1168. *Triphenylarsine–Halogen Adducts.*

By A. D. Beveridge and G. S. Harris.

Conductance measurements have been made on methyl cyanide solutions of triphenylarsine dihalides. Molar conductance values for the dichloride and dibromide indicate that these compounds are weak electrolytes, and the nature of their ions has been deduced from electrolysis experiments. The di-iodide and bromide iodide on the other hand form highly conducting solutions because of a product of their disproportionation in methyl cyanide. A conductimetric titration study of some triphenylarsine–halogen systems in methyl cyanide confirms the existence of 1 : 2 adducts, Ph_3AsHal_4, and three new compounds— Ph_3AsBr_4 Ph_3AsIBr_3, and Ph_3AsI_3Br—have been prepared. Members of the series $Ph_3AsI_nBr_{4-n}$ are strong electrolytes in methyl cyanide, ionising as halogenotriphenylarsonium trihalides, and the ambiguity in the mode of ionisation of certain of the compounds ($n = 1$, 2, and 3) has been resolved.

Triphenylarsine, in common with other triaryl- and trialkyl-arsines, reacts under certain conditions with halogens and interhalogens giving products of compositions Ph_3AsHal_2 and Ph_3AsHal_4. In spite of the wide variety of possible tetrahalides only two have been reported ($Hal_4 = I_4$ and I_2Br_2) and these aroused little interest.[1] In contrast, the known dihalides ($Hal_2 = Cl_2$, Br_2, I_2) have received more attention;[1,2] their reactions have been well studied[3] and their structures have been discussed from time to time by various authors.[4–6] By analogy with similar compounds of other group Vʙ elements it is clear that there are two probable structures for the dihalides; either they have a molecular structure based on trigonal bipyramidal (or square pyramidal) covalent units,[4] or else they are ionic with an arsonium-like structure $[Ph_3AsHal]^+Hal^-$.[6] There is also the possibility that the actual structure adopted is variable, depending on the physical state of the compound; there are numerous examples of this type of behaviour amongst halogen derivatives of group Vʙ elements, *e.g.*, antimony pentachloride is molecular (trigonal bipyramidal) in the solid,[7] whereas in solvents of high dielectric constant it is ionic ($SbCl_4^+SbCl_6^-$).[8] It has in fact been suggested by Mann[9] that the triphenylarsine dihalides are probably covalent in the solid but under certain conditions, for example in a good ionising solvent, are likely to exist in the ionic state ($Ph_3AsHal^+Hal^-$). Jensen[10] found that triphenylarsine dichloride has a zero dipole moment in benzene and this suggests a covalent trigonal bipyramidal structure similar to that found by X-ray analysis for the trimethylstibine dihalides (halogen atoms in the axial positions).[11] In comparison it appears that the phosphine dihalides (R_3PHal_2), insofar as they have been studied, are ionic in the solid[12] and in nitrobenzene solution.[13]

To obtain direct information on the nature of the triphenylarsine dihalides it was thought desirable to examine their electrolytic behaviour under conditions which would favour ion formation, and the results of preliminary studies of the conductance of triphenylarsine dichloride and dibromide in methyl cyanide have already been reported.[14]

[1] A. Michaelis, *Annalen*, 1902, **321**, 141.
[2] W. Steinkopf and G. Schwen, *Ber.*, 1921, **54**, 1437.
[3] A. E. Goddard in J. Newton Friend (ed.), "A Text Book of Inorganic Chemistry," Griffin and Co. Ltd., London, 1930, vol. XI, Part 2, p. 122 *et seq.*
[4] F. G. Mann, *J.*, 1945, 65.
[5] F. G. Mann, in A. Weissberger (ed.), "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon," Interscience Publishers, Inc., New York, 1950, p. 66.
[6] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organo-metallic Compounds," John Wiley and Sons, Inc., New York, 1957, p. 215.
[7] S. M. Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811.
[8] I. R. Beattie and M. Webster, *J.*, 1963, 38.
[9] F. G. Mann, personal communication.
[10] K. A. Jensen, *Z. anorg. Chem.*, 1943, **250**, 257.
[11] A. F. Wells, *Z. Krist.*, 1938, **99**, 367.
[12] J. Goubeau and R. Baumgärtner, *Z. Elektrochem.*, 1960, **64**, 598.
[13] K. Issleib and W. Seidel, *Z. anorg. Chem.*, 1956, **288**, 201.
[14] G. S. Harris, *Proc. Chem. Soc.*, 1961, 65.

The triphenylarsine dihalides studied are all crystalline with melting points in the range 140—215°. They are moderately soluble in methyl cyanide which was chosen as solvent on account of its favourable dielectric properties and the stability of the solutions. Precautions taken to ensure dry conditions are described later. The conductance measurements were made at 25° in a sealed cell. In contrast with the behaviour of certain closely similar compounds, *e.g.*, $(CF_3)_3PCl_2$,[15] the conductance of the solutions did not change on storage and values obtained are shown in Table 1.

TABLE 1.

The electrolytic conductance of triphenylarsine dihalides in methyl cyanide at 25°.
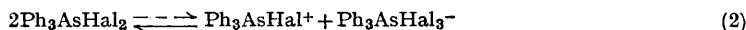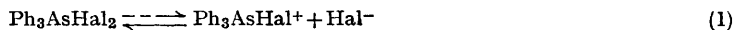
Compound	$10^4\varkappa$ (ohm^{-1} cm.$^{-1}$)	C_m (mole l.$^{-1}$)	Λ_m (ohm^{-1} cm.^{2} mole^{-1})
Ph_3AsCl_2	0·18	0·0016	11·0
	0·24	0·0033	7·3
	0·47	0·0120	3·9
Ph_3AsBr_2	4·14	0·0250	16·6
	4·70	0·0301	15·6
	4·56	0·0364	12·4
Ph_3AsI_2	3·04	0·0048	63·9
	4·01	0·0068	59·6
	6·13	0·0114	54·0
Ph_3AsIBr	6·06	0·0094	64·5
	9·31	0·0202	46·1
	11·97	0·0295	40·7

The magnitudes of the molar conductance values point to a difference in conducting properties of the dichloride and dibromide on the one hand compared with the di-iodide and bromide iodide on the other. It has in fact been shown that the molar conductance values of the latter two compounds are not "real" since the high conductance does not arise from direct ionisation of the dihalides in solution (this point is discussed later). Thus true values of molar conductance of methyl cyanide solutions of triphenylarsine dihalides are rather low ($\Lambda_m < 20$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0.0016$—0·036) as compared with those expected for solutions of strong 1:1 electrolytes in the same solvent at similar concentrations [*e.g.*, $Cu(MeCN)_4NO_3$,[16] $\Lambda_{m,25°} \approx 100$—120 ohm^{-1} cm.^{2} mole^{-1} at $C_m \approx 0.09$—0·026; $AgNO_3$,[17] $\Lambda_{m,25°} = 155.2$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0.00228$] and it is concluded that triphenylarsine dichloride and dibromide are behaving as weak electrolytes in methyl cyanide

$$e.g., \quad Ph_3AsBr_2 \rightleftharpoons Ph_3AsBr^+ + Br^-$$
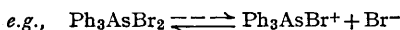
This strongly suggests that these dihalides are molecular in the solid and that only under the influence of the solvent do they undergo partial ionisation. The di-iodide and bromide iodide also would be expected to have molecular lattices.

There are two likely ways in which these compounds might ionise, namely,

$$Ph_3AsHal_2 \rightleftharpoons Ph_3AsHal^+ + Hal^- \qquad (1)$$

$$2Ph_3AsHal_2 \rightleftharpoons Ph_3AsHal^+ + Ph_3AsHal_3^- \qquad (2)$$

and these should be distinguishable by observing quantitatively the migration of halogen when solutions of the compounds are electrolysed. The change in halogen content of the solution at each electrode (in a Hittorf-type cell) depends on the transport numbers of the ions and the relationship varies depending on the mode of ionisation adopted by the compound. If there is no loss of halogen from the solution during electrolysis, then for ionisations (1) and (2), when 1 farad of current is passed,

$$\Delta Hal = 2t_+ - 1$$

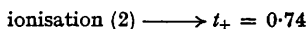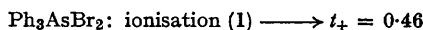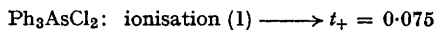and $$\Delta Hal = 4t_+ - 3, \quad \text{respectively,}$$

[15] H. J. Eméleus and G. S. Harris, *J.*, 1959, 1494.
[16] B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J.*, 1961, 3215.
[17] P. Walden and E. J. Birr, *Z. phys. Chem.*, 1929, **144**, 269.

where t_+ is the cation transport number and ΔHal is the increase in moles of halogen atoms at the cathode after electrolysis.

Values of t_+ may then be obtained by substituting observed ΔHal values in these equations. The results were

$$Ph_3AsCl_2: \text{ ionisation (1)} \longrightarrow t_+ = 0\cdot075$$

$$\text{ionisation (2)} \longrightarrow t_+ = 0\cdot54$$

$$Ph_3AsBr_2: \text{ ionisation (1)} \longrightarrow t_+ = 0\cdot46$$

$$\text{ionisation (2)} \longrightarrow t_+ = 0\cdot74$$

For substances undergoing ionisation according to scheme (2) cation transport numbers close to 0·5 are to be expected, and hence it is concluded that triphenylarsine dichloride onises in this manner, *i.e.*,

$$2Ph_3AsCl_2 \rightleftharpoons Ph_3AsCl^+ + Ph_3AsCl_3^-$$
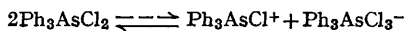
Triphenylarsine dibromide on the other hand undergoes ionisation according to scheme (1),

$$Ph_3AsBr_2 \rightleftharpoons Ph_3AsBr^+ + Br^-$$
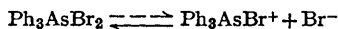
A conductimetric titration of triphenylarsine with bromine (both in methyl cyanide) was carried out in order to confirm the occurrence of the process

$$Ph_3As + Br_2 \longrightarrow Ph_3AsBr_2 \rightleftharpoons \text{ ions}$$
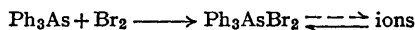
Since triphenylarsine and bromine are effectively non-conductors in methyl cyanide [$Ph_3As, \Lambda_m = 0\cdot004$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0\cdot055$; $Br_2, \Lambda_m = 0\cdot22$ ohm^{-1} cm.^{2} mole^{-1}, at $C_m = 0\cdot033$] such a system would be expected to yield a conductance–composition graph of gently rising slope up to the 1:1 mole ratio, at or near which a change of slope should occur. This was in fact observed and after the 1:1 ratio the conductance rose sharply until the 2:1 ratio ($Br_2:Ph_3As$) was reached at which point there was another marked change in gradient (Fig. 1). This break in the graph along with the high molar conductance of the solution at
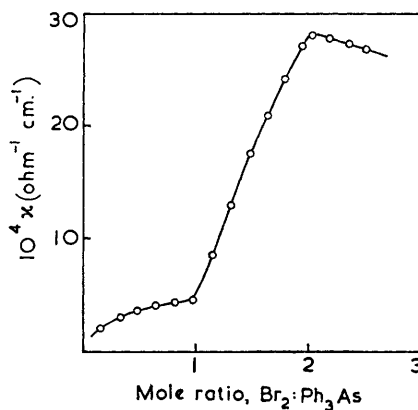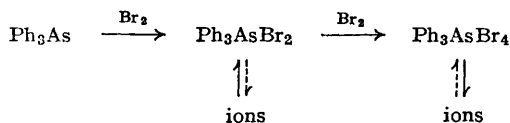

FIG. 1.

this point ($\Lambda_m = 104\cdot2$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0\cdot027$) indicates a conducting species of composition Ph_3AsBr_4. The reaction of triphenylarsine with excess of bromine in methyl cyanide therefore occurs in two distinct stages:

$$Ph_3As \xrightarrow{Br_2} Ph_3AsBr_2 \xrightarrow{Br_2} Ph_3AsBr_4$$
$$\text{ions} \qquad\qquad \text{ions}$$

Beyond the 2:1 ratio the slight decrease in specific conductance may be attributed to dilution of the conducting Ph_3AsBr_4 solution by the added methyl cyanide solution of bromine since the latter does not react further.

In parallel with the conductance changes during the titration, distinct colour changes were observed; the solution remained colourless up to the 1:1 ratio (solid Ph_3AsBr_2 is white) but thereafter became yellow.

Similar experiments were carried out using as titrants iodine and iodine bromide in methyl cyanide and these produced titration graphs which resembled one another very closely (iodine *versus* triphenylarsine is shown in Fig. 2). They differ from the graph of the triphenylarsine–bromine system in that there is no break at the 1:1 mole ratio; a definite break occurs, however, at the 2:1 ratio. The graphs suggest that Ph_3AsI_2 and Ph_3AsIBr do not exist as stable species in methyl cyanide, and that the reactions produce, straight away, the highly-conducting 2:1 adducts, Ph_3AsI_4 and $Ph_3As(IBr)_2$, respectively [$Ph_3AsI_4, \Lambda_m = 100\cdot4$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0\cdot0117$; $Ph_3As(IBr)_2$, $\Lambda_m = 122\cdot0$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0\cdot0127$]. In these titrations the triphenylarsine solutions became red after the first addition of halogen.
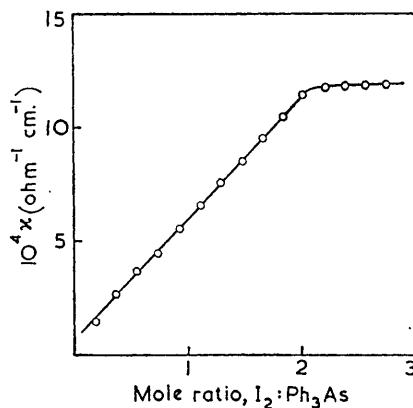

FIG. 2.

It has been possible to obtain these triphenylarsine tetrahalides crystalline by freeze-drying or by adding ether to methyl cyanide solutions containing the halogen and triphenylarsine in the correct ratio.

The magnitude of the molar conductance values of methyl cyanide solutions of these tetrahalides (Table 2) suggests that they are strong 1:1 electrolytes in this solvent and in each case it has been shown by examination of the ultraviolet spectrum of the solution that trihalide ions are present, arising from the ionisation

$$Ph_3AsHal_4 \rightleftharpoons Ph_3AsHal^+ + Hal_3^-$$
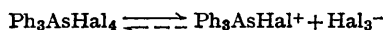
The case of $Ph_3As(IBr)_2$ is of particular interest since there are two possible ionisation schemes:

$$Ph_3As(IBr)_2 \begin{cases} \longrightarrow Ph_3AsI^+ + IBr_2^- & (3) \\ \longrightarrow Ph_3AsBr^+ + I_2Br^- & (4) \end{cases}$$
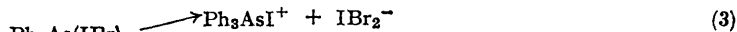
and the ultraviolet spectrum indicates that ions are produced in accordance with the second of these, scheme (4). This is not what would be expected on the basis of the known relative stabilities of the IBr_2^- and I_2Br^- ions:[18] however, in this type of system in which the cation as well as the anion differs in the two possible ionisation schemes, it is clear that the properties of the As–Hal bond in the Ph_3AsHal^+ cation will play a part (apparently in this case a decisive part) in directing the course of ionisation.

[18] E. H. Wiebenga, E. E. Havinga, and K. H. Boswijkt, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 133.

In the titration of triphenylarsine with iodine and iodine bromide (but not bromine) examination of the ultraviolet spectrum of the solution at regular intervals showed that trihalide ion was present from the first addition of titrant onwards. This supports the idea that in these reactions the tetrahalide is formed from the beginning without the intermediate formation of a dihalide. Related to this is the problem of the unexpectedly high molar conductance values found for methyl cyanide solutions of triphenylarsine di-iodide and bromide iodide. These solutions do in fact contain I_3^- and I_2Br^- ions respectively which suggests the occurrence of the disproportionation reactions:

$$2Ph_3AsI_2 \qquad Ph_3As + Ph_3AsI^+ + I_3^-$$

$$2Ph_3AsIBr \rightleftharpoons Ph_3As + Ph_3AsBr^+ + I_2Br^-$$
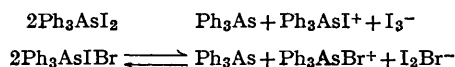
and the apparent molar extinction coefficients of the trihalide ions indicate that these equilibria lie well to the right-hand side. The abnormally high conductance values of these two dihalides are therefore attributed to the tetrahalides formed on disproportionation, although the occurrence, to a small extent, of direct ionisation of Ph_3AsI_2 and Ph_3AsIBr (cf. Ph_3AsBr_2 and Ph_3AsCl_2) cannot be ruled out.

The triphenylarsine tetrahalides so far discussed are members of a series $Ph_3AsI_nBr_{4-n}$, the remaining members of which ($n = 1$ and 3) have been obtained by the reaction of a dihalide and halogen in a suitable solvent:

$$Ph_3AsIBr_3 \longleftarrow Ph_3AsBr_2 + IBr \qquad \qquad (5)$$

$$Ph_3AsI_3Br \longleftarrow Ph_3AsIBr + I_2 \qquad \qquad (6)$$
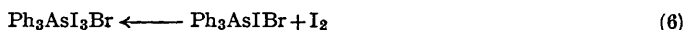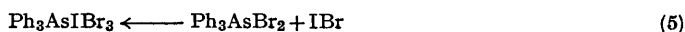
These are crystalline solids the methyl cyanide solutions of which, like those of their analogues, are good electrolytic conductors (Table 2), and from the ultraviolet spectra of these solutions it is clear that these compounds also are halogenotriphenylarsonium trihalides of the forms

$$Ph_3AsIBr_3 \equiv [Ph_3AsBr^+][IBr_2^-]$$

$$Ph_3AsI_3Br \equiv [Ph_3AsBr^+][I_3^-],$$
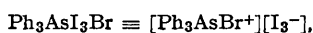
and not the possible alternatives with iodine in the cation.

The pattern of ionisation followed by the compounds in this series leads us to suggest that in similar series involving mixtures of other halogens, the halogen of lower atomic number will reside in the cation. That is, the formation of the cation containing the arsenic–halogen bond of greater strength is the favoured process and preliminary results of a study of the series $Ph_3AsI_nCl_{4-n}$ in methyl cyanide are in keeping with this.

The formation of Ph_3AsIBr_3 and Ph_3AsI_3Br [equations (5) and (6)] can be followed conductimetrically in methyl cyanide when it is found that a distinct break occurs in the conductance–composition graphs at the 1:1 mole ratio of Ph_3AsHal_2 to Hal_2 (at the breaks, $\Lambda_m = 97\cdot4$, $88\cdot7$ ohm^{-1} cm.^{2} mole^{-1} at $C_m = 0\cdot0402$, $0\cdot0272$, respectively, for Ph_3AsIBr_3 and Ph_3AsI_3Br). The two graphs are very similar to each other, and that of the Ph_3AsBr_2–IBr system is shown in Fig. 3. In this system which gives rise to Ph_3AsIBr_3 the process occurring is simply the addition of IBr to the Br^- ion, thus:

$$Ph_3AsBr_2 \rightleftharpoons Ph_3AsBr^+ + Br^- \xrightarrow{\text{IBr}} Ph_3AsBr^+ + IBr_2^-$$
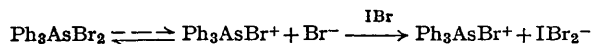
but in the other system (Ph_3AsI_2–IBr) the situation is less simple since the triphenylarsine di-iodide is present essentially as an equimolar mixture of triphenylarsine and triphenylarsine tetraiodide in methyl cyanide solution and the iodine bromide added will react with the triphenylarsine in the usual way:

$$2Ph_3AsI_2 \rightleftharpoons Ph_3As + Ph_3AsI_4$$

$$\Big\updownarrow \text{ 2 IBr}$$

$$Ph_3As(IBr)_2$$
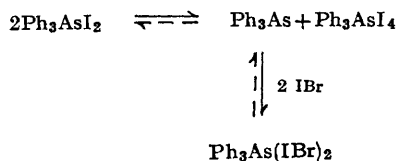
Thus the solution at the 1:1 ratio should contain a mixture of $Ph_3AsI^+I_3^-$ and $Ph_3AsBr^+I_2Br^-$. However, the ultraviolet spectrum of the solution shows absorption due to I_3^- but not I_2Br^- which implies the occurrence of the process

$$Ph_3AsI^+ + I_2Br^- \rightleftharpoons Ph_3AsBr^+ + I_3^- \qquad (7)$$
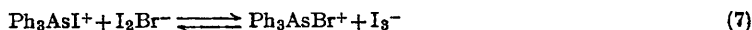
so that at the 1:1 ratio only $Ph_3AsBr^+I_3^-$ is present in detectable amounts. From the nature of the four ions involved in this exchange it is not surprising that the equilibrium lies well to the right-hand side, and by way of confirmation a comparison was made of the ultraviolet spectra of methyl cyanide solutions of $Ph_3AsI^+I_3^-$ and $Me_4N^+I_2Br^-$ with the spectrum of a solution containing equimolar amounts of these compounds; again it was found that the latter solution showed absorption due to I_3^- ion but that due to I_2Br^- was not detected.
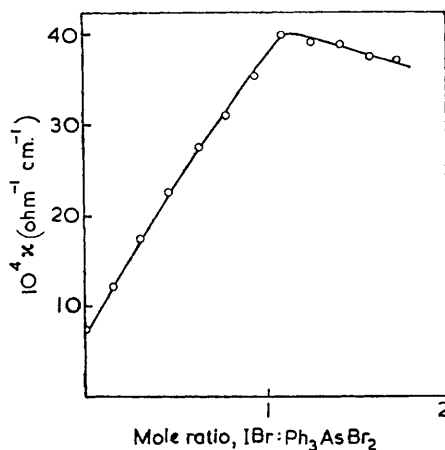

FIG. 3.

An X-ray crystallographic examination of the compounds in the series $Ph_3AsI_nBr_{4-n}$ is being undertaken by Dr. G. A. Sim* and Mr. R. S. McEwen of this Department and the results obtained so far show that Ph_3AsIBr_3 and $Ph_3AsI_2Br_2$ have lattices built of the same ions as those which have been found to be present in the methyl cyanide solutions of the compounds.

EXPERIMENTAL

Since many of the halides involved in this work are moisture sensitive, special care was taken to prevent their hydrolysis. Apparatus, designed so that compounds and solutions were not exposed to a moist atmosphere, was baked-out before use and solvents were thoroughly purified and dried. The compounds were transferred and solutions prepared within a nitrogen-filled dry-box containing phosphoric oxide. Pure anhydrous methyl cyanide suitable for conductance studies was prepared by the method of Smith and Witten[19] (the specific conductance of the purified product was *ca.* 10^{-7} ohm^{-1} cm.$^{-1}$ at 25°). Triphenylarsine was prepared by the Wurtz-type reaction between arsenic trichloride and chlorobenzene.[20]

Preparation of Triphenylarsine Dihalides.—Triphenylarsine dichloride. Dry chlorine gas in a stream of nitrogen was bubbled into a solution of triphenylarsine in carbon tetrachloride until the solvent assumed a pale yellow colour. Cooling was necessary. White crystals of the dichloride precipitated and were filtered off and washed with anhydrous ether; they had m. p. 205° (Found: Cl, 19·1. Calc. for $C_{18}H_{15}AsCl_2$: Cl, 18·8%).

Triphenylarsine dibromide. A solution of bromine (1809 mg.) in methyl cyanide (30 ml.) was

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* Department of Chemistry, University of Illinois, Urbana, Ill. U.S.A.

[19] J. W. Smith and L. B. Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.
[20] R. L. Shriner and C. N. Wolf, *Org. Synth.*, 1950, **30**, 95.

added to a solution of triphenylarsine (3468 mg.) in methyl cyanide (20 ml.). Heat was evolved and white crystals precipitated, m. p. 215° (Found: Br, 34·1. Calc. for $C_{18}H_{15}AsBr_2$: Br, 34·3%).

Triphenylarsine di-iodide. The method described by W. Steinkopf and G. Schwen[2] was used. A saturated solution of iodine (2·500 g.) in anhydrous petroleum (b. p. 100—120°) was added to a saturated solution of triphenylarsine (3·014 g.) in the same solvent. Heat was evolved and at first some purple crystals of triphenylarsine tetraiodide appeared on the wall of the vessel. The solution was decanted and subsequently yellow crystals of the di-iodide were deposited: they had m. p. 138—140° (Found: I, 45·4. Calc. for $C_{18}H_{15}AsI_2$: I, 45·4%).

Triphenylarsine bromide iodide. Iodine bromide (2·601 g.) in methyl cyanide (15 ml.) was added to triphenylarsine (3·850 g.) dissolved in the minimum amount of methyl cyanide. Heat was evolved and yellow *crystals*, m. p. 154—155°, were deposited (Found: C, 42·1; H, 2·9; Br, 15·1; I, 24·2. $C_{18}H_{15}AsBrI$ requires C, 42·2; H, 2·9; Br, 15·6; I, 24·7%).

Preparation of Triphenylarsine Tetrahalides.—Triphenylarsine tetrabromide. Bromine (3501 mg.) in methyl cyanide (20 ml.) was added to triphenylarsine (3360 mg.) in methyl cyanide (30 ml.). Heat was evolved and white crystals of triphenylarsine dibromide were precipitated at first but redissolved on continued addition of the bromine solution. Anhydrous ether was then added until an orange oil separated and when this oil was shaken with ether hygroscopic orange *crystals* formed. These were washed with anhydrous ether and dried under vacuum; they had m. p. 89° (Found: C, 34·9; H, 2·8; Br, 51·6. $C_{18}H_{15}AsBr_4$ requires C, 34·5; H, 2·4; Br, 51·1%). The compound was also obtained by freeze-drying a methyl cyanide solution of triphenylarsine plus excess of bromine.

Triphenylarsine tribromide iodide. Iodine bromide (2358 mg.) in methyl cyanide (20 ml.) was added to a suspension of triphenylarsine dibromide (5291 mg.) in methyl cyanide (50 ml.). The dibromide dissolved, heat was evolved, and on the addition of ether orange *crystals* were precipitated; they had m. p. 120—121° (Found: C, 32·4; H, 2·4; As, 11·1; Br, 35·4; I, 18·7. $C_{18}H_{15}AsBr_3I$ requires C, 32·1; H, 2·2; As, 11·1; Br, 35·6; I, 18·9%).

Triphenylarsine dibromide di-iodide. Iodine bromide (3610 mg.) in methyl cyanide (50 ml.) was added to triphenylarsine (2680 mg.) in methyl cyanide (30 ml.). Heat was evolved, and the addition of anhydrous ether brought the precipitation of red *crystals*, m. p. 104° (Found: C, 30·9; H, 2·2; As, 10·2; Br, 22·1; I, 35·0. $C_{18}H_{15}AsBr_2I_2$ requires C, 30·0; H, 2·1; As, 10·4; Br, 22·2; I, 35·3%). An alternative route to this compound is the reaction of iodine with triphenylarsine dibromide in methyl cyanide.

Triphenylarsine bromide tri-iodide. Iodine (992 mg.) in carbon tetrachloride (200 ml.) was added to triphenylarsine bromide iodide (2005 mg.) suspended in carbon tetrachloride (50 ml.) and the mixture shaken for 24 hr., after which the carbon tetrachloride contained in suspension red *crystals*, m. p. 115—116° (Found: Br, 10·8; I, 49·1. $C_{18}H_{15}AsBrI_3$ requires Br, 10·4; I, 49·7%). Attempts to prepare this compound from methyl cyanide solution gave a purple substance of low bromine content (Found: C, 27·0; H, 1·9; Br, 2·8; I, 60·4%) which is thought to be a mixture containing triphenylarsine tetraiodide as chief component. This could arise on account of the occurrence, in methyl cyanide, of equilibrium (7) coupled with the low solubility of the tetraiodide; and during crystallisation of the tetraiodide, Ph_3AsBr^+ (or, less likely, I_2Br^-) ions may replace to some extent the geometrically similar Ph_3AsI^+ (or I_3^-) ions. For example, the formulation $[(Ph_3AsI^+)_{0.7}(Ph_3AsBr^+)_{0.3}]I_3^-$ requires C, 27·0; H, 1·9; Br, 3·0; I, 58·7%.

Triphenylarsine tetraiodide. Iodine (5000 mg.) dissolved in methyl cyanide (50 ml.) was added to triphenylarsine (3019 mg.) in methyl cyanide (20 ml.). Heat was evolved and purple crystals appeared immediately, m. p. 139—140° (Found: I, 62·1. Calc. for $C_{18}H_{15}AsI_4$: I, 62·4%).

Methods of Analysis.—Halogen was determined by Volhard's method after preliminary treatment of the compounds. Before analysis the solids were hydrolysed with excess of 2M-sodium hydroxide solution for several hours in a sealed flask. This solution was then boiled to ensure complete reaction, cooled, acidified with sulphuric acid, and then treated with sulphur dioxide to reduce any hypohalite ion present. Excess of sulphur dioxide was removed by boiling and the solution was cooled and neutralised with ammonium hydroxide solution. Halide ion was then estimated by the Volhard method.

In the case of compounds containing both iodine and bromine, the total halogen content was measured as above. To determine bromine and iodine individually a modification of Jannasch's method of selective oxidation was used.[21] Aliquot portions of the hydrolysate were acidified with

[21] F. Sutton, "A Systematic Handbook of Volumetric Analysis" (revised by J. Grant), Butterworths Scientific Publications, London, 1955, p. 351.

glacial acetic acid, and addition of hydrogen peroxide (20 vol.) brought about selective oxidation of I^- to I_2 which was steam-distilled in an all-glass apparatus into an ammoniacal hydrazine solution and the resultant I^- determined by Volhard's method. The residual solution containing Br^- was neutralised with ammonium hydroxide solution, acidified with sulphuric acid, then treated with hydrogen peroxide. The liberated Br_2 was distilled into ammoniacal hydrazine as before and the Br^- estimated in the usual way.

Carbon, hydrogen, and arsenic analyses were carried out microanalytically (by A. Bernhardt, Max-Planck-Institut, Mülheim, Germany).

Conductance Measurements.—The conductance cell was of the dipping electrodes type. The electrode supports passed through a standard ground glass cone (B 24) which fitted a vessel containing the solution. In this way the solution was not in contact with the atmosphere during the measurement of conductance. The electrodes consisted of smooth platinum discs of radius *ca.* 0·4 cm. and placed *ca.* 1 cm. apart. The cell constant was 0·5280 cm.$^{-1}$. Measurements were made at 25° using a Phillips resistance bridge (Type GM 4249). Conductance values for the triphenylarsine dihalides have been given in Table 1 and those of the tetrahalides are recorded below (Table 2).

TABLE 2.

The electrolytic conductance of the compounds $Ph_3AsI_nBr_{4-n}$ in methyl cyanide at 25°.

Compound	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	C_m (mole l.$^{-1}$)	Λ_m (ohm^{-1} cm.^{2} mole^{-1})
Ph_3AsBr_4	0·49	0·0042	116·6
	0·77	0·0068	113·2
	1·20	0·0120	100·0
Ph_3AsIBr_3	0·35	0·0028	125·0
	1·08	0·0098	110·2
	1·56	0·0161	97·5
$Ph_3AsI_2Br_2$	0·54	0·0042	128·5
	1·10	0·0091	120·8
	1·80	0·0161	112·5
Ph_3AsI_3Br	0·27	0·0021	128·5
	0·70	0·0066	106·0
	0·82	0·0085	96·5
Ph_3AsI_4	0·29	0·0021	138·0
	0·71	0·0057	124·5
	1·16	0·0100	116·0

Conductimetric Titrations.—The apparatus and techniques were the same as those illustrated and described elsewhere.[22]

Electrolysis Experiments.—These were carried out in a Hittorf-type cell with a U-shaped middle compartment, and the results were considered valid only if the composition of the solution in this compartment after electrolysis differed negligibly from the initial composition. A full description of the technique has been given previously.[22]

Ultraviolet Spectra.—These were recorded using a Perkin-Elmer Model 137 u.v.-vis. Spectrophotometer. Stoppered quartz cells (path lengths 0·2 cm. and 0·5 cm.) were used to contain the solutions being investigated, and measurements were made at room temperature (*ca.* 20°). The absorption data of the triphenylarsine tetrahalides in methyl cyanide are [λ_{max} (mμ), ε in parentheses]: Ph_3AsBr_4, 269 (53,900); Ph_3AsIBr_3, 257 (53,100); $Ph_3AsI_2Br_2$, 275, 351 (44,500, 9670); Ph_3AsI_3Br, 289, 360 (41,500, 14,200); Ph_3AsI_4, 292, 362 (57,700, 31,000).

These wavelengths can be used as a qualitative indication of the particular trihalide ion present in solution. Ions of type $I_nBr_{3-n}^-$ have a high absorption peak in the far ultraviolet and a low peak in the visible or near ultraviolet (this latter was not always observed), and Popov and Swensen[23] have quoted the following figures: Br_3^-, 269 mμ (ε 55,000); IBr_2^-, 256 and 370 mμ (ε 54,000 and 606); I_2Br^-, 280 (our value 277) and 351 mμ (ε 40,600 and 11,600); I_3^-, 291 and 360 mμ (ε 38,800 and 25,500). Benzenoid absorption at about 250 mμ due to the phenyl groups in the triphenylarsine tetrahalides can be ignored on account of its much lower magnitude.

Conductimetric Titrations.—*Iodine against triphenylarsine:* from 0:1 to 2:1 mole ratio, peaks at 291 and 360 mμ.

[22] G. S. Harris and D. S. Payne, *J.*, 1956, 3038.
[23] A. I. Popov and R. F. Swensen, *J. Amer. Chem. Soc.*, 1955, **77**, 3724.

Iodine bromide against triphenylarsine: from 0:1 to 2:1 mole ratio, peaks at 275 and 351 mμ.
Iodine bromide against triphenylarsine dibromide: from 0:1 to 1:1 mole ratio, peak at 257 mμ
Iodine bromide against triphenylarsine di-iodide: from 0:1 to 1:1 mole ratio, peaks at 289 and 360 mμ.

Triphenylarsine tetraiodide (1 *mole*) + *tetramethylammonium bromoiodoiodate* (*I*) (1 *mole*) *in methyl cyanide:* peaks at 292 and 360 mμ.

Triphenylarsine di-iodide in methyl cyanide: peaks at 292 and 362 mμ ($\varepsilon = 28{,}900$ and $15{,}300$).

Triphenylarsine bromide iodide in methyl cyanide: peaks at 275 and 353 mμ ($\varepsilon = 22{,}600$ and $4{,}490$).