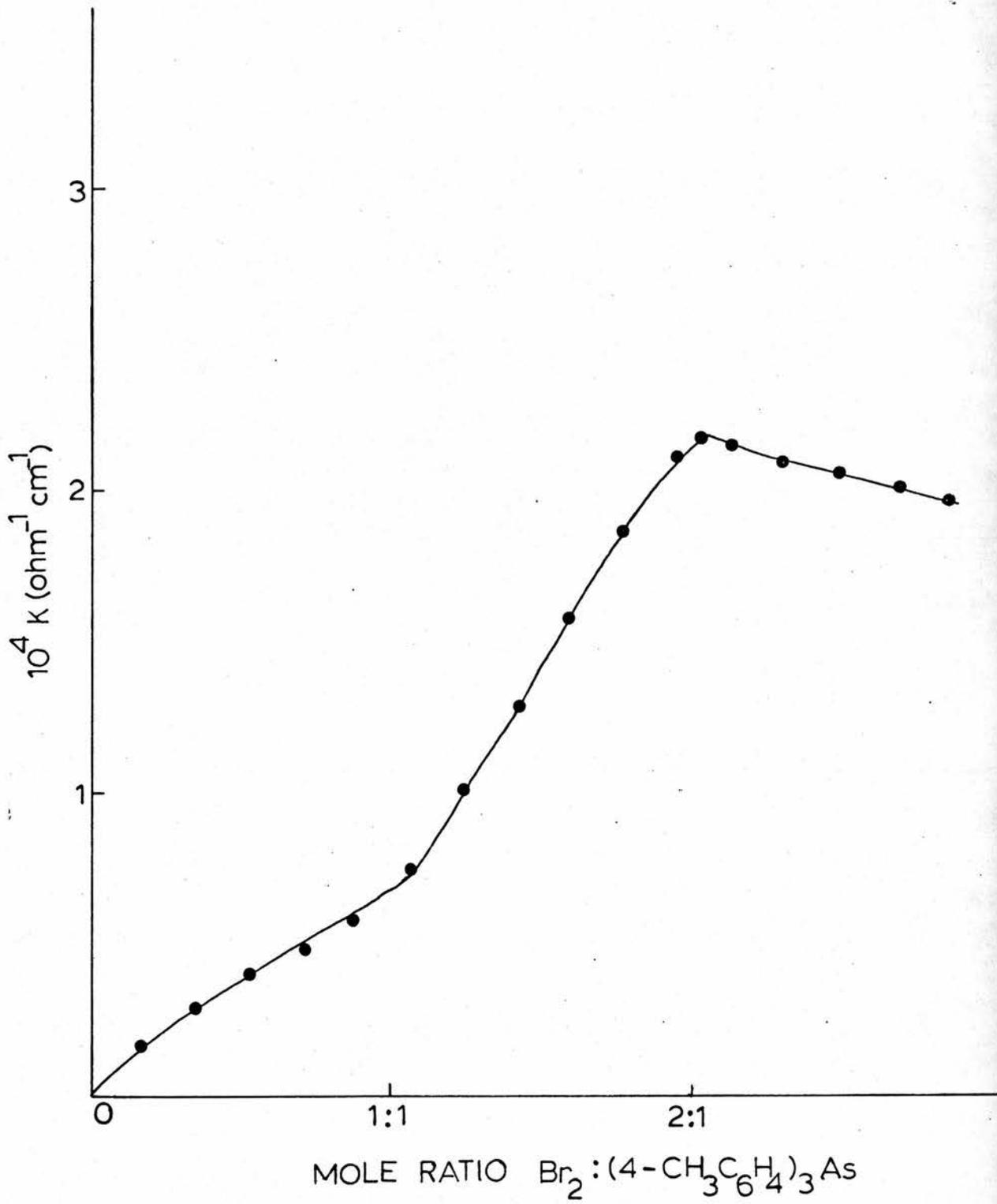
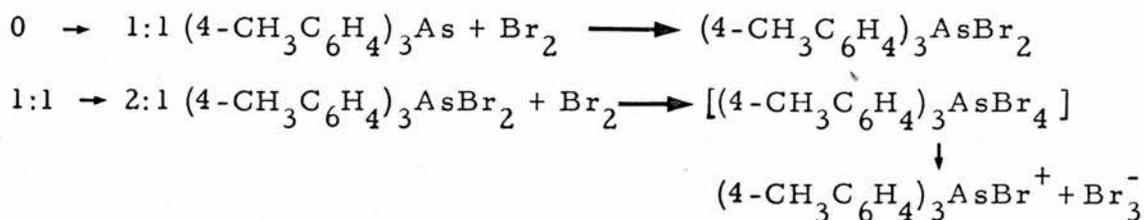


Figure 10. Conductometric Titration of $\text{Br}_2 : (4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

two stage one and may be represented:



The molar conductance values at 1:1 and 2:1 molar ratio were:

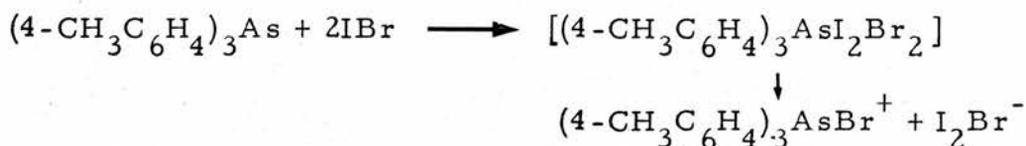
$$1:1 \quad \Lambda_m = 8.81 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.007825 \text{ mol l}^{-1})$$

$$2:1 \quad \Lambda_m = 31.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.006814 \text{ mol l}^{-1})$$

(b) Reaction of Tris(4-methylphenyl)arsine with Iodine Bromide

The results of the conductometric titration of tris(4-methylphenyl)arsine with iodine bromide in nitrobenzene are recorded in Table 15 and illustrated graphically in figure 11.

The solution showed a bright yellow colouration from the first addition of IBr solution and it became intense bright yellow up to the 2:1 [IBr:(4-CH₃C₆H₄)₃As] mole ratio. Conductance rose uniformly up to the 2:1 mole ratio and thereafter fell gradually giving a distinct break at 2:1, indicating formation of (4-CH₃C₆H₄)₃AsI₂Br₂. The reaction occurring therefore is,



The molar conductance value at the 2:1 mole ratio was:

$$\Lambda_m = 29.93 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.006950 \text{ mol l}^{-1})$$

(c) Reaction of Tris(4-methylphenyl)arsine with Iodine

The results of the conductometric titration of tris(4-methylphenyl)arsine with iodine are recorded in Table 16 and illustrated graphically in figure 12.

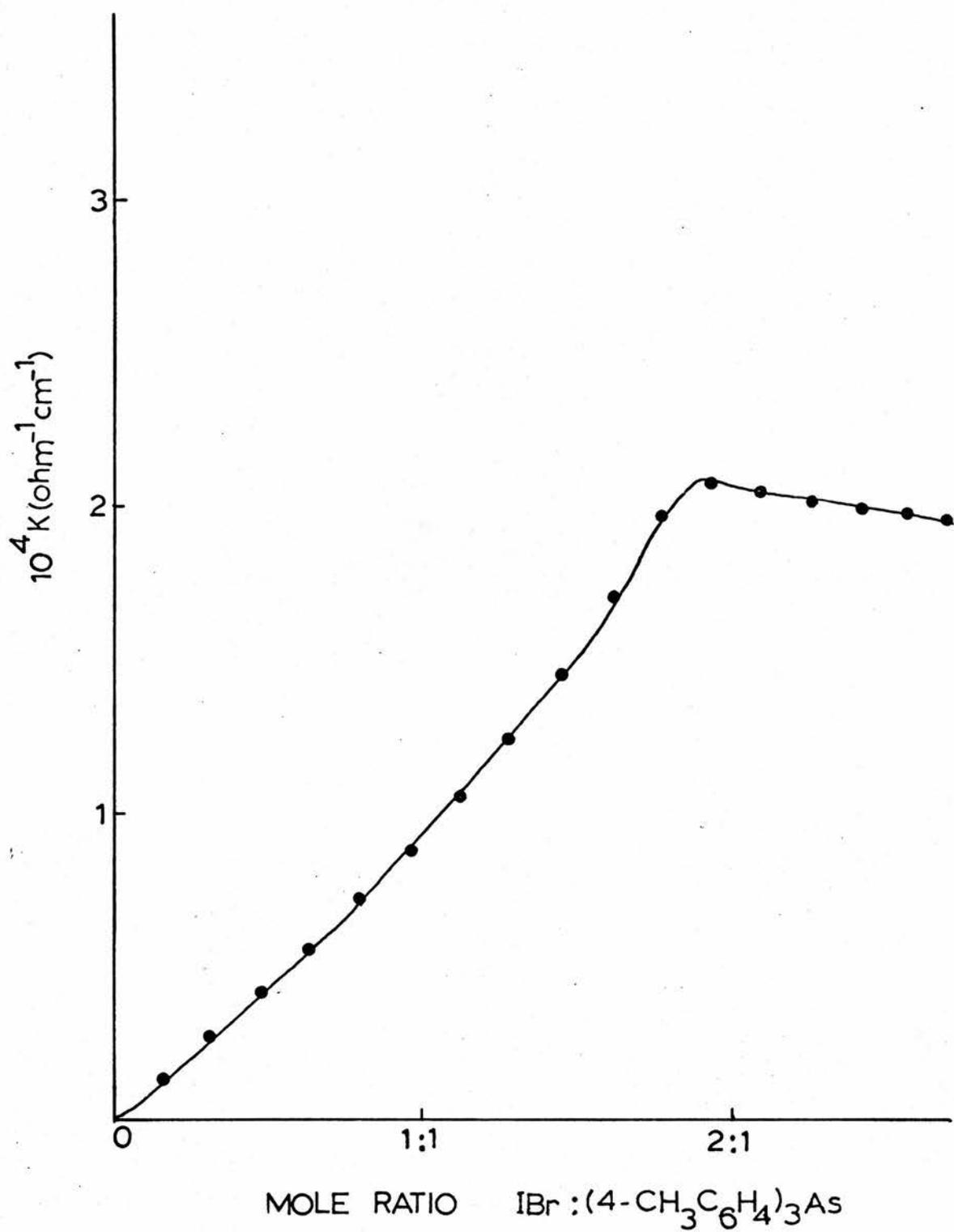


Figure 11. Conductometric Titration of IBr:(4-CH₃C₆H₄)₃As in Nitrobenzene

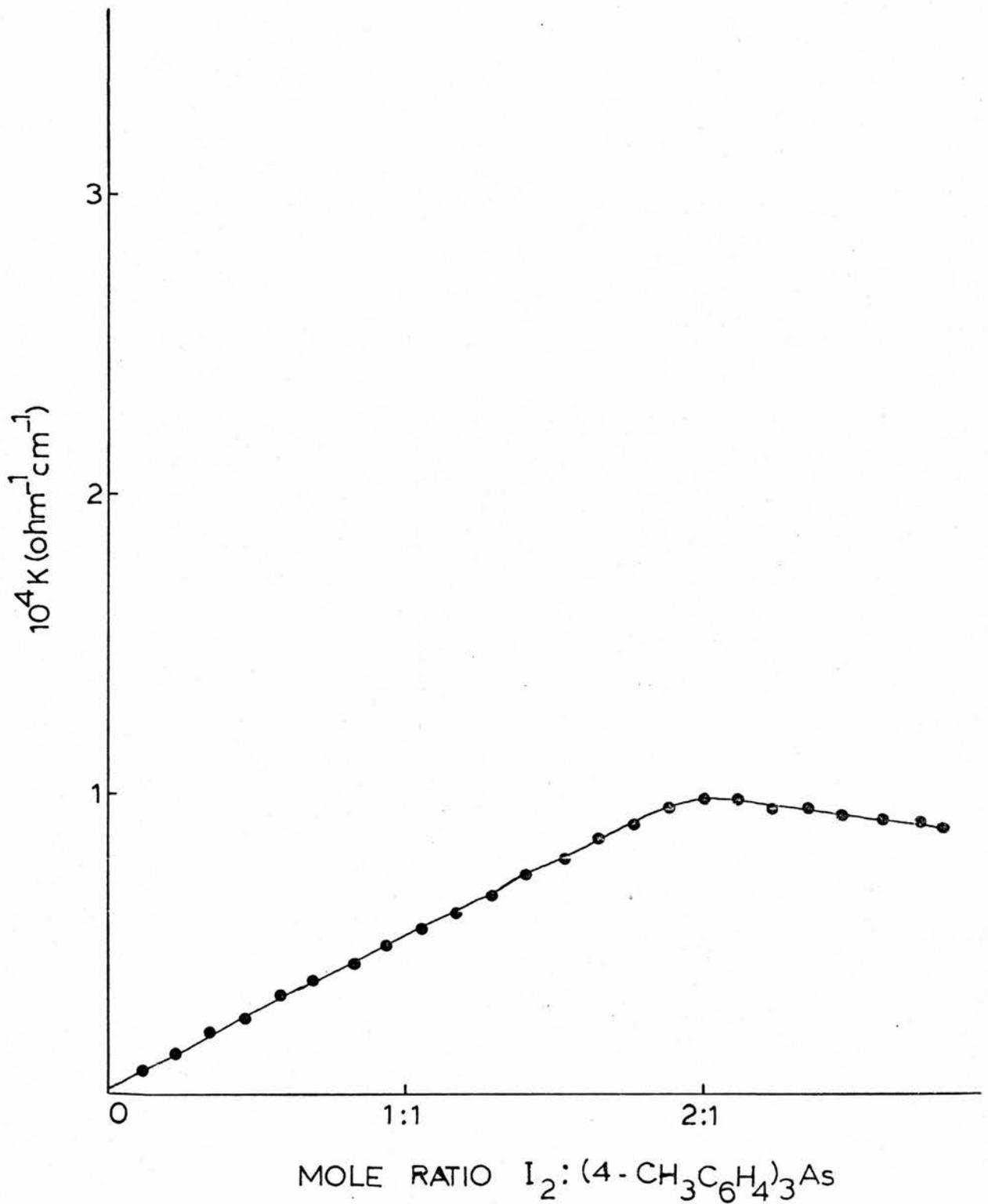


Figure 12. Conductometric Titration of $\text{I}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

As in the titration with IBr the bright yellow colour of the trihalide ion (this time I_3^-) appeared after the first addition of I_2 solution, and the conductance rose uniformly up to the 2:1 mole ratio. After that the conductance fell slowly giving a distinct break at the 2:1 [$I_2:(4-CH_3C_6H_4)_3As$] mole ratio. Thus $(4-CH_3C_6H_4)_3AsI_4$ is the only compound formed in the nitrobenzene solution of $(4-CH_3C_6H_4)_3As$ and I_2 .



The molar conductance value at the 2:1 mole ratio was

$$\Lambda_m = 29.40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (C_m = 0.003402 \text{ mol l}^{-1})$$

(d) Adducts Isolated

All the 2:1 adducts i.e. $(4-CH_3C_6H_4)_3AsBr_4^*$, and $(4-CH_3C_6H_4)_3AsBr_2I_2^*$ and $(4-CH_3C_6H_4)_3AsI_4^*$ whose existence was suggested by conductometric titration were isolated as crystalline solids by addition of ether to mixtures of the reactants in the appropriate ratio in methyl cyanide. The other two tetrahalogeno adducts $(4-CH_3C_6H_4)_3AsBr_3I$ and $(4-CH_3C_6H_4)_3AsBrI_3$ which belong to this series $(R_3AsBr_nI_{4-n}, n=4, 3, 2, 1 \text{ and } 0)$ were also obtained as crystalline solids from the appropriate mixtures of $(4-CH_3C_6H_4)_3As$ and $I_2 + Br_2$.

Dibromotris(4-methylphenyl)arsorane^{*}, formation of which was indicated by conductometric titration, was isolated by reacting

* F. Inglis prepared these adducts¹²¹ in some preliminary experiments.

equimolar amounts of Br_2 and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in methyl cyanide followed by precipitation with ether. Although the formation of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}^*$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2^*$ were not indicated by conductometric titration, these compounds were also isolated as crystalline solids by addition of ether to 1:1 mixtures of the reactants in methyl cyanide. Dichlorotris(4-methylphenyl)arsorane^{*} was prepared by passage of chlorine into a chloroform solution of arsine. Difluorotris(4-methylphenyl)arsorane was isolated by reacting tris(4-methylphenyl)arsine oxide hydrate with aqueous hydrofluoric acid (40%) in boiling water. Unlike the dichloro-, dibromo-, bromoiodo- and diiodo- difluorotris(4-methylphenyl)arsorane is stable in presence of moisture. The properties of all these compounds are summarised in Table 17 on page 48.

D. SUMMARY

Breaks at the 2:1 ratio in conductometric titrations of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$, $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$, and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Br_2 , IBr and I_2 indicate the formation of adducts of composition R_3AsBr_4 , $\text{R}_3\text{AsBr}_2\text{I}_2$ and R_3AsI_4 in solution [$\text{R}=(2\text{-CH}_3\text{C}_6\text{H}_4)$, $(3\text{-CH}_3\text{C}_6\text{H}_4)$, and $(4\text{-CH}_3\text{C}_6\text{H}_4)$]. The high values of molar conductance found at this ratio in each case are indicative of strong 1:1 electrolytes, suggesting that the adducts should be formulated as $\text{R}_3\text{AsBr}^+\text{Br}_3^-$, $\text{R}_3\text{AsBr}^+\text{I}_2\text{Br}^-$ or $\text{R}_3\text{AsI}^+\text{IBr}_2^-$ and $\text{R}_3\text{AsI}^+\text{I}_3^-$. Attempts to prepare these adducts gave them

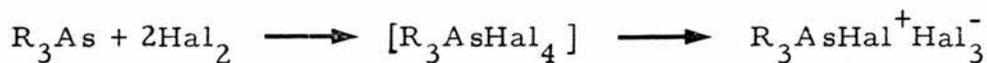
Table 17 Crystalline Adducts of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Halogens

Compound	colour	mp ($^{\circ}\text{C}$)	Hal $^{\bar{3}}$ ion present	$\lambda_{\text{max}} =$ m μ
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsF}_2$	white	95-96	-	-
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$	white	240-242	-	-
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$	white	238-240	-	-
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$	bright yellow	149-151	I_2Br^-	275, 353
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$	rust	166-167	I_3^-	291, 357
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	dark orange	120-121	Br_3^-	269
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	rust	125-126	IBr_2^-	258, 370
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	chocolate brown	132-133	I_2Br^-	273, 351
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	chocolate brown	144-146	I_3^-	291, 357
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	dark brown	152-153	I_3^-	291, 356

1. shown by uv spectrum of methyl cyanide solution of the adduct

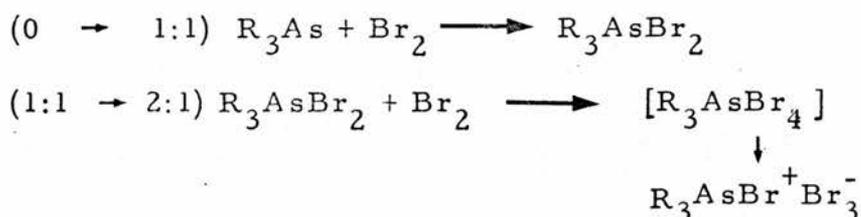
all as crystalline solids. The ultraviolet spectrum of methyl cyanide solutions of $R_3AsBr_2I_2$ showed the presence of I_2Br^- ions indicating that $R_3AsBr^+I_2Br^-$ is the correct formulation for this compound. These three tetrahalogeno compounds belong to the series $R_3AsBr_nI_{4-n}$ ($n=4, 3, 2, 1$ and 0) of which there are another two members, R_3AsBr_3I and R_3AsBrI_3 . These compounds have also been isolated from the appropriate mixtures of R_3As and $I_2 + Br_2$.

The absence of 1:1 breaks in the graphs of the conductometric titrations of $(2-CH_3C_6H_4)_3As$, $(3-CH_3C_6H_4)_3As$ and $(4-CH_3C_6H_4)_3As$ with IBr and I_2 indicate that the dihalogeno adducts R_3AsIBr and R_3AsI_2 are not formed in solution. It is therefore reasonable to assume that these reactions go straight to 2:1 $[Hal_2:R_3As]$ molar composition i.e.



The 1:1 adducts (R_3AsIBr and R_3AsI_2) could however be obtained as solids by reacting equimolar amounts of R_3As with IBr , and R_3As with I_2 in an appropriate solvent.

The presence of 1:1 breaks in conductometric titrations of $(3-CH_3C_6H_4)_3As$ and $(4-CH_3C_6H_4)_3As$ with Br_2 indicate formation of adducts of composition R_3AsBr_2 . From this we can conclude that reaction occurs in two stages, i.e.



These dibromotris(methylphenyl)arsoranes were obtained by reacting $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Br_2 and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Br_2 in a 1:1 molar ratio in appropriate solvents.

The absence of a 1:1 break in the conductometric titration of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ with Br_2 is surprising in view of the fact that other arsines give 1:1 breaks and in view of the apparent colour change in the solution at the 1:1 ratio. It is difficult to find a satisfactory explanation of this observation. A break in a conductometric titration depends on the rate of change of specific conductance of the solution being different before and after the equivalence point. This in turn is dependent on the variation of the number and the mobility of the ions in the solution as the titration proceeds. It is just possible that in this particular case the combined effect of number and mobility of ions is fortuitously the same before and after the 1:1 equivalence point and if this were the case no break could appear.

Attempts to prepare $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ proved difficult and a compound of composition $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ was not obtained. However a solvated compound of composition $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2] \cdot \text{CCl}_4$ was obtained. It is presumed that the reason for the lack of success in preparing the compound $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ lies in crystal packing effects rather than to any inherent instability of the R_3AsBr^+ ion. R_3AsBr_2 in the trigonal bipyramidal molecular form may be unstable for steric reasons (there is conductivity evidence for this which will appear later). Thus this may be an example of an ionic dihalide, $\text{R}_3\text{AsBr}^+\text{Br}^-$. But it would seem that these ions have difficulty

in packing to form a stable lattice unless molecules of carbon tetrachloride are present too.

E. Electrolytic Conductance of $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ and $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$ Adducts in Nitrobenzene

The molar conductance of various dihalogeno and tetra-halogeno adducts were measured at different concentrations in nitrobenzene (dielectric constant $\epsilon = 34.8$ at 25°C) at 25°C . Solutions of each solid contained in conductance cell were prepared in a dry-box and then immersed in a thermostat at 25°C . A slight change in conductance occurred as the solution warmed to the temperature of the thermostat, but thereafter, a steady value was obtained, and this was used to calculate molar conductance. In each case, the molar conductance decreased with increasing concentration [except in the case of the $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ compounds ($\text{Hal}_2 = \text{Cl}_2$ and Br_2) at lower concentrations].

Electrolytic Conductance of R_3AsHal_2 Adducts

[$\text{R} = (2\text{-CH}_3\text{C}_6\text{H}_4)$, $(3\text{-CH}_3\text{C}_6\text{H}_4)$, and $(4\text{-CH}_3\text{C}_6\text{H}_4)$;
 $\text{Hal}_2 = \text{F}_2, \text{Cl}_2, \text{Br}_2, \text{IBr}$ and I_2]

The electrolytic conductance of the adducts R_3AsHal_2 were measured and their molar conductance calculated. The values are given in Tables 18-22 on pp.172-175. A plot of molar conductance (Λ_m) against square root of molar concentration ($\sqrt{C_m}$) was constructed for each compound. These curves are reproduced in

figures 13-18 .

The electrolytic conductance of the dihalogeno compounds of triarylar sine may be discussed in two parts: I, R_3AsHal_2 adducts which ionise and give 'real' value of molar conductance ie. R_3AsF_2 , R_3AsCl_2 and R_3AsBr_2 ; and II. R_3AsHal_2 adducts which do not give 'real' value of molar conductance because of their disproportionation⁹² in solution ie. R_3AsIBr and R_3AsI_2 .

I. Electrolytic Conductance of R_3AsHal_2 Adducts

For a concise comparison of the values of Λ_m at $C_m = 0.01$ mol l⁻¹ were obtained from the graph and these are given below for the difluoro, dichloro, and dibromo compounds

Compound.	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsF ₂	19.00
(4-CH ₃ C ₆ H ₄) ₃ AsF ₂	0.14
(C ₆ H ₅) ₃ AsF ₂	0.0
(2-CH ₃ C ₆ H ₄) ₃ AsCl ₂	9.2
(3-CH ₃ C ₆ H ₄) ₃ AsCl ₂	0.8
(4-CH ₃ C ₆ H ₄) ₃ AsCl ₂	1.0
(C ₆ H ₅) ₃ AsCl ₂	0.4
(2-CH ₃ C ₆ H ₄) ₃ AsBr ₂ CCl ₄	14.1
(3-CH ₃ C ₆ H ₄) ₃ AsBr ₂	5.1
(4-CH ₃ C ₆ H ₄) ₃ AsBr ₂	4.9
(C ₆ H ₅) ₃ AsBr ₂	2.5

It is observed that the values of the molar conductance of dihalogenotris(methylphenyl)arsoranes [with the exception of

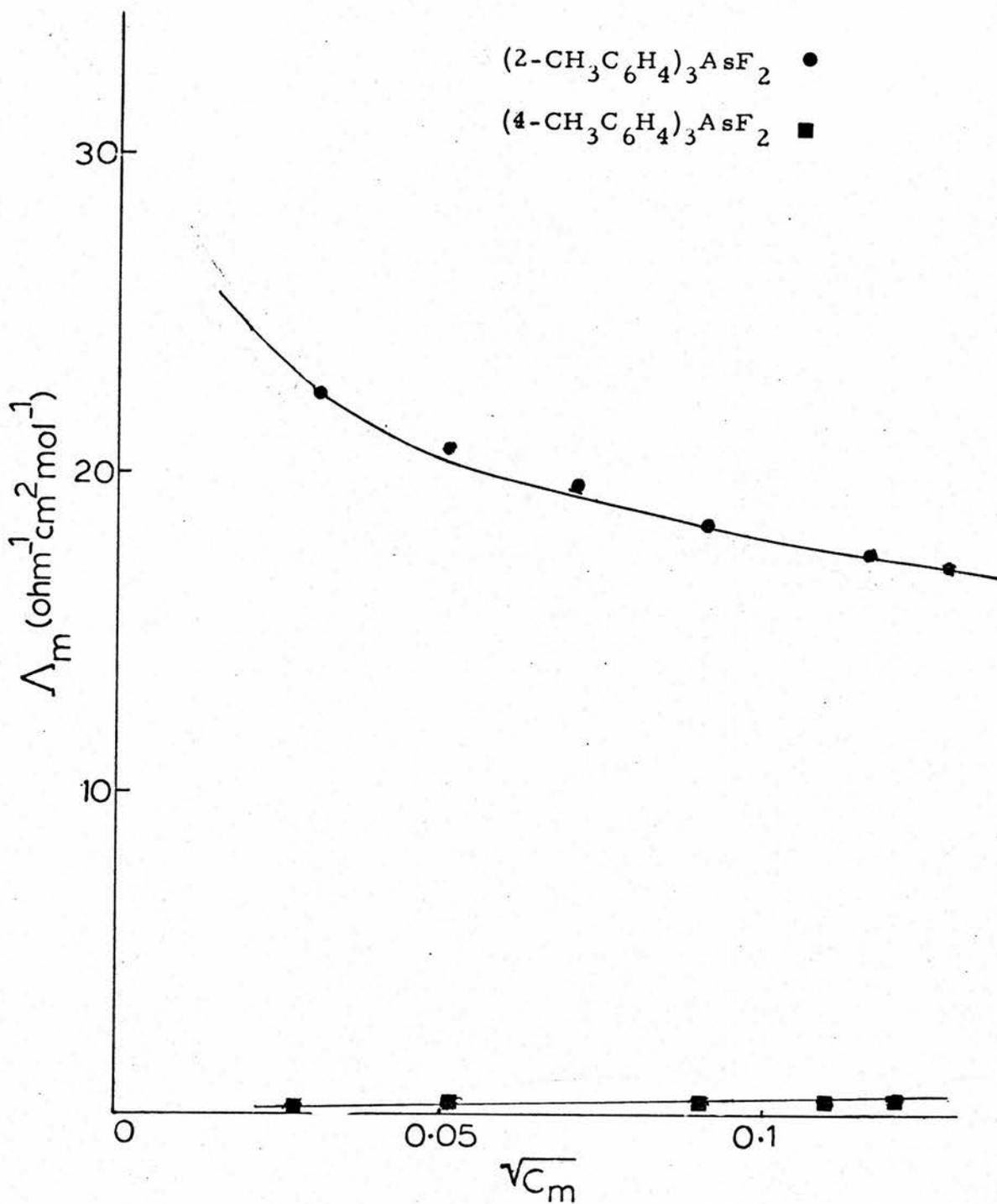


Figure 13. Electrolytic Conductance of R_3AsF_2 Adducts
in Nitrobenzene at 25°C

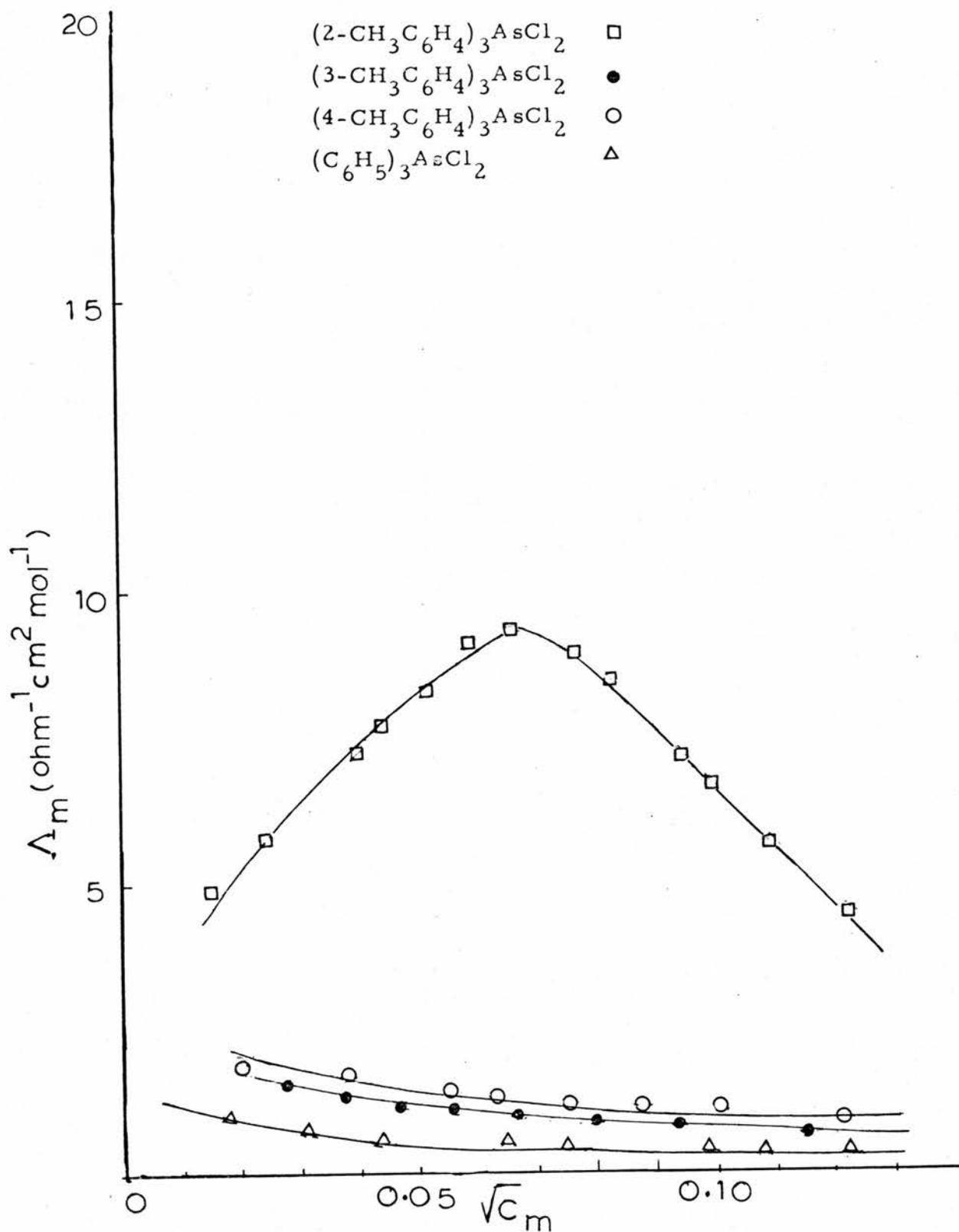


Figure 14. Electrolytic Conductance of R_3AsCl_2 Adducts in Nitrobenzene at 25°C

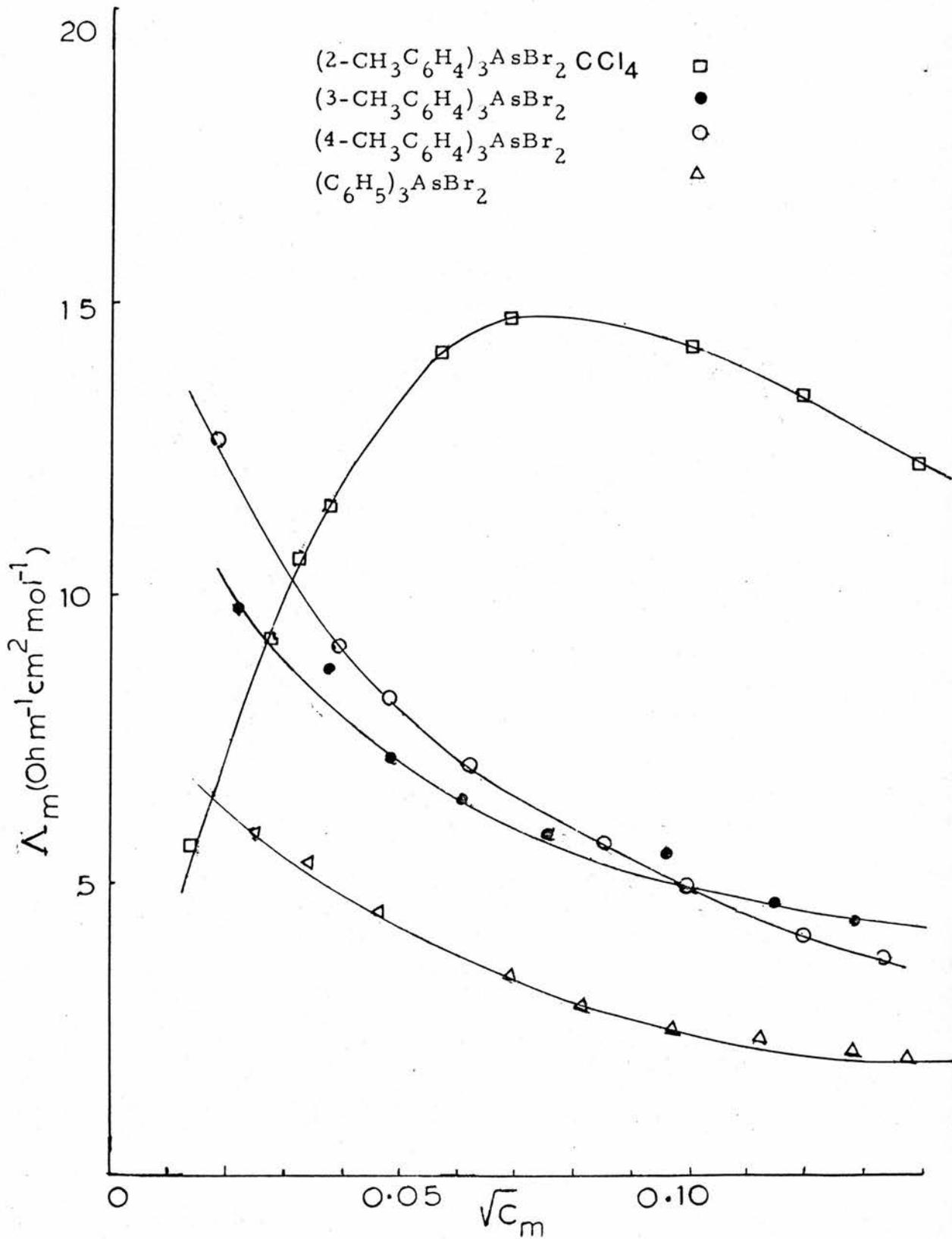
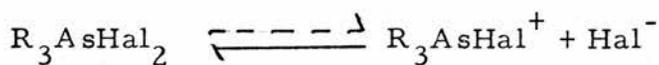


Figure 15. Electrolytic Conductance of R_3AsBr_2 Adducts in Nitrobenzene at 25°C

$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$] are all rather low compared with those expected for solutions of strong 1:1 electrolytes in the same solvent at similar concentration [e. g. for $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$, Λ_m , 25°C , $25.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at $C_m = 0.01 \text{ mol l}^{-1}$].^{p-58}

The dibromo, dichloro and difluoro adducts of tris(methylphenyl)arsoranes thus behave as weak to very weak electrolytes in nitrobenzene.



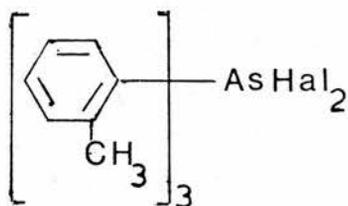
The conductance behaviour strongly suggests that these compounds are molecular in the solid state and that only under the influence of solvent do they undergo ionisation.

As mentioned earlier Harris and co-workers have observed that there is a relation between the electronegativity of the group R and tendency of R_3MHal_2 compound to behave in an ionic form. They showed that increasing the electronegativity of the group R increases the covalent character of the molecule. Conversely, decreasing the electronegativity of the group R weakens the As-Hal bond in the covalent molecules thus making ionisation easier. Considering from this point of view the dibromo compounds show the expected variation in conductance since the electronegativity of the tolyl group is slightly less than that of the phenyl group. Thus the value of molar conductance of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ is slightly higher than that of $(\text{C}_6\text{H}_5)_3\text{AsBr}_2$. There is however little difference between the molar conductance of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$. In case of dichloro compounds the values of molar conductance are much closer together, nevertheless the tolyl compounds have a slightly

higher molar conductance than the phenyl compound. The values of Λ_m of difluoro compounds are so low that they may be regarded as non-electrolytes in nitrobenzene.

The molar conductance values for the $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ adducts differ from those of the $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ adducts in two respects.

(i) The values are much higher and approach those expected for strong electrolytes. This could be attributed to the substitution of methyl group in 2-position of the phenyl ring. The nearness of the methyl group to the arsenic atom may produce a steric effect which results in overcrowding round the As atom in the

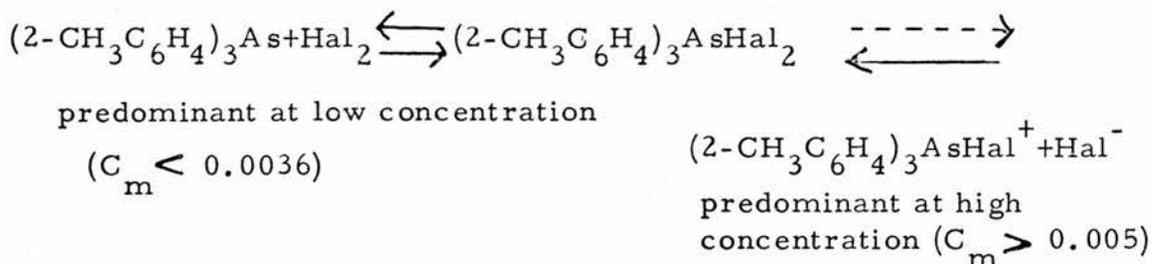


covalent trigonal bipyramidal molecule. This overcrowding would be relieved by ionisation to form a species with 4 coordinate arsenic i.e. the R_3AsX^+ ion. The higher molar conductance values for these compounds may thus be explained.

(ii) From the graphs of molar conductance (Λ_m) against square root of molar concentration $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ and $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ adducts] it is observed that up to a certain concentration (ca. $0.0025 - 0.0036 \text{ C}_m \text{ mol l}^{-1}$) molar conductance increases with increase of concentration and at higher concentration (ca: $0.005 \text{ C}_m \text{ mol l}^{-1}$) the value of molar conductance decreases with increase in concentrations.

Thus a humped graph as shown in figure 14 is obtained. The

anomalous behaviour is believed to be due to the increasing importance of molecular dissociation (giving non-conducting species) at the low concentration.



Considering the effect of different halogens on the molar conductance of $R_3\text{MHal}_2$ compounds by keeping the R group constant and changing the halogens from $F_2 \rightarrow Cl_2 \rightarrow Br_2$

increase in electronegativity	Compound	Λ_m ohm ⁻¹ cm ² mol ⁻¹ at 0.01 C_m mol l ⁻¹
	$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsF}_2$	0.14
	$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$	1.0
	$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$	4.9

it is observed that increase in electronegativity of the halogen group lowers the value of molar conductance, therefore less ionic tendency of the $R_3\text{MHal}_2$ compounds. This view is in agreement with the previous study of $(C_6H_5)_3\text{AsHal}_2$ compounds by Harris and co-workers¹²⁶.

II. Electrolytic Conductance of $R_3\text{AsHal}_2$ Adducts

For a concise comparison the values of Λ_m at $C_m = 0.01 \text{ mol l}^{-1}$ were obtained from the graph and these are given below for the bromiodo, and diiodo compounds.

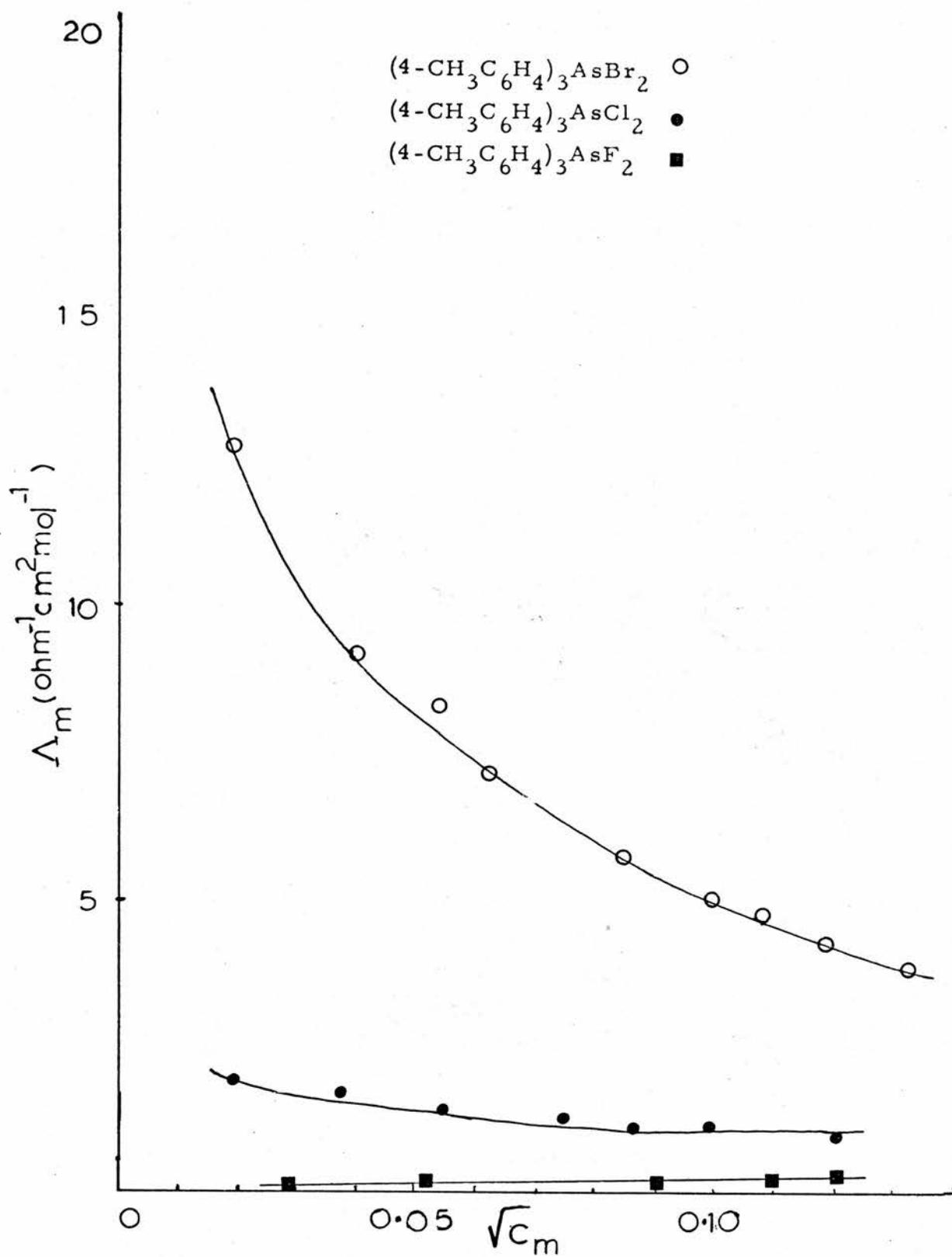
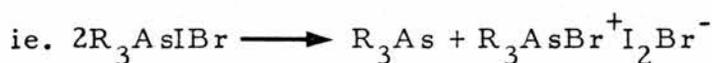


Figure 16. Electrolytic Conductance of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsHal}_2$ Adducts in Nitrobenzene at 25°C

Compound	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsIBr	11.3
(3-CH ₃ C ₆ H ₄) ₃ AsIBr	8.3
(4-CH ₃ C ₆ H ₄) ₃ AsIBr	8.5
(2-CH ₃ C ₆ H ₄) ₃ AsI ₂	11.4
(3-CH ₃ C ₆ H ₄) ₃ AsI ₂	10.3
(4-CH ₃ C ₆ H ₄) ₃ AsI ₂	7.9

The molar conductance values of diiodo- and bromo-iodotris(methylphenyl)arsoranes are not 'real' since they are unstable in solution, disproportionating to the corresponding tetrahalogeno adducts¹²³.



The conductance of the solutions is therefore due to the presence of tetrahalogeno compound (strong 1:1 electrolytes) in solution. Disproportionation has been confirmed from the ultraviolet spectra of R₃AsIBr and R₃AsI₂ in methyl cyanide. These showed the presence of the I₂Br⁻ and I₃⁻ ions from the R₃AsIBr and R₃AsI₂ adducts respectively. The observed disproportionation of these compounds fits in with their non-appearance during conductometric titration of these arsines with IBr and I₂. There is no question of the high molar conductance values for (2-CH₃C₆H₄)₃AsBr₂ having a similar explanation since solutions of this compound do not show ultraviolet absorption due to Br₃⁻ (which they would do if

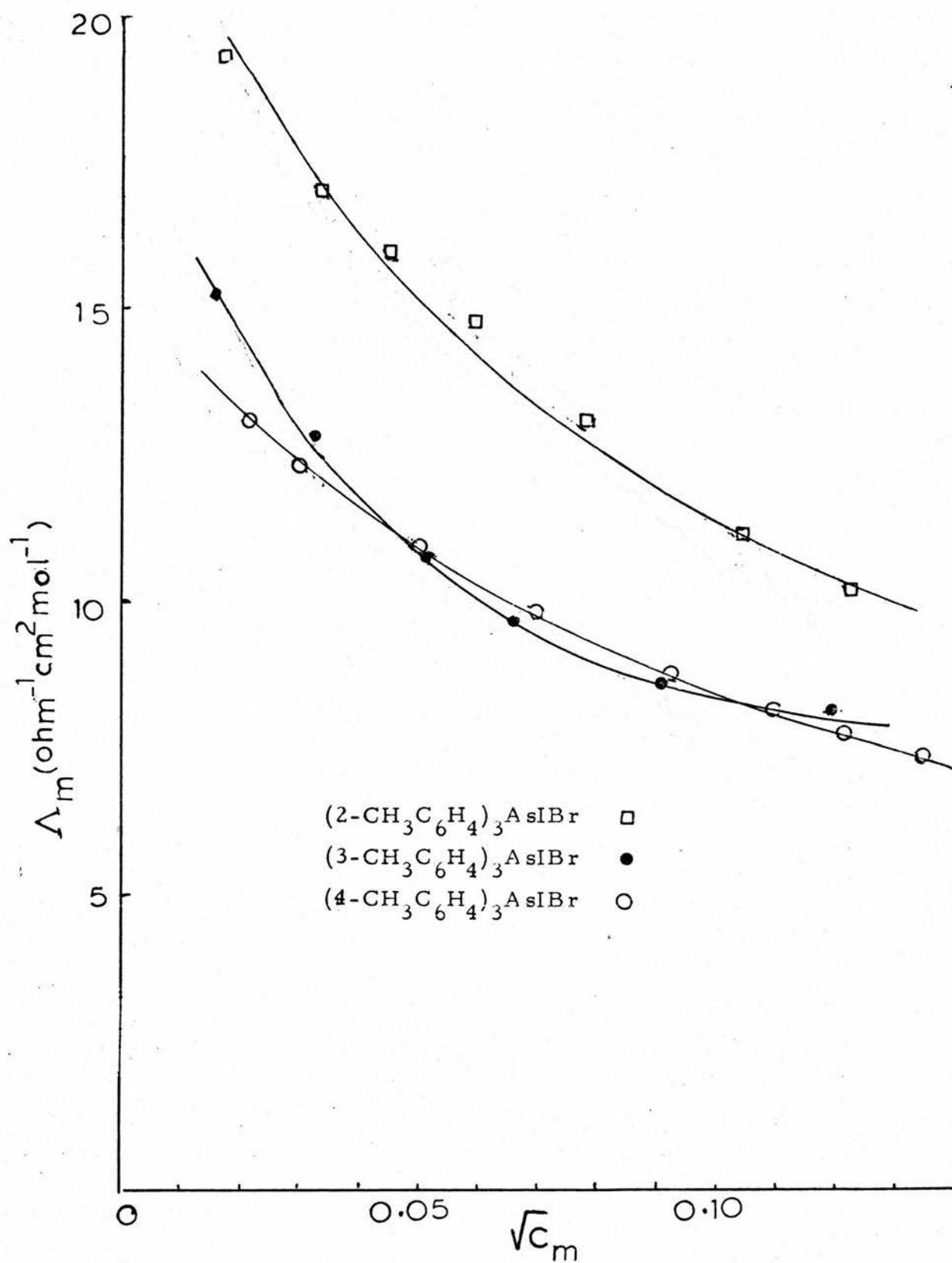


Figure 17. Electrolytic Conductance of R₃AsIBr Adducts
in Nitrobenzene at 25°C

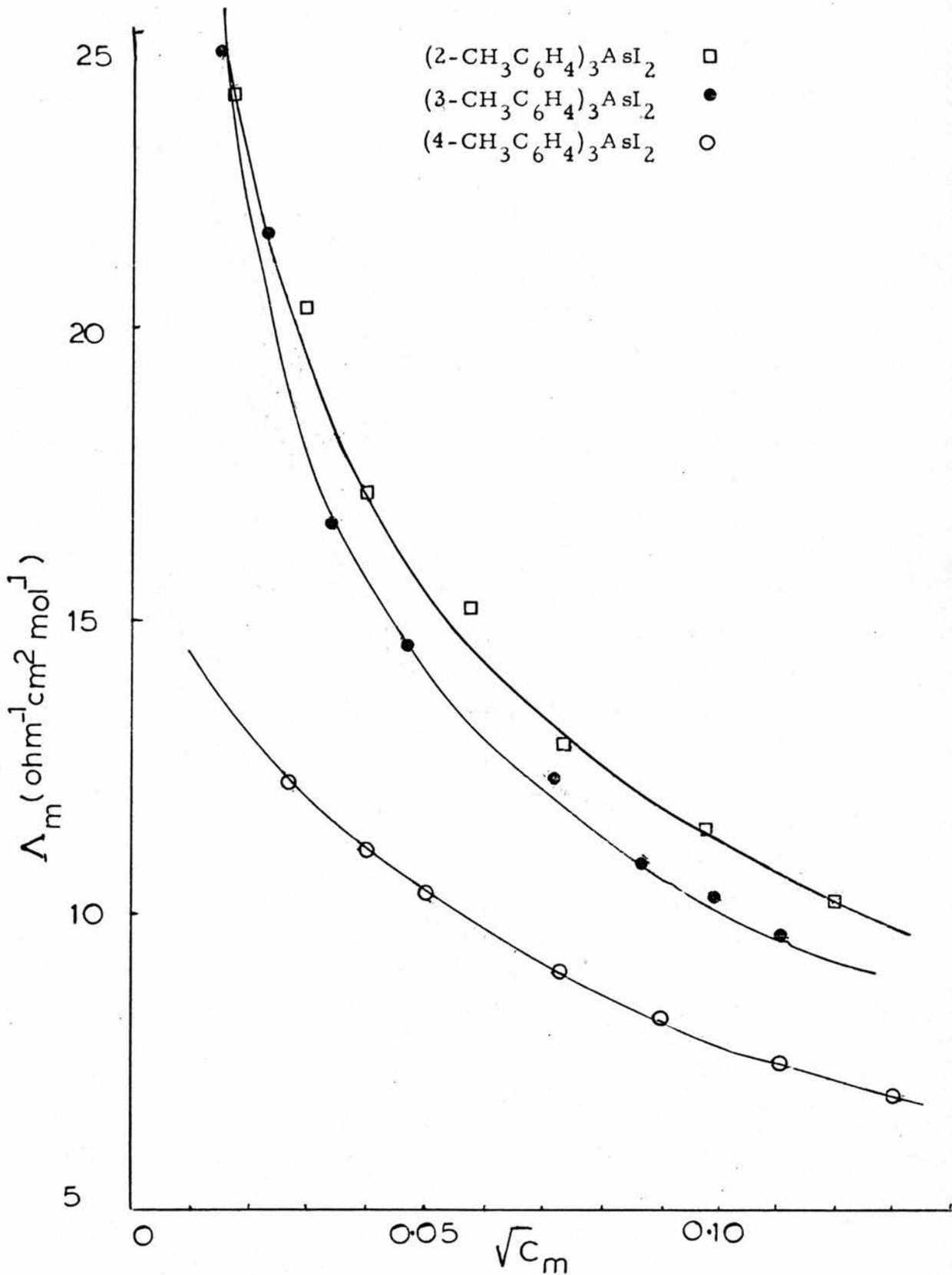


Figure 18. Electrolytic Conductance of $R_3\text{AsI}_2$ Adducts
in Nitrobenzene at 25°C

disproportionation occurred). Likewise it is very unlikely that $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ would undergo disproportionation.

Electrolytic Conductance of $\text{R}_3\text{AsBr}_n\text{I}_{4-n}$ Adducts

[$\text{R}=(2\text{-CH}_3\text{C}_6\text{H}_4)$; $(3\text{-CH}_3\text{C}_6\text{H}_4)$, and $(4\text{-CH}_3\text{C}_6\text{H}_4)$;
 $n=4, 3, 2, 1$ and 0]

The electrolytic conductances of all the adducts of formula $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$ were measured at different concentrations and their molar conductance values were calculated on the basis of their respective formula. These values are given in Tables 23-25 on pp. 175-178. These values when plotted against the square root of the molar concentration ($\sqrt{C_m}$) fall in straight lines [except in case of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$] and are displayed in figures 19-21 .

For comparative purposes the values of conductance at $C_m=0.01 \text{ mol l}^{-1}$, were obtained by interpolation of the graphs, and were found to be:

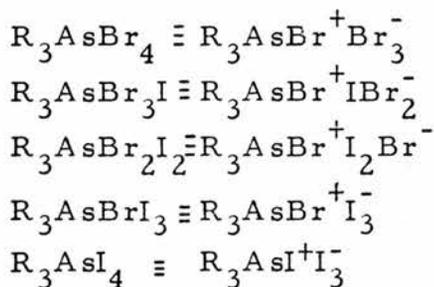
Compound	$\Lambda_m \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	22.6
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	25.4
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	15.9
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	18.4
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	14.9
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	25.4
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	26.0
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	23.9

$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	22.0
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	20.4
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$	25.8
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$	24.3
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	24.2
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$	21.4
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$	20.4

The magnitude of the molar conductance values of nitrobenzene solution of these adducts (as shown above) suggest that they are strong 1:1 electrolytes in the solvent. (For a strong 1:1 electrolyte in nitrobenzene Λ_m 20-26 ohm⁻¹cm²mol⁻¹ at $C_m = 0.01$ mol l⁻¹)¹²⁴ By analogy with $(\text{C}_6\text{H}_5)_3\text{AsHal}_4$ compounds⁹² we can write



The presence of Hal_3^- ion has been confirmed in each case from the ultraviolet spectrum of methyl cyanide solutions of the tetrahalogeno adducts. From the high values of molar conductance of these compounds it seems reasonable to suggest that all of the tetrahalogeno compounds of tris(methylphenyl)-arsines are ionic in the solid state with the same ions as are present in methyl cyanide solution, ie.



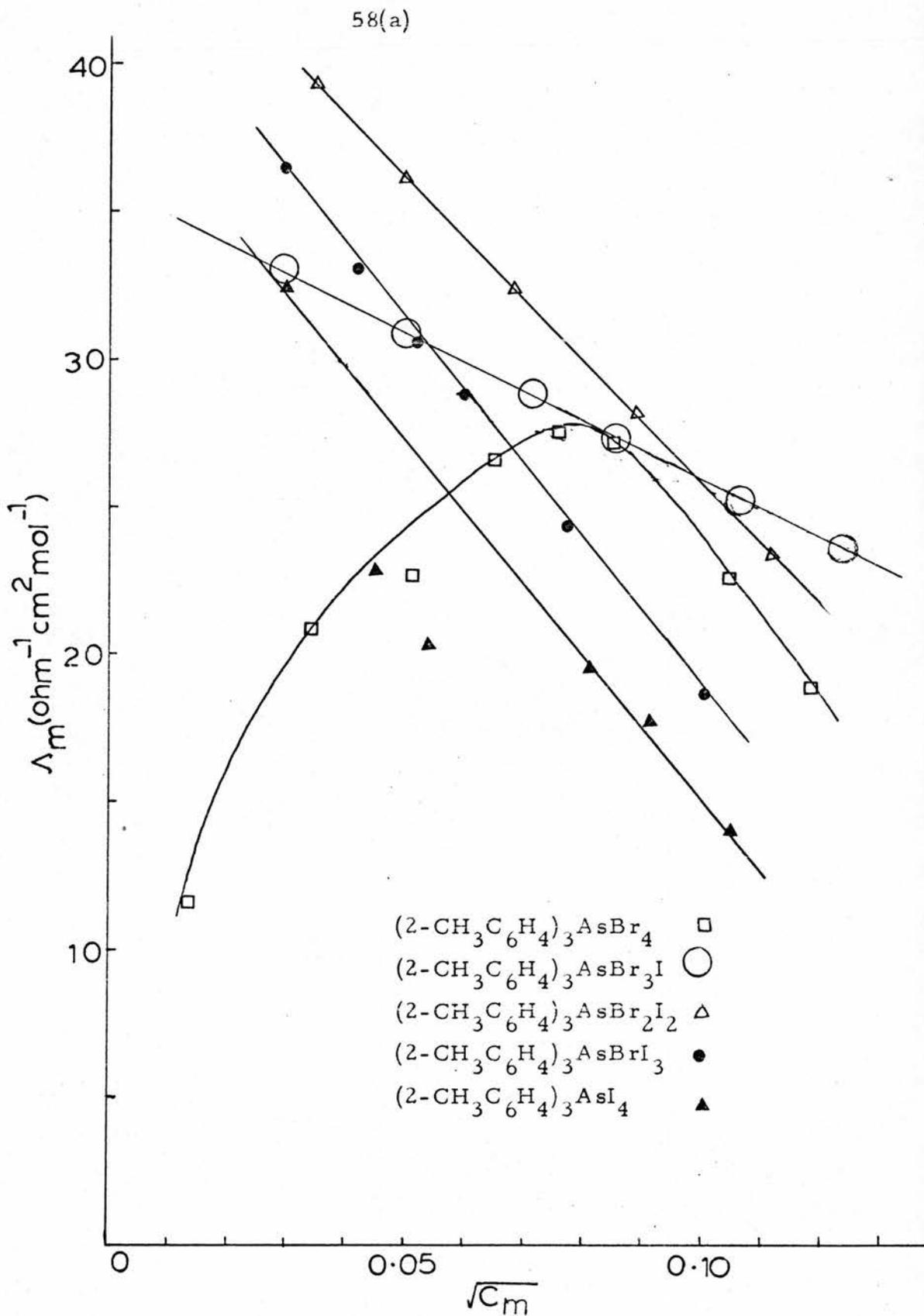


Figure 19. Electrolytic Conductance of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$
 ($n=4, 3, 2, 1, 0$) in Nitrobenzene at 25°C

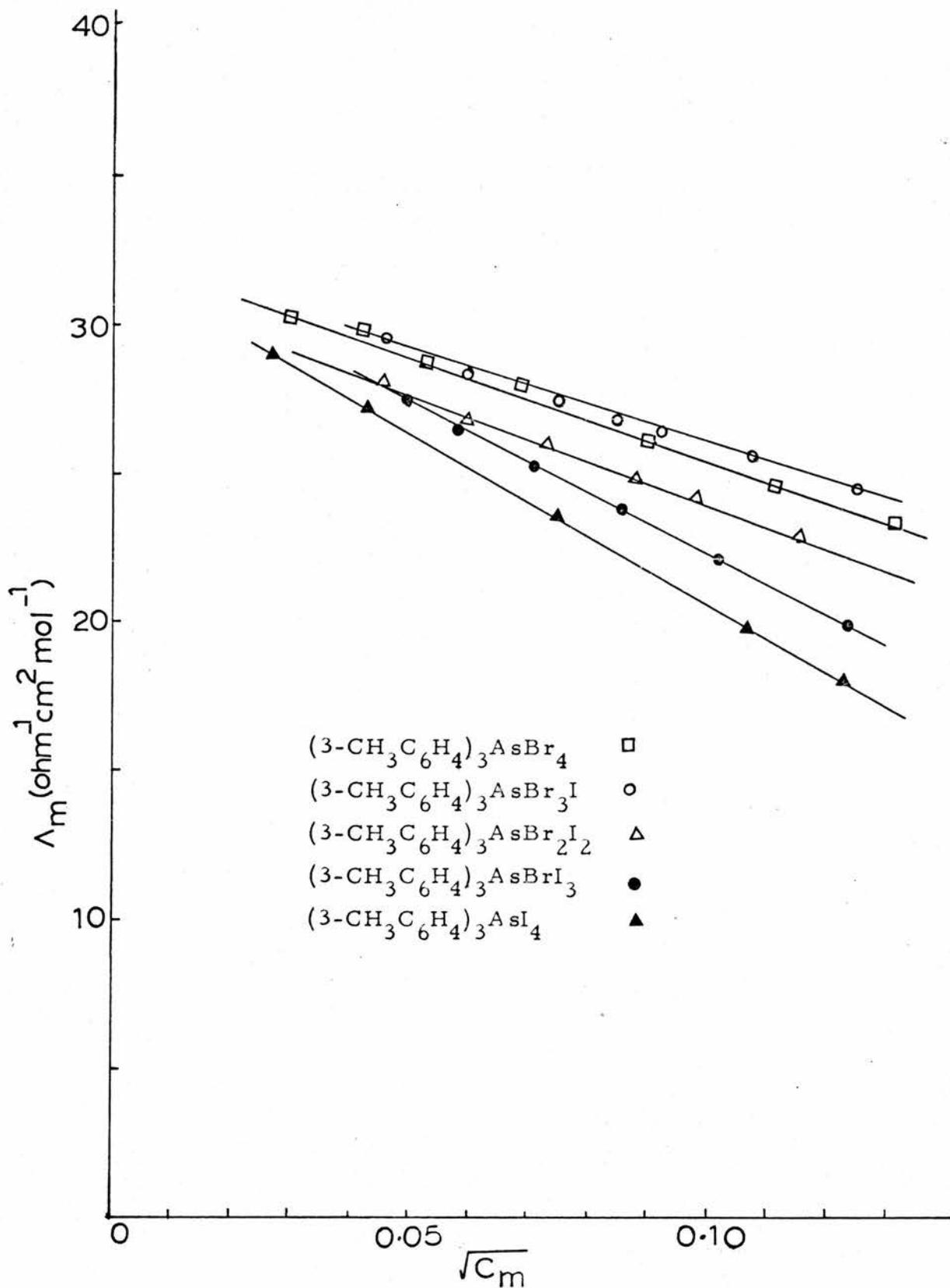


Figure 20. Electrolytic Conductance of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$ in Nitrobenzene at 25°C ($n=4, 3, 2, 1, 0$)

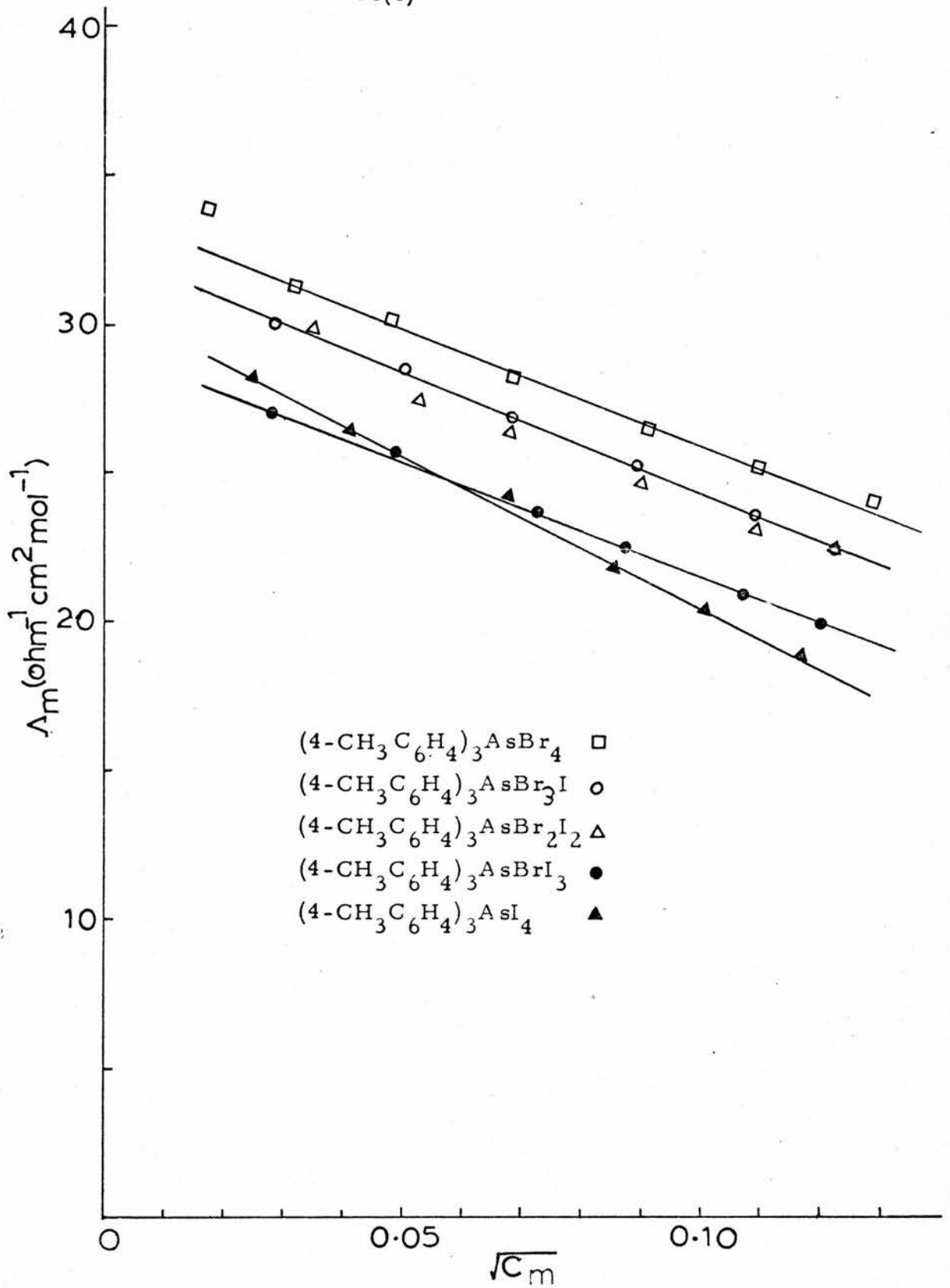


Figure 21. Electrolytic Conductance of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$
 in Nitrobenzene at 25°C
 ($n=4, 3, 2, 1, 0$)

This was shown to be the case for the $(C_6H_5)_3AsHal_4$ compounds⁹².

From figure 19 it is observed that $(2-CH_3C_6H_4)_3AsBr_4$ does not give the normal relationship between molar conductance (Λ_m) and square root of molar concentration ($\sqrt{C_m}$), since at lower concentration the graph develops a positive slope.

The low molar conductance at low concentration is presumably due to a high degree of molecular dissociation [cf. $(2-CH_3C_6H_4)_3AsCl_2$ and $(2-CH_3C_6H_4)_3AsBr_2$]^{p. 54}

F. The Mode of Ionisation of the $R_3AsBr_nI_{4-n}$ Adducts in

Nitrobenzene - Semiquantitative Electrolysis Experiments

[$R=(2-CH_3C_6H_4)$, $(3-CH_3C_6H_4)$, $(4-CH_3C_6H_4)$,
n=3, 2, and 1]

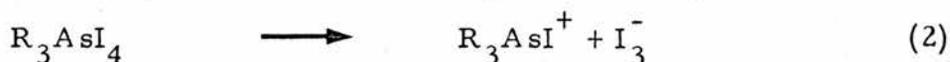
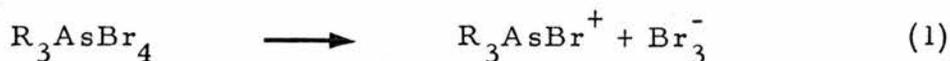
The high values of molar conductance of tetrahalogeno adducts of tris(methylphenyl)arsoranes in nitrobenzene has been interpreted as being due to ionisation as



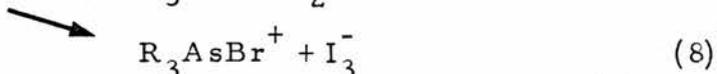
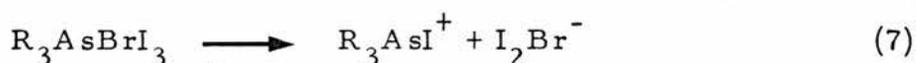
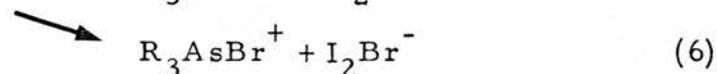
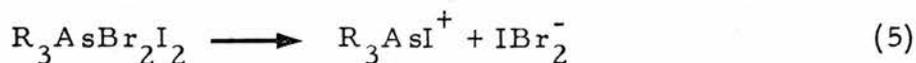
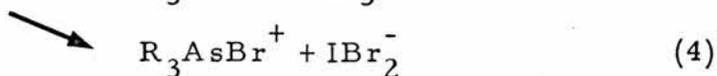
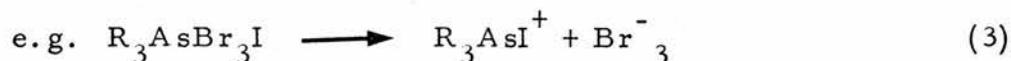
and the exact nature of the ions present has been deduced indirectly from the ultraviolet spectrum of solution of the compound in methyl cyanide¹²⁵. This solvent was used for the ultraviolet work since nitrobenzene is unsuitable for uv studies. It was thought of interest to obtain direct information about the ionisation in nitrobenzene and it was decided to do this using a semiquantitative electrolysis technique.

In the case of tetrahalogeno adducts of triarylsarsines where there is only one type of halogen e.g. R_3AsBr_4 ,

R_3AsI_4 there is only one possible scheme of ionisation^{92, 123}.



In contrast for tetrahalogeno compounds where there are two different halogens present $R_3AsBr_nI_{4-n}$ ($n=3, 2$ and 1) there are two possible schemes of ionisation^{92, 123}.

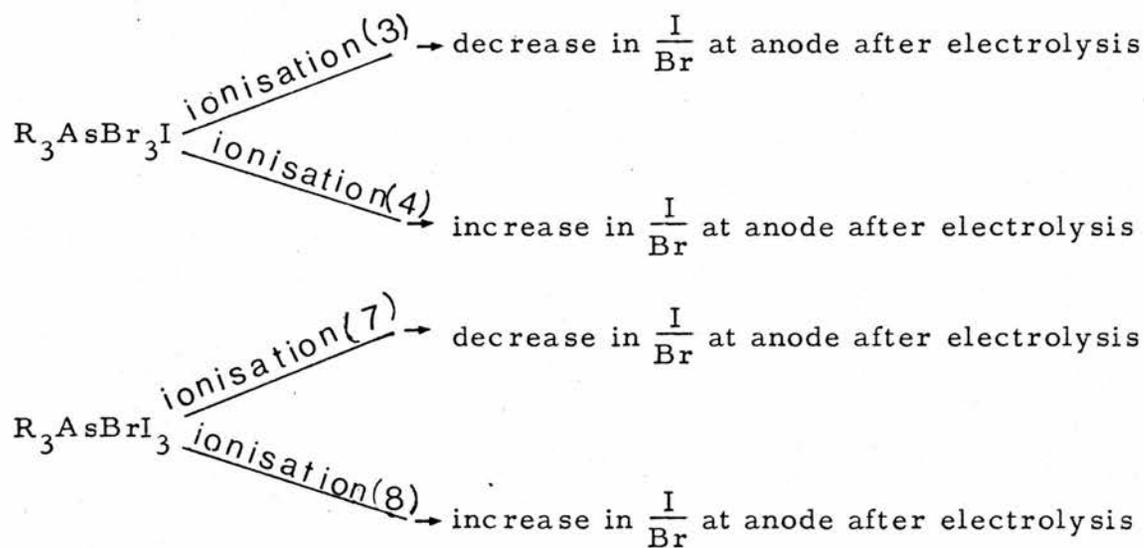


It should be possible to distinguish these by electrolysing a solution of the mixed tetrahalogeno adducts in a Hitroff cell (figure 43) and measuring the change in composition (ratio $\frac{I}{Br}$) of the solution near the electrodes, after the passage of a known amount of current. That is the resultant composition ($\frac{I}{Br}$ ratio) is compared with the composition ($\frac{I}{Br}$ ratio) measured before electrolysis.

The technique assumes that the cation and anion transport numbers are about equal. Thus for $R_3AsBr_2I_2$ it is clear that if ionisation (5) is correct then there will be a build-up of bromine at the anode during electrolysis and the final $\frac{I}{Br}$ ratio in the anode solution will be less than the initial $\frac{I}{Br}$ ratio. On the other hand if ionisation (6) is correct the $\frac{I}{Br}$ ratio in anode solution will increase during electrolysis. The same arguments hold for other

tetrahalogeno adducts containing I and Br ie. R_3AsBr_3I

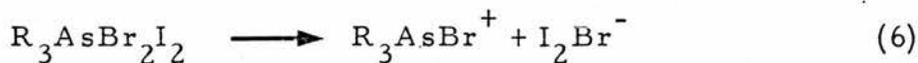
and R_3AsBrI_3



Semiquantitative Electrolysis of $(2-CH_3C_6H_4)_3AsBr_2I_2$ in

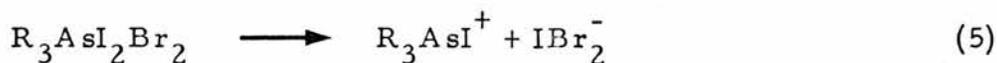
Nitrobenzene

The original colour of the solution before electrolysis was red brown. The ratio $\frac{I}{Br}$ (from analysis) before electrolysis was $\frac{0.95}{0.91} (\approx \frac{1}{1})$ (the theoretical value). The ratio $\frac{I}{Br}$ (at anode) after the electrolysis was $\frac{0.74}{0.67} \approx \frac{1.10}{1}$ ie. the $\frac{I}{Br}$ ratio in the anode solution increases after electrolysis thus favouring ionisation scheme (6)



(ie. the same ionisation scheme as indicated by the ultraviolet spectrum for methyl cyanide solution of this adduct).

On the basis of the known relative stabilities of IBr_2^- and I_2Br^- ions this mode of ionisation is perhaps at first sight unexpected¹²⁷, since if the stability of the trihalide ion controlled the course of ionisation, the possible alternative

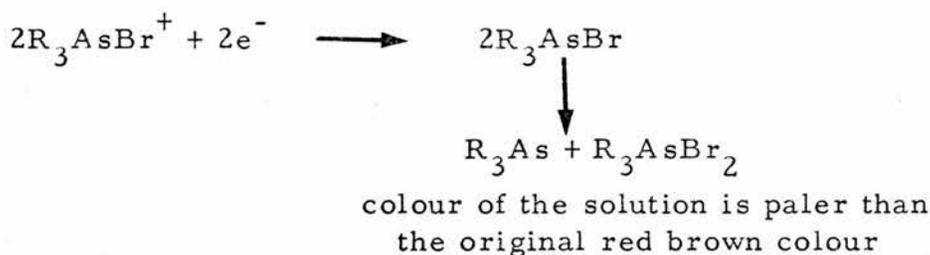


would be expected. Therefore, the factor controlling the mode of ionisation must be the nature of the cation.

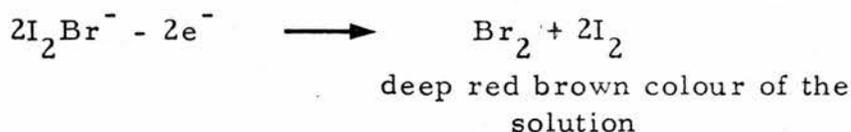
On the one hand, the cation contains an As-Br bond (Scheme 6), and on the other an As-I bond (Scheme 5). Otherwise, they are presumably of a similar size and symmetry. Since in general, the As-Br bond energy is greater than the As-I bond energy (242.44 kJ in AsBr_3 as opposed to 179.74 kJ in AsI_3), it is clear that the bromotriarylarsonium cation is the more favourable species¹²³. Thus, the greater strength of the As-Br bond is the critical factor in determining the mode of ionisation in $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$ compound.

The reactions occurring at the electrodes can be written as:

At cathode:



At anode:



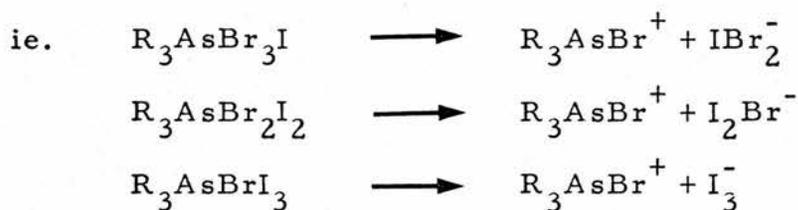
Similarly the semiquantitative electrolysis of adducts $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$, $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$, $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_n\text{I}_{4-n}$ were carried out in nitrobenzene using the same technique and the results are recorded in Table 26 on page 63.

Table 26. Semiquantitative Electrolysis of R_3AsBr I, $n=4-n$ Adducts in Nitrobenzene

Compound	ratio of $\frac{I}{Br}$ before electrolysis found from analysis	ratio of $\frac{I}{Br}$ after the electrolysis found from analysis	change in $\frac{I}{Br}$ ratio observed	Scheme of ionisation observed
$(2-CH_3C_6H_4)_3AsBrI$	$\frac{0.29}{0.91}$ ~ $\frac{1}{3}$	$\frac{0.29}{0.70}$ ~ $\frac{1}{2.41}$	increase	(4)
$(2-CH_3C_6H_4)_3AsBrI_3$	$\frac{0.56}{0.25}$ ~ $\frac{3}{1}$	$\frac{0.72}{0.22}$ ~ $\frac{3.27}{1}$	increase	(8)
$(3-CH_3C_6H_4)_3AsBrI_2$	$\frac{0.45}{0.46}$ ~ $\frac{1}{1}$	$\frac{0.33}{0.22}$ ~ $\frac{1.5}{1}$	increase	(6)
$(3-CH_3C_6H_4)_3AsBrI$	$\frac{0.35}{1.20}$ ~ $\frac{1}{3}$	$\frac{0.27}{0.73}$ ~ $\frac{1}{2.7}$	increase	(4)
$(3-CH_3C_6H_4)_3AsBrI_3$	$\frac{1.38}{0.52}$ ~ $\frac{3}{1}$	$\frac{0.74}{0.21}$ ~ $\frac{3.52}{1}$	increase	(8)
$(4-CH_3C_6H_4)_3AsBrI_2$	$\frac{0.25}{0.25}$ ~ $\frac{1}{1}$	$\frac{0.51}{0.31}$ ~ $\frac{1.64}{1}$	increase	(6)
$(4-CH_3C_6H_4)_3AsBrI$	$\frac{0.51}{1.43}$ ~ $\frac{1}{3}$	$\frac{0.43}{0.93}$ ~ $\frac{1}{2.16}$	increase	(4)
$(4-CH_3C_6H_4)_3AsBrI_3$	$\frac{0.76}{0.23}$ ~ $\frac{3}{1}$	$\frac{0.66}{0.08}$ ~ $\frac{8.25}{1}$	increase	(8)

Summary

(1) The semiquantitative electrolysis experiments show that for all the adducts of type $R_3AsBr_nI_{4-n}$ which contain I and Br [ie. $n=3, 2,$ and 1 ; $R=(2-CH_3C_6H_4), (3-CH_3C_6H_4),$ and $(4-CH_3C_6H_4)$] the ionisation adopted is the one in which the cation contains a bromine atom attached to arsine



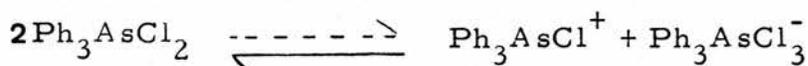
This behaviour follows that observed for $Ph_3AsBr_nI_{4-n}$ compounds⁹².

(2) The ions observed in nitrobenzene solution are the same as those found (from ultraviolet spectrum) in methyl cyanide.

G. The Mode of Ionisation of R_3AsCl_2 Adducts in Nitrobenzene

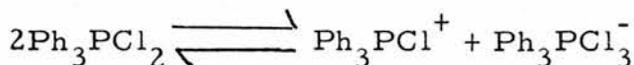
[$R = (3-CH_3C_6H_4),$ and $(4-CH_3C_6H_4)$.]

The mode of ionisation of dichlorotriphenylarsorane in methyl cyanide solution has been deduced from conductance and electrolysis experiments by Harris and Beveridge⁹². It has been suggested that the compound is a weak electrolyte, ionising according to the equation;

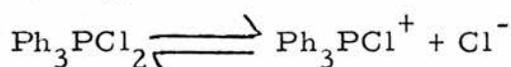


Dichlorotriphenylphosphorane is a strong 1:1 electrolyte ($\Lambda_m = 78.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $C_m = 0.01 \text{ mol l}^{-1}$)⁹² and its ionisation mode in methyl cyanide solution has been investigated by Harris and Ali⁹⁶ who conclude from a conductometric

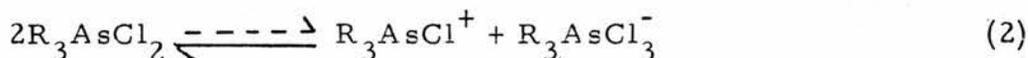
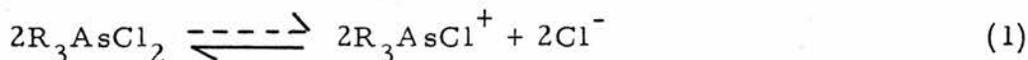
titration study of the reaction of Ph_3PCl_2 with a strong chloride ion donor, Et_4NCl that Ph_3PCl_2 has no tendency to act as a halide ion acceptor. This is believed to eliminate the scheme



involving the $\text{Ph}_3\text{PCl}_3^-$ ion formed by transfer of a chloride ion from one Ph_3PCl_2 molecule to another. They therefore presumed that Ph_3PCl_2 ionises simply as



The electrolytic conductance studies of R_3AsCl_2 compounds in nitrobenzene solution show that they are weak electrolytes in nitrobenzene and so it was of interest to obtain information on the mode of ionisation of these compounds in nitrobenzene. By analogy with Ph_3AsCl_2 and Ph_3PCl_2 the two most probable ionisation schemes for R_3AsCl_2 compounds are:



The ionisation was studied by two methods:

- (1) Quantitative electrolysis
- (2) Conductometric titration of R_3AsCl_2 with $(\text{C}_6\text{H}_5)_4\text{AsCl}$

(1) Quantitative Electrolysis of R_3AsCl_2 in Nitrobenzene

Several attempts were made to determine the transport number of the ions produced in nitrobenzene solution, but it was found difficult to obtain reproducible results, probably because of the very low conductance of the compounds which led to only very small changes in concentration at the electrodes and

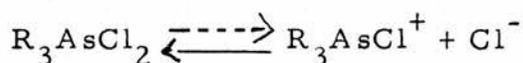
consequent difficulty in accurate analysis. Also, no reactions were observed to take place at the electrodes. Thus no conclusive results could be derived from the quantitative electrolysis of the chloro compounds.

(2) Conductometric Titration of R_3AsCl_2 with $(C_6H_5)_4AsCl$

To get some insight into the ionisation of R_3AsCl_2 in nitrobenzene the reaction of these compounds with $(C_6H_5)_4AsCl$ (a strong chloride ion donor) was studied conductometrically; if R_3AsCl_2 have indeed a tendency to accept a chloride ion in nitrobenzene solution, the following overall process should occur:-



and this should show as a 1:1 break in the conductometric titration graph. The resultant conductance-composition curve (figure 23) was without any discontinuity and did not differ appreciably from that obtained when the same tetraphenylarsonium chloride solution was added to pure solvent. There was thus no indication of the formation of the anion $R_3AsCl_3^-$, and the results suggested that the simple ionisation scheme



is present.

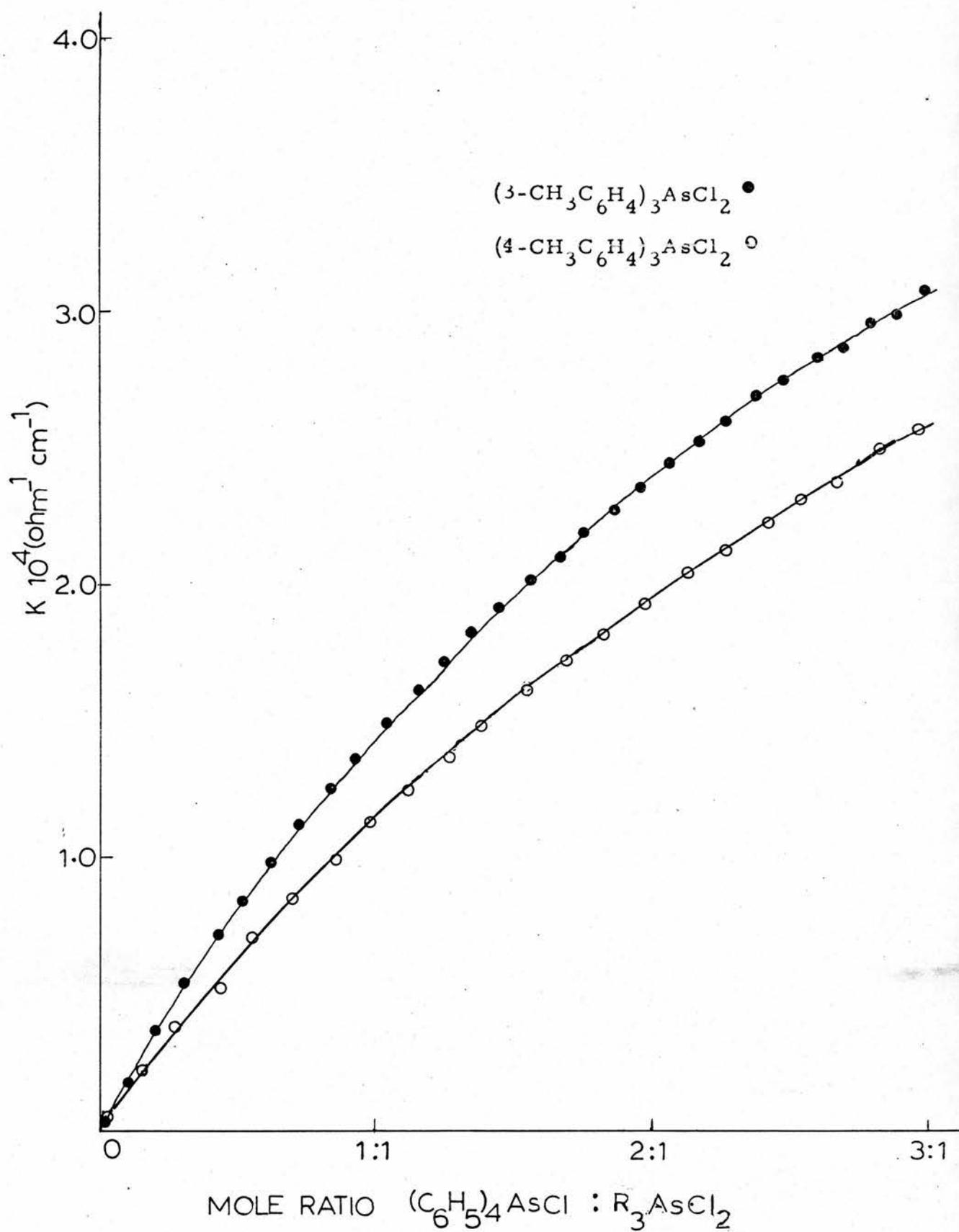


Figure 23. Conductometric Titration of R_3AsCl_2 with $(\text{C}_6\text{H}_5)_4\text{AsCl}$ in Nitrobenzene

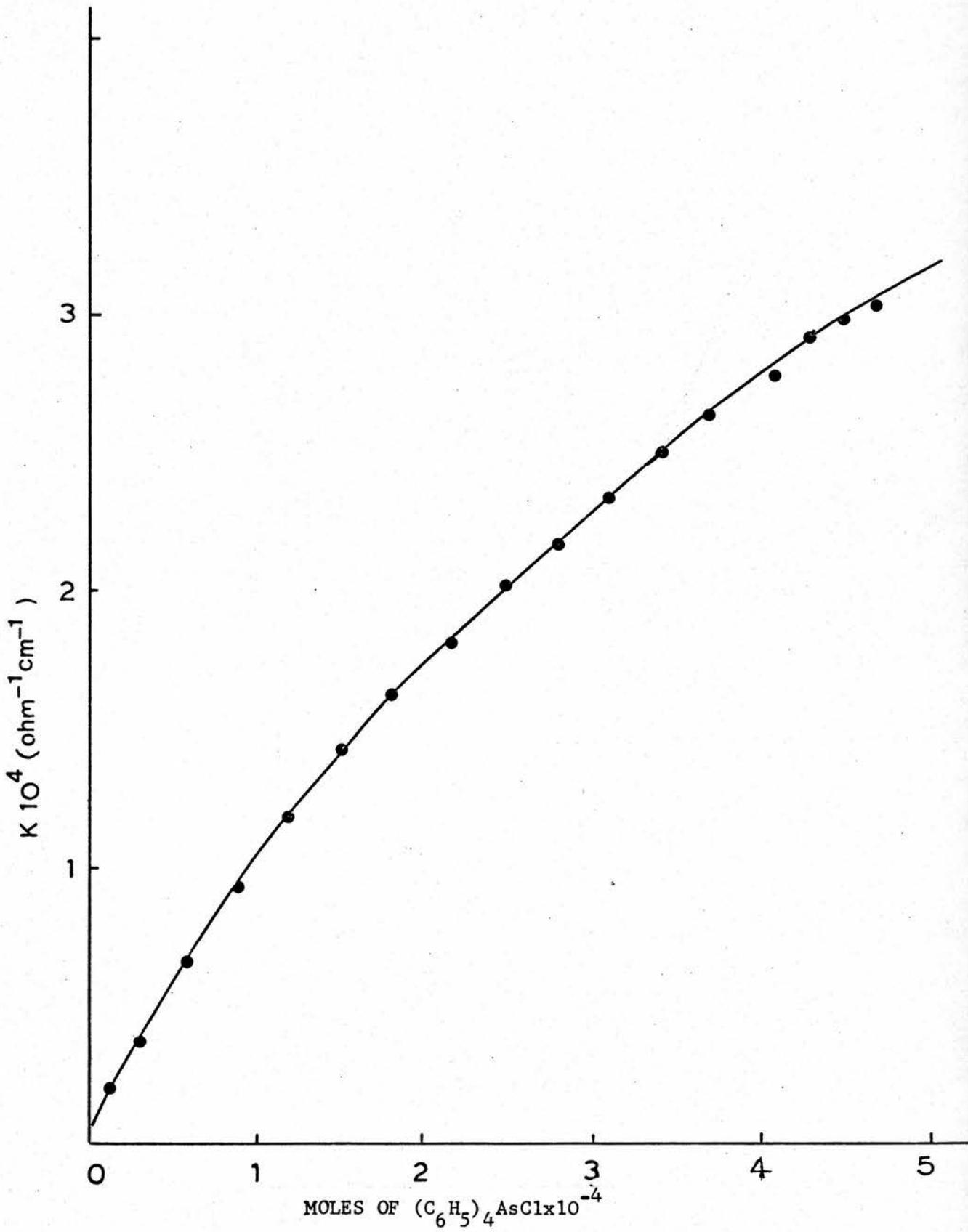


Figure 22. Blank Conductometric Titrations of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ in Nitrobenzene

INTRODUCTION

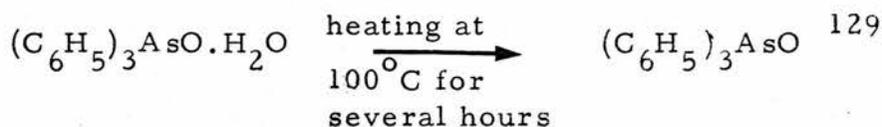
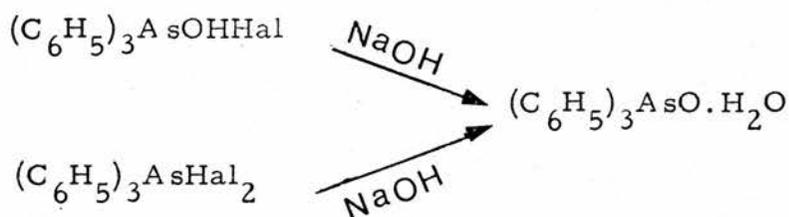
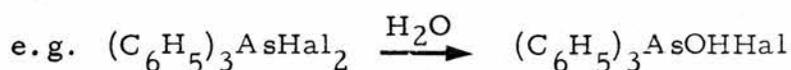
PART II

HYDROLYSIS PRODUCTS OF R_3AsHal_2 COMPOUNDS

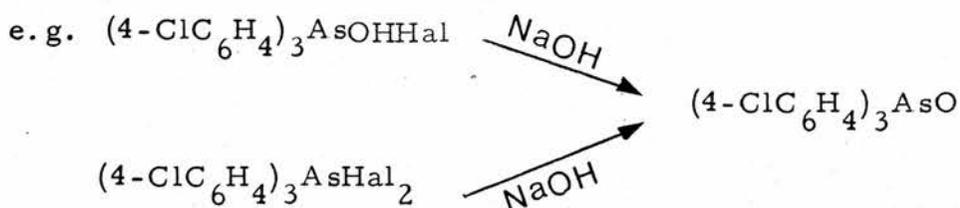
HYDROLYSIS PRODUCTS OF R_3MHAL_2 COMPOUNDS

(R=alkyl or aryl group; M=P, As, Sb and Bi; Hal=Cl, Br)

Like most compounds of the Phosphorus Group elements with halogens, the dihalogeno derivatives of triarylsarsine are hydrolytically unstable. They hydrolyse in two stages^{128a}, corresponding formally to replacement of one or both halogen atoms by an OH group: that is, mild conditions (e. g. the action of cold water) yields $R_3AsOHHal$, generally referred to in the literature as hydroxyhalides, whereas hot caustic alkaline solution gives the hydrated oxide¹²⁹, $R_3AsO \cdot H_2O$ (formerly believed to be the isomeric dihydroxide, $R_3As(OH)_2$). These hydrated oxides dehydrate readily on heating to form the series of oxides R_3AsO ¹²⁹



and the dihalogeno derivatives of some triarylsarsine hydrolyse directly to the oxide without forming a hydrated oxide¹²²



Under appropriate conditions these reactions may be reversed.

(a) Oxides R_3MO

The oxides R_3MO can be obtained by direct oxidation of R_3M as well as by hydrolysis of R_3MHal_2 compounds. Trialkyls in general are fairly readily oxidised by atmospheric oxygen, but triaryls require a stronger oxidising agent such as hydrogen peroxide or permanganate^{130a}.

Vibrational spectroscopy has been extensively used in determining the structure of these compounds by many workers^{129, 131, 130b}, and complete vibrational assignments have been made for $(C_6H_5)_3PO$ ¹³², $(C_6H_5)_3AsO$ ^{129, 133, 134} $(p-XC_6H_4)_3AsO$ and $(m-XC_6H_4)_3AsO$ ¹³⁵. In the former two compounds, bands at 1193 and 880 cm^{-1} , respectively are assigned to the ν (M-O) modes. The As=O stretching frequency in trialkylarsine oxides appear as a well defined band in the 850-910 cm^{-1} region^{136, 137}. Shagidullin and co-workers^{137, 130c} have recently examined the infrared spectra of a number of compounds containing the As=O group. From their observations they concluded that the stretching frequency of this group varies with the electronegativity of the substituents attached to the arsenic atom. Harris and Inglis have studied the ir spectra of triphenylarsine oxide¹²⁹, tris(4-methylphenyl)arsine oxide and tris(4-chlorophenyl)arsine oxide¹²² in the solid state and have found the stretching frequency of the As=O group to be at near 888 cm^{-1} , 890 cm^{-1} and 893 cm^{-1} respectively. They also studied the infrared spectra of triphenylarsine oxide in chloroform solution. This was found to be the same as in

the solid state except for a slight splitting of ν (As-O) ($899/885 \text{ cm}^{-1}$), and the appearance of a strong and rather broad absorption at 2960 cm^{-1} . In the absence of any hydroxyl groups the latter was interpreted as ν (C-H) of chloroform, lowered from 3030 cm^{-1} by formation of a strong complex with the oxide. In support of this, splitting of ν (As-O) is characteristically found in transition metal complexes in which an arsine oxide is co-ordinated through the oxygen¹³⁸.

The oxides R_3PO and R_3AsO are Lewis bases and often used as ligands in transition metal complexes, many of which have been analysed by x-ray diffraction techniques. The molecules have the tetrahedral configuration expected for tetraco-ordinate M, and bonding is adequately described by the use of Sp^3 hybrid orbitals of M to form four σ bonds. The M-O distance is shortened by additional bonding arising from overlap of filled $\text{p}\pi$ orbitals on the oxygen with the empty $\text{d}\pi$ orbitals on M. A similar explanation of bonding in triphenylarsine oxide monohydrate has been proposed by Ferguson and Macaulay¹³⁹. Here it is worth noting the contrast with amine oxides, in which N-O bond must be a very polar single bond because such π bonding is not possible.

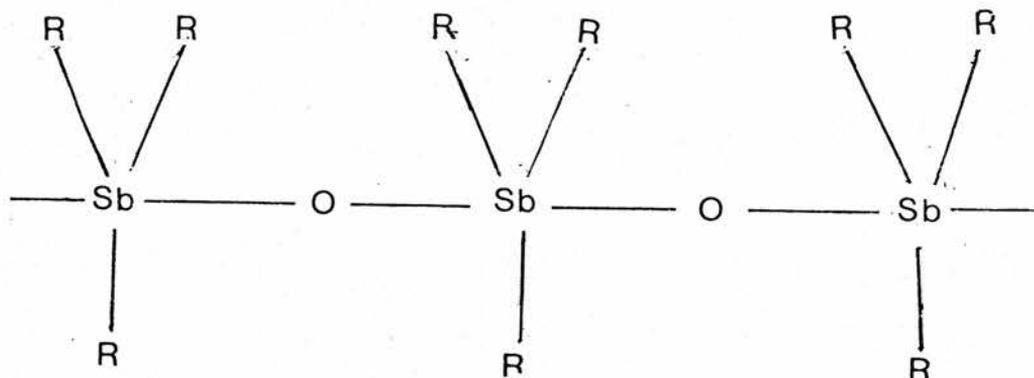


An x-ray diffraction analysis¹⁴⁰ of Ph_3PO has shown the P-O bond length to be 1.46 \AA and corresponding to the value for a strong double bond, being very similar to that obtained from spectroscopic studies¹⁴¹ for the free P-O bond (1.47 \AA)

in the diatomic phosphorus oxide molecule. Very recently the crystal structure of tris(2-methylphenyl)phosphine oxide has been studied by T.S. Cameron¹⁴² and the P-O bond length is reported to be 1.402 Å. The crystal structure study of triphenylarsine oxide monohydrate* has shown the As-O bond length to be 1.644 ± 0.007 Å¹³⁹. (which is compatible with a large amount of double bond character).

Several workers^{130d} have reported on the structure of triarylantimony oxides, but the data are conflicting and no definite conclusions can be drawn. An infrared spectrum of the oxide failed to show any bands in the 900-740 cm⁻¹ region, where the Sb=O grouping might be expected to absorb. On the basis of these results the authors¹³⁴ suggested that (C₆H₅)₃SbO does not contain the Sb=O grouping but is probably polymeric. Venezky and coworkers¹⁴³ found that the infrared spectrum of triphenylantimony oxide exhibits two strong absorption peaks in the 800-600 cm⁻¹ region, which were attributed to symmetrical and asymmetrical O-Sb-O stretching modes; both absorptions were absent in the Raman spectrum. Venezky concluded that his results support a polymeric structure for this oxide. Chremos and Zingaro^{130e} have reported that the ir spectrum of

* The crystals of triphenylarsine oxide monohydrate were provided by Dr. G.S. Harris, Department of Chemistry, University of St. Andrews.

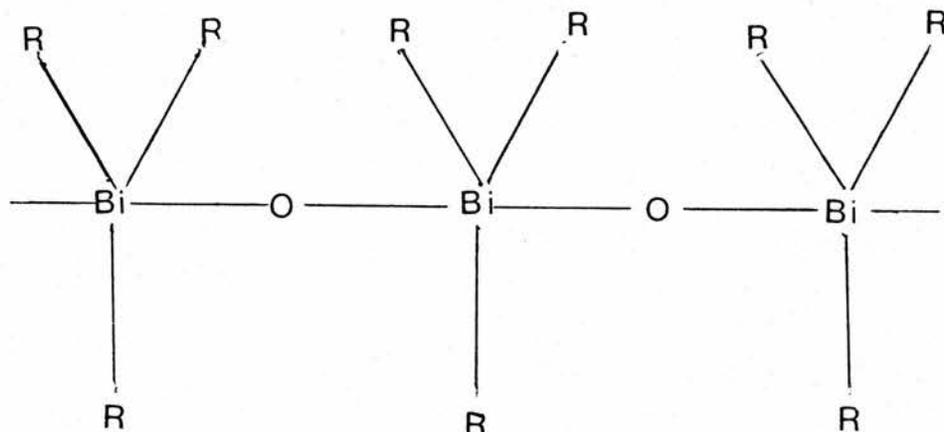


Five co-ordinate polymeric structure of R_3SbO

trialkylantimony oxide contains a single peak between 650 and 550 cm^{-1} which they believe should be assigned to the fundamental $\text{Sb}=\text{O}$ stretching frequency. It seems that further studies are required before the question of the structure of R_3SbO compounds can be decided unequivocally.

R_3BiO compounds are not common and have not been reported earlier. Triphenylbismuth oxide is isolated recently by Goel and Prasad¹⁴⁴ in small yield by treatment of a benzene solution of $(\text{C}_6\text{H}_5)_3\text{BiCl}_2$ with the solid or aqueous silver oxide. It is a white solid, unaffected by atmospheric moisture. Its infrared spectrum in the $4000\text{-}200\text{ cm}^{-1}$ region has shown no bands which can be attributed to O-H stretching or Bi-OH bending frequencies. However, the presence of a band which can be attributed to Bi-O-Bi stretching and the marked similarity of the spectrum to that of the oxybis(triphenylbismuth) derivatives e.g. $(\text{Ph}_3\text{BiX})_2\text{O}$ where $\text{X}=\text{Cl}, \text{Br}$, suggest

that triphenylbismuth oxide has a five co-ordinate polymeric structure involving -Bi-O-Bi- units¹¹⁰.



Five co-ordinate polymeric structure of R_3BiO

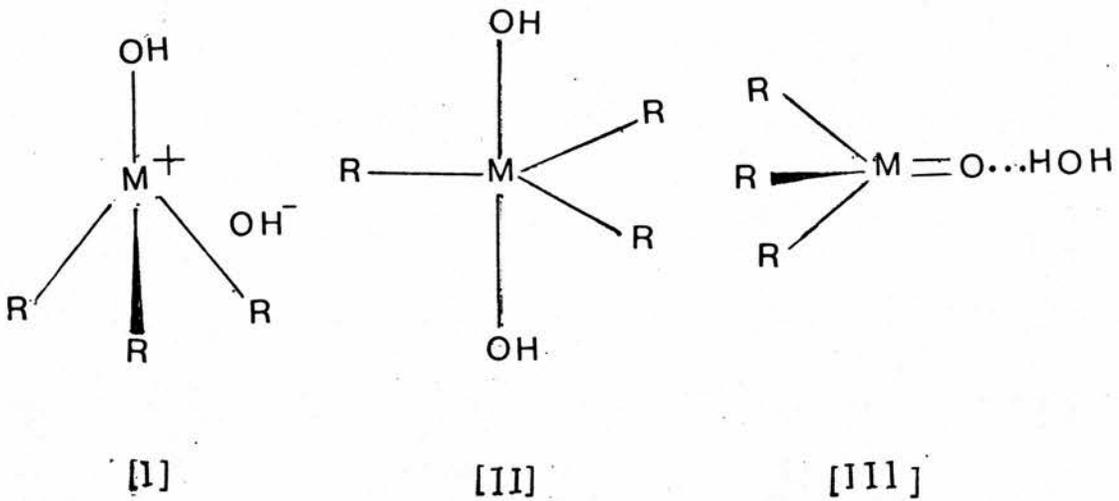
The polymeric structure is also in accord with the low solubility of this compound in organic solvents.

(b) Fully Hydrolysed Derivatives of R_3MHal_2 Compounds

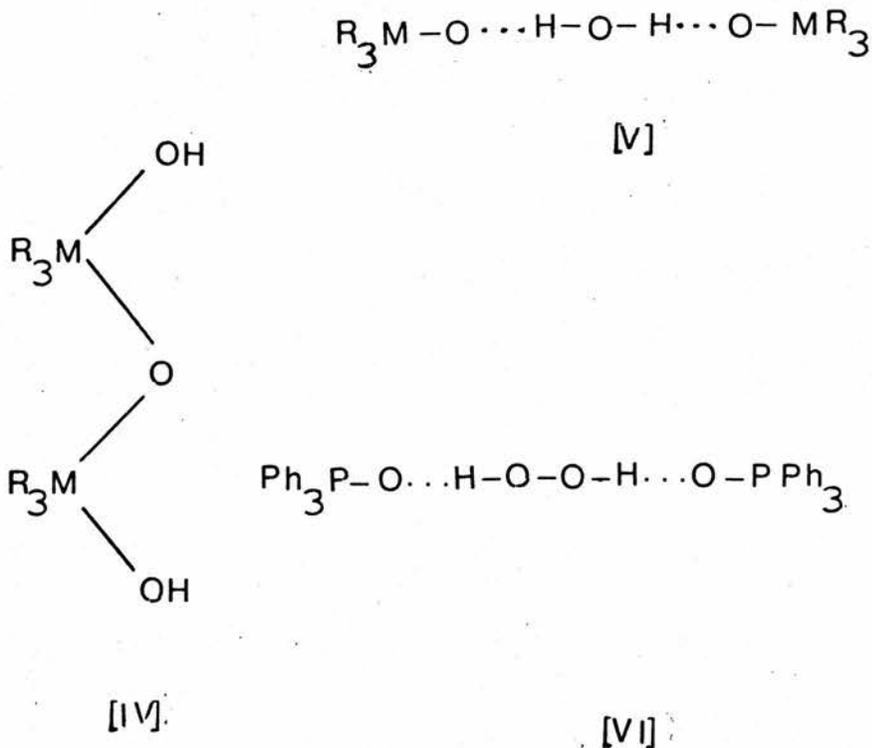
(i) $\text{M}=\text{P}$ and As

$\text{Hal}=\text{Cl}$ and Br

The structure of the fully hydrolysed derivatives of the R_3PHal_2 and R_3AsHal_2 compounds, generally referred to in the literature as dihydroxides has been a matter of controversy. Mann⁸⁹ has discussed the three probable formulations [I], [II] and [III] and suggested that the one adopted may depend on R, as reflected in the very different stabilities of the various $\text{R}_3\text{M}(\text{OH})_2$ compounds. Some dihydroxides are reported to decompose



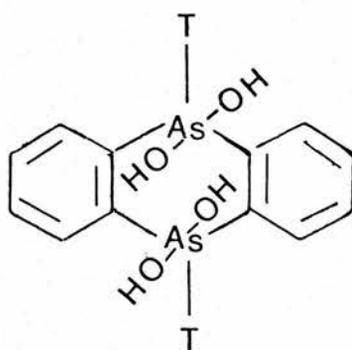
immediately to the oxide R_3MO , others to an intermediate 'sesqui' stage, generally formulated as $(R_3MOH)_2O$ [IV]



However, several workers have recognised that certain 'dihydroxides' are in fact monohydrates of the oxide [III]. In particular Jensen¹⁴⁵ deduced that the dihydroxides of triphenylphosphine and triphenylarsine should be formulated as $\text{Ph}_3\text{MOH}_2\text{O}$ from measurement of their dipole moments in benzene. Sidgwick¹⁴⁶ suggested the same formulation for amine oxide hydrates, but Mann⁸⁹ opposed the hydrate type structures on the grounds that the 'sesqui' compound [IV] would then have to be reformulated as [V]. But there seems to be no particular objection to this, and indeed the exactly analogous structure [VI] has been suggested for a 2:1 adduct of triphenylphosphine oxide with hydrogen peroxide on the evidence of its infrared spectrum¹⁴⁷.

No comparable evidence has been presented for the existence of a true dihydroxide. The work of Meisenheimer¹⁴⁸ who showed that optically active phosphine oxides $\text{RR}'\text{R}''\text{PO}$ do not racemise in the presence of base as they would on formation of $\text{RR}'\text{R}''\text{P}(\text{OH})_2$ [II], strongly suggests that such a structure does not occur. The one arsine for which Mann proposes a structure of type [II] is 5,10-dihydro-5,10-ditolyl arsanthrene¹⁴⁹, [figure VII] and in the light of more recent work the tetrahydroxide of this compound is equally well explained as a hydrate of the dioxide.

The same work of Meisenheimer¹⁴⁸ was used by Mann⁸⁹ to argue for the existence of ionic form [I], but only in that this preserves the tetrahedral configuration of the central atom;



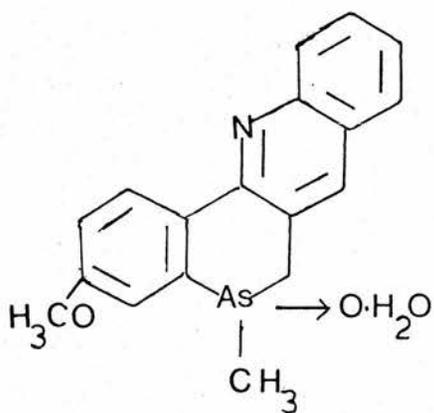
[VII]

however this point is met by the oxide hydrate structure

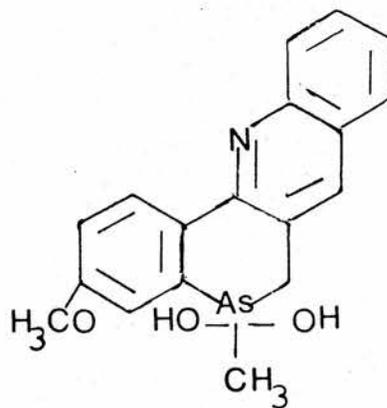
[III]. Further evidence for the hydrated oxide structure

has been advanced by Mann and Wilkinson¹⁵⁰, from the infrared spectrum of 1,2-dihydro-7-methoxy-1-methyl quinolo [3':2'-3:4)-arsoline oxide monohydrate.

In the infrared



[VIII]



[IX]

spectrum of this compound there is a broad band in the 3380-3470 cm^{-1} region (2.88-2.96 μ region), which they attribute to the presence of a water molecule. Thus the compound must be formulated as a hydrated oxide [VIII]. They have stated that if the compound possessed the dihydroxide form [IX] it would give broad absorption above ca. 3030 cm^{-1} due to the presence of $-\text{As}(\text{OH})$.

Recently the structure of " $\text{Ph}_3\text{As}(\text{OH})_2$ " was formulated as $\text{Ph}_3\text{AsOH}_2\text{O}$ in the solid state and in chloroform solution by Harris and Inglis^{129, 122}. In the infrared spectrum of the solid state they observed a strong band at 888 cm^{-1} which is characteristic of the $\text{As}=\text{O}$ stretching frequency^{133, 134, 151}; strong broad bands at ca. 3400 and 1665 cm^{-1} are also present and these have been attributed to lattice water^{152 a}. The spectrum of this compound in chloroform solution showed the absorption at 2960 cm^{-1} , and $\nu(\text{As}-\text{O})$ at 899/885 cm^{-1} (this is the same as shown in the ir spectrum of anhydrous oxide in chloroform solution), but in addition weak, broad absorptions at 3320 and 3180 cm^{-1} , attributed to hydrogen bonded water. Chloroform absorptions at 3680 and 3010 cm^{-1} also appeared in this spectrum. From these results they concluded that the fully hydrolysed derivative of $\text{Ph}_3\text{AsHal}_2$ is the hydrated oxide and does not contain a five-co-ordinate arsenic atom in solid state or in solution. It is not therefore structurally analogous to the R_3AsHal_2 compounds and in agreement with this they have found that the compound is non-conducting in methyl cyanide ($\Lambda_m = 0.43 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$;

$C_m = 0.0028 \text{ mol l}^{-1}$)¹²⁹. They have also examined¹²² the infrared spectrum of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}(\text{OH})_2$ and have shown that the distinctive As=O stretch appeared as a very strong absorption at 890 cm^{-1} and the absorption characteristic of lattice water were observed at 3440, 3280 and 1645 cm^{-1} . There was no absorptions which could be attributed to As-OH groups.

Similar conclusions regarding the structure of "Ph₃As(OH)₂" were reached by Armstrong et al¹³¹. They also took the existence of bands at 885 cm^{-1} (As=O stretch) and 1660 cm^{-1} (lattice water) as indicating the structure Ph₃AsO.H₂O. Infrared spectroscopy and H₂O exchange experiments likewise confirm the existence of the phosphorus analogue as Ph₃POH₂O rather than Ph₃P(OH)₂ in the solid state and in aqueous solution¹⁵³. X-ray analysis of Ph₃AsO.H₂O¹³⁹ is also in agreement with the hydrated structure.

(ii) M=Sb and Bi

Hal=Cl, Br, I

There seems however, to be a distinction between the dihydroxides of triphenylphosphine and triphenylarsine on one hand and those of involving antimony and bismuth on the other. The dihydroxides of triphenylantimony and triphenylbismuth are insoluble in water whereas those of phosphine and arsine are soluble. The "dihydroxides" of triphenylphosphine and arsine dehydrate readily to the corresponding oxides on heating; those of antimony and bismuth do not^{72c}. Ph₃Sb(OH)₂, for instance, is stable up to its melting point of 212°C at atmospheric pressure^{72b},

and though $\text{Ph}_3\text{Bi}(\text{OH})_2$ decomposes at 100°C it does not form an oxide^{72c}.

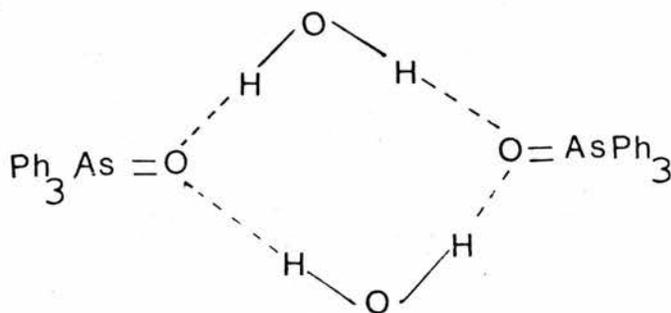
Triphenylantimony "dihydroxides" have been prepared by the hydrolysis of dihalogenotriphenylantimony^{130g}. Thus $(\text{C}_6\text{H}_5)_3\text{SbBr}_2$ and $(\text{C}_6\text{H}_5)_3\text{SbI}_2$ hydrolyse on treatment with alcoholic potassium hydroxide solution to give triphenylantimony "dihydroxide". Challenger and Richards¹⁵⁴ have reported that Ph_3BiCl_2 reacts with silver oxide to give $\text{Ph}_3\text{Bi}(\text{OH})_2$. Recently Goel and Prasad¹⁴⁴ have studied the hydrolysis products of $\text{Ph}_3\text{Bi}(\text{hal})_2$ compounds (hal=Cl, Br) and they have found that the reaction between equimolar portions of dihalogenotriphenyl bismuth and alcoholic sodium or potassium hydroxide affords polymeric $[(\text{Ph}_3\text{Bi})_2\text{O}]\text{X}_2$ compounds. These compounds are white crystalline solids, are unaffected by atmospheric moisture but decompose slowly on exposure to light. They have also reported the compound $[(\text{Ph}_3\text{Bi})_2\text{O}](\text{ClO}_4)_2(\text{H}_2\text{O})_2$ and its anhydrous form. Conductance and infrared spectroscopic data for the anhydrous as well as the hydrated diperchlorate in dichloromethane suggest the presence of ion-pairs or non-ionic species.

(c) Interconversion of Oxides and Dihydroxides

The anhydrous oxides vary in their affinity for water¹²¹. Aqueous alkaline hydrolysis of dihalogeno adducts of triphenylarsine and tris(4-methylphenyl)arsine yielded only the hydrated oxides, from which the anhydrous compounds were obtained by the action of heat. At 100°C prolonged heating was necessary to

remove the last traces of water from these oxides, and they picked up moisture slowly from the atmosphere at room temperature. In contrast, tris(4-chlorophenyl)arsine oxide, obtained directly from aqueous alkali solution, was not hydrated, and did not become hydrated under the action of boiling water.

X-ray analysis of triphenylarsine oxide monohydrate has shown that in the crystals the oxide molecules are linked in pairs by hydrogen bonds through water molecules¹³⁹. Harris and Inglis¹²⁹ on the basis of their observations and x-ray analysis of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ ¹³⁹ have suggested that the ease of hydration of an oxide could be related to the nature of the aryl substituent: an electron-withdrawing group such as 4-chlorophenyl



[X]

would render the oxide a poorer Lewis base (by increasing π -bonding between the oxygen and arsenic atoms) and therefore less likely to form hydrogen bonds. However, a survey of triarylarisines and their hydrates did not support this idea. For instance, the hydrolysis product of dihalogeno adducts of triphenylarsine and tris(4-methylphenyl)arsine are the hydrated oxides whereas that

of the corresponding adduct of intermediate diphenyl-4-methylphenylarsine is the oxide^{128c, d}. But much of the data found in the literature of organoarsenic chemistry is old and possibly inaccurate, and a new investigation might find such a relationship.

(d) Partially Hydrolysed Derivatives of R_3MHal_2 Compounds.



These compounds have been prepared by many different methods^{130h},

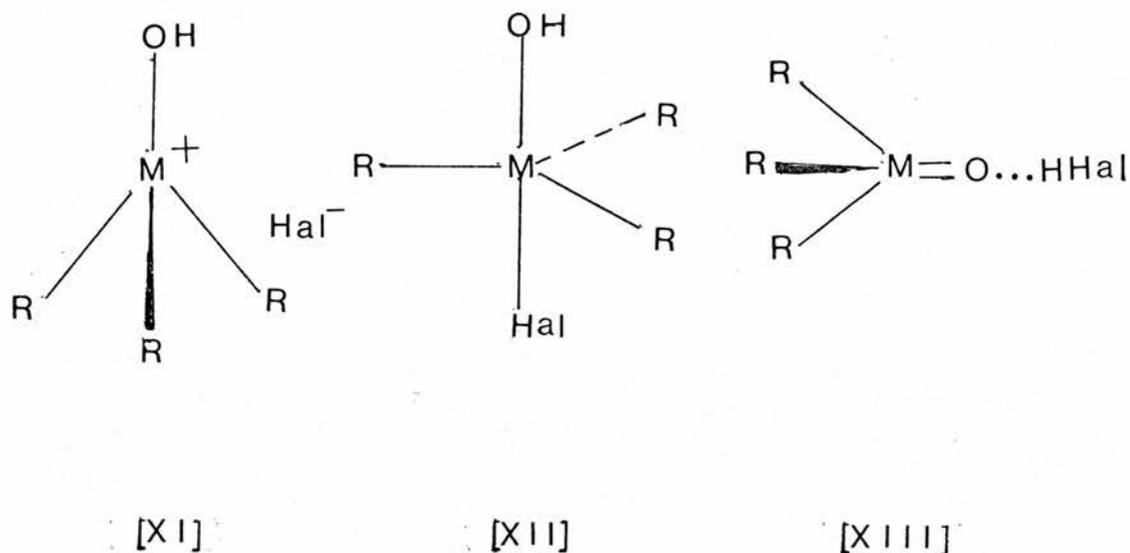
- (i) By the reaction of the appropriate acid with the tertiary arsine oxide or dihydroxide e.g. methylphenylarsine oxide hydrogen chloride has been prepared from the corresponding oxide by treatment with 5N hydrochloric acid.
- (ii) By the partial hydrolysis of the dihalogeno derivatives as mentioned earlier (page 67). Many $R_3AsOHHal$ compounds have been prepared by this procedure^{129, 155, 156}.
- (iii) By the action of lead tetrachloride on dimethylphenylarsine gives the corresponding hydroxychloride^{130h}. Presumably, the dichloro derivative is first formed and then yields the hydroxyhalide on partial hydrolysis.
- (iv) By electrochemical oxidation¹⁵⁷. Recently, triphenylarsine oxide hydrogen chloride has been prepared by the electrochemical oxidation of triphenylarsine in wet methyl cyanide in presence of suitable reagent (e.g. $LiCl$, $LiClO_4$). Controlled-potential coulometric experiments carried out at 0.45V showed that two moles of electrons per molecule of triphenylarsine were involved

in the anodic process. On the basis of these findings the authors have suggested the following reaction,



The structure of compounds of this type was first studied by Steinkopf and Schwen¹⁵⁸. On the basis of thermal cleavage studies they concluded that the hydroxyl group rather than the halogen atom of $\text{R}_3\text{AsOHHal}$ should be associated with the arsenic atom, and they formulated the compounds as hydroxyarsonium salts, $[\text{R}_3\text{AsOH}]^+\text{Br}^-$. The hydroxyhalides are alternatively available from the addition of halogen acid to the corresponding oxides, and may therefore be regarded as acid-base adducts, whatever their exact structure. Hadzi¹⁵⁹ has examined the crystalline adducts of triphenylphosphine oxide with hydrochloric acid and hydrobromic acid, as part of a general study of hydrogen bonded systems, and is of the opinion that proton transfer to the oxygen base does not occur, though he expresses some doubt in the case of hydrogen bromide. The adducts must therefore be formulated as $\text{Ph}_3\text{PO}\dots\text{HHal}$ [XIII] rather than $\text{Ph}_3\text{POH}^+\text{Hal}^-$ [XI]. The covalent structure [XII] he regards as unlikely because of the absence of an identifiable P-Hal stretching frequency in the infrared spectrum.

Comparison¹²¹ of these results with the corresponding derivatives of dihalogenotriphenyl arsoranes suggests that the arsorane derivatives are more likely to be covalent than the



phosphorane derivatives, but the greater basicity of Ph_3AsO when compared with Ph_3PO ¹⁵⁹ suggests that formation of Ph_3AsOH^+ is more likely than Ph_3POH^+ . The acidity of the solutions of $\text{Ph}_3\text{AsOHHal}$ has been taken as evidence for the presence of R_3AsOH^+ ions^{72a} and certainly they react as ionic halides in solution, which had led Mann to state that they are true salts and indeed to use them as evidence for an ionic formulation of the derived dihydroxides. But no measurements have been made to determine the degree of ionisation, which may be only slight, as in the dihalogeno adducts of triarylsarsine.

The evidence for the structure [XI] for these compounds was advanced by Mann and Watson¹⁶⁰. They demonstrated that both diphenyl- α -pyridylarsine oxide and tri- α -pyridylarsine oxide form only monopicates when treated with picric acid. Since tri- α -pyridylarsine forms a dipicrate, the authors assumed that

the structure of the cation of the monopicrate must be $[R_3AsOH]^+$. The failure of the oxides to form dipicrates was then attributed to the deactivating influence of the positively charged arsenic on the pyridine nitrogen atom or atoms.

In one of his valuable papers on the structure of pentavalent derivatives of the Group VB elements Jensen¹⁴⁵ records the very high dipole moment of 9.2D for $Ph_3AsOHCl$, and explains it by means of a resonance hybrid formulation $[XIV] \longleftrightarrow [XV]$



In the past few years there have been several investigations of the structure of these hydroxy compounds. The infrared spectrum of $(CH_3)_3AsOHCl$ contains bands at 847 and 303 cm^{-1} , which have been assigned to the As-O and As-Cl stretching frequencies, respectively^{155, 156}. Thus it was concluded that in the solid state these compounds contain five groups covalently bonded to arsenic atom. The infrared spectra of $(CH_3)_3AsOHBr$, $(C_6H_5)_3AsOHCl$, $(C_6H_5)_3AsOHBr$ and $(C_6H_5)_3AsOHNO_2$ have also been determined^{129, 155, 156, 161}, but the structure of these compounds could not be unequivocally deduced from the infrared data.

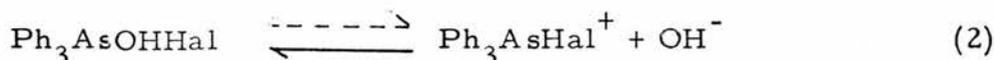
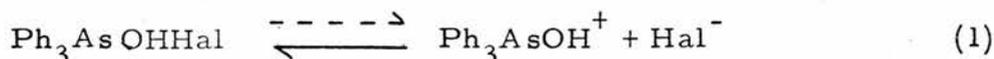
Recently Harris and Inglis¹²⁹ have studied the structure of $Ph_3AsOHHal$ by vibrational spectroscopy and conductance measurements. The infrared spectra of $Ph_3AsOHHal$ do not show a strong band near 888 cm^{-1} , but strong composite absorption occurs in the region $2750-2000\text{ cm}^{-1}$, which can be assigned to OH group vibration under conditions of strong

hydrogen bonding. They found low molar conductance values for the $\text{Ph}_3\text{AsOHHal}$ in methyl cyanide indicating that, like the dihalogeno adducts of triphenylarsine, the "halogenohydroxy

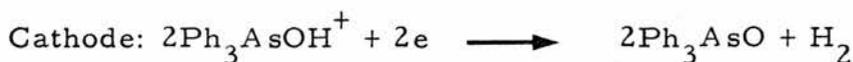
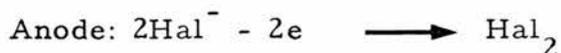
	Λ_m ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	C_m mol l^{-1}
$\text{Ph}_3\text{AsOHHal}$	20-24	0.01-0.05

derivatives" [i.e. $\text{Ph}_3\text{AsOHHal}$] are weak electrolytes and they inferred that the solid consists of molecular $\text{Ph}_3\text{AsOHHal}$ units which ionise partially under the influence of the solvents.

Of the two possible ionisations (1) and (2), the former was indicated



since on electrolysis halogen was produced at the anode and hydrogen at the cathode, according to the following electrode processes:

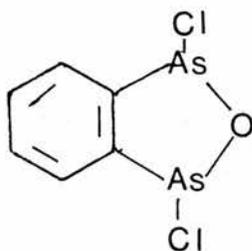


The results of transport number experiment supported ionisation (1). Therefore the structure of $\text{Ph}_3\text{AsOHHal}$ in solution is $\text{Ph}_3\text{AsOH}^+ \text{Hal}^-$ and not $\text{Ph}_3\text{AsHal}^+ \text{OH}^-$. The molar conductances in methyl cyanide and infrared spectra in the solid state of a series of compounds of the type Ph_3AsOHZ where Z is Br_3 , ICl_2 , HgCl_4 or HgBr_4 , showed that these are salts containing the Ph_3AsOH^+ cation.

Failure to locate an absorption in the infrared spectra of

the $\text{Ph}_3\text{AsOHHal}$ compound which could be attributed to an arsenic-halogen stretching frequency cast grave doubts on the validity of a trigonal bipyramidal structure for $\text{Ph}_3\text{AsOHHal}$ ¹⁶². In order to obtain conclusive details of the structures of these compounds Ferguson and Macaulay¹⁶³ studied the crystal structure of Ph_3AsOHCl ^{*} and Ph_3AsOHBr ^{*} by x-ray diffraction. Their results show that the arsenic atoms in the hydroxyhalides are tetrahedrally co-ordinated to three phenyl rings and to an oxygen atom, which is in turn strongly hydrogen bonded to the halogen by an unusually short hydrogen bond .

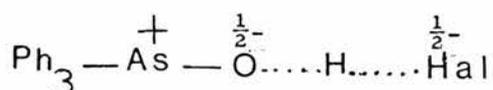
The As-O distances [1.702 and 1.697 ± 0.014 in Ph_3AsOHCl and $1.712 \pm 0.012 \text{ \AA}$ in Ph_3AsOHBr] are significantly longer (by $\sim 0.06 \text{ \AA}$) than the As=O bond in triphenylarsine oxide monohydrate ($1.644 \pm 0.007 \text{ \AA}$)¹³⁹ and are comparable with the As-O single bond length ($1.69 \pm 0.01 \text{ \AA}$) found for example in o-phenylenediarsine oxychloride¹⁶⁴ [XVI].



[XVI]

* The crystals of Ph_3AsOHCl and Ph_3AsOHBr were provided by Dr. G.S. Harris, Department of Chemistry, University of St. Andrews

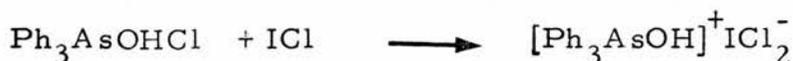
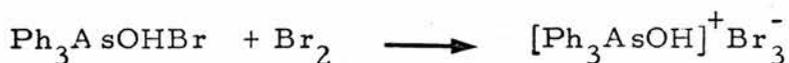
From these observations it is concluded that the following formulation [XVII] which is essentially similar to that proposed earlier by Jensen¹⁴⁵ and Hadzi¹⁵⁹ is a reasonable representation of the structure of triphenylarsine oxide hydrogen chloride [ie. Ph_3AsOHCl] and triphenylarsine oxide hydrogen bromide [ie. Ph_3AsOHBr].



[XVII]

Harris and Inglis have studied¹²⁹ the reaction of $\text{Ph}_3\text{AsOHHal}$ with bromine and iodine chloride in methyl cyanide by conductometric titrations. In each case these gave a rise in conductance followed by a break close to the 1:1 mole ratio.

The reactions were therefore indicated as:



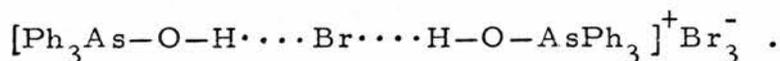
They could not however isolate solid $[\text{Ph}_3\text{AsOH}]^+\text{Br}_3^-$ by this reaction, the product obtained being $\text{Ph}_3\text{AsOHBr}_2$ which they formulated as $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$. $[\text{Ph}_3\text{AsOH}]^+\text{Br}_3^-$ was obtained however by careful hydrolysis of Ph_3AsBr_4 in moist acetonitrile, but on treatment with ether it reverted to $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$.

The adduct $[\text{Ph}_3\text{AsOH}]^+\text{ICl}_2^-$ indicated by conductometric titration

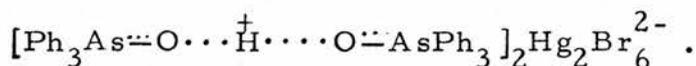
was prepared readily, without complication, by ether precipitation as stable yellow crystals. Thus in their reactions with halogens and interhalogens in methyl cyanide the triphenylarsine oxide hydrogen halides behave similarly to the dihalogenotriphenylarsoranes.

The crystal structure of $[\text{Ph}_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^+$ ¹⁶⁵ and $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ ¹⁶⁶ have been determined by x-ray analysis. The adduct $[\text{Ph}_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$ is formulated $[\text{Ph}_3\text{As}-\text{O}-\text{H}\cdots\text{Cl}\cdots\text{H}-\text{OAsPh}_3]^+\text{ICl}_2^-$ with two tetrahedral triphenylarsine hydroxide groups linked by strong $\text{O}-\text{H}\cdots\text{Cl}-$ hydrogen bonds to a single chlorine ion and with independent, discrete ICl_2^- ions.

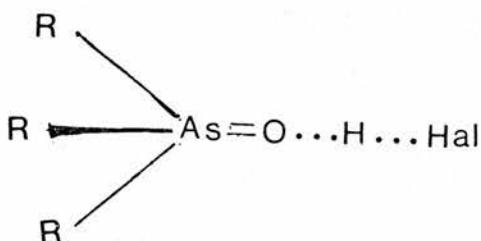
The $\text{OH}\cdots\text{Cl}^-$ distances [2.946 and 2.953(8) Å] are intermediate between the very short distances found¹⁶³ in Ph_3AsOHCl [2.854 and 2.817(17) Å] and the mean [3.08(1) Å] reported in triphenylarsine oxide monohydrate¹³⁹. Mean $\text{O}-\text{H}$ and $\text{H}\cdots\text{Cl}$ distances are 0.89 and 2.13 Å. The As^+-O distances [1.727(7) and 1.716(7) Å] are as expected^{163, 139}. The mean As^+-C distance [1.901(10) Å] is also close¹⁶⁸ to those found in similar molecules^{163, 139, 167}. The ICl_2^- group is almost linear [$\text{Cl}-\text{I}-\text{Cl}$ 176.3(2)°]. The structure closely resembles that of the isomorphous bromide derivative $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ ¹⁶⁶ in which the Ph_3AsOH groups are coupled by strong $\text{O}-\text{H}\cdots\text{Br}\cdots\text{H}-\text{O}$ hydrogen bonds i.e.



A compound possessing this type of hydrogen bonded structure has been reported earlier¹⁶⁸ i.e.



Regarding the structure of compounds of type $\text{Ph}_3\text{AsOHHal}$, we have seen that conductance studies suggested they were weak electrolytes¹²⁹, which leads to the assumption that these are covalent species in solution and almost certainly in the solid state. Covalent $\text{Ph}_3\text{AsOHHal}$ molecules would, by analogy with other compounds of the group (e.g. Ph_3AsF_2 ¹¹⁴), be expected to be trigonal bipyramidal in structure. However, x-ray analysis of $\text{Ph}_3\text{AsOHHal}$ leads to the conclusion that the triphenylarsine hydroxyhalides have a structure essentially similar to that of Jensen's formulation $[\text{XIII}]$ ¹⁴⁵. Infrared spectra of the solid and



[XIII]

solutions as well as nmr studies of solutions indicate strong hydrogen bonding in $\text{R}_3\text{AsOHHal}$ (Hal=Cl, Br).

No hydroxyfluoride $[\text{R}_3\text{AsOHF}]$ has been reported, which is not surprising in view of the affinity of fluoride for hydrogen¹²¹. The number of hydroxyiodides which have been reported is small.

This is difficult to explain since many di-iodides are known and the hydroxyiodides which have been reported (such as those of phenyldimethylarsine¹⁵⁸ and phenyldipseudocumylarsine¹⁶⁹) were obtained by the same methods as were used to prepare the chlorides and bromides. Lyon and Mann¹⁷⁰ have reported the isolation of Ph_3AsOHI from the reaction of Ph_3AsO and HI ($\text{KI} + \text{HOAc}$), but do not give sufficient evidence in support of their claim. Recently Harris and Inglis have investigated the hydrolysis products of Ph_3AsI_2 ¹²¹. Several attempts to prepare triphenylarsine oxide hydrogen iodide following the same method as for Ph_3AsOHCl and Ph_3AsOHBr , yielded only a mixture of products and there was no evidence for the presence of a hydroxy compound. It would seem that the existence of Ph_3AsOHI is in doubt and the products claimed as Ph_3AsOHI ¹⁷⁰ may not be the same as Ph_3AsOHCl and Ph_3AsOHBr compounds.

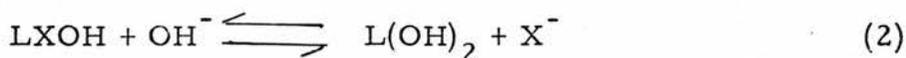
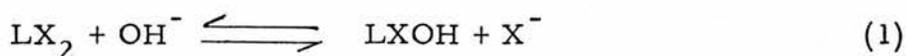
The hydroxyhalides of triphenylphosphine have been obtained by saturating an ethanol solution of triphenylphosphine oxide with hydrogen halide gas. In this way Hadzi¹⁵⁹ obtained $(\text{Ph}_3\text{AsO})_2\text{HCl}$ and $(\text{Ph}_3\text{AsO})_2\text{HBr}$. The 1:1 adducts of triphenylphosphine oxide with hydrogen halides are not stable under ordinary conditions; slow loss of hydrogen halide occurs and the final product is a hemi-hydrogen halide ie. $(\text{Ph}_3\text{PO})_2\text{HHal}$. The hemi-hydrogen chloride adduct of triphenylphosphine oxide $(\text{Ph}_3\text{PO})_2\text{H}\cdot\text{Cl}$, is reported to be stable for several months. Hadzi¹⁵⁹ has studied the infrared spectra of the hydroxyhalides of phosphine and arsine and has suggested that they are salts of hydrogen-bonded adducts

of the type that was later shown by x-ray analysis to be present in the $\text{Ph}_3\text{AsOHHal}$ compounds.

Recently it has been reported¹⁷¹ that $[(\text{Ph}_3\text{PO})_2\text{H}]^+\text{ClO}_4^-$ is formed by the reaction of Ph_3PO with HClO_4 in ethanol. Attempts¹⁷¹ to prepare the compound $(\text{Ph}_3\text{PO})_2\text{HCl}$ were unsuccessful and resulted only in the isolation of the compound Ph_3POHCl . The authors reported that its infrared spectrum and elemental analysis were invariant after one year. They found the spectrum of this compound to be identical with that obtained by Hadzi for $(\text{Ph}_3\text{PO})_2\text{HCl}$.

Compounds of the type $\text{R}_3\text{SbOHHal}$ (R=aryl group; Hal=Cl, Br) have been reported by several investigators. Morgen, Micklethwait and Whitby¹⁷² reported the preparation of Ph_3SbOHCl by the hydrolysis of Ph_3SbCl_2 in aqueous alcohol, and Wittig and Clauss¹⁷³ have reported the preparation of Ph_3SbOHBr by a similar procedure. Other workers, however, have been unable to obtain these hydroxy compounds, but have obtained instead compound of the type $(\text{Ph}_3\text{SbHal})_2\text{O}$ ¹⁷⁴. The latter authors established the structure by analyses and molecular weight determinations. In addition, they did not observe any hydroxyl bands in the infrared spectrum. Long and co-workers^{98,99} have made a detailed study of the hydrolysis products of R_3SbHal_2 compounds and found that no compounds with analyses corresponding to $\text{R}_3\text{SbOHHal}$ could be prepared; nor could hydroxyl bands for the hydrolysis products be found in their infrared spectra.

Accordingly these authors concluded that compounds of the type $R_3SbOHHal$ probably do not exist in the solid state and that reports of such compounds in the earlier literature are based on analytical errors. Recently the hydrolysis of the compounds LX_2 ($L=R_3Sb$ and $X=F, Cl, Br$ or I) has been studied by Benmalek and co-workers¹⁷⁵. They have reported the equilibrium constant values for the following:



For equilibrium (1) k_1 values fell in the range $10^7 - 10^{10}$ and for equilibrium (2) the values of k_2 were in the range $10^5 - 10^{7.5}$.

Challenger and co-workers have reported the preparation of compounds of the type Ph_3BiOHX ; $X=Cl, Br$ ^{176, 177}.

$Ph_3BiOHCl$ is formed by the action of moist ammonia gas on dichlorotriphenylbismuth in chloroform solution; from sodium and Ph_3BiCl_2 in diethyl ether containing a trace of moisture; by the action of aqueous ammonia on Ph_3BiCl_2 . $Ph_3BiOHBr$ and Ph_3BiBr_2 ¹⁷⁶ were obtained by the action of excess of aqueous sodium bromide on triphenylbismuth hydroxide. Similarly, Ph_3BiOH_2 when treated with excess of aqueous sodium chloride gave dichlorotriphenylbismuth and triphenylbismuth oxide hydrogen chloride. Solomakhina¹⁷⁸ has recently isolated $Ph_3BiOHCl$ as a byproduct (presumably, hydrolysis product) from the reaction of triphenylbismuth with iodine trichloride.

Harris and co-workers as a corollary to their extensive studies of the conductance of triphenylarsine-halogen compounds

have, as has been mentioned in Part I, made some preliminary studies of the halogen adducts of tris(4-methylphenyl)arsine and tris(4-chlorophenyl)arsine and this has included the hydrolysis of these compounds. In this part of the thesis a full study of the hydrolysis of the following dihalogenotris(methylphenyl)arsoranes has been made:

dihalogenotris(2-methylphenyl)arsorane

dihalogenotris(3-methylphenyl)arsorane

dihalogenotris(4-methylphenyl)arsorane

Hal=Cl or Br

It was hoped that in this way we would gain information on the effect, if any, variation of the substituent in the phenyl ring would have on the course of the reactions and the properties of the products of the hydrolysis reactions.

RESULTS AND DISCUSSION

Results and Conclusions

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A. Fully Hydrolysed Products of R_3AsHal_2

($R=2-CH_3C_6H_4$, $3-CH_3C_6H_4$, $4-CH_3C_6H_4$; $Hal_2=Cl_2$ and Br_2)

(a) Tris(methylphenylarsine oxide and 'Dihydroxides')

Hydrolysis of $(2-CH_3C_6H_4)_3AsBr_2$ and $(4-CH_3C_6H_4)_3AsBr_2$ with aqueous alkali yielded colourless crystalline solids which were identified as $(2-CH_3C_6H_4)_3AsO.H_2O$ and $(4-CH_3C_6H_4)_3AsO.H_2O$ by their elemental analysis and infrared spectra. In contrast, attempts to isolate $(3-CH_3C_6H_4)_3AsO.H_2O$ (or its anhydrous form) by aqueous alkaline hydrolysis of the corresponding dibromo adduct were not successful. A sticky viscous, colourless product was obtained which did not yield a crystalline solid on trituration or cooling. However, the compound was obtained in anhydrous form [ie. $(3-CH_3C_6H_4)_3AsO$] by the oxidation of $(3-CH_3C_6H_4)_3As$ with potassium permanganate in acetone¹⁷⁹. This anhydrous oxide when treated with water gave a sticky product which on keeping in water for two weeks was converted into a white crystalline solid. This was shown, by analysis and from its infrared spectrum, to be $(3-CH_3C_6H_4)_3AsO.H_2O$. The anhydrous oxides $(2-CH_3C_6H_4)_3AsO$ and $(4-CH_3C_6H_4)_3AsO$ were obtained by heating the corresponding hydrated oxides at $100^\circ C$ for several hours.

In the infrared spectra of $R_3AsO.H_2O$ the absorption characteristics of lattice water^{152a} which were observed as strong broad bands, are shown in Table 27 on p. 94. There was no observable absorption due to OH stretching which could be attributed to the $-AsOH$ linkage^{130f}. The distinctive absorptions due to ν (As-O) in the hydrated oxides ($R_3AsO.H_2O$) appeared as

Table 27.

Compound	frequency cm^{-1}	
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}\cdot\text{H}_2\text{O}$	3560-3180,	1640-1600
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}\cdot\text{H}_2\text{O}$	3600-3100,	1670-1610
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}\cdot\text{H}_2\text{O}$	3560-2600,	1670-1610

strong bands between $900\text{-}860\text{ cm}^{-1}$, (in most cases these As-O bands are split into two peaks). The frequencies are given in Table 28 below, and ν As-O bands of triphenylarsine oxide and

Table 28.

 ν As=O

compound	frequency cm^{-1}		change in frequency
	Hydrated	Anhydrous	
$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}$	880s, 868vs	885vs, 870s	$\sim +5, +2$
$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}$	880vs	882vs	$\sim +2$
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsO}$	890vs, 894s	882vs, 888s	$\sim -8, -6$
$(\text{C}_6\text{H}_5)_3\text{AsO}^{121}$	888vs	899, 885	$\sim +11, -3$

its hydrated form are included for comparison.

In the infrared spectra of the anhydrous oxides (ie. R_3AsO), the absorption characteristic of lattice water were absent as expected. Further, it was noted that the distinctive ν As-O peaks were slightly shifted from those of the hydrated oxides as shown in Table 28 above. Since these shifts are slight and not in the same direction in every case it is not easy to state categorically the reason for the observed shifts. Since, by analogy with hydrated triphenylarsine oxide¹²⁹ the hydrated compounds almost certainly

contain hydrogen-bonds involving the oxygen of As=O it would be expected that the As=O frequency would increase on going to the anhydrous compound. The splitting of ν As-O presumably indicates the presence of non-equivalent ligand molecules¹³⁸ or coupling between the As-O vibration of two ligands co-ordinated to the same acceptor¹³⁸.

B. Partially Hydrolysed Products of the R_3AsHal_2 Adducts:

$R_3AsOHCl$ and $R_3AsOHBr$

($R=2-CH_3C_6H_4$, $3-CH_3C_6H_4$, $4-CH_3C_6H_4$; $Hal_2 = Cl_2$ and Br_2)

The partially hydrolysed compounds, $R_3AsOHCl$ and $R_3AsOHBr$, were obtained by aqueous hydrolysis of R_3AsCl_2 and R_3AsBr_2 respectively. These are white crystalline solids at room temperature and their properties are listed in Table 29 on page 96. By analogy with the structures of $Ph_3AsOHCl$ and $Ph_3AsOHBr$ which have been established as to be a simple hydrogen bonded 1:1 adduct of triphenylarsine oxide with the appropriate hydrogen halide^{121, 163}, the likely structures for the compounds $R_3AsOHHal$ are



It would be expected therefore that they would form only slightly conducting solutions in ionising solvents and that their infrared spectra would show a strong composite band in the region ca. $2750-2000\text{ cm}^{-1}$, due to hydrogen bonded OH^{121, 129}. Again by analogy with $Ph_3AsOHHal$ it might be expected that the $R_3AsOHHal$ compounds would add a molecule of halogen to produce the ionic trihalides of type $[R_3AsOH]^+ Hal_3^-$. To obtain

Table 29. Partially Hydrolysed Products of R_3AsHal_2 Adducts

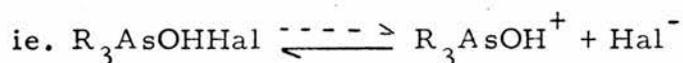
Compound	Colour	m. p. ($^{\circ}C$)
$(2-CH_3C_6H_4)_3AsOHCl$	white	218-220
$(2-CH_3C_6H_4)_3AsOHBr$	white	217-218
$(3-CH_3C_6H_4)_3AsOHCl$	white	200-202
$(3-CH_3C_6H_4)_3AsOHBr$	white	185-186
$(4-CH_3C_6H_4)_3AsOHCl$	white	179-181
$(4-CH_3C_6H_4)_3AsOHBr$	white	207-208

further information about the properties of the compounds $R_3AsOHHal$, their conductance behaviour, infrared spectra and reactions with halogens have been studied.

(a) Conductance Measurements

The conductance of the $R_3AsOHCl$ and $R_3AsOHBr$ compounds in nitrobenzene at $25^{\circ}C$ were measured over a range of concentrations and values for their molar conductance calculated. These values are given in Tables 30 and 31 on p. 179. A plot of molar conductance (Λ_m) against the square root of molar concentration ($\sqrt{C_m}$) was constructed for each compound. These curves are reproduced in figures 24 and 25. For the purpose of comparison, values of Λ_m at $C_m = 0.01 \text{ mol l}^{-1}$ were obtained from the graph and these are given overleaf.

The low values of molar conductance obtained suggests that only slight ionisation takes place in nitrobenzene,



Within the chloride or bromide series, the values of Λ_m do not vary with the position of the methyl group in the phenyl ring.

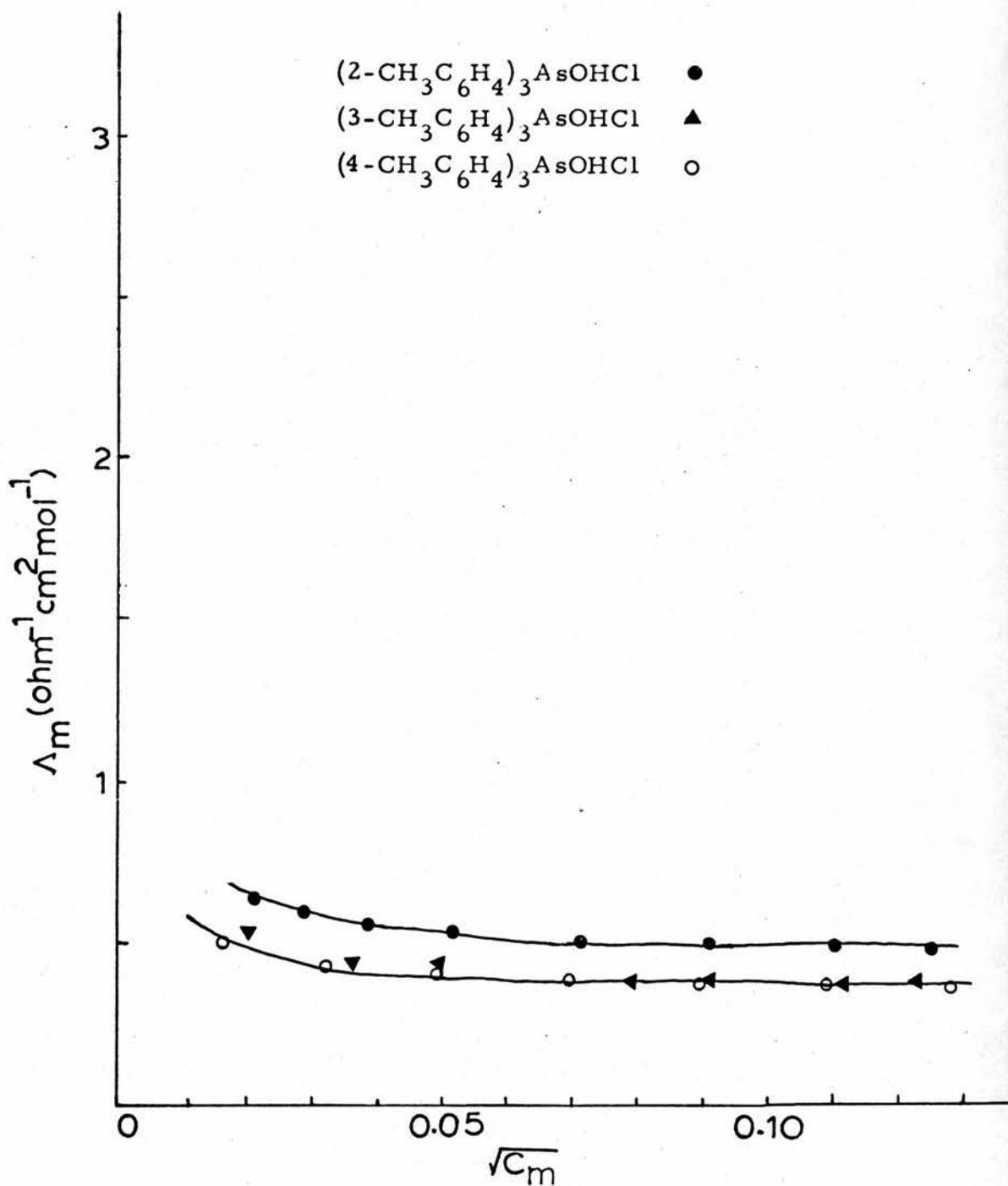


Figure 24. Electrolytic Conductance of $R_3\text{AsOHCl}$ Compounds in Nitrobenzene at 25°C

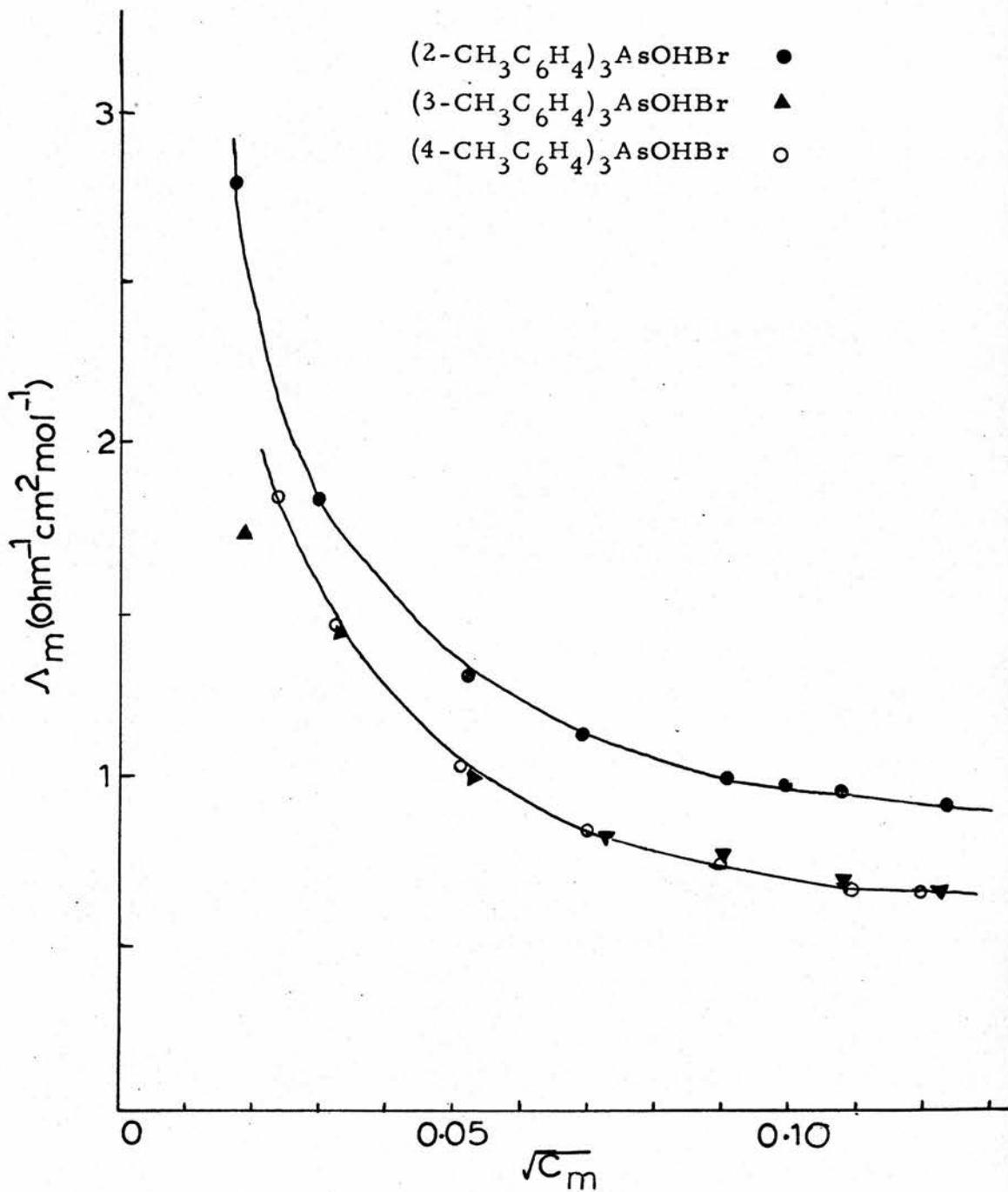
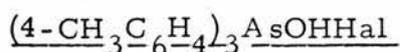


Figure 25. Electrolytic Conductance of $R_3\text{AsOHBr}$ Compounds
in Nitrobenzene at 25°C

compound	Λ_m (ohm ⁻¹ cm ² mol ⁻¹)
(2-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.50
(3-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.38
(4-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.38
(2-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.98
(3-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.70
(4-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.70

This is in contrast to the behaviour of dihalogenotriarylarsonanes, and would seem to support Jensen's¹⁴⁵ structure (tetrahedral As) in preference to the conventional one (trigonal bipyramidal As). Since, if the molecules were trigonal bipyramidal their conductance behaviour in nitrobenzene would be expected to resemble that of the R₃AsHal₂ adducts. In the proposed structure, the halogen (which forms the anion) is not directly attached to the arsenic atom and is thus less influenced by the steric effects of the aryl groups attached to the arsenic atom, and the degree of ionisation in solution would be expected to depend principally on the nature of the halogen atom.

(b) Hydrogen Bonding in the R₃AsOHHal Compounds



(Hal=Cl or Br)

The infrared spectra of solid (4-CH₃C₆H₄)₃AsOHCl and (4-CH₃C₆H₄)₃AsOHBr were similar to one another. Their most prominent feature was very strong broad absorption in the region 2750-1720 cm⁻¹ [2700-1720 cm⁻¹ for (4-CH₃C₆H₄)₃AsOHCl and

2750-2000 cm^{-1} for $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$] (figure 26 on p. 98a) which can be attributed only to an O-H stretching mode under the influence of very strong hydrogen bonding¹²⁹. ν (O-H) is reported in this region for the related amine oxide hydroxyhalide¹⁸⁰ and arsenic acids¹⁸¹. $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ also had a strong, rather broad absorption at 1600-1500 cm^{-1} (resolved into two peaks at 1593 and 1558 cm^{-1}), close to the reported stretching frequency of the H-Cl bonds in the hydrogen dichloride ion HCl_2^- (1565 cm^{-1})¹⁸². A similar interpretation [in the ir spectrum of $(\text{C}_6\text{H}_5)_3\text{AsOHCl}$ ¹²¹] of the 1593 cm^{-1} absorption as an H-Cl stretch supports the presence of extremely strong hydrogen bonding between the oxygen and chlorine atom, and suggests a structure in which the hydrogen atom is shared more or less equally between them¹²¹. Likewise an absorption at 2250 cm^{-1} in the spectrum of HClNO_3^- ion is attributed to H-Cl stretching¹⁸³.

In the spectrum of the $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$, on the other hand, there is no absorption which can be compared with the H-Br stretching frequency of HBr_2^- ion, at 1690 cm^{-1} ¹⁸⁴. However there is a broad peak at ca. 1435 cm^{-1} [not present in the spectrum of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ or $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ itself] whose intensity and exact position are obscured by the strong phenyl ring absorption at 1440 cm^{-1} (figure 26 on p. 98a). This may indicate a relatively weaker H-Br bond corresponding to the higher O-H frequency which implies a stronger O-H bond than in the hydroxychloride.

In further support of the hydrogen bonded structure, $\text{R}_3\text{AsO}\cdots\text{H}\cdots\text{Cl}$, no absorption was observed in the infrared spectrum of the hydroxychloride which could be attributed to an As-Hal bond^{152b}.

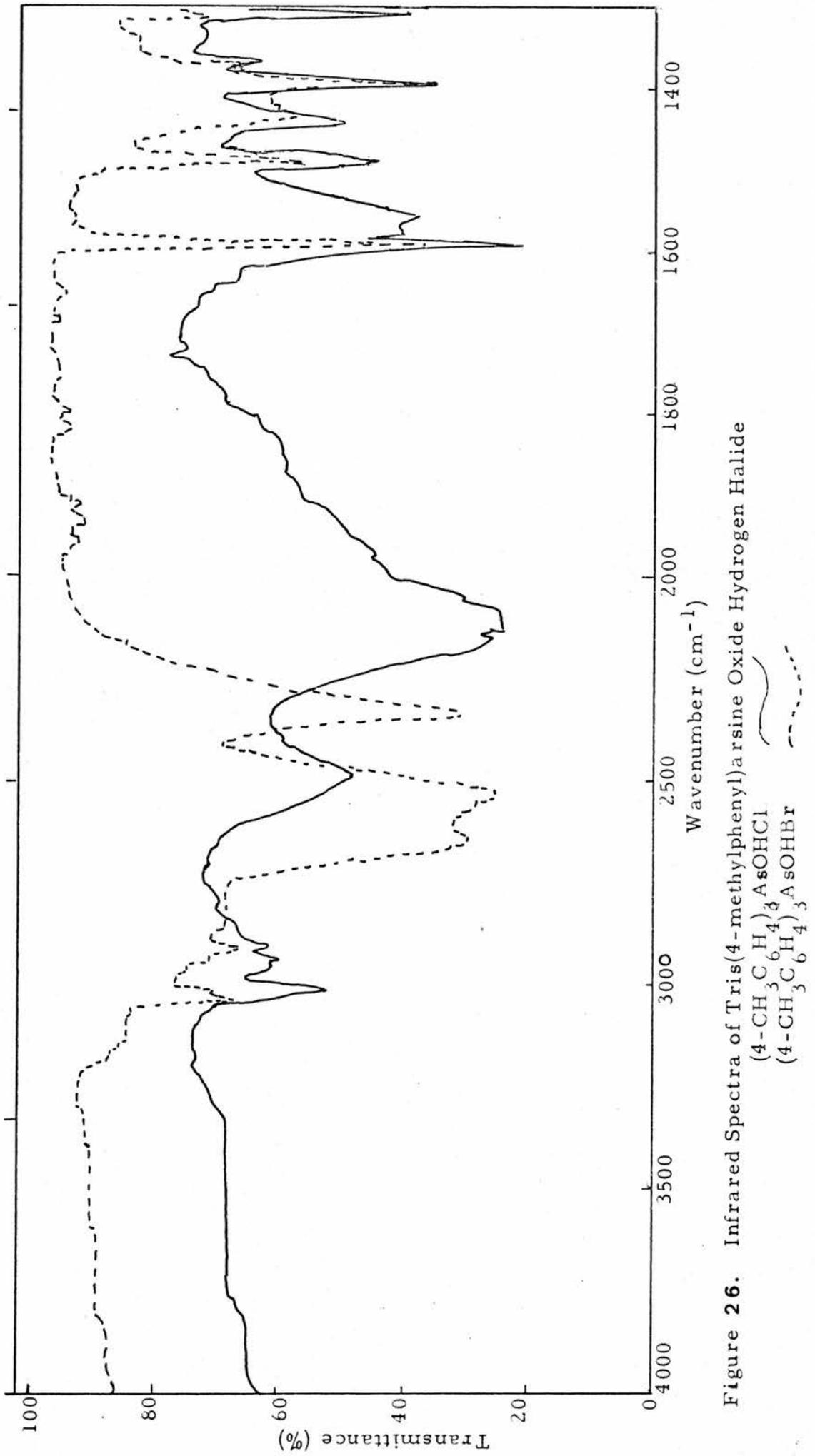
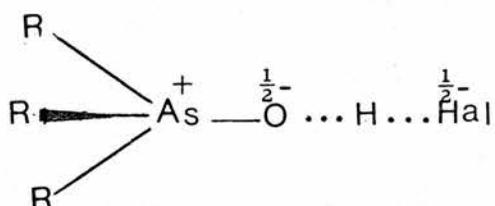


Figure 26. Infrared Spectra of Tris(4-methylphenyl)arsine Oxide Hydrogen Halide

The infrared spectra of the tris(2-methylphenyl)arsine oxide hydrogen halide $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHHal}]$ and tris(3-methylphenyl)arsine oxide hydrogen halide $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHHal}]$ compounds are very similar to those of the tris(4-methylphenyl)arsine oxide hydrogen halide [ie. $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHHal}]$. Also they differ from the corresponding arsine in exactly the same way. These facts suggest that they have similar structure.

(c) Conclusion

The results of conductance measurements and infrared spectra of all the tris(methylphenyl)arsine compounds $[\text{R}_3\text{AsOHCl}]$ and $\text{R}_3\text{AsOHBr}]$ studied are consistent with those of Ph_3AsOHCl and Ph_3AsOHBr ¹²¹ and by analogy with the structures of $\text{Ph}_3\text{AsOHHal}$ ¹²¹ it is reasonable to conclude that these tolyl compounds $\text{R}_3\text{AsOHHal}$ have the same structure as that of $\text{Ph}_3\text{AsOHHal}$: shown by crystal structure analysis¹⁶³.



C. The Reaction of $\text{R}_3\text{AsOHHal}$ with Halogens and Interhalogens

($\text{R} = 2\text{-CH}_3\text{C}_6\text{H}_4, 3\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{Hal} = \text{Cl}, \text{Br}$)

Previous work on the reaction of triarylsarsines^{* I} with halogens has shown that conductometric titration is a valuable technique for following the course of the reaction.

* Harris and co-workers Ref. 92, 120, 121, 185

I Part I of this thesis

Likewise the technique has been used for studying the reactions of triphenylarsine oxide hydrogen halide with halogens¹²¹. The conductometric titration of the tris(methylphenyl)arsine compounds $R_3AsOHCl$ and $R_3AsOHBr$ with Br_2 , I and ICl were therefore carried out in nitrobenzene using the same apparatus and technique as had been used in the previous studies^I.

The conductance-composition graphs for conductometric titration of all the tris(methylphenyl)arsine oxide hydrogen bromide compounds $R_3AsOHBr$ with Br_2 and I in nitrobenzene were remarkably alike (figures 27 and 28 on pp. 101a, 101b). They showed a rapid rise in conductance up to the 1:1 $[Hal_2:R_3AsOHHal]$ mole ratio, followed by a slow, steady drop. In every case the solution acquired the strong colour of a trihalide ion from the first addition of halogen. The results of the conductometric titration of $R_3AsOHBr$ with Br_2 and I are listed in Table 32 on p. 101. Values of molar conductance at the 1:1 mole ratio were between 20.0 and 26.0 $ohm^{-1} cm^2 mol^{-1}$ (ca. $C_m = 0.01-0.019 mol l^{-1}$), and these results were therefore interpreted as showing formation of the strong electrolyte $[R_3AsOH]^+ Hal_3^-$:



In every case the end point in these titrations were sharp indicating that the products of the reaction were not dissociated. The results of conductometric titration of $R_3AsOHCl$ with ICl in nitrobenzene are listed in Table 33 on p. 102 and represented in figure 29 on p. 102a.

These conductometric titration results therefore indicate

^I Part I of this thesis

Table 32. Conductometric Titration of $R_3AsOHBr$ with Br_2 and IBr in Nitrobenzene

Compound	titration with	Λ_m at 1:1 [Hal ₂ :R ₃ AsOHHal] mole ratio	C_m mol l ⁻¹	indicating formation of
(2-CH ₃ C ₆ H ₄) ₃ AsOHBr	Br ₂	22.72	0.01318	→ [R ₃ AsOH] ⁺ Br ₃ ⁻
(3-CH ₃ C ₆ H ₄) ₃ AsOHBr	Br ₂	20.31	0.01752	
(4-CH ₃ C ₆ H ₄) ₃ AsOHBr	Br ₂	23.09	0.01345	
(2-CH ₃ C ₆ H ₄) ₃ AsOHBr	IBr	24.57	0.01378	→ [R ₃ AsOH] ⁺ IBr ₂ ⁻
(3-CH ₃ C ₆ H ₄) ₃ AsOHBr	IBr	20.47	0.01993	
(4-CH ₃ C ₆ H ₄) ₃ AsOHBr	IBr	25.32	0.01066	

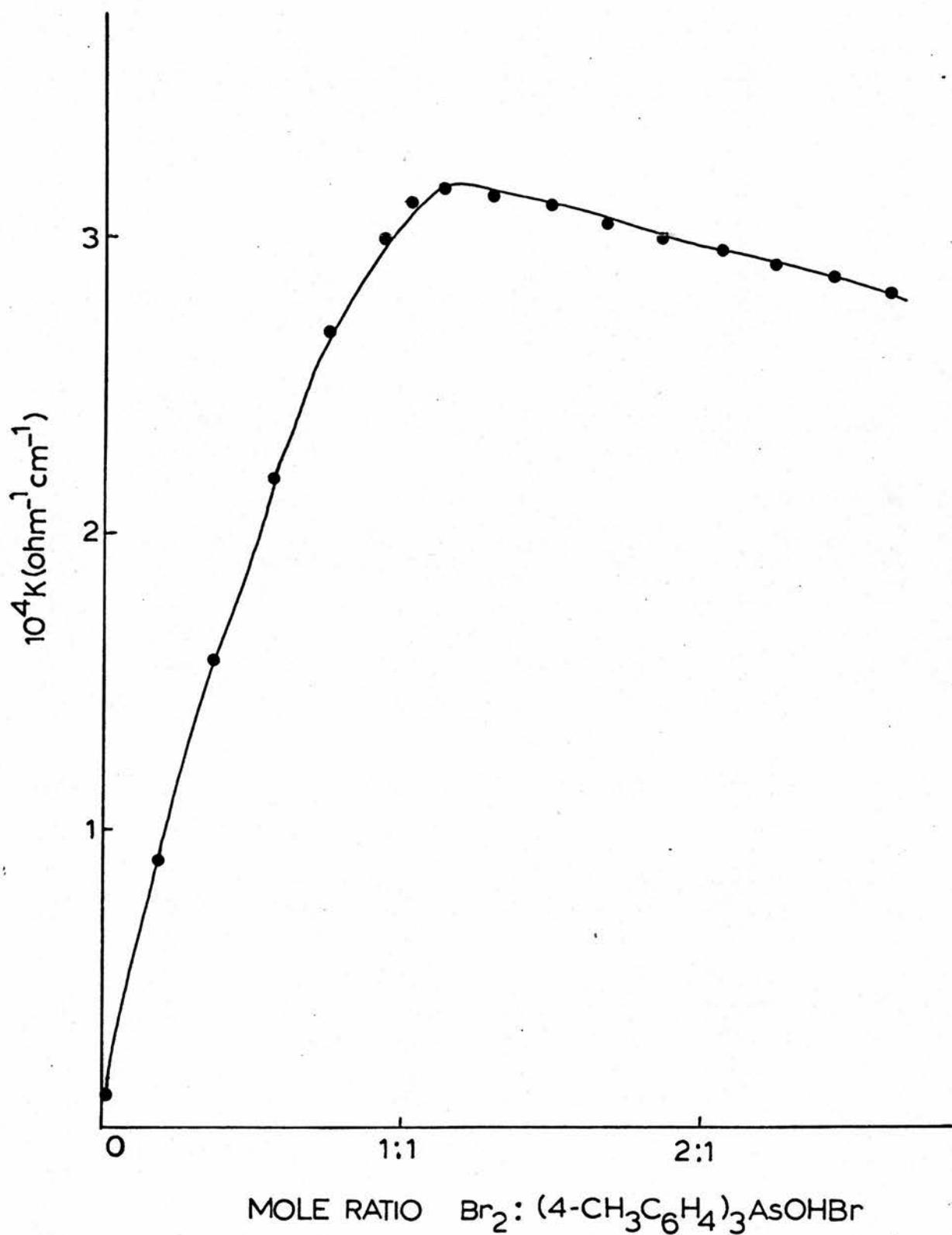


Figure 27. Conductometric Titration of $\text{Br}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ in Nitrobenzene

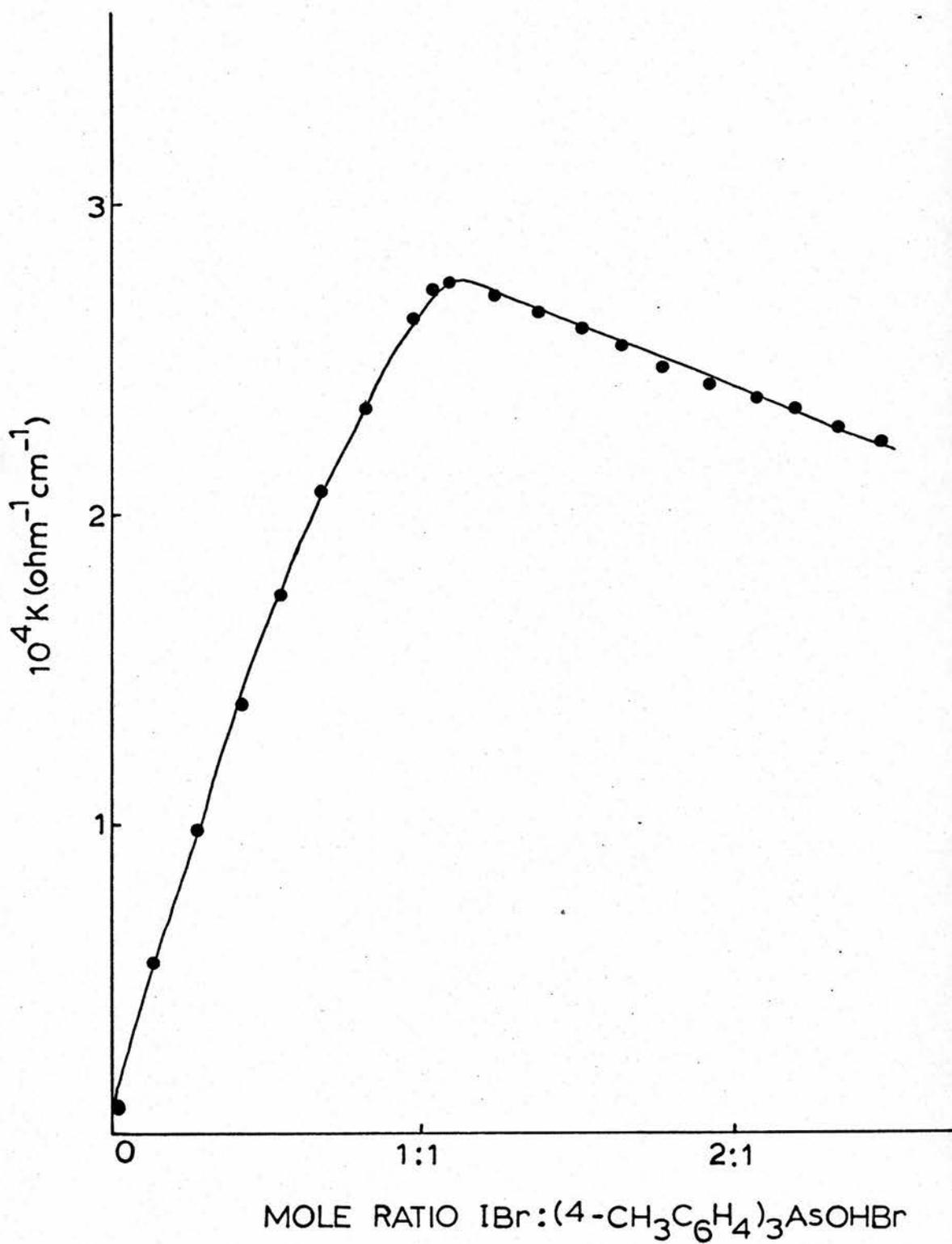
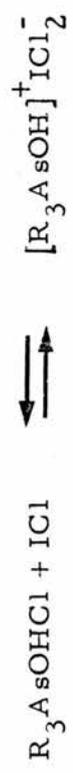


Figure 28. Conductometric Titration of $\text{IBr}:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ in Nitrobenzene

Table 33. Conductometric Titration of $R_3AsOHCl$ with ICl in Nitrobenzene

Compound	Λ_m $ohm^{-1} cm^2 mol^{-1}$ at 1:1 $[ICl:R_3AsOHCl]$ mole ratio	C_m = $mol l^{-1}$	indicating formation of
$(2-CH_3 C_6 H_4)_3 AsOHCl$	23.62	0.00972	$\left[\begin{array}{c} \rightarrow [R_3AsOH]^+ ICl_2^- \end{array} \right]$
$(3-CH_3 C_6 H_4)_3 AsOHCl$	21.84	0.00972	
$(4-CH_3 C_6 H_4)_3 AsOHCl$	21.90	0.01188	

The conductometric titration of $R_3AsOHCl$ with ICl in nitrobenzene showed the same general features as observed in the conductometric titration of $R_3AsOHBr$ with Br_2 and IBr , but the break at 1:1 $[ICl:R_3AsOHCl]$ mole ratio was not sharp but slightly rounded, figure 29 on p.102a. This is presumed to be due to the system being at equilibrium at the end-point, thus the reaction does not lie completely on the right hand side of the equation i.e.



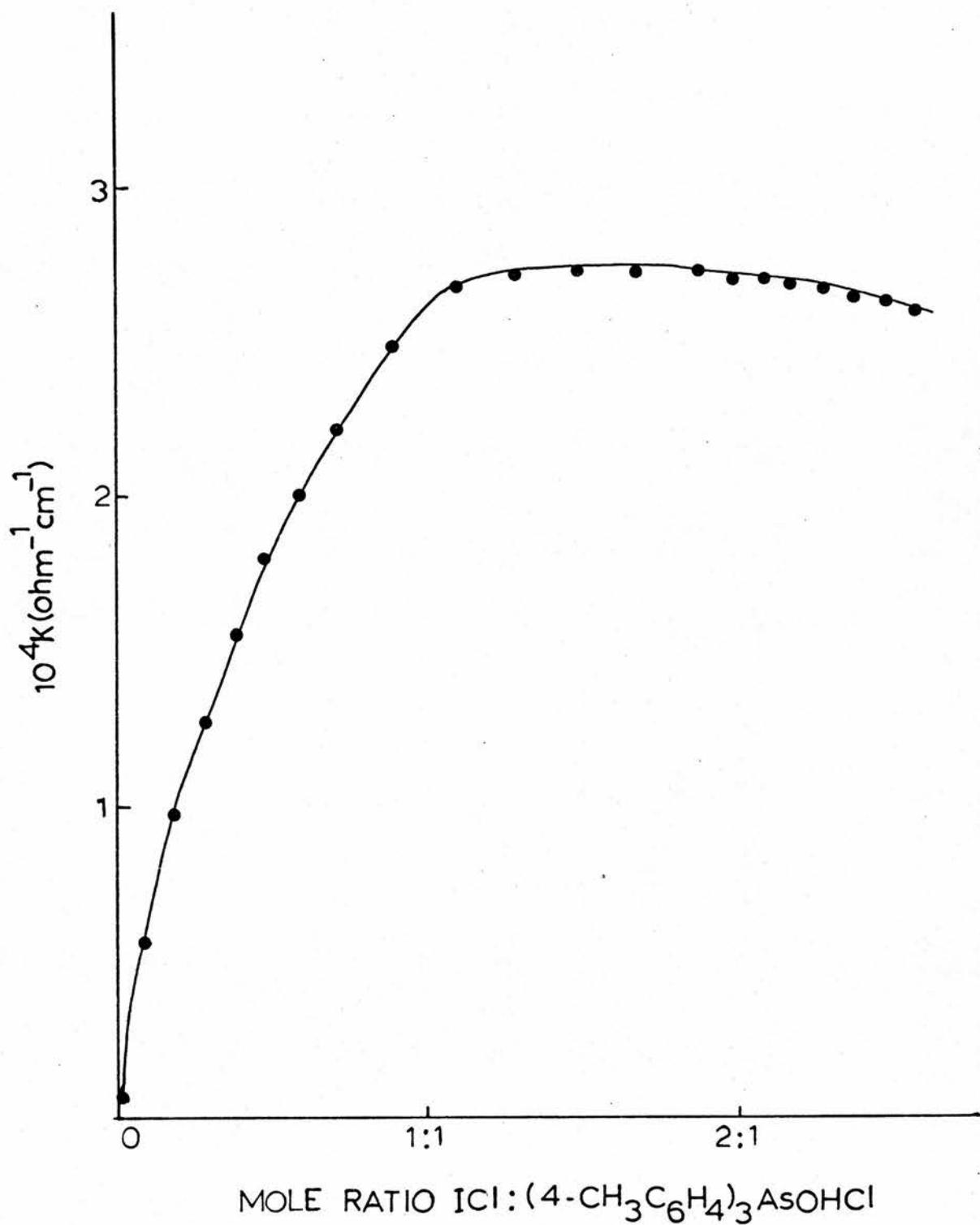


Figure 29. Conductometric Titration of $\text{ICl}:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ in Nitrobenzene

the formation of hydroxytris(methylphenyl)arsonium salts containing the anions Br_3^- , IBr_2^- and ICl_2^- in nitrobenzene solution.

D. Isolation of the Compounds $[\text{R}_3\text{AsOH}]^+\text{Hal}_3^-$ Indicated by Conductometric Titration

(R = 2- $\text{CH}_3\text{C}_6\text{H}_4$, 3- $\text{CH}_3\text{C}_6\text{H}_4$, 4- $\text{CH}_3\text{C}_6\text{H}_4$; $\text{Hal}_3^- = \text{Br}_3^-$, IBr_2^- and ICl_2^-)

(1) $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Hal}_3^-$

(a) $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}_3^-$

Great difficulty was experienced in the isolation of the polyhalogen compounds whose formation in solution was indicated by conductometric titration of $\text{R}_3\text{AsOHHal}$ with halogens and interhalogens. A convenient route to the isolation of the compounds of type R_3AsHal_2 and R_3AsHal_4 adducts was the addition of ether to a methyl cyanide solution of R_3As and halogen in correct proportion* ; precipitation of the crystalline dihalogeno or tetrahalogeno adduct usually occurred. However, attempts to prepare in this way, $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}_3^-$ from a methyl cyanide solution of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and Br_2 in 1:1 mole ratio invariably produced dark yellow crystals, m.p. 145-146°C of empirical formula $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}_2$. The infrared spectrum showed in the O-H region a strong band at ca. 3000 cm^{-1} (figure 30 on p.103a) quite different in appearance from that of the hydroxyhalide (figure 26 on p. 98a). This band is similar in appearance and position to that present in the infrared spectrum of hydroxytriphenylarsonium $(\text{C}_6\text{H}_5)_3\text{AsOH}^+$ salts¹²¹ and is therefore assigned to the O-H stretching vibration of the $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}^+$ ion. The uv spectrum of the

* isolation of adducts pp. 37, 42, and 46 of this thesis

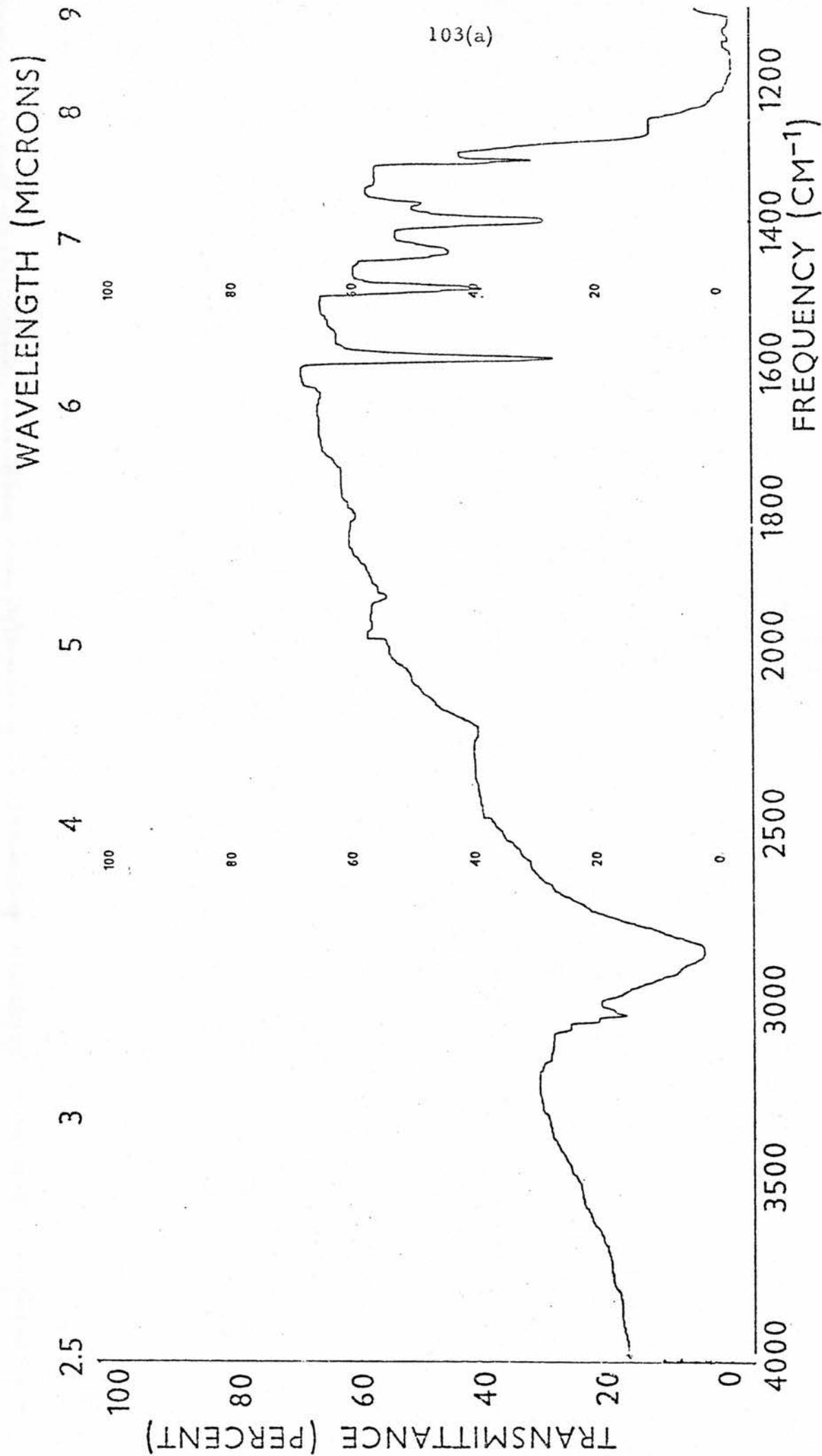
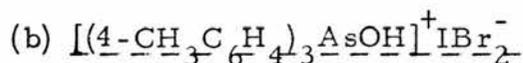


Figure 30. The Characteristic Hydroxyl Stretching Frequency in the Infrared Spectrum of
 $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2\text{Br}^-\text{Br}_3^-$

compound showed the presence of Br_3^- ions. These data can best be explained by assuming the compound to be the mixed anion compound $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$. In support of this the extinction coefficient of the tribromide ion peak in the uv spectrum calculated on the basis of this formula was in good agreement with the published values ^{*125, 129}. A conductometric titration of this compound with bromine in nitrobenzene was carried out, a break occurred at the 1:1 mole ratio, indicating that the reaction $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^- + \text{Br}_2 \longrightarrow 2[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+ + \text{Br}_3^-$ was taking place (figure 31 on p. 104a).



Attempts to isolate the compound $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{IBr}_2^-$ by addition of ether to a methyl cyanide solution of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and IBr in 1:1 mole ratio gave orange crystals whose analysis was in keeping with the formulation $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{IBr}_3^-$, m.p. 138-140°C. The infrared spectrum of this compound contained a strong broad peak at 3000 cm^{-1} which suggested the presence of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}^+$ ion, and the uv spectrum of its methyl cyanide solution indicated the

* $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ isolated from Ph_3AsOHBr and Br_2 under similar conditions by Harris and Inglis ¹²⁹ also supported the above formulation of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$

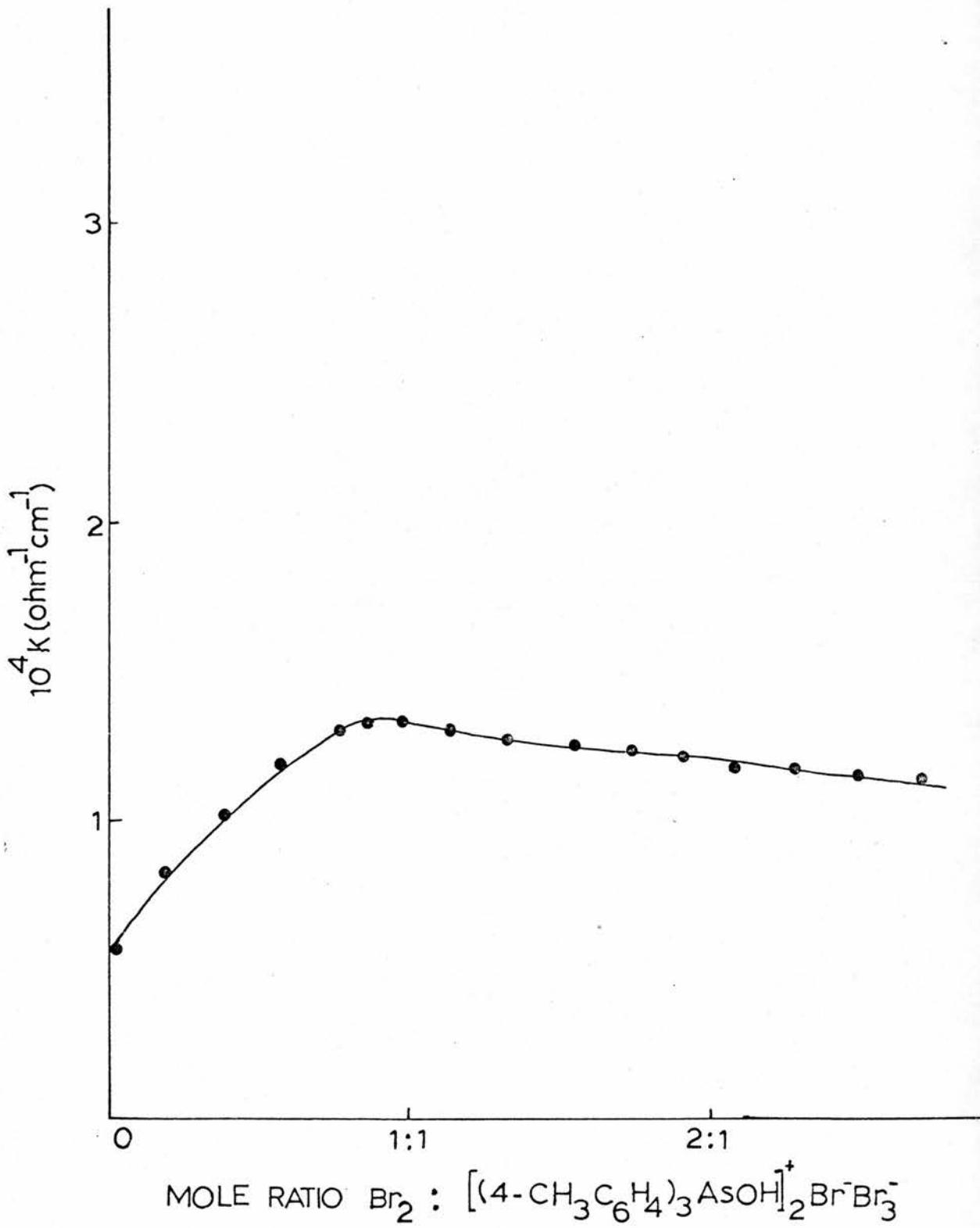
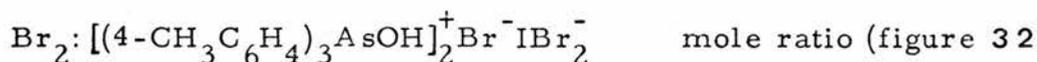
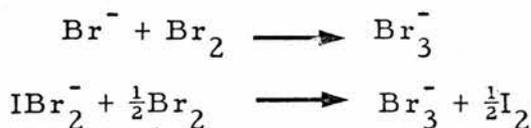


Figure 31. Conductometric Titration of $\text{Br}_2 : [(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ in Nitrobenzene

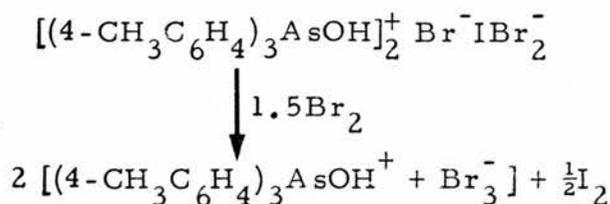
presence of IBr_2^- ions. These data can be best explained by the formulation of the compound as $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$ containing both bromide and dibromideiodide ions. To confirm this a conductometric titration of this compound with Br_2 in nitrobenzene was carried out. A break occurred in the conductance-composition graph close to the 1.5:1



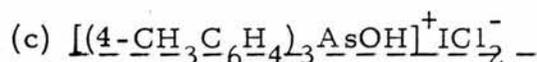
on p. 105a). The formation of a break at this ratio is presumed to be due to the following two reactions



The overall reaction is therefore



The uv spectrum of a methyl cyanide solution containing a mixture of bromine and $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$ in 1.5:1 ratio showed that only Br_3^- ion was present (peak at $\lambda_{\text{max}} = 269\text{m}\mu$). This observation supports to the above interpretation.



Attempts to prepare $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{ICl}_2^-$ by reacting an equimolar mixture of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ and ICl in methyl cyanide and ether gave a pale yellow crystalline compound, whose analysis suggested the composition $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{ICl}_3^-$. By analogy with the reaction of Ph_3AsOHCl with ICl under similar conditions¹²⁰ and its x-ray crystallographic study¹⁶⁵ it was thought

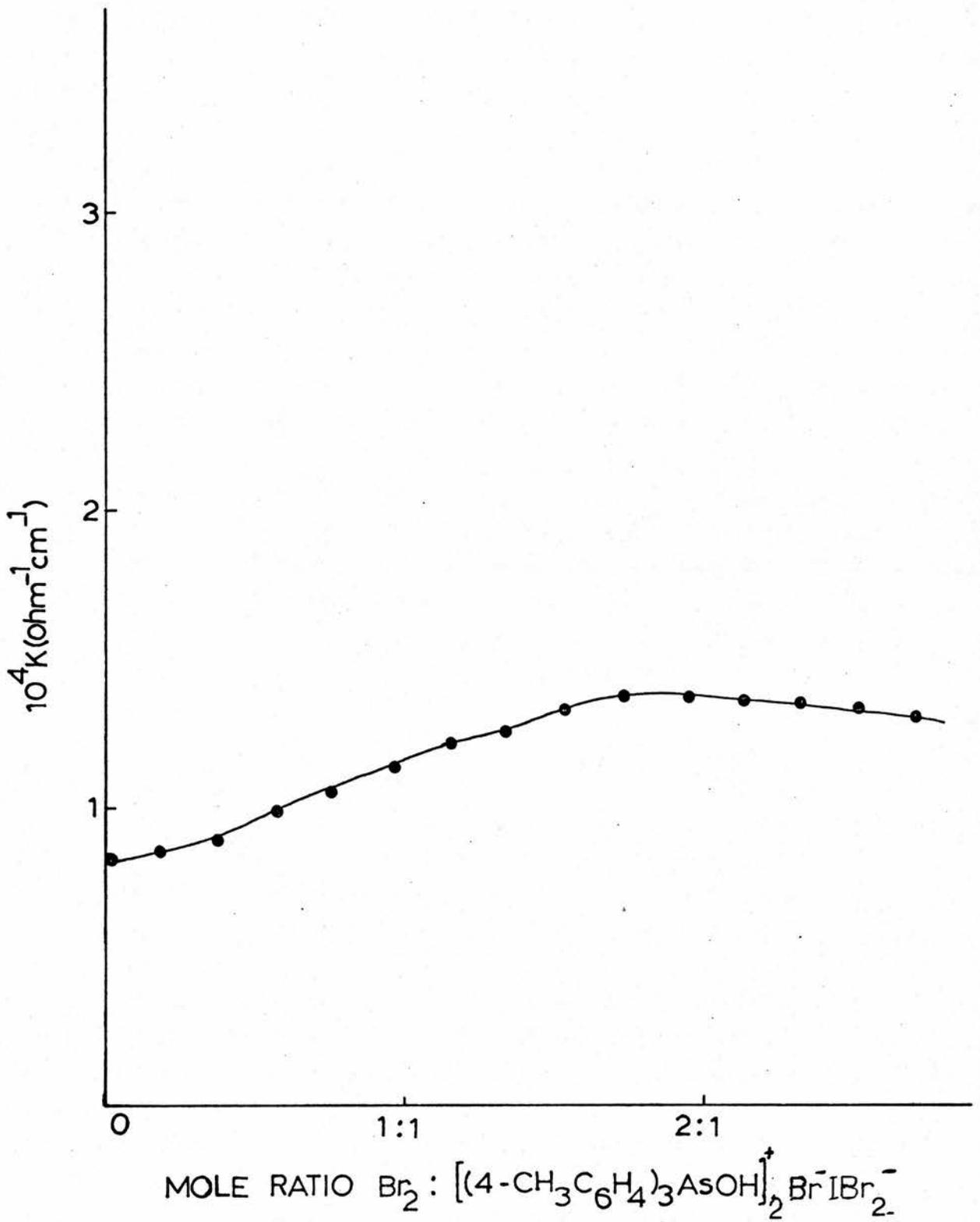
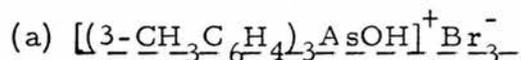
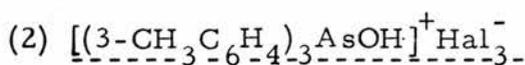


Figure 32. Conductometric Titration of $\text{Br}_2 : [(\text{4-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+ \text{Br}^- \text{IBr}_2^-$ in Nitrobenzene

that the product might be $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$. Its infrared spectrum showed the characteristic peak at 3000 cm^{-1} , indicating presence of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}^+$ ion, and the ICl_2^- ion was confirmed from its uv spectrum in methyl cyanide solution. A conductometric titration of this compound with ICl in nitrobenzene gave a break (not sharp) figure 33 on p.106a at the 1:1 $\text{ICl}:[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$ mole ratio presumably due to the reaction $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^- + \text{ICl} \longrightarrow 2[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}^+ + \text{ICl}_2^-]$



Repeated attempts to isolate $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}_3^-$ whose existence in solution was indicated by the conductometric titration of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ with Br_2 in nitrobenzene, were not successful. Attempts included (i) addition of ether to an equimolar mixture of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and Br_2 in methyl cyanide solution, (ii) using carbon tetrachloride as solvent. An oily product was obtained in each case and this solidified into yellow crystals with great difficulty. These gave the analytical data C, 46.12; H, 3.67; Br, 37.26% which do not tally with the required C, 41.68; H, 3.67; Br, 39.61%. for $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}_3^-$ or the required C, 48.02; H, 4.23; Br, 30.43% for $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$. The uv spectrum of this solid dissolved in methyl cyanide indicated presence of Br_3^- ion, but its infrared spectrum does not show the characteristic peak of the R_3AsOH^+ ion. It was therefore difficult to assign a

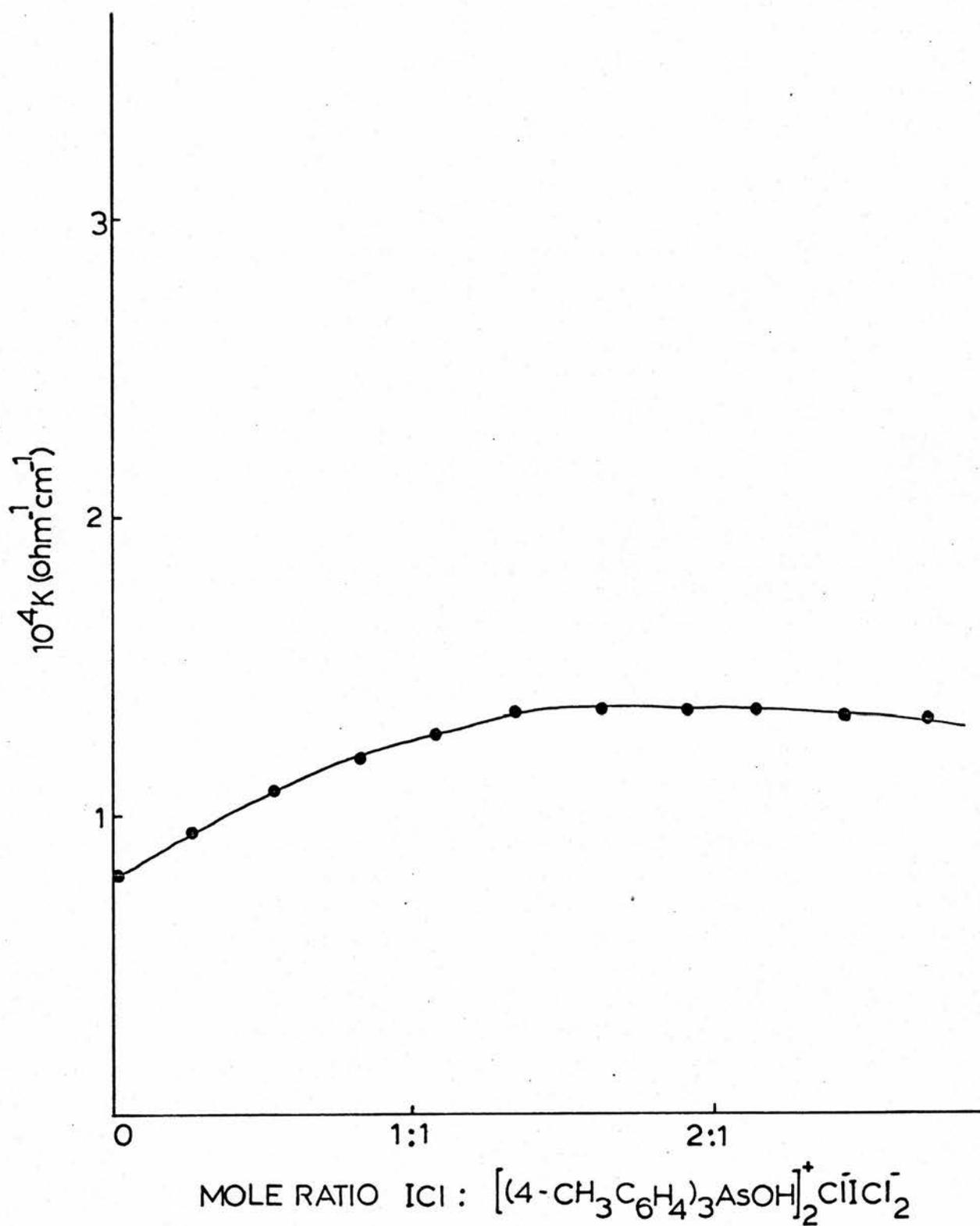
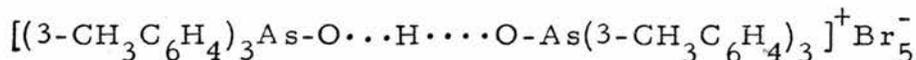
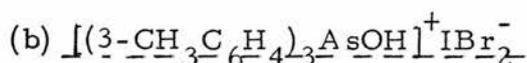


Figure 33. Conductometric Titration of
 ICl: $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+ \text{Cl}^- \text{ICl}_2^-$ in Nitrobenzene

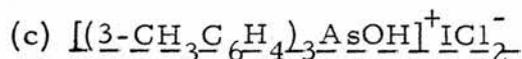
structure to this substance. The only reasonable structure whose analytical data were close to those found, was a hydrogen bonded one,



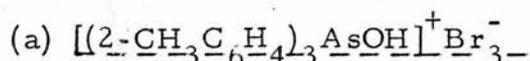
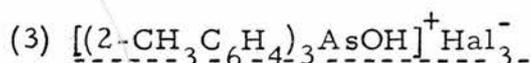
Anions containing more than four halogen atoms are known for I_5^- , I_7^- , I_9^- ^{127b} and Br_9^- ¹⁸⁶. Harris and co-workers have recognised the presence of Br_7^- and Br_9^- in the vapour pressure study of Br_2 -triarylphosphine system^{82, 120}.



Hydroxytris(3-methylphenyl)arsonium dibromide iodide was isolated from an equimolar mixture of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and IBr in methyl cyanide. An orange oil separated and this solidified into an orange crystalline product with great difficulty. m.p. 58-60°C. Analysis in keeping with $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{IBr}_2^-$. Uv spectrum confirmed the presence of IBr_2^- ion. Its infrared spectrum confirmed the presence of R_3AsOH^+ ion.

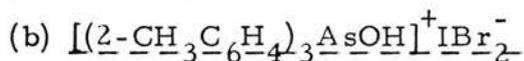


Attempts to isolate hydroxytris(3-methylphenyl)arsonium dichloride iodide were not successful. A yellow-brown oily product was obtained and this could not be converted to a solid.

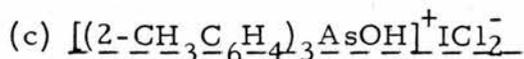


Attempts to isolate $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}_3^-$ from a carbon tetrachloride solution containing an equimolar mixture of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and Br_2 gave a yellow crystalline solid of

empirical composition $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}_2$. Its infrared spectrum suggested the presence of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}^+$ ion and the ultraviolet spectrum was consistent with presence of the Br_3^- ion. By analogy with the product obtained from similar systems $[(\text{C}_6\text{H}_5)_3\text{AsOHBr} + \text{Br}_2]^{129}$ and $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and Br_2 (p. 103] previously studied this compound is formulated as $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$. In support of this the extinction coefficient of the tribromide ion calculated on the basis of the formula was in good agreement with the published values^{125, 129}.



Although hydroxytris(2-methylphenyl)arsonium dibromide iodide was suggested from conductometric titration as being present in nitrobenzene solution of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and IBr , attempts to prepare this as a crystalline compound were not successful. A yellow crystalline product was obtained and the uv spectrum of this compound showed presence of IBr_2^- ions, but the analytical figures obtained (C, 41.41; H, 3.49; Br, 24.08; I, 11.39%) did not fit any reasonably likely structure expected from the given reactants. It is presumed that the product is impure but attempts to prepare a pure compound were not successful.



From the reaction of equimolar amounts of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ with ICl in methyl cyanide, two different products were isolated. The product precipitated out from the reaction mixture (using ether) was $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$ and the second product obtained

Table 34. Crystalline Adducts of $R_3AsOHHal$, with Halogens and Interhalogens

Compound	Colour	m.p. ($^{\circ}C$)	Hal_3^- ion present ¹	$\lambda_{max} = m\mu$
$[(4-CH_3C_6H_4)_3AsOH]_2^+ Br^- Br_3^-$	dark yellow	145-146	Br_3^-	269
$[(4-CH_3C_6H_4)_3AsOH]_2^+ Br^- IBr_2^-$	orange	138-140	IBr_2^-	257, 370
$[(4-CH_3C_6H_4)_3AsOH]_2^+ Cl^- ICl_2^-$	pale yellow	145-147	ICl_2^-	233
$[(3-CH_3C_6H_4)_3AsOH]_2^+ IBr_2^-$	orange	58-60	IBr_2^-	257, 370
$[(2-CH_3C_6H_4)_3AsOH]_2^+ Br^- Br_3^-$	dark yellow	132-134	Br_3^-	269
$[(2-CH_3C_6H_4)_3AsOH]_2^+ Cl^- ICl_2^-$	yellow	136-138	ICl_2^-	228
$[(2-CH_3C_6H_4)_3AsOH]_2^+ ICl_2^-$	yellow	110-112	ICl_2^-	228

1. Shown by uv spectrum of methyl cyanide solution of the adduct¹²⁵

was the expected one $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$

The properties of all the crystalline compounds isolated and discussed above are given in Table 34 on page 109.

E. Electrolytic Conductance of Compounds Obtained from the

Reaction of $\text{R}_3\text{AsOHHal}$ with Halogens and Interhalogens

($\text{R}=2\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{Hal}=\text{Cl}$ or Br)

The electrolytic conductance of all the compounds isolated from the reaction of $\text{R}_3\text{AsOHHal}$ with Br_2 , IBr and ICl in methyl cyanide/ether or carbon tetrachloride were measured in nitrobenzene at different concentrations and their molar conductance values were calculated on the basis of their respective formula. These values are given in Tables 35-40 on pages 180-181. The values of molar conductance (Λ_m) when plotted against the square root of molar concentration ($\sqrt{C_m}$) fall in straight lines except in the case of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ and are displayed in figures 34-39 on pp. 111a-111f.

For comparative purposes the values of conductance at $C_m = 0.01 \text{ mol l}^{-1}$, were obtained by interpolation from the graphs and were found to be:

Compound	$\Lambda_m \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
$[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$	26.8
$[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$	27.9
$[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$	27.0
$[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{IBr}_2^-$	26.6

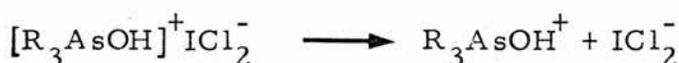
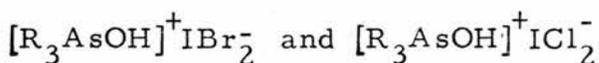
cont. on p. 111

Compound	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$	22.6
$[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$	27.9
$[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$	24.4

The magnitude of these molar conductance values suggest that the compounds are strong 1:1 electrolytes in nitrobenzene.

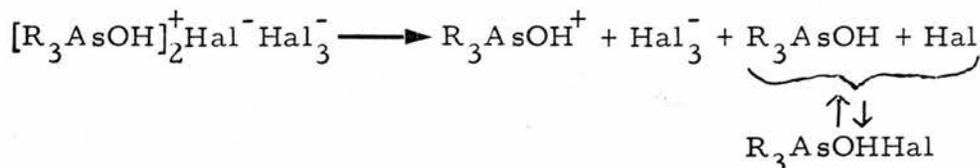
(For a strong 1:1 electrolyte in nitrobenzene $\Lambda_m = 20\text{-}26$ ohm⁻¹ cm² mol⁻¹ at $C_m = 0.01$ mol⁻¹).¹²⁴

By analogy with R_3AsHal_4 compounds we can write for



respectively.

As for the mixed anion compounds e. g. $[\text{R}_3\text{AsOH}]_2^+\text{Hal}^-\text{Hal}_3^-$ by analogy with $[\text{Ph}_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ ¹²⁹, it could be expected that on dissolving $[\text{R}_3\text{AsOH}]_2^+\text{Hal}^-\text{Hal}_3^-$ in nitrobenzene the following equilibria would result:



that is, the solution is equivalent to an equimolar mixture of

$\text{R}_3\text{AsOH}^+\text{Hal}_3^-$ and $\text{R}_3\text{AsOHHal}$ in nitrobenzene. $[\text{R}_3\text{AsOH}]_2^+\text{Hal}^-\text{Hal}_3^-$

should, therefore, behave approximately as a simple, strong 1:1

electrolyte (producing two ions per formula unit). The presence

of the Hal_3^- ion has been confirmed in each case from the ultraviolet

spectrum of the methyl cyanide solutions of the polyhalogen adducts

(as discussed in previous section). From the high values of molar

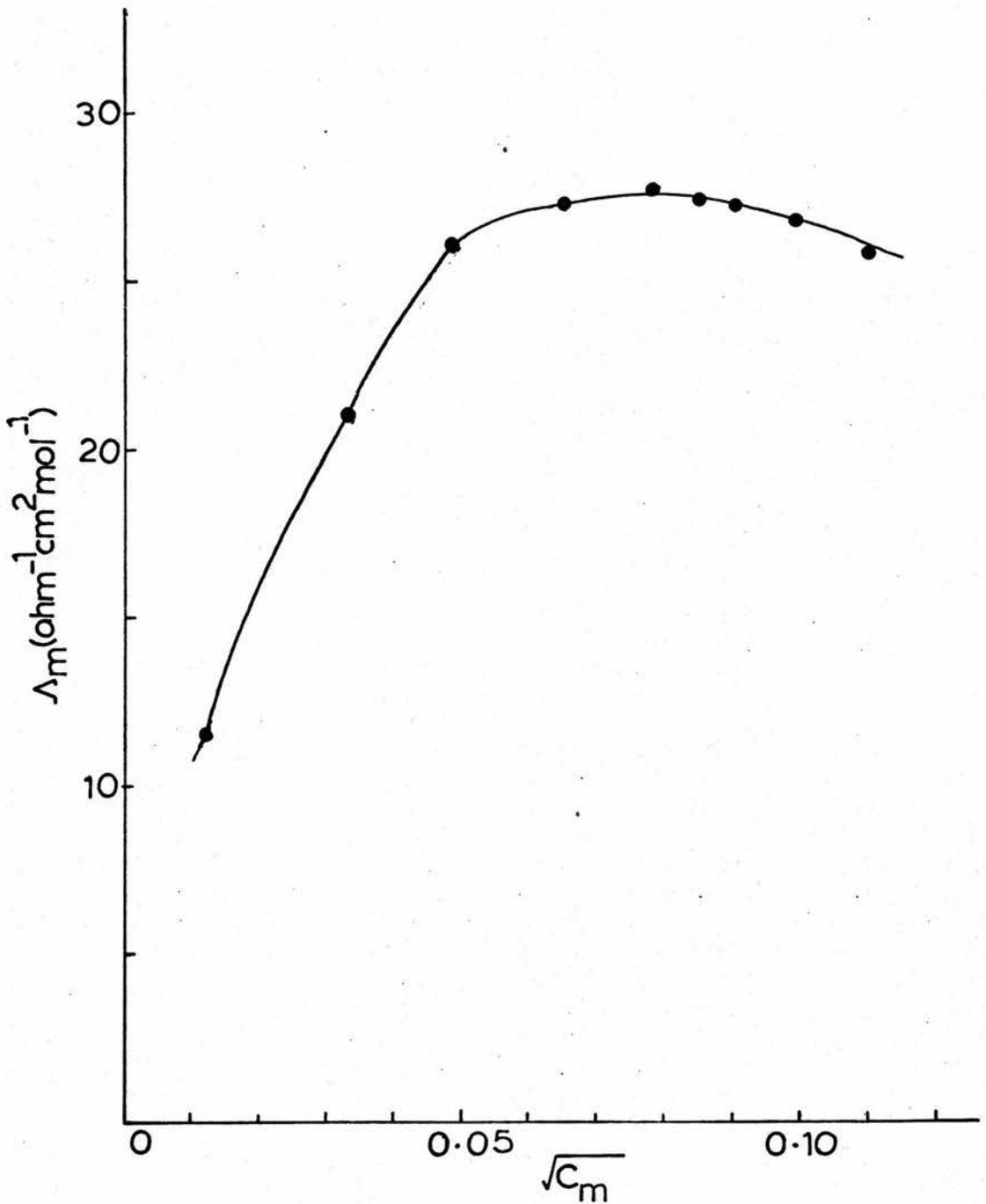


Figure 34. Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ in Nitrobenzene at 25°C

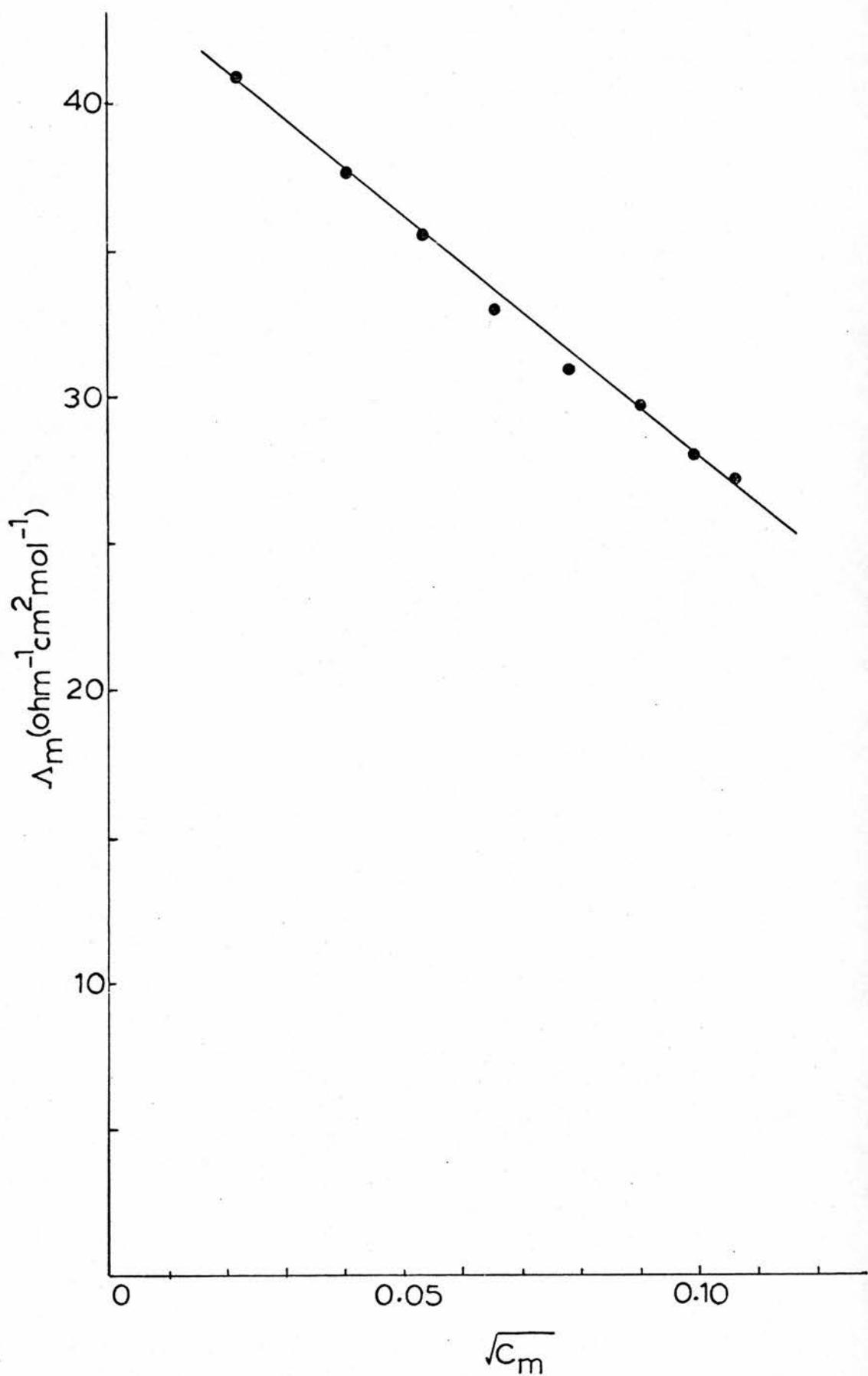


Figure 35 . Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$ in Nitrobenzene at 25°C

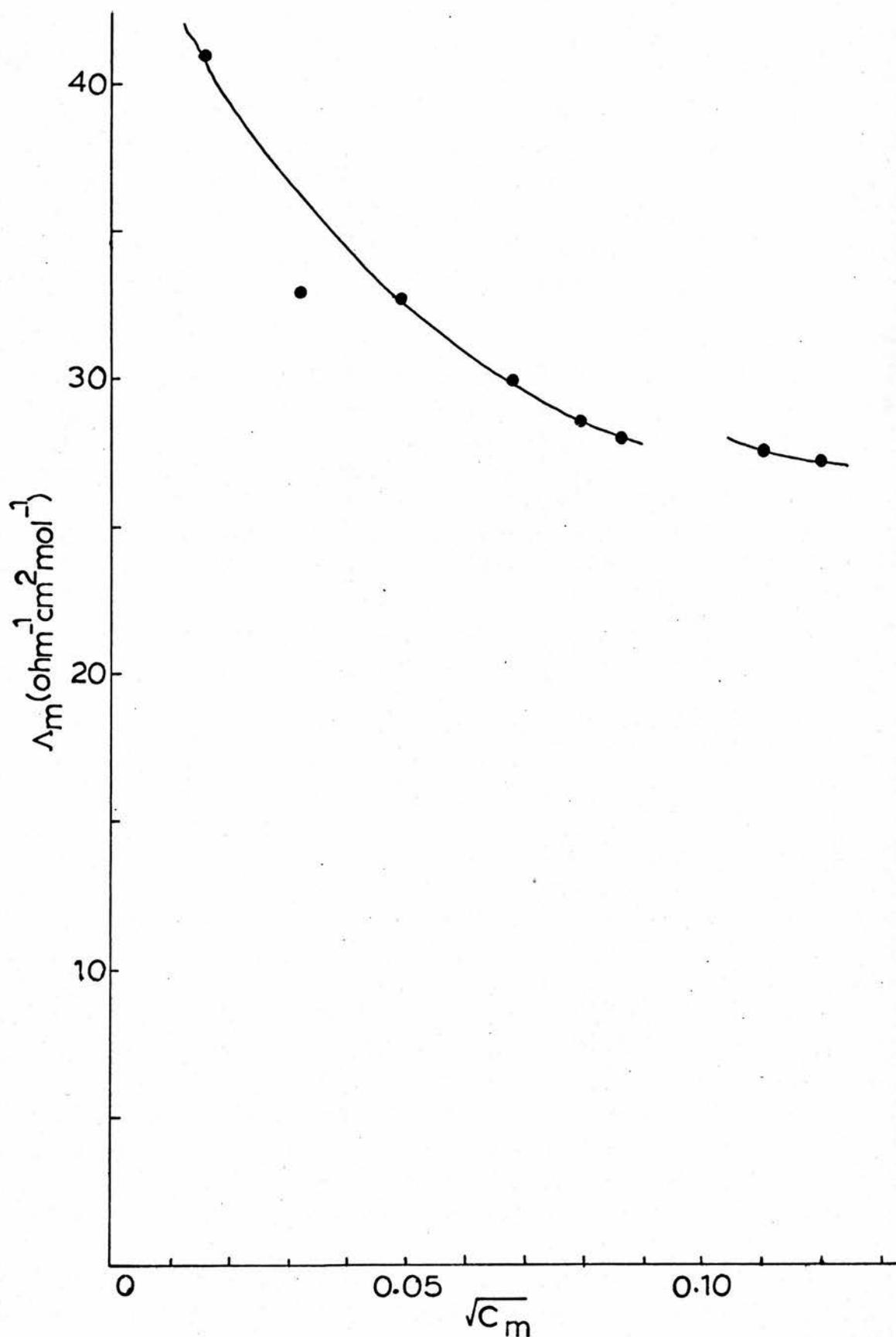


Figure 36. Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2\text{Cl}^-\text{ICl}_2^-$ in Nitrobenzene at 25°C

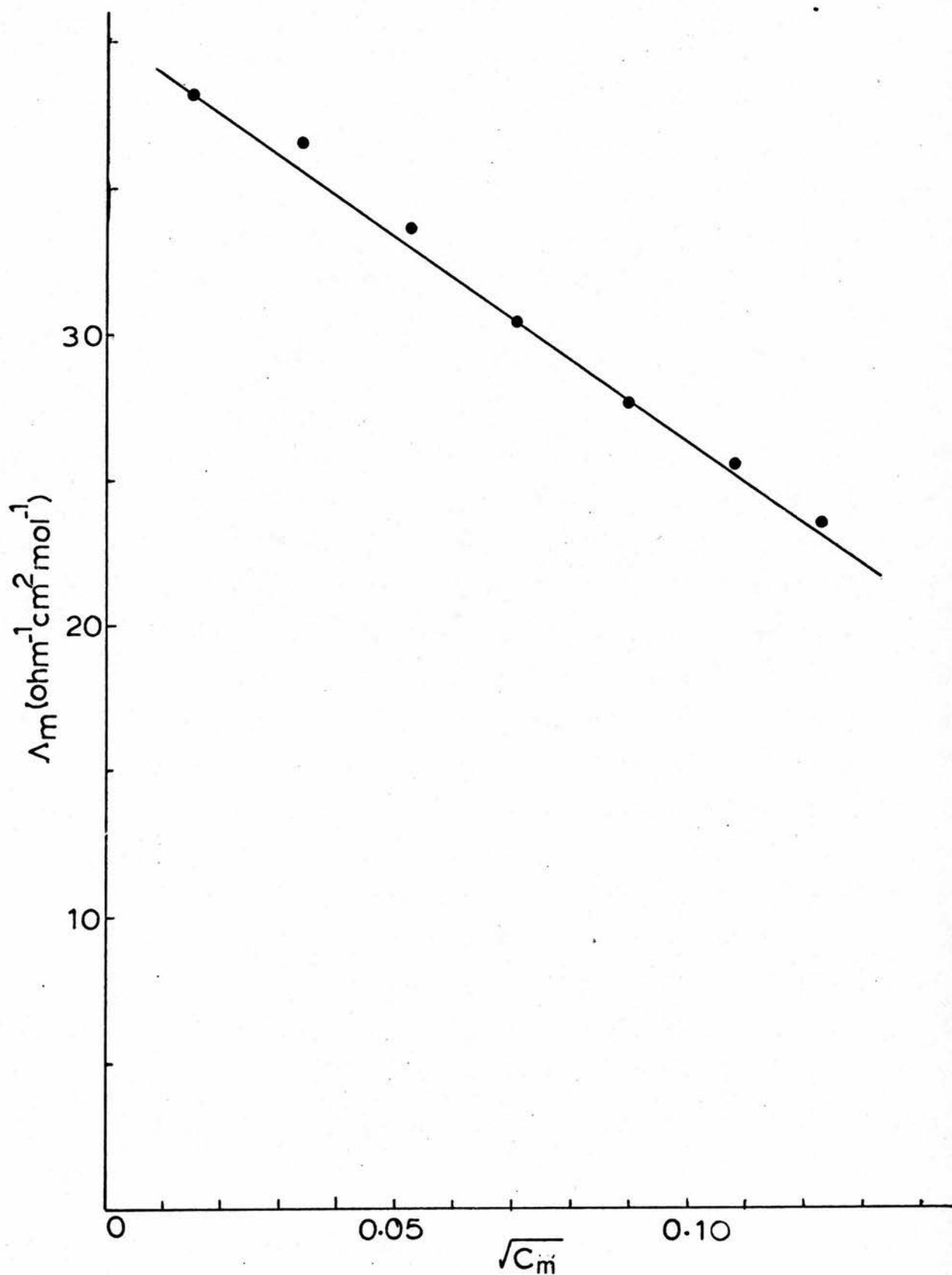


Figure 37. Electrolytic Conductance of $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{IBr}_2^-$
in Nitrobenzene at 25°C

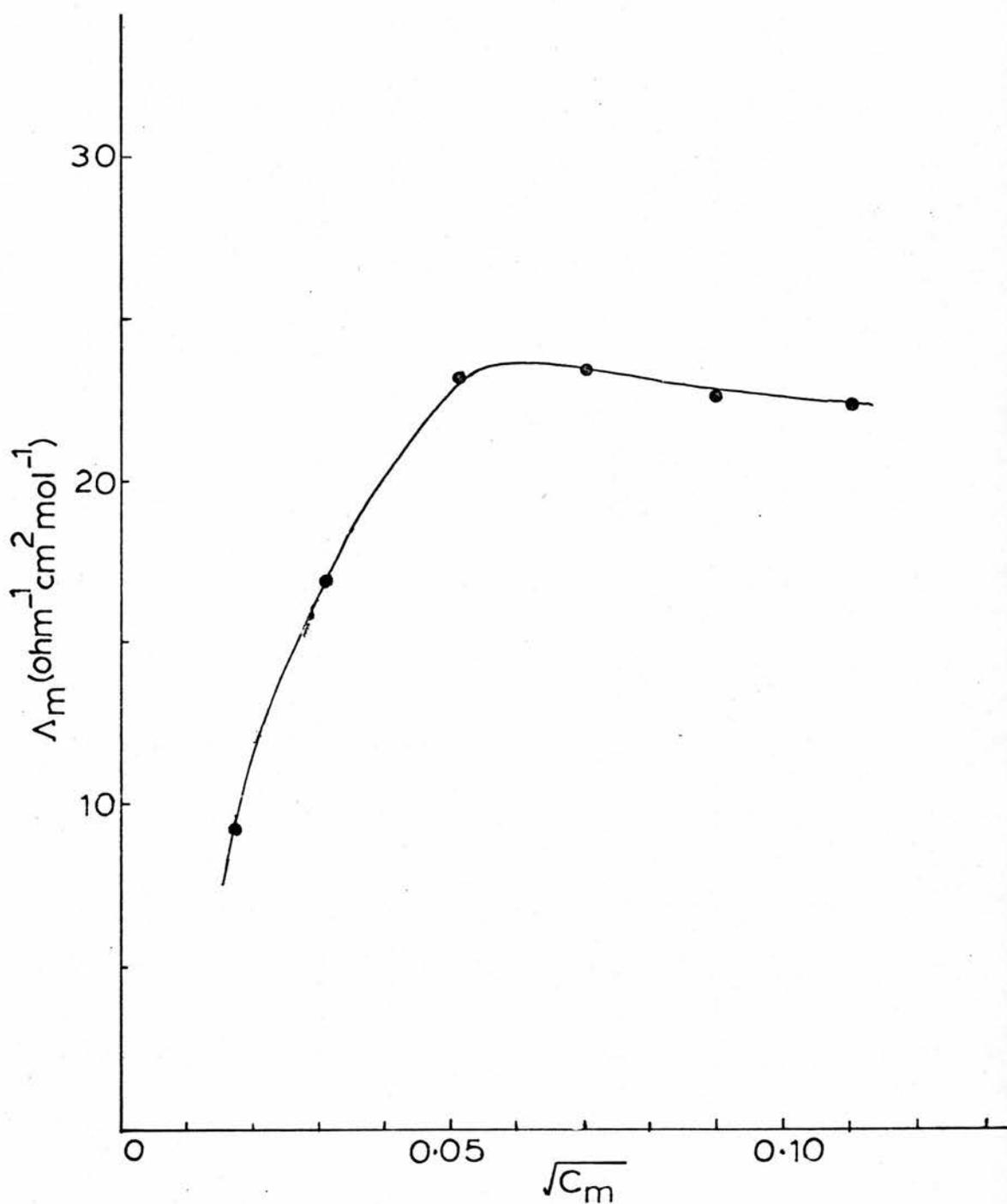


Figure 38. Electrolytic Conductance of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$ in Nitrobenzene at 25°C

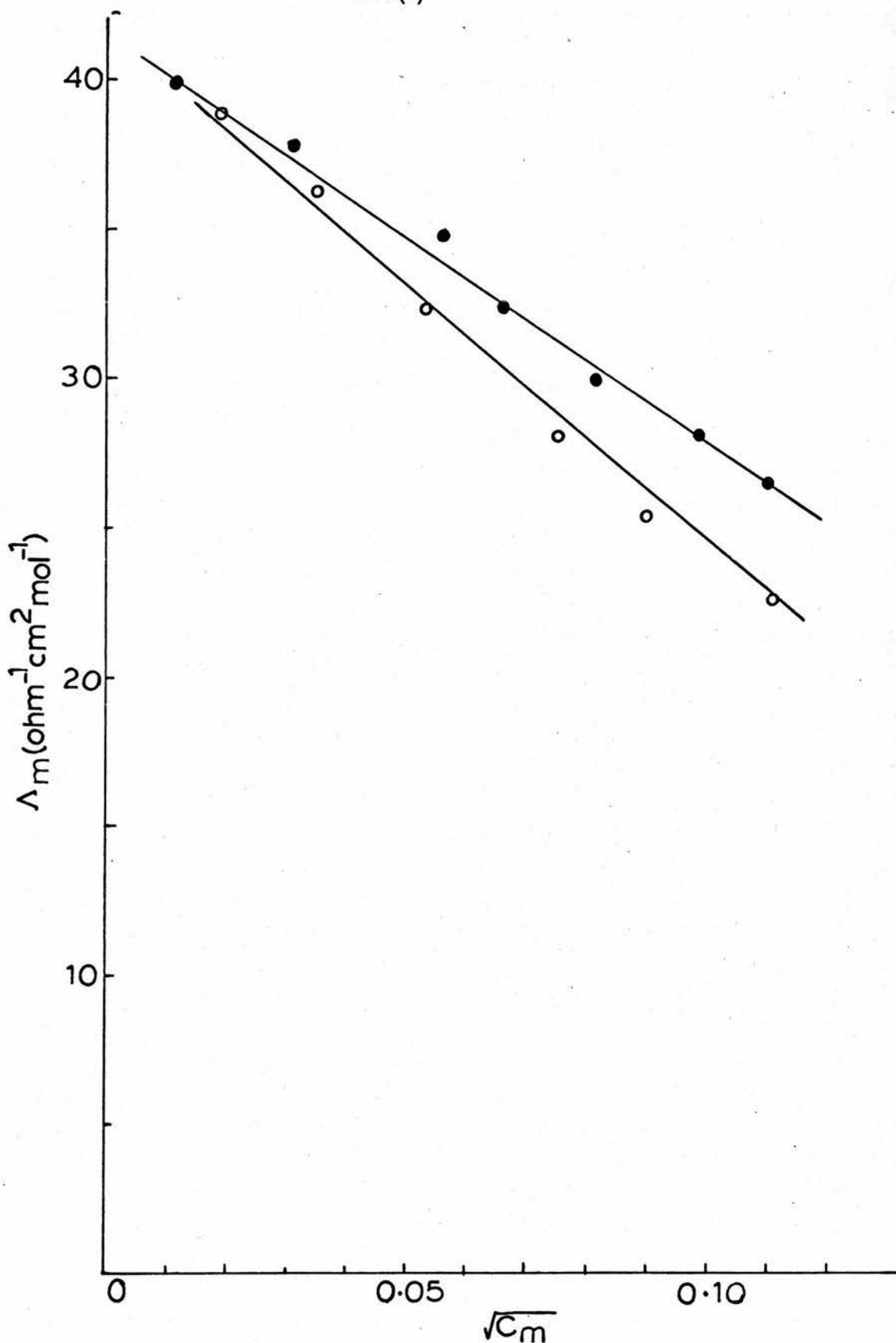


Figure 39. Electrolytic Conductance of
 $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2\text{Cl}^-\text{ICl}_2^-$ ●
 $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$ ○

in Nitrobenzene at 25°C

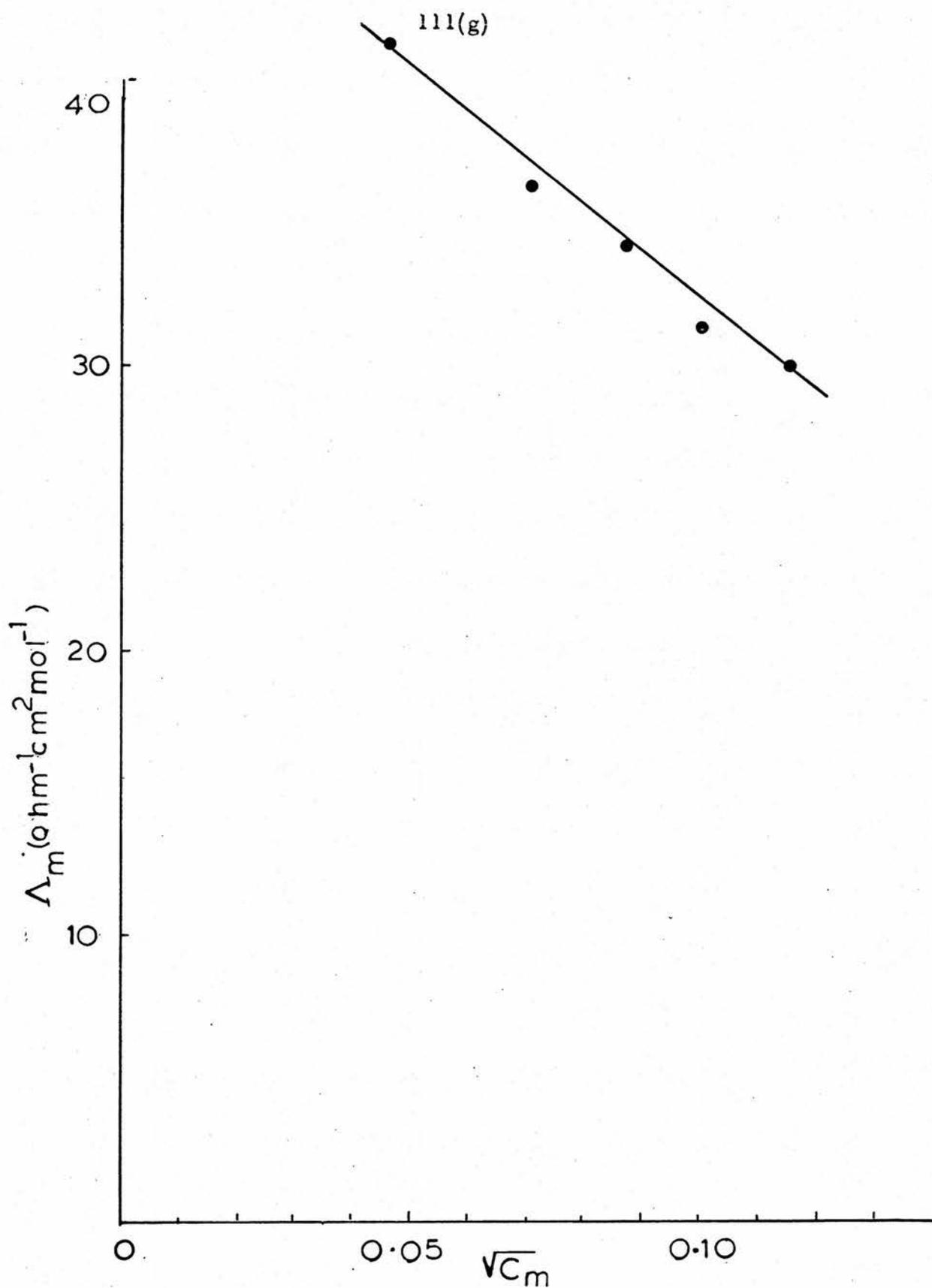


Figure 40. Electrolytic Conductance of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ in Nitrobenzene in Nitrobenzene at 25°C

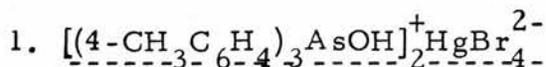
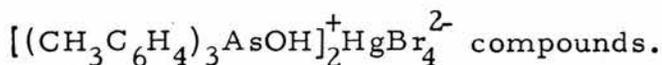
conductance of these compounds it seems reasonable to suggest that all of the compounds obtained from the reaction of tris(methylphenyl)arsine oxide hydrogen halides with Br_2 , IBr and ICl are ionic in the solid state.

From figures 34 and 38 on pp. 111a, 111e it is observed that $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+ \text{Br}^- \text{Br}_3^-$ and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+ \text{Br}^- \text{Br}_3^-$ do not give the normal relationship between molar conductance (Λ_m) and square root of molar concentration ($\sqrt{C_m}$), since the graphs develop a positive slope at lower concentration. The abnormal behaviour at low concentration is presumably due to a high degree of molecular dissociation. [cf. $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$, $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ and $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$ (p. 54 of this thesis)].

F. Reaction of R_3AsOHBr with HgBr_2

($\text{R}=2\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$)

Harris and Inglis¹²⁹ have mentioned that $\text{Ph}_3\text{AsOHHal}$ ($\text{Hal}=\text{Cl}, \text{Br}$) behave as a halide ion donor to mercury (II) halide. In this connection it was thought of interest to study the reaction of tris(methylphenyl)arsine oxide hydrogen bromide with mercuric bromide. It was expected that these would react to give

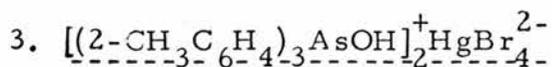


Attempts to isolate bis [hydroxytris(4-methylphenyl)arsonium] - tetrabromo mercurate from ethanol containing $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ and HgBr_2 in a 2:1 molar proportion were unsuccessful. A colourless viscous oily product was obtained and this solidified to

white crystals with great difficulty. Analysis of the solid gave C, 33.56; H, 3.27; Br, 25.27%. This does not tally with figures required for the expected compound $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ nor with $[\text{R}_3\text{AsO}\cdots\overset{\oplus}{\text{H}}\cdots\text{OAsR}_3]_2\text{Hg}_2\text{Br}_6^{2-}$ which might also be a reasonable product to expect¹⁶⁸. The infrared spectrum of the solid did not show the peak at 3000 cm^{-1} characteristic of the R_3AsOH^+ cation nor was there any indication of showing hydrogen bonded $\text{O}\cdots\text{H}\cdots\text{O}$ groups. The uv spectrum showed absorption at $\lambda_{\text{max}} = 263\text{ m}\mu$, this could be due to the Br_3^- ion ($\lambda_{\text{max}} = 269\text{ m}\mu$) but is shifted downwards. Solution of the solid in nitrobenzene have a high specific conductance. It is difficult to formulate a structure for this product which is in keeping with all of the above mentioned observations, although the one which comes closest to the analytical data is the R_3AsO adduct $\text{R}_3\text{AsO}\cdot\text{HgBr}_2$. This reaction obviously requires further investigation.

2. $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$

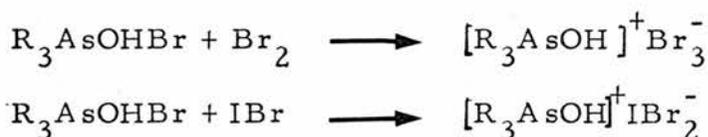
Ethanol containing $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (2 mols) and HgBr_2 (1 mol) gave a viscous oily product. As in the previous reaction extreme difficulty was experienced in isolating a solid product. However, a workable but still slightly sticky white product was obtained and the analytical data for this tallied with the expected product, $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$. This compound is very hygroscopic and on exposure to the atmosphere it reverted to an oil.



This compound was prepared by the addition of ether to $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (2 mols) and HgBr_2 (1 mol) contained in acetone/chloroform. Its infrared spectrum had a strong broad peak at 3000 cm^{-1} which indicated presence of the R_3AsOH^+ cation. The uv spectrum of its methyl cyanide solution surprisingly suggested presence of Br_3^- ions. The molar conductance of the compound in nitrobenzene solution was found to be $31.20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at $C_m = 0.01 \text{ mol l}^{-1}$. figure 40 on p. 111g. Thus it behaves, as expected as a strong 1:1 electrolyte. From the analytical data, ir spectrum and conductance studies of this compound and by analogy with $[\text{Ph}_3\text{AsOH}]_2^+ \text{HgBr}_4^{2-}$ ¹²⁹ this compound was formulated $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+ \text{HgBr}_4^{2-}$.

G. Conclusion

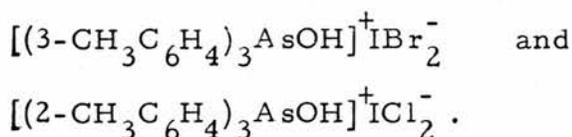
In the conductometric titration of $\text{R}_3\text{AsOHHal}$ ($\text{R} = 2\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{Hal} = \text{Cl}, \text{Br}$) with Br_2 , IBr and ICl , breaks at the 1:1 $[\text{Hal}_2 : \text{R}_3\text{AsOHHal}]$ mole ratio indicate the formation of compounds of composition $\text{R}_3\text{AsOHBr}_3$, $\text{R}_3\text{AsOHIBr}_2$ and $\text{R}_3\text{AsOHICl}_2$. The high values of molar conductance at the 1:1 mole ratio found in each case indicate strong 1:1 electrolyte behaviour suggesting that the compounds should be formulated as $[\text{R}_3\text{AsOH}]^+ \text{Br}_3^-$, $[\text{R}_3\text{AsOH}]^+ \text{IBr}_2^-$ and $[\text{R}_3\text{AsOH}]^+ \text{ICl}_2^-$. In the conductometric titration of R_3AsOHBr with Br_2 and IBr the breaks in the graph at the 1:1 ratio are sharp indicating that the reactions are complete at the end-point.



In contrast, in the titration of R_3AsOHCl with ICl the breaks at the 1:1 mole ratio are not sharp, but slightly rounded. This is presumed to be due to the system being at equilibrium at the end-point, thus the reaction does not lie completely on the right hand side of the equation i.e.



Though the formation of these compounds was indicated by conductometric titration, great difficulty was experienced in their isolation from equimolar mixtures of $\text{R}_3\text{AsOHHal}$ and Hal_2 in methyl cyanide/ether or carbon tetrachloride. In many cases oily products were obtained which crystallised with great difficulty. Out of the nine compounds whose preparation was attempted only two were isolated with the expected formula. These were



Five compounds were isolated as mixed-anion compounds, viz.,

1. $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$
2. $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$
3. $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$
4. $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$
5. $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$

The difficulty experienced in obtaining these compounds is hard to explain. It is however obvious that several factors will come into

play, such as (i) the presence of complex equilibria in solution (ii) the solubility of the compound (iii) crystal packing effects (cf. $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$ which could only be obtained as a CCl_4 solvate, p. 50 of this thesis).

In an attempted preparation of $[\text{R}_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ from the reaction of R_3AsOHBr and HgBr_2 , it was observed that $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ was obtained readily, whereas $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$ could only be obtained with great difficulty as a rather sticky product whose analytical results nevertheless were in keeping with those expected. The reaction product of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ with mercuric bromide HgBr_2 was not identified. These reactions require further investigation.

EXPERIMENTAL

EXPERIMENTAL

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I General Techniques

(a) Handling of Materials

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

All the oxygen containing compounds described could be handled without special precautions, except for a few polyhalides which tended to lose halogen unless kept in tightly sealed containers.

(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 branched various sub-sections designed for special operations.

(c) Conductance Measurements

Conductance measurements were made at 25°C in a sealed cell. A standard pair of smooth platinum dipping electrodes was used. The cell constant was determined using a 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 solution was complete, the cell was placed in a thermostat bath at 25°C and the specific conductance measured using a Wayne Kerr B 641 Autobalance Bridge. For higher concentrations, successive additions of the compound from small sample tubes were made inside the dry-box into the same cell (figure 41). Molar conductances were then calculated and plotted against $\sqrt{C_m}$.

(d) Conductometric Titrations

Conductometric titration is a useful technique for investigating the course of certain types of reaction, giving information not only on the stoichiometry of the reaction products but also on their electrolytic nature.

Methyl cyanide was usually employed as a solvent by Harris et al^{120,121,123}, due to its high dielectric constant (36.7 at 25°C) which results in high conductances of electrolytes and consequent easy distinction between non-electrolytes and weak electrolytes. However, commercial methyl cyanide varied in quality from batch to batch and for some of the compounds studied in this thesis good consistency of conductometric results could not be obtained,

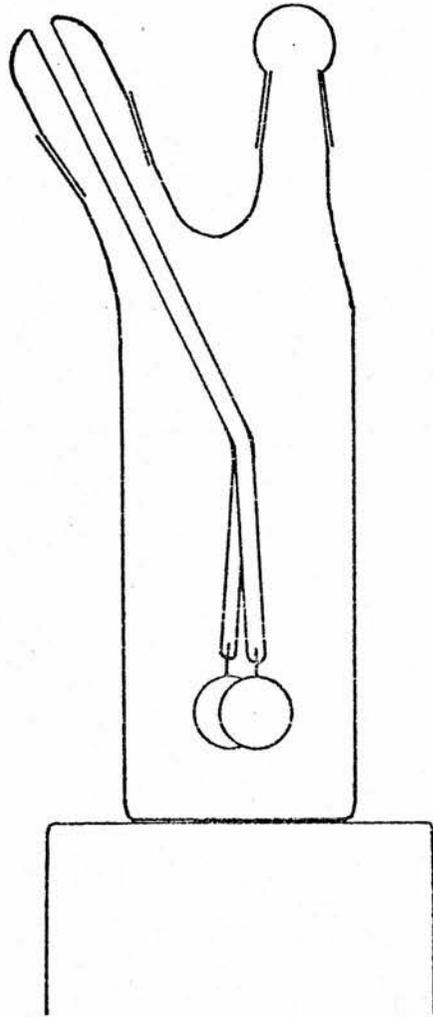


Figure 41. Conductance Cell

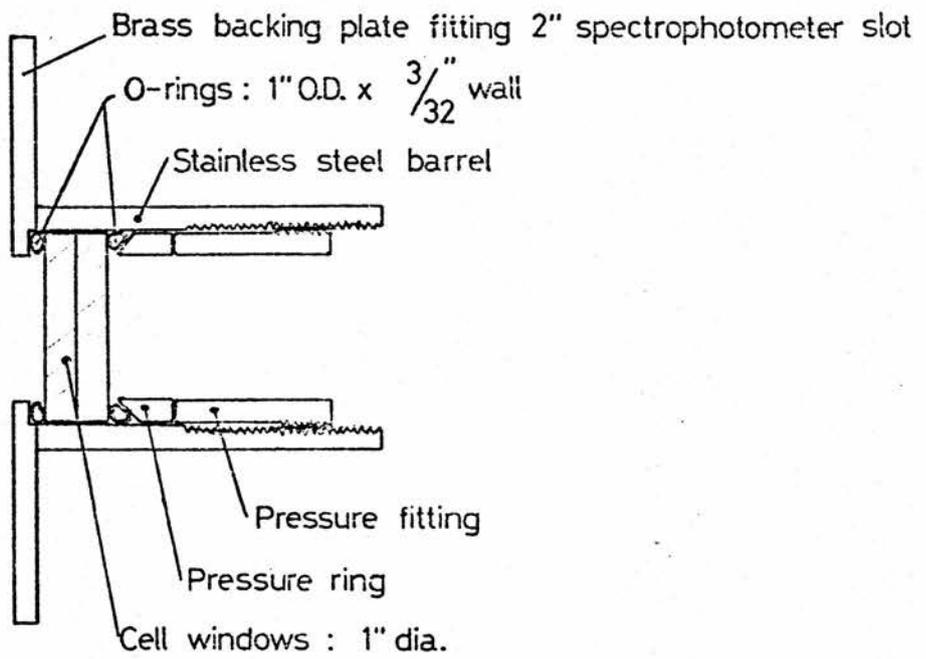
even after repetition three to four times. No such problem was encountered with nitrobenzene and even though its dielectric constant is much lower (34.8 at 25°C) than that of methyl cyanide, it was found to be a much more suitable solvent for the aforementioned compounds. The specific conductance of the purified nitrobenzene was less than 10^{-7} ohm⁻¹ cm⁻¹ at 25°C.

Titration were carried out in an apparatus designed to exclude moisture and to keep halogen solutions from contact with tap grease: a description of the apparatus and its operation has been published by Harris and Inglis⁹³. The conductance bridge used was a Wayne Kerr B 641 Autobalance Bridge. During a titration the conductance was measured when equilibrium had been attained after each addition of halogen solution to the arsine solution.

(e) Infra-red Spectra

Infra-red spectra were recorded on a Perkin-Elmer Model 621 (and in some cases Model 257) Grating Infrared Spectrophotometer over the range 4000-200 cm⁻¹ (and 4000-625 cm⁻¹ in the case of the latter). Although infra-red spectroscopy was extensively used throughout this work, it was only with respect to the partial hydrolysis products of dihalo-tris(methylphenyl)arsoranes and tris(methylphenyl)arsine oxides that much useful information could be obtained.

The samples were prepared in the dry-box as mulls in nujol or voltalef and placed between either potassium bromide or sodium chloride plates. A special type of sample holders was



Demountable Cell for Air Sensitive Samples

Figure 42.

constructed (figure 42) , in order to protect the sample from air or moisture. A mull was prepared and placed between a pair of one inch (1") alkali halide windows in the dry-box as usual and inserted in the barrel of the cell between o-rings. The pressure ring and pressure fitting were assembled and tightened so that the circumference of the windows was sealed before removal from the dry-box. This assembled cell could then be inserted into the standard 2" sample slot of any infra-red spectrophotometer.

(f) Ultra-Violet Spectra

Ultra-violet spectra were recorded on a Unicam SF 800B UV/visible recording spectrophotometer. Stoppered quartz cells of 1 cm or 0.5 cm path length were used, measurements being made at room temperature (ca. 20°C).

(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 by Mr. James Bews.

Halogen analyses were carried out potentiometrically using an adaptation of the method described by Lingane¹⁸⁷. A description of the method is as follows:

Approximately 50 mg of sample was accurately weighed into a stoppered 100 ml Quickfit conical flask, the addition of sample being made in the dry-box. The sample was then hydrolysed with 20 ml of 2M sodium hydroxide solution, the hydrolysis being performed in a closed system to prevent the possible escape of

hydrogen halide. The resultant solution or suspension was left to stand for one hour before boiling for a minimum of fifteen minutes to ensure complete hydrolysis. It was then cooled and made just acidic with concentrated sulphuric acid before immediately bubbling sulphur dioxide gas through the solution, for two minutes to reduce any hypohalite ion present. Further boiling served both to drive off excess sulphur dioxide and reduce the bulk of the solution. After cooling, the solution was neutralised with concentrated ammonia. It was then thoroughly washed with distilled water into a 250 ml beaker, 2.5 g analar barium nitrate added, followed by 10 ml of analar acetone and 3-5 drops of boiled out 6M nitric acid, before titrating with 0.1M silver nitrate. The solution was stirred throughout the titration by the use of a magnetic stirrer. A silver wire was used as an indicator electrode and a saturated calomel electrode as the reference electrode, with a salt bridge containing 3M ammonium nitrate solution.

The 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 6M nitric acid resulted in the oxidation of halide to halogens, giving low results.

The electrode potential (mV) of the initial halide solution was determined, and corresponding measurements taken at 0.1 ml intervals of silver nitrate until the end-point was being approached.

This was detected by a more rapid increase in the change in potential and, when this was observed, the addition of silver nitrate solution was reduced to 0.02 ml between each reading. A graph of mV readings against ml of silver nitrate added was plotted, the points of inflection being regarded as the end-points of the titration.

Before each titration the silver wire indicator electrode was cleaned by immersion in 50% nitric acid for one minute, washed with distilled water, then immersed in concentrated ammonia for two minutes before a final thorough washing with distilled water. For some of the compounds reported in this thesis, the analytical results obtained were not as good as expected. This was attributed partly to the inherent instability of the compounds at room temperature and partly to the experimental difficulties involved in handling them.

(h) Electrolysis

The electrolysis cell was of the H-type as shown in figure 43 the electrodes consisting of smooth platinum foil. The apparatus was thoroughly washed with acetone and then baked in an oven for a few hours. The cell was transferred to the dry-box, rinsed with the solution to be electrolysed and after it was filled, the solution was electrolysed for 15-20 minutes by the passage of direct current (12V).

(i) Column Chromatography

The compound was dissolved in benzene and applied to an alumina or silica column prepared with petroleum-ether (40-60°C).

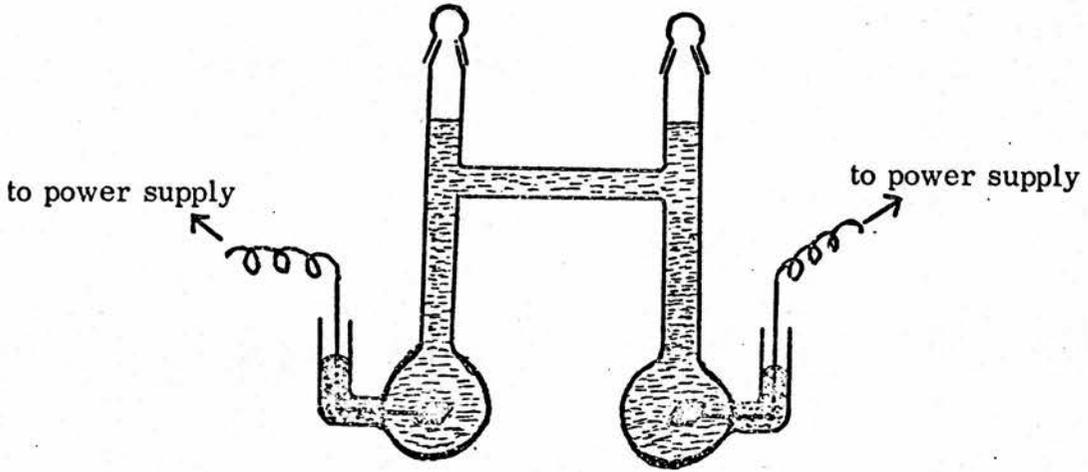


Figure 43 Electrolysis Cell

It was eluted in turn with the following solvents:

Petroleum-ether (40-60°C)

2% benzene-petroleum ether

5% benzene-petroleum ether

10% benzene-petroleum ether

20% benzene-petroleum ether

Benzene

Chloroform

II Solvents and Purification of Materials

(a) Solvents

(i) Methyl cyanide

Pure anhydrous methyl cyanide suitable for conductance studies was prepared by a modification of the method described by Smith and Witten¹⁸⁸. The commercial material (Hopkin and Williams) was allowed to stand for one week over potassium hydroxide pellets, with occasional 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 with vigorous stirring to remove ammonia and water. It was filtered again and distilled on to phosphorus pentoxide; the distillate was refluxed and distilled on to fresh phosphorus pentoxide. This procedure was repeated until the phosphorus pentoxide did not cake and turn yellow, but formed a fine suspension in the liquid. The resultant pure, dry methyl cyanide was stored in a tightly stoppered round bottom flask; in a large desiccator over silica gel. Finally, before use it was refluxed and distilled, using a nine inch column of glass helices (which had been oven dried) into individual flasks containing a little fresh phosphorus pentoxide. From these individual flasks, the dry solvent was distilled on the vacuum line as required, to remove any traces of phosphorus pentoxide. The specific conductance of methyl cyanide purified by this method was always ca. $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . The boiling range was $81-82^{\circ}\text{C}$.

(ii) Nitrobenzene

Analar grade nitrobenzene was distilled twice, once at

atmospheric pressure, when the fraction boiling at 207-208°C was collected and the other at reduced pressure (65-68°C, ca 2 mm). The specific conductance of this nitrobenzene was less than $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C.

(iii) Carbon tetrachloride

The method used to obtain pure carbon tetrachloride was a variation of that described by Popov and Schmor¹⁸⁹. The crude solvent (500 ml) was refluxed for ten hours with a saturated solution of potassium permanganate in 2M sodium hydroxide solution (100 ml). The carbon tetrachloride was then separated and washed several times with water. After a preliminary drying with anhydrous magnesium sulphate, the carbon tetrachloride was filtered and distilled on to phosphorus pentoxide, and then distilled several times on to fresh phosphorus pentoxide. The fraction boiling between 75.5-76.0°C, at atmospheric pressure was collected. Finally, before use, the dry solvent was distilled on the vacuum line, to remove any traces of phosphorus pentoxide.

(iv) Chloroform^{190a}

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, 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 vacuum line to remove traces of phosphorus pentoxide. Boiling range 61-62°C.

(v) Diethyl ether^{190b}

Diethyl ether was preliminary dried over anhydrous calcium chloride and filtered before sodium wire was added. The ether was allowed to stand over the sodium wire for several days. It was then refluxed for an hour, distilled and fresh sodium wire added. The ether was distilled before use. Boiling range 34-35°C.

(vi) Petroleum-ether (40-60°C)^{190c}

The commercial grade solvent was well-shaken twice with concentrated sulphuric acid (10% of the volume). After removing the sulphuric acid vigorous shaking was continued with successive portions of a concentrated solution of potassium permanganate in 10% sulphuric acid until the colour of permanganate remained unchanged. The petroleum ether layer was separated and washed thoroughly with a large volume of water before drying over anhydrous calcium chloride. After twenty-four hours it was filtered and twice distilled over sodium wire, the fraction boiling between 40-60°C being collected. This petroleum ether was stored in a tightly stoppered flask in a desiccator containing phosphorus pentoxide. Immediately before use it was redistilled.

(vii) Methylene chloride^{190d}

Commercial grade methylene chloride was shaken with portions of concentrated sulphuric acid, until the acid layer remained colourless, then washed successively with water, aqueous (5%) sodium carbonate and finally with water. It was then dried over anhydrous calcium chloride for twenty-four hours, filtered

on to phosphorus pentoxide and distilled on to fresh phosphorus pentoxide. This process was repeated 2-3 times. It was stored away from light in a brown bottle with Linde type 4A molecular sieve. Before use, the methylene chloride was distilled on the vacuum line to remove traces of drying agents. Boiling range 40-41°C.

(b) Reagents

(i) Bromine

Analar bromine was first kept over anhydrous calcium bromide for 2-3 days. It was filtered into a small flask under a nitrogen hood, attached to the vacuum system, cooled and pumped off to remove the more volatile impurities. The bromine was then distilled in vacuo into small previously weighed ampoules, cooled to liquid nitrogen temperature. The ampoules were sealed off and reweighed. Thus, known weights of bromine could be stored in sealed ampoules. Standard solutions of bromine were made by breaking a given ampoule under a known weight of solvent.

(ii) Iodine

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

(iii) Iodine monobromide

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

(iv) Iodine monochloride

Commercial iodine monochloride was purified by distillation on vacuum line.

(v) Chlorine

Chlorine, obtained from a cylinder, was dried by passage through two-three traps containing anhydrous calcium chloride. It was diluted with dry nitrogen for synthetic use.

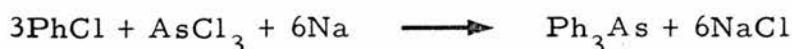
(vi) General

Reagents used in the preparation of tris(2-methylphenyl)arsine, tris(3-methylphenyl)arsine and tris(4-methylphenyl)arsine were of analytical grade and were distilled before use: arsenic trichloride; 1-bromo, 2-methylbenzene; 1-bromo, 3-methylbenzene and 1-bromo, 4-methylbenzene.

(c) Starting Materials

Triphenylarsine, tris(2-methylphenyl)arsine, tris(3-methylphenyl)arsine and tris(4-methylphenyl)arsine were the starting materials in this work and were prepared as follows:

(i) Triphenylarsine was prepared by a standard Wurtz-type reaction between chlorobenzene and arsenic trichloride¹⁹¹;



The arsine was recrystallised from 95% ethanol: m.p. 61°C.

(ii) Tris(2-methylphenyl)arsine¹⁹² was prepared by reacting the Grignard reagent of 1-bromo, 2-methylbenzene with arsenic trichloride in diethyl ether; the reaction finally completed by heating.

The crude product contained tris(2-methylphenyl)arsine and some by-products. It was purified by column chromatography using petroleum-ether as solvent. Colourless needles of tris(2-methylphenyl)arsine were obtained on concentration of the eluant.

m.p. 98°C . (Found: C, 72.47; H, 5.94. Calculated for

$\text{C}_{21}\text{H}_{21}\text{As}$: C, 72.44; H, 6.03%)

(iii) Tris(3-methylphenyl)arsine^{128b} was prepared by reacting the Grignard reagent of 1-bromo, 3-methylbenzene with arsenic trichloride in diethyl ether and the reaction finally completed by heating. The product was purified by column chromatography as in the above preparation. Colourless needles of tris(3-methylphenyl)arsine were obtained. m.p. 95°C . (Found: C, 72.48; H, 6.04.

Calculated for $\text{C}_{21}\text{H}_{21}\text{As}$: C, 72.44; H, 6.03%)

(iv) Tris(4-methylphenyl)arsine¹⁹³ was prepared by a standard Wurtz-type reaction, between 1-bromo, 4-methylbenzene and arsenic trichloride in diethyl ether. The product was purified by column chromatography as mentioned in the purification of tris(2-methylphenyl)arsine. m.p. 146°C . (Found: C, 72.42; H, 5.96. Calculated for $\text{C}_{21}\text{H}_{21}\text{As}$: C, 72.44; H, 6.03%)

III Preparation of Halogen Adducts

General Remarks

Many of the compounds made during the course of this work were prepared in several different ways. The method described below is the one which was found to give the purest product. Crystallisation of solids in general was effected by adding ether or petroleum ether to a solution of the compound in a polar solvent, usually methyl cyanide (but occasionally chloroform, carbon tetrachloride or acetone was used). Yields were usually almost quantitative if care was taken to extract successive crops of crystals from the filtrates, but normally the initial crop only (generally ca. 70%) was taken, particularly in the case of hydrolytically unstable compounds in order to avoid repeated handling.

Melting point determinations were carried out in sealed tubes which had been stored in the dry-box. These include the preparation of solutions, mixing of reactants, filtering and drying. The trays which contained the phosphorus pentoxide were regularly replaced. When a prepared compound was to be removed from the dry-box, so that it could be pumped on the vacuum line, it was taken in a small tube with B-24 cone, attached to a B-24 tap-cap adapter which would be attached directly to the vacuum line. The apparatus was of suitable size to facilitate entry into the dry-box (figure 44) .

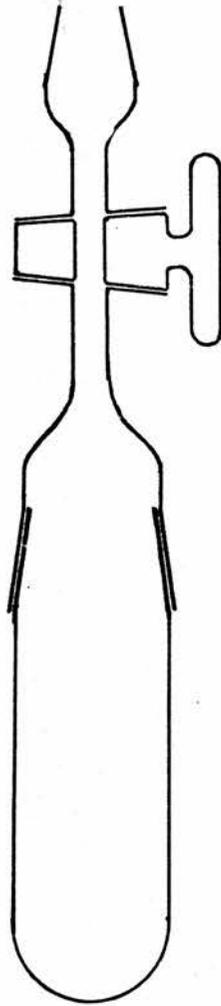
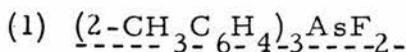


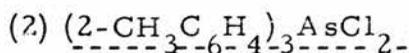
Figure 44. A small tube with B-24 cone, attached to a B-24 adapter

PART I

PART I(a) Halogen Adducts of Tris(2-methylphenyl)arsine

Tris(2-methylphenyl)arsine oxide hydrate (1.00 g, 2.615 mmol) and water (50 ml) were heated together to boiling and stirred vigorously. Hydrofluoric acid (30 ml of 40% acid) was then added slowly. A white precipitate formed and the warm mixture was stirred for a further 30 minutes. The product difluorotris(2-methylphenyl)arsorane was isolated by filtration, washed with water and dried (yield, 0.86 g, 85%). Recrystallised from acetone/ether. m.p. 178-180°C. (Analysis, Found: C, 65.60; H, 5.85%. $\text{C}_{21}\text{H}_{21}\text{AsF}_2$ requires: C, 65.28; H, 5.49%)

ir spectrum: 1590m, 1582w, 1580-1555 vwb, 1300 vw, 1290m, 1280m, 1220-1190wb, 1160w, 1128w, 1120-910vsb, 900-850mb, 795-712sb, 710w, 702m cm^{-1}



Tris(2-methylphenyl)arsine (1.742 g, 5 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 solvent was now reduced to \approx 5 ml on the vacuum line before adding ether to produce white crystals of dichlorotris(2-methylphenyl)arsorane. The product was filtered, washed with ether and dried in vacuo. m.p. 200-206°C. (Analysis: Found: C, 59.62; H, 4.85; Cl, 16.70%. $\text{C}_{21}\text{H}_{21}\text{AsCl}_2$ requires: C, 60.15; H, 5.05; Cl, 16.91%)

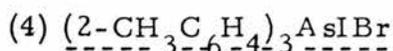
ir spectrum: 2160-1900mb, 1825vw, 1599ms, 1568w, 1282vs,
 1208s, 1200s, 1165m, 1125s, 1060w, 1030s, 1000-970wb,
 945w, 870m, 862m, 798s, 780m, 770ms, 760vs, 748vs, 695s,
 530m, 485m, 435vs, 432vs, 415s, 395m cm^{-1}

(3) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$

Bromine (0.3196 g, 1.999 mmol) in carbon tetrachloride (25 ml) was added dropwise with shaking to a solution of tris(2-methylphenyl)arsine (0.6966 g, 1.999 mmol) in carbon tetrachloride (20 ml). Pale yellow crystals precipitated out during the addition of bromine solution, the reaction mixture was shaken for half an hour, filtered, washed with 40/60 petroleum ether and dried on the vacuum line, m.p. 92°C . (Analysis: Found: C, 39.58, H, 3.30, Br, 23.51% $\text{C}_{21}\text{H}_{21}\text{AsBr}_2 \cdot \text{CCl}_4$ requires: C, 39.91; H, 3.20; Br, 24.15%) (The material was triturated with petroleum ether, filtered, dried and analysed for C, H; the results were consistent with the first analysis. The preparation was repeated using the same solvent and it also showed solvated molecule of CCl_4 . The presence of CCl_4 molecule was confirmed by (i) ir spectrum showed C-Cl absorption (ii) when treated with aqueous 2M NaOH solution, it gave clear smell of CCl_4 .)

uv spectrum showed no Br_3^- ions

ir spectrum: 1975vw, 1890vw, 1870vw, 1840vw, 1790-1610wb,
 1600ms, 1570m, 1290vs, 1210vs, 1172ms, 1165ms, 1140ms,
 1132ms, 1060vw, 1042m, 1000vw, 965w, 888w, 872w, 810-710vsb,
 702ms, 660w, 535m, 480m, 475w, 435vs, 420m cm^{-1}



A solution of iodine bromide (0.6760 g, 3.268 mmol) in methyl cyanide (30 ml) was added, with shaking, to a solution of tris(2-methylphenyl)arsine (1.1386 g, 3.268 mmol) in the same solvent (30 ml). After addition of IBr was complete, dry ether was added but no product was obtained. The dark coloured solution was now concentrated to a volume of approximately 10 ml by removing the solvent on the vacuum line by the method of freeze drying. More ether was now added and fine rust coloured crystals of bromiodotris(2-methylphenyl)arsorane separated out. These were filtered, washed with ether and dried in vacuo.

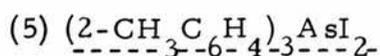
m.p. 162-163°C (Analysis: Found: C, 44.90; H, 3.76; Br, 13.73; I, 22.24% $\text{C}_{21}\text{H}_{21}\text{AsIBr}$ requires: C, 45.42; H, 3.82; Br, 14.40; I, 22.87%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 271$ and $351 \text{ m}\mu$;

Lit. $\lambda_{\text{max}} =$ at $280 \text{ m}\mu^{125}$ and $275 \text{ m}\mu^{123}$ for I_2Br^- ion).

Observed $\lambda_{\text{max}} = 271 \text{ m}\mu$ showed complex ionisation.

ir spectrum: 1990vw, 1950vw, 1870vw, 1840vw, 1700vw, 1630vw, 1590m, 1565w, 1285m, 1280s, 1205s, 1168m, 1130m, 1050 w, 1030mw, 982w, 948vw, 865m, 791s, 750vs, 696s, 528m, 480ms, 430vs, 400 m cm^{-1}



Iodine (0.5076 g, 1.999 mmol) dissolved in petroleum ether (150 ml) was added dropwise, with shaking to a solution of tris(2-methylphenyl)arsine (0.6966 g, 1.999 mmol) in 40 ml of the same solvent. After addition of several ml of halogen solution brown-

black crystals began to form on the wall of the flask. These were subsequently shown to be $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$. On addition of a little more of the halogen solution no more dark product appeared and so the mother liquor was decanted into another flask and the addition of halogen solution continued. When approximately 60% of the halogen solution had been added a dark brown crystalline solid began to separate out. After addition was complete the flask and the contents were shaken for 15-20 minutes before filtering, washing with petroleum ether and drying on the vacuum line.

This product was found to be the expected diiodotris(2-methylphenyl)arsorane. m.p. 163-164°C (Analysis: Found: C, 41.73; H, 3.53; I, 41.17% $\text{C}_{21}\text{H}_{21}\text{AsI}_2$ requires: C, 41.88; H, 3.52; I, 42.15%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $360 \text{ m}\mu$)

ir spectrum: 1810vw, 1585w, 1560w, 1280ms, 1205s, 1165m, 1125ms, 1052vw, 1032m, 990w, 952vw, 870w, 794m, 750vs sh, 705w, 630vw, 530m, 490ms sh, 435vs, 405 cm^{-1}

(6) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$

Bromine (0.5025 g, 3.144 mmol) dissolved in methyl cyanide (25 ml) was added dropwise to a solution of tris(2-methylphenyl)arsine (0.5476 g, 1.572 mmol) in the same solvent (30 ml), with stirring. After complete addition of bromine solution, the volume of the solvent was reduced on the vacuum line before adding ether to produce bright yellow crystals of bromotris(2-methylphenyl)arsonium tribromide. These were filtered, washed with ether and dried on vacuum line. m.p. 154°C (Analysis: Found: C, 37.64;

H, 3.19; Br, 47.06% $C_{21}H_{21}AsBr_4$ requires: C, 37.76; H, 3.17; Br, 47.85%)

uv spectrum showed Br_3^- ion (peak at $\lambda_{269} m\mu$)

ir spectrum: 2710vw, 1985vw, 1975vw, 1950vw, 1835vw, 1808vw, 1685vw, 1640vw, 1630vw, 1610vw, 1590ms, 1565m, 1285s, 1208s, 1170m, 1165m, 1150vw, 1140w, 1132s, 1055w, 1030ms, 1000w, 962w, 880w, 872vw, 870vw, 800ms, 762vs, 748vs, 720w, 700w, 692w, 660vw, 630vw, 535w, 498w, 485w, 440ssh, 420ms, $325s\text{ cm}^{-1}$

(7) $(2-CH_3C_6H_4)_3AsBr_3I$

A 1:1 mixture of iodine bromide and bromine (IBr 0.3054 g, 1.476 mmol + Br_2 0.2360 g, 1.476 mmol) in methyl cyanide (60 ml) was added dropwise to a solution of tris(2-methylphenyl)arsine (0.5144 g, 1.476 mmol) in the same solvent (35 ml) with continuous stirring. After complete addition of the mixed halogen solution the reaction mixture was shaken for fifteen minutes. The bulk of the solvent was removed on the vacuum line before adding ether to produce orange coloured crystals of $(2-CH_3C_6H_4)_3AsBr_3I$. These were filtered, washed with ether and dried on the vacuum line. m.p. $171^\circ C$. (Analysis: Found: C, 35.33; H, 2.80; Br, 33.36, I, 17.70% $C_{21}H_{21}AsBr_3I$ requires: C, 35.28; H, 2.96; Br, 33.55; I, 17.75%)

uv spectrum showed IBr_2^- ions (peaks at $\lambda_{max} = 257$ and $370 m\mu$)

ir spectrum: 1985vw, 1960vw, 1845vw, 1832vw, 1815vw, 1722vw, 1695vw, 1645vw, 1635vw, 1612vw, 1590ms, 1565m, 1530vw, 1280ssh, 1200s, 1166m, 1160m, 1145w, 1128s, 1050w, 1025ms,

990m, 955m, 872m, 865w, 860w, 792s, 755vs, 740vs, 690m,
685w, 525m, 485m, 472w, 430vssh, 420s, 415ms, 390w, 315vs cm^{-1}

(8) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$

A 1:1 mixture of iodine and bromine (I_2 0.4911 g, 1.9349 mmol + Br_2 , 0.3092 g, 1.9348 mmol) in methyl cyanide (50 ml) was added dropwise to a solution of tris(2-methylphenyl)arsine (0.6740 g, 1.9349 mmol) also in methyl cyanide (25 ml) with continuous stirring. The volume of the solvent was then reduced on the vacuum line before adding ether, at which stage rust coloured crystals of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$ separated out. These were filtered, washed with ether and dried on the vacuum line.
m.p. 149-150°C. (Analysis: Found: C, 33.22; H, 2.70; Br, 20.34; I, 34.66% $\text{C}_{21}\text{H}_{21}\text{AsBr}_2\text{I}_2$ requires: C, 33.10; H, 2.78; Br, 20.97; I, 33.22%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 265$ and $351 \text{ m}\mu$
Lit. I_2Br^- peaks at $\lambda_{\text{max}} = 280, 351 \text{ m}\mu^{125}$ and at $\lambda_{\text{max}} = 275, 351 \text{ m}\mu^{123}$). From the observation it appears to be complex ionisation.

ir spectrum: 1980vw, 1970vw, 1950vw, 1825vw, 1810vw, 1635w,
1610w, 1590ms, 1565m, 1282s, 1205s, 1170ms, 1165m, 1150w,
1140w, 1132s, 1055w, 1032ms, 998m, 962w, 880w, 872w, 800ms,
762vs, 748vs, 700m, 692m, 535m, 495m, 485m, 440vs, 430s,
420ms, 325s cm^{-1}

(9) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$

A 1:1 mixture of iodine bromide and iodine (IBr , 0.8598 g, 4.157 mmol + I_2 , 1.0552 g, 4.157 mmol) in methyl cyanide (80 ml)

was added as before to tris(2-methylphenyl)arsine (1.448 g, 4.157 mmol) dissolved in carbon tetrachloride (35 ml). After complete addition of the mixed halogen solution, the reaction mixture was shaken for half an hour. The volume of solvent was reduced on vacuum line, more carbon tetrachloride added when chocolate brown crystals of $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ started to separate. These were filtered, washed with ether and dried on vacuum line. m.p. 132°C (Analysis: Found: C, 31.48; H, 2.58; Br, 9.37; I, 48.72% $\text{C}_{21}\text{H}_{21}\text{AsBrI}_3$ requires: C, 31.18; H, 2.62; Br, 9.87; I, 47.07%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 285$ and $355 \text{ m } \mu$
 Lit. value $\lambda_{\text{max}} = 291$ and $360 \text{ m } \mu$ ¹²⁵)

ir spectrum: 1990vw, 1960vw, 1700vw, 1640vw, 1620vw, 1592m, 1570w, 1282s, 1205s, 1170m, 1165m, 1145vw, 1135w, 1130ms, 1055w, 1040ms, 990w, 955vw, 872w, 865w, 795s, 755vw, 740vs, 692m, 690m, 530m, 489m, 476m, 430vs, 422s, 409ms, 315ms cm^{-1}

(10) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$

Iodine (0.7303 g, 2.877 mmol) dissolved in methyl cyanide (50 ml) was added dropwise with shaking to a suspension of tris(2-methylphenyl)arsine (0.50 g, 1.435 mmol) in the same solvent (20 ml). The arsine reacted with the iodine and after complete addition of halogen, a dark violet coloured solution resulted. The total volume was reduced in the usual manner and brown-black crystals of iodotris(2-methylphenyl)arsonium triiodide were isolated on the addition of ether. These were filtered, washed

with ether and dried on vacuum line. m.p. 114°C (Analysis:

Found: C, 28.50; H, 2.33; I, 60.43% $C_{21}H_{21}AsI_4$ requires:

C, 29.46; H, 2.45; I, 59.30%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{max} = 291$ and 360 m μ)

ir spectrum: 1970vw, 1930vw, 1810w, 1695vw, 1615vw, 1578m,

1555w, 1270s, 1198s, 1160s, 1120ms, 1048w, 1025m, 982m,

945m, 862m, 790ms, 748vs, 698w, 688w, 525m, 478m, 430s,

400w cm^{-1}

(b) Halogen Adducts of Tris(3-methylphenyl)arsine

(1) $(3-CH_3C_6H_4)_3AsCl_2$

Dichlorotris(3-methylphenyl)arsorane was prepared in exactly the same manner as dichlorotris(2-methylphenyl)arsorane, white crystals of $(3-CH_3C_6H_4)_3AsCl_2$ melt at 173-175°C (Analysis: Found: C, 59.84; H, 5.47; Cl, 17.33% $C_{21}H_{21}AsCl_2$ requires: C, 60.15; H, 5.05; Cl, 16.91%)

ir spectrum: 1970w, 1895vw, 1790vw, 1740vw, 1730vw, 1692w,

1600s, 1575m, 1310ms, 1270w, 1170ms, 1116w, 1099s, 1040m,

990s, 980m, 975m, 920vw, 900m, 875w, 865m, 860w, 835vw,

770vs, 712w, 670vs, 620vw, 560vw, 500ms, 430w, 420s,

410ms, 380s, 355vw, 330ms, 312 m cm^{-1}

(2) $(3-CH_3C_6H_4)_3AsBr_2$

Bromine (0.3444 g, 2.155 mmol) dissolved in carbon tetrachloride (20 ml) was added dropwise with shaking to a solution of tris(3-methylphenyl)arsine (0.7507 g, 2.155 mmol) in the same solvent (20 ml). After complete addition of the halogen, the resultant solution was shaken for half an hour. Excess of solvent

was removed on vacuum line when white crystals of dibromotris-(3-methylphenyl)arsorane separated out. These were filtered, washed with ether and dried on vacuum line. m.p. 185-186°C.

(Analysis: 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%)

uv spectrum showed no Br_3^- ions

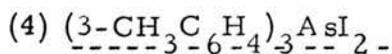
ir spectrum: 1960vw, 1940vw, 1890vw, 1870vw, 1810vw, 1770vw, 1725w, 1670vw, 1588s, 1562w, 1305s, 1268w, 1190vw, 1168m, 1112ms, 1090s, 1035m, 990vw, 969m, 900m, 868m, 862m, 830w, 778vs, 762vs, 754w, 670vs, 625vw, 500s, 430ms, 412vs, 380s, 320ms cm^{-1}

(3) $(\text{---}3\text{---}6\text{---}4\text{---}3\text{---})_3\text{AsIBr}$

A solution of iodine bromide (0.6702 g, 3.240 mmol) in methyl cyanide (40 ml) was added with shaking to a suspension of tris(3-methylphenyl)arsine (1.1286g, 3.240 mmol) in the same solvent (20 ml). The total volume of the resultant clear solution was reduced in the usual manner. Bright yellow crystals of bromoiodotris(3-methylphenyl)arsorane were isolated on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 136°C. (Analysis: Found: C, 45.15; H, 3.70; Br, 14.30; I, 22.80% $C_{21}H_{21}AsIBr$ requires: C, 45.42; H, 3.82; Br, 14.40; I, 22.87%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{\max} = 279$ and 355 m μ)

ir spectrum: 1580m, 1560w, 1305m, 1210w, 1165m, 1112mw, 1090s, 1068mw, 1040mw, 1032m, 990s, 968vw, 908w, 900mw, 875m, 862w, 782vs, 772vs, 675vw, 510mw, 498ms, 490ms, 428ms, 420ms, 412s, 380w, 365mw, 300w, 282m cm^{-1}



Iodine (0.5076 g, 1.999 mmol) dissolved in ether (30 ml) was added dropwise with shaking to a suspension of tris(3-methylphenyl)arsine (0.6966 g, 1.999 mmol) in petroleum ether (20 ml). The arsine reacted with iodine and light brown crystals of diiodo-tris(3-methylphenyl)arsorane began to separate during the addition of halogen. After addition of halogen was complete the flask and the contents were shaken for half an hour before filtering, washing with ether and drying on vacuum line. m.p. 185-186°C.

(Analysis: Found: C, 41.61; H, 3.49; I, 41.86% $\text{C}_{21}\text{H}_{21}\text{AsI}_2$ requires: C, 41.88; H, 3.52; I, 42.15%)

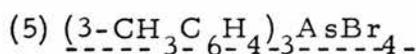
uv spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 292$ and $358 \text{ m}\mu$)

ir spectrum: 1580m, 1560wb, 1305m, 1265w, 1210w, 1170ms,

1168ms, 1115m, 1095s, 1060mw, 1035m, 990s, 970vw, 905m,

875m, 865vw, 780vw, 772vs, 770vs, 680vs, 510w, 500m, 492m,

430ms, 412ms, 375-350wb cm^{-1}



Bromine (0.933 g, 5.838 mmol) dissolved in methyl cyanide (15 ml) was added dropwise to a suspension of tris(3-methylphenyl)arsine (1.017 g, 2.915 mmol) in the same solvent (10 ml) with continuous stirring. A clear orange solution remained, which did not produce a solid adduct even after reducing the volume to ≈ 5 ml and adding ether. The volume was again reduced to the minimum quantity and on triturating with petroleum ether bright yellow crystals of bromotris(3-methylphenyl)arsonium tribromide

were obtained. These were filtered, washed with ether and dried on vacuum line. m.p. 65°C . (Analysis: Found: C, 37.57; H, 3.15; Br, 47.51% $\text{C}_{21}\text{H}_{21}\text{AsBr}_4$ requires: C, 37.76; H, 3.17; Br, 47.85%)

uv spectrum showed Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$)

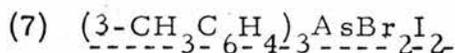
ir spectrum: 1970vw, 1900vw, 1740vw, 1590m, 1565w, 1310ms, 1210w, 1165ms, 1110m, 1090ms, 1068m, 1030m, 980s, 915w, 870m, 840m, 765vs, 760s, 665vs, 480mw, 420ms, 400ms, 380-340wb cm^{-1}

(6) $\text{---3---6---4---3---3---}$ $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$

A 1:1 mixture of iodine bromide and bromine (IBr 0.265 g, 1.281 mmol + Br_2 0.2048 g, 1.281 mmol) in methyl cyanide was added dropwise with shaking to a suspension of tris(3-methylphenyl)-arsine (0.4462 g, 1.281 mmol) in the same solvent (15 ml). The total volume of the resultant clear solution was reduced in the usual manner and rust coloured crystals of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_3\text{I}$ were separated on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. $99\text{-}100^{\circ}\text{C}$. (Analysis: Found: C, 35.22; H, 2.84; Br, 33.86; I, 17.93% $\text{C}_{21}\text{H}_{21}\text{AsBr}_3\text{I}$ requires: C, 35.28; H, 2.96; Br, 33.55; I, 17.75%)

uv spectrum showed IBr_2^- ions (peaks at $\lambda_{\text{max}} = 256$ and $370 \text{ m}\mu$)

ir spectrum: 1970vw, 1910vw, 1875vw, 1812vw, 1720vw, 1710vw, 1675vw, 1590vw, 1565vw, 1312m, 1278vw, 1220w, 1175w, 1170m, 1122vw, 1115w, 1099s, 1082ms, 1040m, 1012w, 990s, 972vw, 925w, 920w, 905vw, 890w, 875ms, 860m, 840vw, 735vs, 730vs, 720vw, 700vs, 682vs, 672vs, 509ms, 499mw, 490w, 430ms, 420vs, 388ms, 380ms, 370ms, 322s, 290w cm^{-1}



A 1:1 mixture of iodine and bromine (I_2 0.6720 g, 2.647 mmol + Br_2 0.4231 g, 2.647 mmol) in methyl cyanide (30 ml) was added dropwise to a suspension of tris(3-methylphenyl)arsine (0.922 g, 2.647 mmol) in the same solvent (30 ml) with continuous stirring. On complete addition of the mixed halogen solution, the flask and the contents were shaken for 15 minutes. The bulk of the resultant clear solution was reduced on vacuum line before adding ether to obtain red brown crystals of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$. These were filtered, washed with ether and dried on vacuo. m.p. 102°C .

(Analysis: Found: C, 32.86; H, 2.71; Br, 20.54; I, 33.24%

$\text{C}_{21}\text{H}_{21}\text{AsBr}_2\text{I}_2$ requires: C, 33.10; H, 2.78; Br, 20.97, I, 33.30%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 276$ and $351 \text{ m}\mu$)

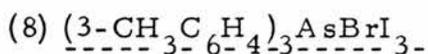
ir spectrum: 1670vw; 1590m, 1570vw, 1312m, 1220w, 1175mw,

1170m, 1118w, 1100s, 1080m, 1040m, 1000m, 999s, 925vw,

920w, 910vw, 880m, 860mw, 840vw, 782vs, 780vs, 770vs,

720vw, 685s, 675vs, 510m, 500m, 490vw, 435ms, 420vs,

380m, 370m, 325ms, 290 w cm^{-1}



Iodine (0.6045 g, 2.382 mmol) dissolved in carbon tetrachloride (145 ml) was added to a suspension of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$ (1.3226 g, 2.382 mmol) in the same solvent (35 ml) with continuous stirring. After complete addition of the halogen solution, the flask and the contents were shaken for half an hour. On keeping the reaction mixture for 24 hours, brown crystals of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ were separated. These were filtered, washed with CCl_4 and dried

on vacuum line. m.p. 103-104°C. (Analysis: Found: C, 31.08; H, 2.58; Br, 8.25; I, 45.40% $C_{21}H_{21}AsBrI_3$ requires: C, 31.18; H, 2.62; Br, 9.87; I, 47.07%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{max} = 287$ and $355 \text{ m}\mu$
Lit. 291 and $360 \text{ m}\mu^{125}$)

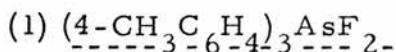
ir spectrum: 1950vw, 1760vw, 1582ms, 1560vw, 1555vw, 1300m,
1270vw, 1210w, 1168m, 1160ms, 1110m, 1090s, 1072m, 1032m,
1005vw, 995ms, 982s, 910mw, 900vw, 880m, 876m, 852mw,
770vs, 762vs, 710w, 670vs, 500m, 490m, 482w, 428ms, 415vs,
372m, 365mw, 315ms cm^{-1}

(9) $(3-\text{CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$

Iodine (0.6345 g, 2.499 mmol) dissolved in methyl cyanide (30 ml) was added dropwise to a suspension of tris(3-methylphenyl)-arsine (0.4352 g, 1.249 mmol) in the same solvent (15 ml) with continuous stirring. The flask and the contents were shaken for half an hour before removing the excess of solvent on vacuum line, shining dark violet crystals of iodotriphenylarsonium triiodide were separated on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 101-102°C. (Analysis: Found: C, 29.55; H, 2.49; I, 59.30% $C_{21}H_{21}AsI_4$ requires: C, 29.45; H, 2.45; I, 59.32%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{max} = 291$ and $360 \text{ m}\mu$)

ir spectrum: 1955vw, 1890vw, 1875vw, 1760vw, 1588m, 1562w,
1315w, 1310m, 1270vw, 1212vw, 1170m, 1165m, 1112w, 1092ms,
1078w, 1035w, 1000m, 990ms, 980vw, 970vw, 912w, 902vw,
880vw, 872ms, 860w, 775vs, 770vs, 715vw, 680s, 672vssh,
508m, 499m, 488vw, 432m, 420vs, 378m, 320m cm^{-1}

(c) Halogen Adducts of Tris(4-methylphenyl)arsine

Tris(4-methylphenyl)arsine oxide hydrate (0.95 g, 2.484 mmol) and water (50 ml) were heated together to boiling and stirred vigorously. Hydrofluoric acid (30 ml of 40% acid) was then added slowly. A white precipitate formed and the warm mixture was stirred for a further 30 minutes. The product was isolated by filtration, washed with water and dried (yield, 0.84 g, 87%).

Recrystallised from acetone-ether m.p. 95-96°C (Analysis: Found:

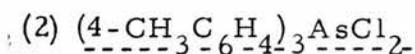
C, 65.57; H, 5.90% $\text{C}_{21}\text{H}_{21}\text{AsF}_2$ requires: C, 65.28; H, 5.49%)

ir spectrum: 1600ms, 1500s, 1312m, 1215w, 1190s, 1090m, 1080ms,

1035wb, 1020ms, 970-960vwb, 820m, 800vssh, 720-710wb,

695m, 630w, 590s, 520-488vsb, 488-432vsb, 430w, 372-360sb,

358-315msb cm^{-1}



Dichlorotris(4-methylphenyl)arsorane was prepared in exactly the same manner as dichlorotris(2-methylphenyl)arsorane.

White crystals of $(\text{4-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ melt at 240-242°C. (Analysis:

Found: C, 59.76; H, 5.40; Cl, 17.04% $\text{C}_{21}\text{H}_{21}\text{AsCl}_2$ requires:

C, 60.15; H, 5.05; Cl, 16.91%)

ir spectrum: 2070vw, 2040vw, 1909m, 1790w, 1625m, 1590ms,

1310s, 1278vw, 1210ms, 1188vs, 1120ms, 1072vs, 1035m,

1010s, 980vw, 956vw, 818w, 795vs, 755vw, 715w, 688m, 618w,

585ms, 480vs, 432m, 365ms, 322ms, 285m cm^{-1}

(3) $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$

Bromine (0.9392 g, 5.877 mmol) dissolved in methyl cyanide (30 ml) was added dropwise to a suspension of tris(4-methylphenyl)arsine (2.0472 g, 5.877 mmol) in the same solvent (20 ml). The arsine reacted with bromine and a clear solution resulted on complete addition of halogen solution. White crystals of dibromotris(4-methylphenyl)arsorane were obtained on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 238-240°C (Analysis: Found: C, 50.47; H, 4.03; Br, 31.06% $\text{C}_{21}\text{H}_{21}\text{AsBr}_2$ requires: C, 49.63; H, 4.17; Br, 31.45%)
 uv spectrum showed no Br_3^- ions
 ir spectrum: 1900m, 1780vw, 1618w, 1590m, 1310s, 1275w, 1210m, 1189vs, 1120ms, 1070vs, 1035mw, 1010s, 950vw, 930vw, 812w, 790vs, 715vw, 688w, 588s, 475vs, 430m cm^{-1}

(4) $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$

A solution of iodine bromide (1.2037 g, 5.820 mmol) in methyl cyanide (60 ml) was added dropwise to a suspension of tris(4-methylphenyl)arsine (2.0274 g, 5.820 mmol) in the same solvent (40 ml) with continuous stirring. The total volume of the resultant clear solution was reduced in the usual manner. Bright yellow crystals of bromiodotris(4-methylphenyl)arsorane were obtained on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 149-151°C (Analysis: Found: C, 44.96; H, 3.93; Br, 14.00; I, 22.24% $\text{C}_{21}\text{H}_{21}\text{AsIBr}$ requires: C, 45.42; H, 3.82; Br, 14.40; I, 22.87%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{max}=275$ and $353\text{ m}\mu$)

ir spectrum: 1592m, 1310s, 1276vw, 1210m, 1190ms, 1182vs,

1115m, 1070s, 1030w, 1010ms, 936w, 832m, 790vs, 745vw,

710w, 615w, 580ms, 465vs, 429ms cm^{-1}

(5) $(\text{4-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$

Iodine (1.269 g, 4.999 mmol) dissolved in methyl cyanide (50 ml) was added dropwise to a solution of tris(4-methylphenyl)arsine (1.7416 g, 4.999 mmol) in the same solvent (50 ml) with continuous stirring. After complete addition of halogen solution, the volume of the solvent was reduced on the vacuum line before adding ether to produce rust coloured crystals of diiodotris(4-methylphenyl)arsorane. These were filtered, washed with ether and dried on vacuum line. m.p. $166-167^\circ\text{C}$ (Analysis: Found: C, 42.04; H, 3.46; I, 41.42% $\text{C}_{21}\text{H}_{21}\text{AsI}_2$ requires: C, 41.88; H, 3.52; I, 42.15%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{max}=291$ and $357\text{ m}\mu$)

ir spectrum: 1595m, 1565vw, 1310s, 1280w, 1212m, 1191s,

1189vs, 1116m, 1075s, 1030s, 1015s, 940w, 835m, 790vs,

712w, 688m, 620w, 580m, 468vs, 430ms, 450wb cm^{-1}

(6) $(\text{4-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$

Bromine (0.7725 g, 4.833 mmol) dissolved in methyl cyanide (35 ml) was added dropwise to a solution of tris(4-methylphenyl)arsine (0.8419 g, 2.416 mmol) in diethyl ether (40 ml) with continuous stirring. After complete addition of bromine solution, the volume of the solvent was reduced on vacuum line before adding

ether to obtain dark orange crystals of bromotris(4-methylphenyl)-
 arsonium tribromide. These were filtered, washed with ether
 and dried on vacuum line. m.p. 120-121°C (Analysis: Found:
 C, 37.77; H, 3.14, Br, 47.43% $C_{21}H_{21}AsBr_4$ requires: C, 37.76;
 H, 3.17; Br, 47.85%)

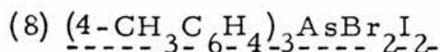
uv spectrum showed Br_3^- ions (peak at $\lambda_{max} = 269 \text{ m}\mu$)

ir spectrum: 1940-1900vwb, 1810vw, 1645vw, 1625vw, 1595ms,
 1570vw, 1312ms, 1290vw, 1215m, 1188s, 1122ms, 1075s,
 1032m, 1012ms, 968m, 945w, 830ms, 922w, 800vs, 798vs,
 788vs, 715w, 690ms, 620m, 592vs, 580m, 465vs, 430ms,
 360ms, 320msb cm^{-1}

(7) $(4-CH_3C_6H_4)_3AsBr_3I$

A 1:1 mixture of iodine bromide and bromine (IBr 1.0464 g,
 5.059 mmol + Br_2 0.8086 g, 5.059 mmol) in methyl cyanide (80 ml)
 was added dropwise to a suspension of tris(4-methylphenyl)arsine
 (1.7625 g, 5.059 mmol) in the same solvent (50 ml) with continuous
 stirring. After complete addition of the mixed halogen solution
 the flask and the contents were shaken for fifteen minutes. Excess
 of the solvent was removed on vacuum line before adding ether to
 obtain rust coloured crystals of $(4-CH_3C_6H_4)_3AsBr_3I$. These
 were filtered, washed with ether and dried on vacuum line. m.p.
 125-126°C (Analysis: Found: C, 34.71; H, 2.93; Br, 30.11; I, 21.11%
 $C_{21}H_{21}AsBr_3I$ requires: C, 35.28; H, 2.96; Br, 33.55; I, 17.75%)
 uv spectrum showed IBr_2^- ions (peaks at $\lambda_{max} = 258$ and $370 \text{ m}\mu$)
 ir spectrum: 1920vw, 1810vw, 1640vw, 1592ms, 1565vw, 1312ms,
 1215m, 1188s, 1122m, 1076vs, 1055vw, 1035w, 1012ms, 968w

962w, 942vw, 832m, 799vs, 790vs, 715w, 688m, 618m, 590vs,
575m, 468vs, 430ms, 358ms, 320ms cm^{-1}



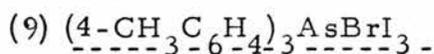
A 1:1 mixture of iodine and bromine (I_2 1.2823 g, 5.052 mmol + Br_2 0.8074 g, 5.052 mmol) in methyl cyanide (80 ml) was added dropwise to a suspension of tris(4-methylphenyl)arsine (1.7599 g, 5.052 mmol) in the same solvent (20 ml) with continuous stirring. On complete addition of the mixed halogen solution, the flask and the contents were shaken for 15 minutes. The bulk of the resultant clear solution was reduced on vacuum line before adding ether to obtain chocolate brown crystals of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$. These were filtered, washed with ether and dried as usual. m.p. 132-133°C. (Analysis: Found: C, 33.10; H, 2.76; Br, 19.12; I, 33.42% $\text{C}_{21}\text{H}_{21}\text{AsBr}_2\text{I}_2$ requires: C, 33.10; H, 2.78; Br, 20.97; I, 33.32%)

uv spectrum showed I_2Br^- ions (peaks at $\lambda_{\text{max}} = 273$ and $351 \text{ m}\mu$)

ir spectrum: 1920vw, 1592ms, 1312ms, 1215m, 1188ms, 1122m,

1075s, 1035w, 1012m, 965w, 940vw, 830m, 795vs, 715w, 685m

618m, 592s, 580m, 468vs, 430ms, 360ms, 320ms cm^{-1}



A 1:1 mixture of iodine bromide and iodine (IBr 0.9413 g, 4.551 mmol + I_2 1.1552 g, 4.551 mmol) in methyl cyanide (115ml) was added dropwise to a solution of tris(4-methylphenyl)arsine (1.5855 g, 4.551 mmol) in the same solvent (50 ml) with continuous stirring. The flask and contents were shaken for half an hour before reducing the bulk of the solvent on vacuum line. Chocolate brown

of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBrI}_3$ were obtained on addition of ether.

These were filtered, washed with ether and dried on vacuum line.

m.p. 144-146°C. (Analysis: Found: C, 31.34; H, 2.60; Br, 7.96; I, 48.77% $\text{C}_{21}\text{H}_{21}\text{AsBrI}_3$ requires: C, 31.18; H, 2.62, Br, 9.87; I, 47.07%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $357\text{m}\mu$)

ir spectrum: 1585ms, 1305ms, 1208m, 1180s, 1115m, 1068vs, 1015w, 1005ms, 955vw, 935vw, 820m, 785vs, 710vw, 680m, 610w, 580ms, 460vs, 422ms, 350ms cm^{-1}

(10) $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$

Iodine (0.846 g, 3.175 mmol) dissolved in methyl cyanide (50 ml) was added dropwise to a solution of tris(4-methylphenyl)-arsine (0.5528 g, 1.587 mmol) in ether (15 ml) with continuous stirring. The flask and contents were shaken for half an hour, before removing the excess of solvent on the vacuum line. Dark brown crystals of iodotrist(4-methylphenyl)arsonium triiodide were isolated on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 152-153°C. (Analysis: Found: C, 29.57; H, 2.40; I, 58.58% $\text{C}_{21}\text{H}_{21}\text{AsI}_4$ requires: C, 29.45; H, 2.45; I, 59.30%)

uv spectrum showed I_3^- ions (peaks at $\lambda_{\text{max}} = 291$ and $356\text{m}\mu$)

ir spectrum: 1920vw, 1810vw, 1630vw, 1592s, 1570vw, 1310s, 1215m, 1188s, 1120m, 1072vs, 1035w, 1010ms, 960w, 940w, 830w, 795vs, 715vw, 685w, 618vw, 588ms, 470vs, 430ms, $355\text{m}, 315\text{m cm}^{-1}$

(d) Halogen Adducts of Triphenylarsine(1) $(C_6H_5)_3AsF_2$

Triphenylarsine oxide hydrate (0.65 g, 1.91 mmol) and water (30 ml) were heated together to boiling and stirred vigorously. Hydrofluoric acid (20 ml of 40% acid) was then added slowly. A white precipitate formed and the warm mixture was stirred for a further 30 minutes. The product was isolated by filtration, washed with water and dried (yield, 0.57 g, 87%).

Recrystallisation from acetone gave white lath-shaped crystals

m.p. 134-136°¹²⁶.

(Analysis: Found: C, 62.7; H, 4.3; F, 11.3% calculated for $C_{18}H_{15}AsF_2$: C, 62.8; H, 4.4; F, 11.1%)

ir spectrum: 3095w, 3060s, 1990-1950vwb, 1930-1890vwb,

1830-1800vwb, 1318ms, 1188ms, 1160m, 1090s, 1082s, 1000m,

995m, 930m, 925m, 855vw, 750vssh, 690vs cm^{-1}

(2) $(C_6H_5)_3AsCl_2$

Triphenylarsine (1.531 g, 4.999 mmol) was dissolved in methyl cyanide (35 ml) and dry chlorine gas diluted in a stream of dry nitrogen was passed, until the solvent assumed a pale yellow colour. Cooling was necessary during the reaction. The volume of the solvent was reduced to \approx 5 ml, on the vacuum line before adding ether to obtain white crystals of dichlorotriphenylarsorane. These were filtered, washed with ether and dried on vacuum line.

m.p. 212°⁹² (Analysis: Found: C, 56.66; H, 5.94; Cl, 18.65%

Calculated for $C_{18}H_{15}AsCl_2$: C, 57.33; H, 4.01; Cl, 18.80%)

(3) $(C_6H_5)_3AsBr_2$

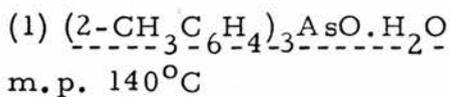
Bromine (0.9780 g, 6.119 mmol) dissolved in methyl cyanide (25 ml) was added dropwise to a solution of triphenylarsine (1.8739 g, 6.119 mmol) in the same solvent (35 ml) with continuous stirring. Excess of the resultant clear solution was removed on vacuum line and white crystals of dibromotriphenylarsorane were obtained on addition of ether. These were filtered, washed with ether and dried on vacuum line. m.p. 228-232°C.⁹² (Analysis: Found: C, 46.12; H, 3.20; Br, 33.92% Calculated for $C_{18}H_{15}AsBr_2$: C, 46.38; H, 3.24; Br, 34.27%)

PART II

(a) Fully Hydrolysed Products of R_3AsHal_2 Adducts and Their Oxides

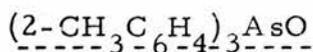
The dibromotris(2-methylphenyl)arsorane and dibromotris(4-methylphenyl)arsorane were hydrolysed completely by 2M sodium hydroxide solution. The partially hydrolysed compounds $(2-CH_3C_6H_4)_3AsOHBBr$ and $(4-CH_3C_6H_4)_3AsOHBBr$ were prepared as described in (b) on p. 154 but instead of being dissolved in aqueous acetone the solid material left when the methyl cyanide/ether solvent was decanted and stirred into 2M sodium hydroxide solution which was then brought to boil. When the solution was cooled white precipitates of $(2-CH_3C_6H_4)_3AsO.H_2O$ and $(4-CH_3C_6H_4)_3AsO.H_2O$ were obtained. These were filtered, washed with water and dried as usual. The anhydrous oxides of tris(2-methylphenyl)arsine and tris(4-methylphenyl)arsine were obtained by heating the hydrated oxide for several hours at $100^\circ C$. Identity was confirmed from the infrared spectrum and C,H analysis. $(3-CH_3C_6H_4)_3AsO$ was prepared by the oxidation of $(3-CH_3C_6H_4)_3As$ with potassium permanganate in acetone¹⁷⁹. Tris(3-methylphenylarsine) was dissolved in acetone, stirred and potassium permanganate, dissolved in the same solvent, added until the pink colour of $KMnO_4$ remained permanent for one hour; excess of permanganate was destroyed by alcohol, the mixture filtered. On complete removal of the solvent a residue is obtained which is extracted in ether. $(3-CH_3C_6H_4)_3AsO$ is obtained as a white crystalline solid by concentrating ether extract m.p. $125-126^\circ C$ identified by its analysis and infrared spectrum. When this anhydrous oxide treated with water gave a sticky product which on keeping with water for two weeks converted into a white crystalline compound identified from

its infrared spectrum

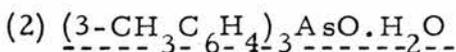


(Analysis: Found: C, 65.20, H, 5.94% $\text{C}_{21}\text{H}_{23}\text{AsO}_2$ requires:
 C, 65.69; H, 6.07%)

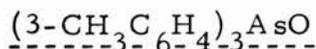
ir spectrum: 3560-3180vsb, 3080-3020wb, 1640-1600msb, 1585ms,
 1560w, 1315m, 1275ms, 1200ms, 1120s, 1050m, 1030vw, 880s,
 868vsm, 795ms, 762vssh, 705m cm^{-1}



ir spectrum: 3080vw, 3060vw, 3022w, 2970vw, 2940vw, 1950-1920wb,
 1750-1720vwb, 1640-1610vwb, 1540mssh, 1562m, 1555mw, 1285ms
 1281s, 1202s, 1165mssh, 1132m, 1124ms, 1058ms, 1032mssh,
 885vs, 870s, 800s, 768vs, 762vs 710m, 655w cm^{-1}



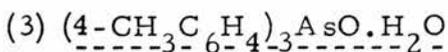
ir spectrum: 3600-3100vsb, 1670-1610msb, 1585ms, 1310-1280mb,
 1170-1150mb, 1095ms, 1070w, 1065-1010mb, 988ms, 880vs, 830m,
 800s, 780s, 690vs, 668mw cm^{-1}



m.p. 125-126°C

(Analysis: Found: C, 69.79; H, 6.34% $\text{C}_{21}\text{H}_{21}\text{AsO}$ requires:
 C, 69.22; H, 5.82%)

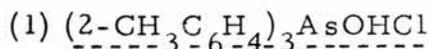
ir spectrum: 1580ms, 1540vw, 1320-1300wb, 1170-1135vwb, 1095s,
 1070vw, 1030m, 985m, 882vs, 830vw, 780s, 715mb, 690s, 665w cm^{-1}



m.p. 94°C

(Analysis: Found, C, 65.15; H, 5.92% Calculated for $\text{C}_{21}\text{H}_{23}\text{AsO}_2$:

was removed on vacuum line and white crystals of R_3AsHal_2 were obtained on addition of ether. When crystallisation appeared to be complete and the solid had settled the supernatant liquid was decanted and the residue (partially hydrolysed R_3AsHal_2 adduct) dissolved in the minimum quantity of boiling acetone. Water (ca. 1 ml) was added to the solution and boiling continued for a few minutes to ensure complete hydrolysis. The solution was then filtered hot and allowed to cool before ether (1 to 2 vol.) was added. White crystals of the hydroxyhalide precipitated immediately or when the filtrate was cooled to $0^\circ C$. They were recrystallised from acetone/ether and dried under vacuum.

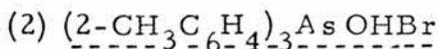


m.p. $218-220^\circ C$

(Analysis: Found: C, 62.65; H, 5.62; Cl, 8.98% Calculated for

$C_{21}H_{22}AsClO$: C, 62.92; H, 5.54; Cl, 8.84%)

ir spectrum: 2760-1670vsb, 1660-1500sb, 1285ms, 1280ms, 1205s, 1165ms, 1130msb, 1060m, 1040m, 990m, 810vw, 840-705vsb resolved into three bands (792vs, 770vs, and 745vs), 702w, 698ms, 658vw, 532ms, 482m, 435vsb, 420vsb cm^{-1}

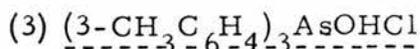


m.p. $217-218^\circ C$

(Analysis: Found: C, 56.83; H, 4.79; Br, 18.12% Calculated for

$C_{21}H_{22}AsBrO$: C, 56.64; H, 4.99; Br, 17.94%)

ir spectrum: 2800-1990vsb, 1590m, 1555wb, 1450-1430msb, 1285m, 1200ms, 1165m, 1128m, 1090wb, 1060mw, 1048mw, 990w, 792s, 770vs, 748vsb, 692ms, 430vs, 408msb cm^{-1}

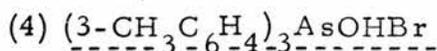


m.p. 200-202°C

(Analysis: Found: C, 62.79; H, 5.53; Cl, 8.74% Calculated for

$C_{21}H_{22}AsClO$: C, 62.92; H, 5.54; Cl, 8.84%)

ir spectrum: 2760-1630vsb, 1600ms, 1560-1500mb, 1340vw, 1325m,
1280vw, 1212m, 1190m, 1165mw, 1125w, 1100ssh, 1038ms,
1010w, 990vs, 922m, 899s, 840s, 780-770vsb, 680vs, 662s, 505vs
420vssh cm^{-1}

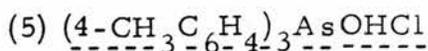


m.p. 185-186°C

(Analysis: Found: C, 56.76; H, 5.01; Br, 17.85% Calculated for

$C_{21}H_{22}AsBrO$: C, 56.64; H, 4.99; Br, 17.94%)

ir spectrum: 2800-2000vsb, 1970wb, 1905w, 1830-1740wb, 1715-1690wb,
1598s, 1565w, 1460-1430msb, 1412ssh, 1332vw, 1320m, 1282vw,
1212m, 1178m, 1170w, 1158ms, 1120w, 1102ms, 1095s, 1090m,
1035mb, 1000w, 982s, 912m, 892m, 882m, 872m, 830ms, 770vsbsh,
710s, 675vs, 660s, 502vs, 430s, 420vs, 360vw, 280msb cm^{-1}

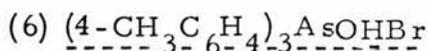


m.p. 179-181°C

(Analysis: Found: C, 62.82; H, 5.64; Cl, 8.97% Calculated for

$C_{21}H_{22}AsClO_4$: C, 62.92; H, 5.54; Cl, 8.84%)

ir spectrum: 2700-1720vsb, 1600-1500vsb (resolved into two peaks at
1593 and 1558 cm^{-1}), 1315s, 1330vw, 1260ms, 1190s, 1122w, 1085vs,
1035ms, 1015s, 985wb, 965w, 958w, 850s, 792vsb, 770vs, 690ms,
618w, 612m, 595s, 460vsb, 422ms, 350mb cm^{-1}



m.p. 207-208°C

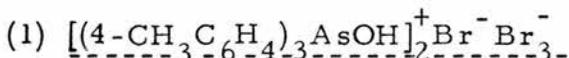
(Analysis: Found: C, 65.94; H, 4.91; Br, 17.97% Calculated for

$C_{21}H_{22}AsBrO$: C, 56.64; H, 4.99; Br, 17.94%)

ir spectrum: 2750-2000vsb, 1600s, 1435msb, 1315ms, 1215wb, 1190s,
1165mb, 1112w, 1085vs, 1035wb, 1015m, 985vwb, 960vw, 899w,
810vssh, 792vs, 755vs, 715ms, 690w, 520w, 590s, 470vsb, 430s,
360wb, 330wb cm^{-1}

(c) Crystalline Compounds Isolated from the Reaction of $R_3AsOHHal$ with Br_2 , IBr and ICl

(R = 2- $CH_3C_6H_4$, 3- $CH_3C_6H_4$, 4- $CH_3C_6H_4$; Hal = Cl, Br)

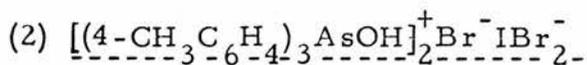


Bromine (0.4162 g, 2.604 mmol) in methyl cyanide (15 ml) was added dropwise to a solution of $(4-CH_3C_6H_4)_3AsOHBr$ (1.1598 g, 2.604 mmol) in methyl cyanide (30 ml), with continuous stirring of the reaction mixture. After complete addition of the bromine solution the flask was shaken for 15 minutes. The volume of the resultant solution was reduced to \approx 5 ml on the vacuum line and on adding ether yellow crystals were obtained. These were filtered, washed with ether, and dried on the vacuum line m.p. 145-146°C. (Analysis: Found: C, 47.97; H, 4.23; Br, 30.24% $C_{42}H_{44}As_2O_2Br_4$ requires: C, 48.02; H, 4.23; Br, 30.43%)

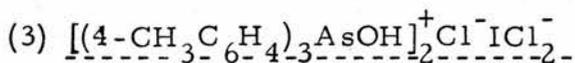
uv spectrum showed Br_3^- ions (peak at $\lambda_{max} = 269 m \mu$)

ir spectrum: 3100-3020wb, 3000-2500vsb, 1600s, 1500ms, 1315msh,
1210wb, 1190m, 1185ms, 1130m, 1120ms, 1082ssh, 1032mb,
1010ms, 975vw, 945wb, 835m, 800vssh, 745vs, 710vw, 690-685wb,

650-630wb, 615vw, 590s, 480vs, 470-465vs, 445s cm^{-1}



Iodine bromide (0.5921 g, 2.863 mmol) in a mixture of solvents methyl cyanide and ether (15 ml + 10 ml respectively), was added dropwise to a suspension of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (1.2748 g, 2.863 mmol) in ether (15 ml) with continuous stirring of the reaction mixture. After complete addition of the mixed halogen solution and adding ether no product was separated. The bulk of the solvent was reduced on vacuum line, more ether was then added to obtain yellow crystalline product. These were filtered, washed with ether and dried on vacuum line. m.p. 138-140°C (Analysis: Found: C, 45.34; H, 4.19; Br, 22.21; I, 11.00% $\text{C}_{42}\text{H}_{44}\text{As}_2\text{O}_2\text{Br}_3\text{I}$ requires: C, 45.96; H, 4.04; Br, 21.84; I, 11.56%) uv spectrum showed IBr_2^- ion (peak at $\lambda_{\text{max}} = 257$ and $370\text{m}\mu$) ir spectrum: 3060-2500vsb, 1600-1550msb, 1500m, 1315ms, 1210wb, 1190ms, 1135m, 1120ms 1085vs, 1035mw, 1015m, 945vw, 835wb, 800vs, 745vs, 620msb, 590sb, 430sb cm^{-1}



Iodine chloride (0.2121 g, 1.306 mmol) in methyl cyanide (2 ml) was added dropwise to a suspension of $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ (0.5235 g, 1.306 mmol) in methyl cyanide (2 ml) with continuous stirring of the reaction mixture. On addition of about approximately half the quantity of ICl solution bright yellow crystals started to separate out, which on complete addition of ICl solution were redissolved leaving a little product which did not dissolve even keeping it overnight. This product (A) was filtered, washed with

ether and dried as usual. From the filtrate of product (A), bright yellow crystals were obtained on addition of ether (B). These were filtered, washed with ether and dried. m.p. of (B) 145-147°C (Analysis: Found for (B): C, 51.98; H, 4.39; Cl, 11.76; I, 13.16% $C_{42}H_{44}As_2O_2ICl_3$ requires: C, 52.32; H, 4.61; Cl, 11.03; I, 13.16%). Analysis found for (A) and its m.p. 144-146°C showed that (A) and (B) were the same products.

uv spectrum showed presence of ICl_2^- ions (peaks at $\lambda_{max} = 233m \mu$ Lit. value for ICl_2^- ions at $\lambda_{max} = 227, 336 m \mu^{125}$. It seems complex ionisation)

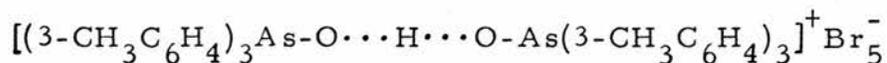
ir spectrum: 3120-2500vsb, 2320-2220wb, 1600-1550msb, 1495m, 1318s, 1210mb, 1190s, 1160m, 1125ms, 1090-1080vs, 1035ms, 1018s, 1000-980wb, 970vw, 960w, 850ms, 830-780sb, 770vs, 755ms, 710vw, 685mw, 615w, 590vs, 480s, 470vs, 430s cm^{-1}

(4) Attempted Preparation of $[(3-CH_3C_6H_4)_3AsOH]^+Br_3^-$

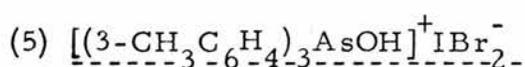
Bromine (0.1997 g, 1.249 mmol) in methyl cyanide (20 ml) was added to a suspension of tris(3-methylphenyl)arsine oxide hydrogen bromide (0.5565 g, 1.249 mmol) in the same solvent (10 ml) with stirring. On complete addition of bromine, a clear solution resulted. An oily product was obtained on removing the solvent and adding ether. This oil was converted to a yellow crystalline solid with great difficulty (stirring on mechanical stirrer for 76 hours, followed by trituration and prolonged pumping on vacuum line and on keeping it in a dry-box for four days a few crystals were separated). On further trituration with ca. 5 ml ether yellow crystalline product was obtained. These were filtered, washed with ether and dried as

usual. (Analysis: Found: C, 46.12; H, 3.67; Br, 37.25%)

uv spectrum showed presence of Br_3^- ion. This compound was not identified but a possible formulation was suggested.



whose analytical data C, 44.67; H, 3.84; Br, 35.38% are closer to the results found for the compound.



Iodine bromide (0.6874 g, 3.323 mmol) in methyl cyanide (15 ml) was added dropwise to a suspension of $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (1.4800 g, 3.323 mmol) in the same solvent (25 ml) with continuous stirring of the reaction mixture. $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ reacted with iodine bromide and after complete addition of the mixed halogen solution, a clear solution resulted which was shaken further for one hour. The bulk of the solvent was reduced on vacuum line to ≈ 5 ml, before adding ether. A red brown oily product was separated which did not solidify on trituration with ether. Again it was stirred for 70 hours, ether layer was decanted and the oily product trituated with petroleum ether for two hours, when a few crystals separated, kept overnight and next day on trituration with petroleum ether the oil was solidified into orange crystals. These were filtered, washed with ether and dried on vacuum line. m.p. $58\text{-}60^\circ\text{C}$ (Analysis: Found: C, 39.66; H, 3.69; Br, 25.02; I, 17.06%.

$\text{C}_{21}\text{H}_{22}\text{AsOIBr}_2$ requires: C, 38.67; H, 3.40; Br, 24.50; I, 19.46%)

uv spectrum showed presence of IBr_2^- ions (peaks at $\lambda_{\text{max}} = 258$ and $370 \text{ m } \mu$)

ir spectrum: 3300-2400sb, 1595ms, 1315m, 1220-1210mb, 1180-1050s

(resolved into 1170mb, 1120ms, 1100s), 1030ms, 988s, 915w, 900vw, 880w, 832m, 790-750vs (resolved into 788s, 775vs, 760s), 620vsb, 580-510msb, 510-430msb, 430s, 420-390sb, 340-300mwb cm^{-1}

(6) Attempted Preparation of $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$

Tris(3-methylphenyl)arsine oxide hydrogen chloride (1.0009 g, 2.497 mmol) was added to a solution of iodine chloride (0.4055 g, 2.497 mmol) in methyl cyanide (2 ml) with continuous stirring.

$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ reacted with ICl and a clear solution was obtained. On addition of ether it gave an oily product which could not be converted to a solid by (i) stirring for 72 hours, (ii) triturating with ether, (iii) petroleum ether and (iv) prolonged pumping on vacuum line.

(7) $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{Br}^-\text{Br}^-$

Bromine (0.2991 g, 1.871 mmol) in carbon tetrachloride (20 ml) was added dropwise to a suspension of tris(2-methylphenyl)arsine oxide hydrogen bromide (0.8332 g, 1.871 mmol) in the same solvent (10 ml) with continuous stirring of the reaction mixture. On complete addition of the halogen a clear solution resulted. Excess of solvent is pumped off on vacuum line, and on adding ether, yellow crystals were separated out. These were filtered, washed with ether, and dried on vacuum line. m.p. 132-134°C. (Analysis: Found: C, 48.95; H, 4.38; Br, 30.43% $\text{C}_{42}\text{H}_{44}\text{As}_2\text{O}_2\text{Br}_4$ requires: C, 48.02; H, 4.23; Br, 30.43%)

uv spectrum showed presence of Br_3^- ions (peak at $\lambda_{\text{max}} = 269 \text{ m}\mu$)

ir spectrum: 3100-3040wb, 3020-2920mb, 2900-2000vsb, 1595ms, 1570m, 1280ms, 1202s, 1165mb, 1130-1128ms, 1100-1080wb, 1065-1045wb, 870-500vsb (resolved into 788s, 770-700vsb, 690-680wb), 430-400vsb cm^{-1}

(8) Attempted Preparation of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{IBr}_2^-$

Iodine bromide (0.7498 g, 3.625 mmol) in methyl cyanide (20 ml) was added to a suspension of tris(2-methylphenyl)arsine oxide hydrogen bromide (1.6141 g, 3.625 mmol) in the same solvent (10 ml). After complete addition of halogen a clear solution was obtained. The excess of solvent was removed on vacuum line and bright yellow crystals were obtained on addition of ether. These were filtered, washed with ether and dried. (Analysis: Found: C, 41.41; H, 3.49; Br, 24.08; I, 11.39%. This result did not tally with the C, 38.67; H, 3.40; Br, 24.50; I, 19.46% of the expected compound $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{IBr}_2^-$ and not with the C, 45.96; H, 4.04; Br, 21.84; I, 11.56% of the mixed anion compound, $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}^-$. It was difficult to assign a formulation for this product.

(9) $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]^+\text{ICl}_2^-$ and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{ICl}_2\text{Cl}^-$

$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ (1.0011 g, 2.497 mmol) was added in small quantity to a solution of ICl (0.4055 g, 2.497 mmol) in methyl cyanide (2 ml) with continuous stirring of the reaction mixture. $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHCl}$ reacted with ICl and a clear solution resulted. Kept overnight and next day, on addition of ether pale yellow crystals were separated (A). These were filtered, washed with ether, and

dried on vacuum line. m.p. 136-138°C. From the filtrate on addition of ether yellow crystals were isolated (B). These were filtered, washed with ether and dried as usual m.p. 110-112°C.

(Analysis: Found for (A): C, 51.98; H, 4.56; Cl, 11.78; I, 13.34%

$C_{42}H_{44}As_2O_2ICl_3$ requires: C, 52.32; H, 4.61; Cl, 11.03; I, 13.16%)

uv spectrum showed presence of ICl_2^- ions (peak at $\lambda_{max} = 228 \text{ m } \mu$)

(Analysis: Found for (B): C, 44.68; H, 4.03; Cl, 11.50; I, 23.11%

$C_{21}H_{22}AsOICl_2$ requires: C, 44.78; H, 3.94; Cl, 12.59; I, 22.53%)

uv spectrum showed presence of ICl_2^- ions (peak at $\lambda_{max} = 228 \text{ m } \mu$)

ir spectrum for (A): 3070-2400vsb, 2300-2000mb, 1590ms,

1560-1550mb, 1280ssh, 1200s, 1150m, 1128ms, 1060mw, 1030mb,

792s, 770-700vs (resolved into 768vs, 760-740vsb), 698ms,

430-350sb cm^{-1}

ir spectrum for (B): 3200-2500vsb, 1600ms, 1570ms, 1285ssh,

1205sb, 1160m, 1142vw, 1135msb, 1055mw, 1040-1030msb, 990m,

950mw, 945w, 872ms, 870m, 860w, 796vs, 780w, 770-700vsb

(resolved into 750vs, 742vs, 732vs), 692mssh, 620-550msb, 530m,

490ms, 480m, 430vssh, 412s, 395ms cm^{-1}

(10) Attempted Preparation of $[(4-CH_3C_6H_4)_3AsOH]^+HgBr_4^{2-}$

$(4-CH_3C_6H_4)_3AsOHBr$ (0.9876 g, 2.218 mmol) dissolved in hot absolute ethanol (10 ml) was added dropwise to a boiling solution of mercuric bromide (0.400 g, 1.109 mmol) in the same solvent (10 ml) with continuous stirring. On cooling, a viscous white oil was obtained. On attempting to redissolve this oil in the hot solvent it converted to a white crystalline solid (which did not redissolve) even after continuous boiling. After cooling,

the crystals were filtered and dried on vacuum line. m.p. 158-159°C
 (Analysis: Found: C, 33.56; H, 3.27; Br, 25.27%. This analysis
 did not tally with the required C, 40.32; H, 3.55; Br, 22.36%
 of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$.

[Adding ether to the alcoholic filtrate yielded 0.48 g of the
 starting material $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$. This was identified
 from its infrared spectrum and m.p.]

(11) Attempted Preparation of $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$

$(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (1.2352 g, 2.774 mmol) in absolute
 ethanol (10 ml) was added dropwise to a boiling solution of mercuric
 bromide (0.50 g, 1.387 mmol) in the same solvent (10 ml). On
 cooling and adding ether a viscous oily product was obtained. Extreme
 difficulty was experienced in attempting to isolate a solid product
 from this reaction product. However, after trituration with
 petroleum ether, followed by concentration of the solvent and
 prolonged pumping under a vacuum of 0.001 mm Hg, a workable,
 but still slightly sticky white solid was obtained. (Analysis: Found:
 C, 41.06; H, 3.91; Br, 20.0% $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$
 requires: C, 40.32; H, 3.55; Br, 22.36%)

(12) $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$

$(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOHBr}$ (1.1131 g, 2.50 mmol) dissolved
 in chloroform (20 ml), was added dropwise to a boiling solution
 of mercuric bromide (0.4504 g, 1.25 mmol) in AR acetone (10 ml)
 with continuous stirring. On cooling and adding ether white
 crystals were obtained. These were filtered, washed with ether,

and dried on vacuum line. m.p. 188-189°C. (Analysis: Found:

C, 40.49; H, 3.50; Br, 25.55% $C_{42}H_{44}As_2Br_4HgO$ requires:

C, 40.32; H, 3.55; Br, 22.36%)

ir spectrum: 3160-2500sb, 1580m, 1560-1495vwb, 1278ms, 1195ms,

1155m, 1120m, 1070-975mb, 795m, 750vs cm^{-1}

Experimental Data

Conductometric Titration Data of the Systems $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{As}:\text{Halogens}$ Table 6. $\text{Br}_2:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{Br}_2:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{Br}_2:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.0010	2.1834	2.2235
0.1679	0.3016	2.3513	2.1741
0.3359	0.4548	2.5193	2.1413
0.5038	0.7866	2.6872	2.0878
0.6718	0.9781	2.8552	2.0459
0.8397	1.1674	3.0231	1.9974
1.0077	1.3480	3.1911	1.9555
1.1756	1.5042	3.3590	1.9078
1.3436	1.6604	3.5270	1.8659
1.5115	1.7960	3.6949	1.8256
1.6795	1.9333	3.8629	1.7919
1.8474	2.0813	4.0308	1.7590
2.0154	1.2563	4.1988	1.7262

Table 7. $\text{IBr}:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{IBr}:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{IBr}:(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.0005508	2.1798	2.1807
0.1676	0.2451	2.3475	2.1487
0.3353	0.4726	2.5152	2.1084
0.5030	0.6863	2.6829	2.0550
0.6707	0.8918	2.8506	2.0139
0.8384	1.0858	3.0183	1.974
1.0061	1.2658	3.1859	1.9193
1.1737	1.4417	3.3530	1.8700
1.3414	1.6111	3.5213	1.8330
1.5091	1.7467	3.6890	1.7960
1.6768	1.8823	3.8567	1.7673
1.8445	2.0303	4.0244	1.7303
2.0122	2.1618	4.1920	1.6896

Table 8. $I_2:(2-CH_3C_6H_4)_3As$ in Nitrobenzene

Mole Ratio $I_2:(2-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio $I_2:(2-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.0000	0.0007235	2.0919	0.9033
0.1162	0.09781	2.2081	0.9140
0.2324	0.1749	2.3243	0.9189
0.3486	0.2480	2.4405	0.9189
0.4648	0.3153	2.5567	0.9157
0.5810	0.3786	2.6730	0.9091
0.6973	0.4389	2.7892	0.9119
0.8135	0.4973	2.9054	0.8902
0.9297	0.5474	3.0216	0.8754
1.0459	0.6460	3.1378	0.8631
1.1621	0.6945	3.2540	0.8515
1.2783	0.7332	3.3703	0.8417
1.3946	0.7718	3.4868	0.8318
1.5108	0.8055	3.6027	0.8220
1.6270	0.8376	3.7189	0.8121
1.7432	0.8647	3.8351	0.8022
1.8594	0.8894	3.9514	0.7915
1.9757			

Table 10. $\text{Br}_2:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{Br}_2:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{Br}_2:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.001521	2.2477	2.3016
0.1873	0.1389	2.4351	2.2522
0.3746	0.2170	2.6224	2.2062
0.5619	0.2794	2.8097	2.1495
0.7492	0.3296	2.9970	2.0919
0.9367	0.3822	2.1843	2.0443
1.1238	0.6584	2.3716	2.0015
1.3112	1.0570	3.5590	1.9604
1.4985	1.4426	3.7463	1.9193
1.6858	1.8141	3.9336	1.8782
1.8731	2.1692	4.1209	1.8412
2.0604	2.3673	4.3082	1.8084

Table 11. $\text{IBr}:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{IBr}:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{IBr}:(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.001331	1.7557	1.3645
0.1097	0.08417	1.8654	1.4713
0.2194	0.1656	1.9752	1.5700
0.3292	0.2445	2.0849	1.5700
0.4389	0.3234	2.1946	1.5412
0.5486	0.4027	2.3044	1.5124
0.6584	0.4816	2.4141	1.4878
0.7681	0.5630	2.5238	1.4631
0.8778	0.6411	2.6336	1.4426
0.9876	0.7233	2.7433	1.4220
1.0973	0.8014	2.8530	1.4056
1.2070	0.8836	2.9628	1.3809
1.3168	0.9773	3.0725	1.3563
1.4265	1.0644	3.1822	1.3316
1.5358	1.1590	3.2920	1.3069
1.6460	1.2601	3.3960	1.2990

Table 12. $I_2:(3-CH_3C_6H_4)_3As$ in Nitrobenzene

Mole Ratio $I_2:(3-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio $I_2:(3-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.0000	0.001677	1.6877	0.8951
0.09376	0.0657	1.7814	0.9469
0.1875	0.1216	1.8752	0.9872
0.2812	0.1726	1.9690	1.0168
0.3750	0.2244	2.0627	1.0233
0.4688	0.2737	2.1565	1.0168
0.5625	0.3263	2.2502	1.0044
0.6563	0.3801	2.3440	0.9888
0.7500	0.4290	2.4378	0.9707
0.8438	0.4759	2.5315	0.9543
0.9376	0.5203	2.6253	0.9387
1.0313	0.5630	2.7190	0.9247
1.1251	0.6074	2.8128	0.9115
1.2189	0.6485	2.9066	0.8943
1.3126	0.6732	3.0003	0.8820
1.4064	0.7480	3.0941	0.8688
1.5001	0.7981	3.1879	0.8557
1.5939	0.8466	3.2749	0.8452

Table 14. $\text{Br}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{Br}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$k \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{Br}_2:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.003132	2.3080	2.1166
0.1775	0.1791	2.4855	2.0697
0.3550	0.3033	2.6631	2.0245
0.5326	0.4110	2.8406	1.9834
0.7101	0.4981	3.0182	1.9407
0.8877	0.5803	3.1957	1.9004
1.0652	0.7562	3.3732	1.8634
1.2427	1.0275	3.5508	1.8273
1.4203	1.3069	3.7283	1.7960
1.5978	1.5946	3.9054	1.7631
1.7754	1.8716	4.0834	1.7344
1.9529	2.1396	4.2609	1.7040
2.1304	2.1659	4.4385	1.6760

Table 15. $\text{IBr}:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ in Nitrobenzene

Mole Ratio $\text{IBr}:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)	Mole Ratio $\text{IBr}:(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$	$K \times 10^4$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0.0000	0.003288	2.0957	2.0599
0.1612	0.1446	2.2569	2.0385
0.3224	0.2860	2.4181	2.0155
0.4836	0.4208	2.5793	1.9974
0.6448	0.5647	2.7405	1.9793
0.8060	0.7208	2.9017	1.9629
0.9672	0.8894	3.0629	1.9481
1.1284	1.0570	3.2241	1.9349
1.2896	1.2535	3.3854	1.9243
1.4508	1.4656	3.5466	1.9169
1.6120	1.7122	3.7078	1.9119
1.7733	1.9711	3.8690	1.9086
1.9345	2.0813	4.1914	1.9045

Table 16. $I_2:(4-CH_3C_6H_4)_3As$ in Nitrobenzene

Mole Ratio $I_2:(4-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)	Mole Ratio $I_2:(4-CH_3C_6H_4)_3As$	$K \times 10^4$ (ohm ⁻¹ cm ⁻¹)
0.0000	0.000329	1.8860	0.9642
0.1178	0.08178	2.0039	0.9946
0.2357	0.1438	2.1217	0.9929
0.3536	0.2079	2.2396	0.9798
0.4715	0.2671	2.3575	0.9633
0.5893	0.3246	2.4754	0.9461
0.7072	0.3814	2.5932	0.9272
0.8251	0.4356	2.7111	0.9132
0.9430	0.4915	2.8290	0.8951
1.0608	0.5482	2.9469	0.8778
1.1787	0.6025	3.0647	0.8639
1.2966	0.6617	3.1826	0.8483
1.4145	0.7217	3.3005	0.8343
1.5323	0.7800	3.4184	0.8214
1.6502	0.8425	3.5363	0.8080
1.7681	0.9017	3.6541	0.7948

Table 18. Electrolytic Conductance of R_3AsF_2 Adducts in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsF ₂	0.0009737	0.03120	0.2205	22.64
	0.002638	0.05136	0.5538	20.94
	0.005139	0.07168	1.0163	19.77
	0.008353	0.09139	1.5517	18.57
	0.01346	0.1160	2.3722	17.62
	0.016512	0.1284	2.8483	17.25
(4-CH ₃ C ₆ H ₄) ₃ AsF ₂	0.0008025	0.02833	0.000779	0.09706
	0.002685	0.05182	0.003661	0.1363
	0.008229	0.09071	0.01225	0.1489
	0.01189	0.1090	0.01747	0.1469
	0.01449	0.12040	0.02098	0.1448
(C ₆ H ₅) ₃ AsF ₂	0.0005977	0.02444	0.0004102	0.06863
	0.002695	0.05192	0.0009538	0.03537
	0.007996	0.08942	0.001640	0.02052
	0.01211	0.11004	0.002574	0.00904

Table 19. Electrolytic Conductance of R_3AsCl_2 Adducts in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsCl ₂	0.000231	0.01521	0.01142	4.93
	0.001661	0.04076	0.1213	7.30
	0.002724	0.05219	0.2301	8.44
	0.004427	0.06653	0.4145	9.36
	0.006949	0.08336	0.5911	8.50
	0.010031	0.10015	0.6758	6.73
	0.011908	0.10912	0.6825	5.73
	0.151413	0.12304	0.6896	4.55
(3-CH ₃ C ₆ H ₄) ₃ AsCl ₂	0.000824	0.02871	0.01300	1.57
	0.001448	0.03805	0.01970	1.36
	0.003223	0.05677	0.03586	1.11
	0.006527	0.08079	0.05950	0.911
	0.008953	0.09462	0.07409	0.827
	0.013516	0.11625	0.09852	0.728

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Table 19. (cont.)

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(4-CH ₃ C ₆ H ₄) ₃ AsCl ₂	0.004129	0.02039	0.00788	1.90
	0.001503	0.03877	0.02593	1.72
	0.003076	0.05546	0.04374	1.42
	0.007719	0.08786	0.08591	1.11
	0.010005	0.10002	0.1123	1.12
	0.014654	0.12105	0.1371	0.935
(C ₆ H ₅) ₃ AsCl ₂	0.000331	0.01820	0.00354	1.07
	0.001942	0.04407	0.01182	0.608
	0.005743	0.07578	0.02561	0.4460
	0.009974	0.09987	0.03743	0.375
	0.011749	0.01083	0.04138	0.352
	0.014935	0.12220	0.04808	0.322

Table 20. Electrolytic Conductance of R₃AsBr₂ Adducts in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsBr ₂ · ·CCl ₄	0.000207	0.01442	0.01192	5.73
	0.000795	0.02820	0.07444	9.36
	0.001481	0.03848	0.1718	11.61
	0.003259	0.05709	0.4641	14.24
	0.006314	0.07946	0.9395	14.87
	0.010005	0.10002	1.4337	14.32
	0.014341	0.11975	1.9295	13.45
(3-CH ₃ C ₆ H ₄) ₃ AsBr ₂	0.00514	0.02269	0.05018	9.74
	0.002461	0.04962	0.1764	7.16
	0.003842	0.06197	0.2528	6.58
	0.005876	0.07665	0.3469	5.90
	0.009344	0.09665	0.5212	5.57
	0.01330	0.11530	0.6310	4.75
	0.01666	0.12910	0.7221	4.33
(4-CH ₃ C ₆ H ₄) ₃ AsBr ₂	0.000359	0.01923	0.04729	12.78
	0.002418	0.04918	0.1986	8.21
	0.003934	0.06272	0.2817	7.16
	0.007309	0.08549	0.4208	5.75
	0.009879	0.09939	0.4959	5.02
	0.011769	0.10848	0.5568	4.73
	0.014225	0.11926	0.6105	4.29

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Table 20. (cont)

Compound	C_m mol l ⁻¹	\sqrt{C}_m	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$(C_6H_5)_3AsBr_2$	0.000652	0.02554	0.0398	6.09
	0.001249	0.03534	0.0685	5.48
	0.002300	0.04796	0.1052	4.57
	0.004779	0.06913	0.1637	3.42
	0.009573	0.09784	0.2561	2.67
	0.012758	0.11295	0.3062	2.40
	0.016544	0.12862	0.3593	2.17

Table 21. Electrolytic Conductance of R_3AsIBr Adducts in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	\sqrt{C}_m	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$(2-CH_3C_6H_4)_3AsIBr$	0.000290	0.01706	0.05633	19.37
	0.001153	0.03394	0.1978	17.16
	0.003642	0.06030	0.5395	14.81
	0.006302	0.07938	0.8280	13.14
	0.011120	0.10545	1.2532	11.27
	0.015252	0.1235	1.5785	10.35
$(3-CH_3C_6H_4)_3AsIBr$	0.0002749	0.01658	0.04168	15.15
	0.001136	0.03370	0.14457	12.73
	0.002601	0.05100	0.2781	10.69
	0.005659	0.07523	0.5306	9.37
	0.008500	0.09219	0.7217	8.491
	0.014544	0.12059	1.189	8.17
$(4-CH_3C_6H_4)_3AsIBr$	0.000468	0.02165	0.06149	13.11
	0.002525	0.05025	0.27810	11.01
	0.004906	0.07005	0.4866	9.91
	0.008607	0.09277	0.7626	8.85
	0.012297	0.11089	1.0085	8.20
	0.015099	0.12287	1.1772	7.79

Table 22. Electrolytic Conductance of R_3AsI_2 in Nitrobenzene

at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$(2-CH_3C_6H_4)_3AsI_2$	0.000288	0.01697	0.06990	24.24
	0.001630	0.04037	0.28050	17.21
	0.003327	0.05768	0.50830	15.28
	0.005337	0.07305	0.6927	12.98
	0.0096461	0.98214	1.1093	11.50
	0.014445	0.12019	1.4950	10.35
$(3-CH_3C_6H_4)_3AsI_2$	0.000541	0.2327	0.11721	21.64
	0.001192	0.03453	0.1990	16.70
	0.002267	0.04760	0.3331	14.69
	0.005266	0.07256	0.6339	12.03
	0.009917	0.09959	1.0251	10.35
	0.012267	0.11075	1.1862	9.57
$(4-CH_3C_6H_4)_3AsI_2$	0.000726	0.02696	0.01359	12.32
	0.001611	0.04014	0.1804	11.19
	0.002503	0.05003	0.2623	10.47
	0.008155	0.09031	0.6813	8.35
	0.012413	0.11141	0.9350	7.53
	0.016932	0.13012	1.1754	6.94

Table 23. Electrolytic Conductance of $(2-CH_3C_6H_4)_3AsBr_nI_{4-n}$

Adducts (n=4, 3, 2, 1 and 0) in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$(2-CH_3C_6H_4)_3AsBr_4$	0.000183	0.01356	0.02170	11.86
	0.001170	0.03421	0.2444	20.89
	0.002601	0.0510	0.5927	22.79
	0.005855	0.07652	1.5667	26.76
	0.007390	0.08597	2.0100	27.20
	0.01119	0.10581	2.5199	22.51
	0.01399	0.1183	2.6567	18.99
$(2-CH_3C_6H_4)_3AsBr_3I$	0.0008761	0.02959	0.2876	32.83
	0.002450	0.04950	0.7424	30.29
	0.005066	0.07118	1.4443	28.50
	0.007076	0.08412	1.9476	27.52
	0.01125	0.1061	2.8496	25.33
	0.10550	0.1244	3.6657	23.65

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Table 23. (cont)

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsBr ₂ I ₂	0.0005027	0.02242	0.2184	43.44
	0.001266	0.03557	0.5003	39.52
	0.002519	0.05019	0.9105	36.15
	0.004737	0.06882	1.537	32.44
	0.008022	0.08957	2.2638	28.22
	0.01306	0.1145	3.060	23.43
(2-CH ₃ C ₆ H ₄) ₃ AsBrI ₃	0.0009387	0.03063	0.3432	36.56
	0.001796	0.04238	0.5943	33.07
	0.002788	0.05280	0.8532	30.60
	0.003691	0.06075	1.0636	28.81
	0.006170	0.07855	1.5150	24.56
	0.010300	0.1014	1.927	18.71
(2-CH ₃ C ₆ H ₄) ₃ AsI ₄	0.0009412	0.03068	0.3052	32.46
	0.002045	0.04522	0.4662	22.80
	0.003013	0.05489	0.6137	20.36
	0.006649	0.08155	1.310	19.70
	0.008441	0.09187	1.493	17.70
	0.01102	0.1050	1.550	14.07

Table 24. Electrolytic Conductance of (3-CH₃C₆H₄)₃AsBr_nI_{4-n}

(n=4, 3, 2, 1 and 0) in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(3-CH ₃ C ₆ H ₄) ₃ AsBr ₄	0.000654	0.02558	0.1980	30.24
	0.002912	0.05397	0.8380	28.76
	0.004802	0.06929	1.3472	28.05
	0.008274	0.09096	2.1571	26.06
	0.01239	0.1113	3.0591	24.68
	0.01726	0.1314	4.0262	23.31
(3-CH ₃ C ₆ H ₄) ₃ AsBr ₃ I	0.002185	0.04673	0.6466	29.61
	0.003707	0.06088	1.056	28.49
	0.005728	0.07568	1.579	27.57
	0.008470	0.09202	2.239	26.42
	0.011707	0.1082	3.022	25.65
	0.01562	0.1250	3.826	24.50

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Table 24. (cont)

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(3-CH ₃ C ₆ H ₄) ₃ AsBr ₂ I ₂	0.002132	0.04616	0.6012	28.19
	0.003652	0.06042	0.9800	26.83
	0.005414	0.07357	1.409	26.02
	0.007857	0.08863	1.955	24.89
	0.009740	0.09870	2.359	24.24
	0.01327	0.1152	3.032	22.85
(3-CH ₃ C ₆ H ₄) ₃ AsBrI ₃	0.0008117	0.02849	0.2464	30.41
	0.002580	0.05079	0.7108	27.55
	0.005075	0.07124	1.287	25.37
	0.007516	0.08670	1.796	23.89
	0.01065	0.1032	2.3536	22.10
	0.01418	0.1191	2.8331	19.98
(3-CH ₃ C ₆ H ₄) ₃ AsI ₄	0.0007431	0.02726	0.2156	29.02
	0.001926	0.04388	0.5272	27.36
	0.005630	0.07502	1.330	23.63
	0.009279	0.09632	1.8892	20.36
	0.01147	0.1071	2.2825	19.90
	0.015153	0.1231	2.7275	18.00

Table 25. Electrolytic Conductance of (4-CH₃C₆H₄)₃AsBr_nI_{4-n}

(n=4, 3, 2, 1 and 0) in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(4-CH ₃ C ₆ H ₄) ₃ AsBr ₄	0.0002956	0.01719	0.1004	33.97
	0.002381	0.04880	0.7184	30.16
	0.004837	0.06955	1.3642	28.20
	0.008405	0.09168	2.2340	26.57
	0.01223	0.11059	3.0900	25.26
	0.01683	0.1297	4.0417	24.00
(4-CH ₃ C ₆ H ₄) ₃ AsBr ₃ I	0.000888	0.02979	0.2665	30.02
	0.002663	0.05160	0.7598	28.53
	0.004864	0.06974	1.3101	26.93
	0.008124	0.09013	2.047	25.20
	0.01230	0.1109	2.9070	23.62
	0.01534	0.1238	3.4144	22.25

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Table 25. (cont)

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(4-CH ₃ C ₆ H ₄) ₃ AsBr ₂ I ₂	0.001266	0.03558	0.3665	28.95
	0.002900	0.05385	0.7948	27.40
	0.004693	0.06850	1.2347	26.30
	0.008110	0.09005	2.0099	24.78
	0.01211	0.11005	2.8280	23.34
	0.01530	0.1237	3.4345	22.44
(4-CH ₃ C ₆ H ₄) ₃ AsBrI ₃	0.0008273	0.02876	0.2240	27.07
	0.002452	0.04952	0.6291	25.64
	0.005387	0.07339	1.2820	23.79
	0.007891	0.08883	1.7767	22.51
	0.01184	0.1088	2.4840	20.97
	0.01461	0.12090	2.9355	20.08
(4-CH ₃ C ₆ H ₄) ₃ AsI ₄	0.0006602	0.02569	0.1863	28.22
	0.001688	0.041086	0.4461	26.43
	0.004704	0.06859	1.138	24.20
	0.007562	0.08696	1.658	21.92
	0.010256	0.10127	2.092	20.40
	0.01393	0.11805	2.630	18.87

Table 30. Electrolytic Conductance of $R_3AsOHCl$ Compounds
in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.0004694	0.02166	0.003028	0.6451
	0.002862	0.05350	0.01557	0.5540
	0.005139	0.07168	0.02657	0.5170
	0.008373	0.09150	0.04233	0.5055
	0.01214	0.1102	0.06180	0.5087
	0.01570	0.1253	0.07749	0.4933
(3-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.0004097	0.02024	0.002224	0.5430
	0.002458	0.04958	0.01056	0.4298
	0.004808	0.06934	0.01841	0.3829
	0.008337	0.09131	0.03241	0.3887
	0.01248	0.1117	0.04962	0.3975
	0.01523	0.1234	0.06056	0.3974
(4-CH ₃ C ₆ H ₄) ₃ AsOHCl	0.0002978	0.01725	0.001514	0.5082
	0.002460	0.04960	0.01022	0.4157
	0.005007	0.07076	0.01996	0.3986
	0.008096	0.08998	0.03185	0.3934
	0.01209	0.1099	0.04672	0.3863
	0.016272	0.1275	0.06192	0.3805

Table 31. Electrolytic Conductance of $R_3AsOHBr$ in Nitrobenzene
at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
(2-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.0003135	0.01770	0.008775	2.79
	0.002752	0.05246	0.03606	1.31
	0.005013	0.07080	0.05667	1.13
	0.008309	0.09115	0.08482	1.02
	0.01187	0.1089	0.1142	0.96
	0.01555	0.1247	0.1435	0.92
(3-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.0003717	0.01927	0.006458	1.73
	0.002813	0.05304	0.02895	1.02
	0.005375	0.07331	0.04560	0.84
	0.008104	0.09002	0.06210	0.76
	0.0118036	0.1086	0.08373	0.70
	0.01532	0.1237	0.1038	0.67
(4-CH ₃ C ₆ H ₄) ₃ AsOHBr	0.0005835	0.02415	0.01075	1.84
	0.002698	0.05194	0.02784	1.03
	0.005004	0.07073	0.04251	0.84
	0.008210	0.09061	0.06139	0.74
	0.01215	0.1102	0.08315	0.68
	0.01462	0.1209	0.09653	0.66

Table 35. Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0001572	0.01253	0.01807	11.49
0.001155	0.03398	0.2438	21.11
0.002440	0.04939	0.6378	26.14
0.006153	0.07844	1.6481	26.78
0.0081	0.0900	2.1340	26.34
0.01216	0.1103	3.1506	25.91

Table 36. Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{IBr}_2^-$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0004923	0.02218	0.2012	40.87
0.001761	0.04197	0.6611	37.52
0.004430	0.06656	1.4541	32.81
0.008201	0.09056	2.4286	29.61
0.009884	0.09941	2.7693	28.01
0.01139	0.1067	3.0762	27.00

Table 37. Electrolytic Conductance of $[(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{Cl}_3^-$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0002283	0.01511	0.09348	40.95
0.002416	0.04915	0.7909	32.72
0.004628	0.06803	1.3878	29.98
0.007476	0.08646	2.0984	28.06
0.01226	0.1107	3.3991	27.71
0.01449	0.1204	3.9579	27.29

Table 38. Electrolytic Conductance of $[(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{IBr}_2^-$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0002358	0.01535	0.09239	39.18
0.001179	0.03433	0.4326	36.69
0.002718	0.05214	0.9174	33.74
0.005087	0.07132	1.5537	30.54
0.008234	0.09074	2.3041	27.98
0.01190	0.1091	3.0464	25.58

Table 39. Electrolytic Conductance of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Br}^-\text{Br}_3^-$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0003173	0.01781	0.02932	9.24
0.001022	0.03197	0.1727	16.89
0.002822	0.05312	0.6551	23.21
0.004903	0.07002	1.1512	23.47
0.008172	0.09039	1.8598	22.75
0.01228	0.1108	2.7524	22.41

Table 40. Electrolytic Conductance of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{ICl}_2^-$
and $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$ in Nitrobenzene at 25°C

Compound	C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
$[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{ICl}_2^-$	0.0003955	0.01988	0.1534	38.79
	0.001274	0.03570	0.4603	36.11
	0.002856	0.05344	0.9198	32.20
	0.005650	0.07517	1.5843	28.03
	0.008126	0.09014	2.06634	25.42
	0.01234	0.11109	2.8054	22.73
$[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{Cl}^-\text{ICl}_2^-$	0.00014	0.01183	0.5583	39.88
	0.001008	0.03176	0.3816	37.82
	0.002604	0.05103	0.9038	34.70
	0.006646	0.08152	1.9924	29.97
	0.009800	0.09899	2.7572	28.13
	0.01215	0.1102	3.5028	28.82

Table 41. Electrolytic Conductance of $[(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsOH}]_2^+\text{HgBr}_4^{2-}$
in Nitrobenzene at 25°C

C_m mol l ⁻¹	$\sqrt{C_m}$	$10^4 K$ ohm ⁻¹ cm ⁻¹	Λ_m ohm ⁻¹ cm ² mol ⁻¹
0.0005301	0.02302	0.2369	44.69
0.002222	0.04714	0.9127	41.06
0.005113	0.07150	1.8532	36.24
0.007580	0.08706	2.5465	33.59
0.010119	0.1005	3.1580	31.26
0.01322	0.1150	3.8389	29.02

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