Chlorine-containing Mixed Halogen Adducts of Triphenylphosphine, Triphenylarsine, and Triphenylstibine

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Conductometric titrations of PPh_3Cl_2 and $AsPh_3Cl_2$ with halogens and interhalogens show that the reactions are simple leading to the formation of adducts of types $MPh_3Cl_2X_2$ (M = P or As; X_2 = Br_2, I_2, ICl, or IBr) and MPh_3Cl_5I (M = P or As) in acetonitrile. The high molar conductances of the adducts suggest their formulation as $MPh_3Cl^+ClX_2^-$ and $MPh_3Cl^+ICl_4^-$ respectively. The polyhalide ions present have been identified from the u.v. spectra of the acetonitrile solutions. The reactions of MR_3 (M = P, As, or Sb) with ICl and ICl_3 also give rise to highly conducting adducts in acetonitrile but the conductometric titration graphs indicate that these reactions are complex. Some of the adducts (PPh_3Cl_3I, $AsPh_3Cl_3I$, and $AsPh_3Cl_5I$) have been obtained as crystalline solids.

THE triphenyl derivatives of phosphorus, arsenic, and antimony have long been known to react with halogens to form 1 : 1 and in some cases 2 : 1 adducts, the so-called 'dihalides' (*e.g.* PPh_3Cl_2) and 'tetrahalides' (*e.g.* PBr_4Ph_3) respectively.[1,2] Recent investigations on this class of compound have included *X*-ray diffraction,[3] spectroscopic,[4,5] and electrolytic conductance [6] studies, and these have revealed variety in the nature of the adducts, showing that some of the compounds are molecular (*e.g.* $AsPh_3F_2$),[3] whereas others consist of ions in the solid state (*e.g.* PBr_2Ph_3).[4] The conductance studies have demonstrated that some of the molecular adducts undergo ionisation under the influence of a suitable solvent (*e.g.* $AsPh_3Cl_2$ in acetonitrile solution).[7]

In earlier papers [6-8] we have reported the preparation and the results of electrolytic conductance studies of a number of halogen adducts of triphenylarsine and triphenylphosphine containing both bromine and iodine. This included compounds in the two series represented by the general formula $MBr_nPh_3I_{4-n}$ (M = P or As; n = 1—3). In these studies the technique of conductometric titration was employed with profit to follow the course of the reaction of MPh_3 with halogen (or interhalogen) and to predict compound formation in the various systems investigated. In this paper we describe an extension of our studies to the investigation of some reactions leading to the formation of chlorine-containing mixed halogen adducts of triphenylphosphine, triphenylarsine, and triphenylstibine.

RESULTS AND DISCUSSION

As one possible route to the chlorine-containing adducts we have examined reactions of MPh_3Cl_2 (M = P, As, or Sb) with certain halogens (I_2 and Br_2) and interhalogens (IBr, ICl, and ICl_3). The graphs obtained from the conductometric titrations of these systems in acetonitrile were of three types, representative examples of which are shown in Figure 1. The reactions of PPh_3Cl_2 and $AsPh_3Cl_2$ with ICl, IBr, and ICl_3 gave graphs of type A; the reactions of PPh_3Cl_2 and $AsPh_3Cl_2$ with Br_2 and I_2 gave graphs of type B. In the reactions involving $SbPh_3Cl_2$ with these halogens and interhalogens graphs of type C were obtained. The type A conductometric titration graph with its distinct break at the 1 : 1 mole ratio gives a clear indication of tetrahalide (MPh_3X_4) formation in these systems, *e.g.* equation (1).

$$PPh_3Cl_2 + ICl \longrightarrow PPh_3Cl_3I \qquad (1)$$

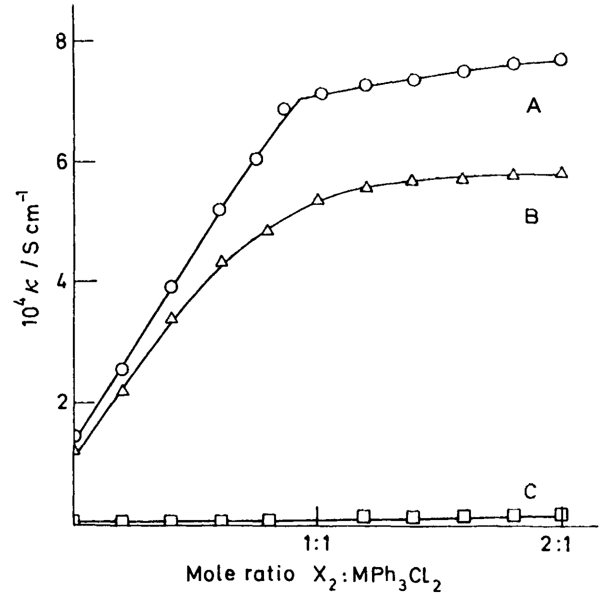


FIGURE 1 Conductometric titrations of MPh_3Cl_2 with X_2: A, PPh_3Cl_2–ICl; B, PPh_3Cl_2–Br_2; C, $SbPh_3Cl_2$–Br_2

The high values of molar conductance at the 1 : 1 ratio (Λ_M *ca.* 100—130 S cm^2 mol^{-1}; concentration *ca.* 0.003 mol dm^{-3}) are indicative of strong 1 : 1 electrolyte behaviour in acetonitrile, thus for example, PPh_3Cl_3I = $PPh_3Cl^+ICl_2^-$. The nature of the ions was in each case deduced from the ultraviolet spectra of the solutions which gave an indication of the particular trihalide ion present.[6,9] In the systems which gave a graph of type B the components interact similarly to give tetrahalides. However the rather blunt break in the conductometric titration graphs indicates incomplete reaction at the

$$PPh_3Cl_2 + Br_2 \rightleftharpoons PBr_2Ph_3Cl_2 \qquad (2)$$
$$(= PPh_3Cl^+Br_2Cl^-)$$

1 : 1 equivalence point, *e.g.* equation (2). Such behaviour is generally attributed to the tendency of a

product of the reaction to dissociate, and in these cases the labile species is the particular trihalide ion formed (Br_2Cl^- or I_2Cl^-). These trihalide ions are members of the category of unsymmetrical trihalide ions which are known to dissociate readily.[9,10] As would be expected the molar conductance at the 1 : 1 ratio is lower in these cases (Λ_M *ca.* 80—85 S cm^2 mol^{-1}; concentration *ca.* 0.003 mol dm^{-3}).

The analogous reactions of $SbPh_3Cl_2$ gave no indication of ionic adduct formation in solution. Addition of halogen or interhalogen to the $SbPh_3Cl_2$ solution produced a negligible rise in conductance.

The detailed findings of the conductometric titrations are summarised in Table 1. It is of interest to note that in these systems chloro-arsonium and chloro-phosphonium cations are invariably formed rather than the possible bromo- or iodo- alternatives. This pattern of behaviour matches that of other triphenylarsine and triphenylphosphine mixed tetrahalides in which it is found that the halogen of lowest atomic number present appears in the cation.[7,8]

TABLE 1

Results of conductometric titrations of MPh_3Cl_2 ($M = P$ or As) with ICl, IBr, ICl_3, Br_2, and I_2

	Reactants	Stoicheiometry of adduct formed in solution	Ions in solution
Type A graph	$PPh_3Cl_2 + ICl$	PPh_3Cl_3I	$[PPh_3Cl][ICl_2]$
	$PPh_3Cl_2 + IBr$	$PBrPh_3Cl_2I$	$[PPh_3Cl][IBrCl]$
	$PPh_3Cl_2 + ICl_3$	PPh_3Cl_5I	$[PPh_3Cl][ICl_4]$
	$AsPh_3Cl_2 + ICl$	$AsPh_3Cl_3I$	$[AsPh_3Cl][ICl_2]$
	$AsPh_3Cl_2 + IBr$	$AsBrPh_3Cl_2I$	$[AsPh_3Cl][IBrCl]$
	$AsPh_3Cl_2 + ICl_3$	$AsPh_3Cl_5I$	$[AsPh_3Cl][ICl_4]$
Type B graph	$PPh_3Cl_2 + I_2$	$PPh_3Cl_2I_2$	$[PPh_3Cl][I_2Cl]$
	$PPh_3Cl_2 + Br_2$	$PBr_2Ph_3Cl_2$	$[PPh_3Cl][Br_2Cl]$
	$AsPh_3Cl_2 + I_2$	$AsPh_3Cl_2I_2$	$[AsPh_3Cl][I_2Cl]$
	$AsPh_3Cl_2 + Br_2$	$AsBr_2Ph_3Cl_2$	$[AsPh_3Cl][Br_2Cl]$

Attempts were made to isolate the adducts shown by conductometric titration to exist in solution but this was successful in only three cases. The adducts isolated as pure crystalline compounds were: PPh_3Cl_3I, $AsPh_3Cl_3I$, and $AsPh_3Cl_5I$. These had high molar conductances in acetonitrile (Λ_M *ca.* 105—115 S cm^2 mol^{-1}; concentration = 0.01 mol dm^{-3}) thus confirming their ionic nature. The partial lack of success in obtaining chlorine-containing adducts as solids contrasts with the relative ease with which all of the compounds in the two series $MBr_nPh_3I_{4-n}$ ($M = P$ or As) were obtained.[6,7] This may be put down to inherent instability of the solid adducts arising from the fact that certain chlorine-containing polyhalide ions, *e.g.* Br_2Cl^-, have a tendency to dissociate to halogen and halide.[9,10] An adduct containing three halogens, $AsBr_2Ph_3ClI$, was suggested from the conductometric titration of $AsBr_2Ph_3$ with ICl in acetonitrile and was subsequently obtained as a red crystalline compound. The graph was of type A giving a distinct break at the 1 : 1 mole ratio and the u.v. spectrum of the solution revealed the presence of the IBr_2^- ion. The reaction occurring was therefore that shown in equation (3). It is noteworthy that the ions

$$AsBr_2Ph_3 + ICl \longrightarrow AsBr_2Ph_3ClI \quad (\equiv AsPh_3Cl^+IBr_2^-) \qquad (3)$$

formed by this adduct are those expected from the above mentioned rule even although no As–Cl bonds were present before adduct formation.

The other route to chlorine-containing mixed-halogen adducts investigated was the reaction of MPh_3 ($M = P$, As, or Sb) with iodine chloride and iodine trichloride. These reactions were studied by conductometric titration and the results are summarised as follows.

The PPh_3–ICl *System*.—Conductometric titration of triphenylphosphine with iodine chloride in acetonitrile gave the graph (D) shown in Figure 2, demonstrating that this system is quite unlike the PPh_3–IBr [6] system in its behaviour with respect to the positions of the breaks in the graph and the occurrence in this case of a conductance maximum (although a conductometric titration graph displaying a maximum has been observed in some systems involving triphenylstibine [6]). The mole ratios at which the breaks occurred were (unexpectedly but reproducibly) close to 0.66 : 1 and 1.33 : 1 (*i.e.* ICl : PPh_3 = 2 : 3 and 4 : 3). In the course of the titration the solution was pale yellow up to the first break and thereafter assumed a red colour which darkened progressively. Ultraviolet spectra of the solution indicated the presence of tri-iodide ion between the conductance maximum (0.66 : 1 ratio) and the conductance minimum (1.33 : 1 ratio). It is clear that this reaction is more complicated than any of the triphenylphosphine–halogen reactions previously studied in acetonitrile [6] and in consequence a simple reaction scheme involving the formation of firstly a 1 : 1 then a 2 : 1 adduct is not adequate; however, Scheme 1, involving the formation of a mixture of adducts at each stage is suggested to explain the con-

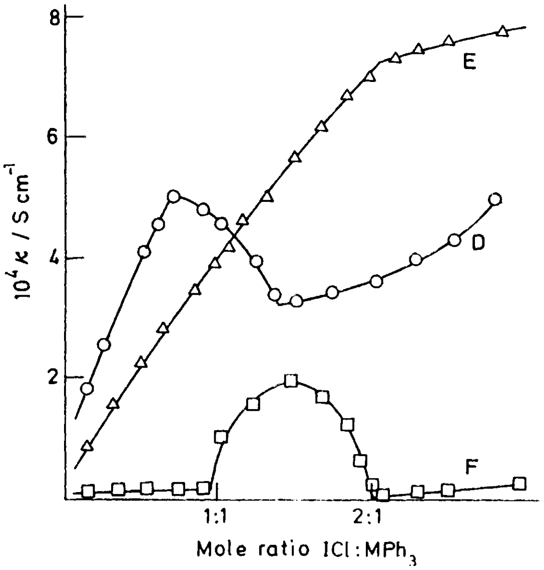
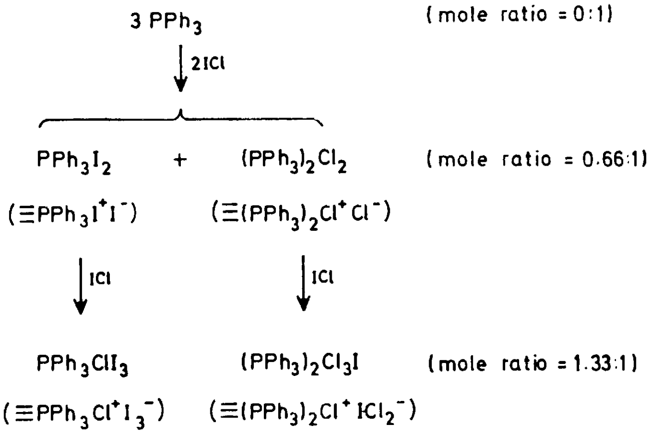


FIGURE 2 Conductometric titrations of MPh_3 with ICl: D, PPh_3–ICl; E, $AsPh_3$–ICl; F, $SbPh_3$–ICl

ductometric titration results. Further support for this scheme comes from the isolation of PPh_3I_2 from the solution at the 0.66 : 1 molar ratio; also, the compound of stoicheiometry $PPh_3Cl_{0.5}I_{1.5}$ [formulated as $(PPh_3)_2Cl^+I_3^-$] [11] was isolated at the 1.33 : 1 ratio thus lending support to the formation of the ionic species suggested in Scheme 1 at this mole ratio. The crystallisation of $(PPh_3)_2Cl^+I_3^-$ rather than $(PPh_3)_2Cl^+ICl_2^-$ is presumably a solubility effect.

The need to postulate the formation of an adduct of formula $(PPh_3)_2Cl_2$ was novel and attempts to obtain this as a crystalline compound were not successful. However, indirect evidence supports its existence in solution: (a) conductometric titration (in acetonitrile) of triphenylphosphine dichloride with triphenylphosphine results in a slight increase in conductance of the dichloride solution and the graph has a 1 : 1 break indicating the occurrence of reaction (4); (b) depression of



SCHEME 1

$$PPh_3Cl_2 + PPh_3 \longrightarrow (PPh_3)_2Cl_2 \quad (4)$$
$$(\equiv PPh_3Cl^+Cl^-) \qquad (\equiv (PPh_3)_2Cl^+Cl^-)$$

freezing point determination of a 1 : 1 molar mixture of PPh_3Cl_2 and PPh_3 in nitrobenzene was in keeping with a two particle system and hence interaction of the components in the manner indicated above [observed molecular weight, 296; calculated average molecular weight for $(PPh_3)_2Cl^+Cl^-$, 297.8].

The $AsPh_3$–ICl *System*.—The plot of conductance against composition for this system (E in Figure 2) resembled that of the triphenylarsine–iodine bromide system giving a break at the 2 : 1 (ICl : $AsPh_3$) ratio only. This shows that iodine chloride reacts with triphenylarsine to produce, immediately, the highly conducting 2 : 1 adduct $AsPh_3Cl_2I_2$ (at 2 : 1 mole ratio, Λ_M 77 S cm^2 mol^{-1}; concentration, 0.007 mol dm^{-3}), equation (5).

$$AsPh_3 + 2ICl \longrightarrow AsPh_3Cl_2I_2 \quad (5)$$
$$(\equiv AsPh_3Cl^+I_2Cl^-)$$

Attempts to isolate the adduct $AsPh_3Cl_2I_2$ from this reaction again failed as in the case of the $AsPh_3Cl_2 + I_2$ reaction. Crystalline products were obtained but these invariably had too high a percentage of iodine; it is thought that this arises from replacement of some I_2Cl^- by I_3^- in the solid since it is known that in solution the I_2Cl^- ion undergoes disproportionation giving I_3^- and ICl_2^-.[9]

The $SbPh_3$–ICl *System*.—This system, like the $SbPh_3$–IBr system [6] gave a conductometric titration graph with a hump at the mole ratio 1.5 : 1 (ICl : $SbPh_3$) (F, Figure 2). There was virtually no rise in conductance when iodine chloride was added to the triphenylstibine solution as far as the 1 : 1 ratio. From that point on the conductance began to rise, reached a maximum at 1.5 : 1 (ICl : $SbPh_3$), then fell to a low value again and levelled off at 2 : 1 giving a break at this ratio. The triphenylstibine dihalides, $SbPh_3ClI$ and $SbPh_3Cl_2$ were isolated from the solution at the 1 : 1 and 2 : 1 ratios respectively. Triphenylstibine dihalides are known to be virtually non-conducting in acetonitrile [6] thus explaining the low conductance values observed at the 1 : 1 and 2 : 1 ratios. The reactions completed in solution at the 1 : 1 and 2 : 1 mole ratios may be represented by equations (6) and (7).

$$SbPh_3 + ICl \longrightarrow SbPh_3ClI \quad (0:1 \longrightarrow 1:1) \quad (6)$$

$$SbPh_3ClI + ICl \longrightarrow SbPh_3Cl_2 + I_2 \quad (1:1 \longrightarrow 2:1) \quad (7)$$

Examination of the u.v. spectrum of the solution at different compositions indicated the presence of tri-iodide ion between mole ratios 1 : 1 and 2 : 1. Therefore it must be assumed that as the reaction proceeds from the 1 : 1 to the 2 : 1 ratio the iodine formed combines with unreacted $SbPh_3ICl$ to produce, temporarily, the ionic tetrahalide $SbPh_3ClI_3$ ($\equiv SbPh_3Cl^+I_3^-$). That is, between these ratios the reaction occurs in two stages, as shown in (8), thus accounting for the conductance

$$SbPh_3ClI \xrightarrow{\frac{1}{2}ICl} \tfrac{1}{2}SbPh_3Cl_2 + \tfrac{1}{2}SbPh_3ClI_3 \xrightarrow{\frac{1}{2}ICl} \quad (8)$$
$$(\equiv SbPh_3Cl^+I_3^-)$$
$$SbPh_3Cl_2 + I_2$$

maximum at the 1.5 : 1 mole ratio. Absorption in the u.v. spectrum due to tri-iodide ion also reaches a maximum at this ratio. That $SbPh_3ClI_3$ does form in acetonitrile has been confirmed from conductometric titration of $SbPh_3ClI$ with I_2. The graph resembled type A (Figure 1) displaying a steep increase in conductance up to the 1 : 1 ratio and at this point a distinct break occurred. However attempts to prepare the tetrahalide $SbPh_3ClI_3$ as a crystalline solid by the usual methods were not successful. Previous studies have also failed to yield crystalline tetrahalides of triphenylstibine even although their existence in solution has been demonstrated.[6]

The PPh_3–ICl_3 *System*.—The conductometric titration for this system (G, Figure 3) showed that the reaction between triphenylphosphine and iodine trichloride is complex and that it gives the same adduct, the 1 : 1 compound PPh_3Cl_3I, as is obtained from the PPh_3Cl_2–ICl system. The graph has three breaks (at mole ratios $ICl_3 : PPh_3 = 0.5 : 1$, 0.66 : 1, and 1 : 1) suggesting that the reaction leading to the 1 : 1 adduct occurs in three stages. During titration the solution was pale yellow until the 0.5 : 1 ratio; thereafter it developed a red colour which subsequently diminished as the 1 : 1 ratio was approached. The u.v. spectrum of the solution between mole ratio 0.5 : 1 and 1 : 1 showed the presence of iodine and beyond the 1 : 1 ratio the presence of the ICl_2^- ion was indicated. The dihalide, PPh_3ClI, was isolated at the 0.5 : 1 ratio, and the tetrahalide, PPh_3Cl_3I, at the 1 : 1 ratio. These observations and the features of the conductometric titration graph may be explained by the occurrence of the sequence of reactions in Scheme 2 from the beginning of the reaction up to the 1 : 1 mole ratio of reactants.

The $AsPh_3$–ICl_3 *System*.—The form of the conductometric titration graph (H, Figure 3) shows that this system behaves quite differently from the preceding one. The solution acquired a deep red colour from the first addition of iodine trichloride and the conductance rose gradually to the 0.66 : 1 ($ICl_3 : AsPh_3$) mole ratio. At this point it began to rise steeply and the colour of the solution turned to an intense yellow; a distinct break occurred at the 1 : 1 ratio. The stoicheiometry of the first stage of the reaction may be represented as equation (9). The products of this stage will interact (as has been shown earlier) to give some $AsPh_3Cl_2I_2$ ($\equiv AsPh_3Cl^+I_2Cl^-$) and this accounts for the increase in conductance and for the colour of the solution up to this point. The second stage of the reaction (from mole ratio 0.66 : 1 to 1 : 1) involves the formation of the adduct, $AsPh_3Cl_3I$, equation (10). Examination of the u.v. spectrum of the solution at points in the titration confirmed the presence of I_2Cl^- from the beginning to the 0.66 : 1 ratio and thereafter the presence of ICl_2^- was indicated. The solid adduct, $AsPh_3Cl_3I$ was obtained as yellow crystals at the 1 : 1 ratio. The reason why this system behaves differently from the PPh_3–ICl_3 system in the first stage is presumably a reflection of the apparent instability of $AsPh_3ClI$ in acetonitrile; this is deduced from the absence of a 1 : 1 break in the conductometric titration graph of the $AsPh_3$–ICl system.

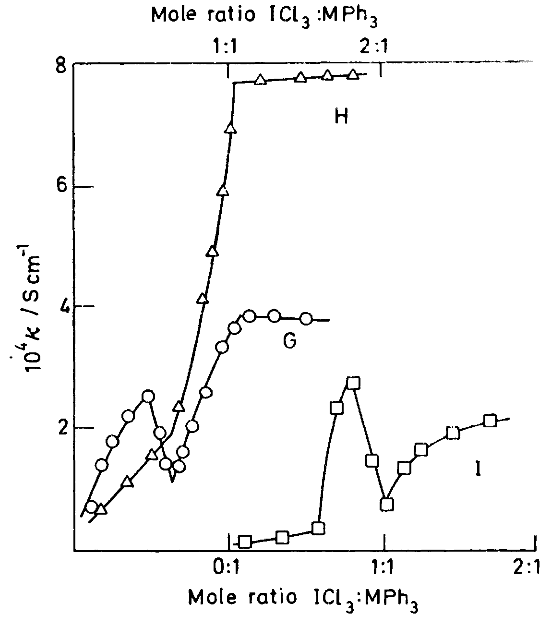
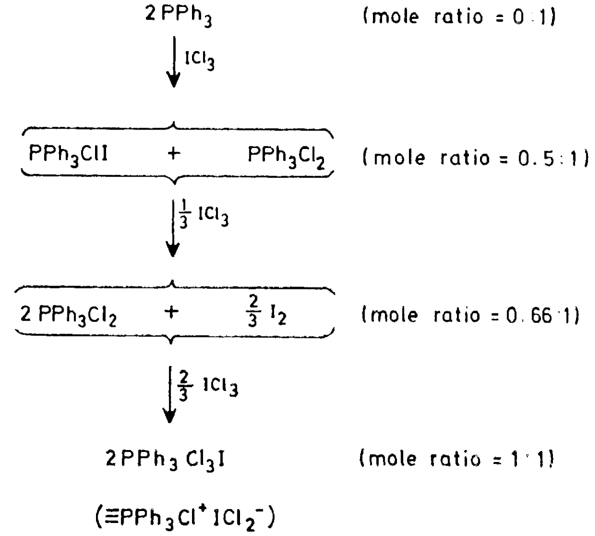


FIGURE 3 Conductometric titrations of MPh_3 with ICl_3: G, PPh_3–ICl_3 (upper abscissa); H, $AsPh_3$–ICl_3 (upper abscissa); I, $SbPh_3$–ICl_3 (lower abscissa)

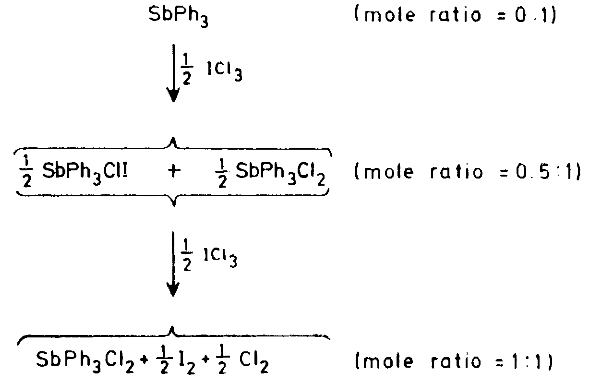
$$AsPh_3 + \tfrac{2}{3}ICl_3 \longrightarrow AsPh_3Cl_2 + \tfrac{1}{3}I_2 \qquad (9)$$

$$(AsPh_3Cl_2 + \tfrac{1}{3}I_2) + \tfrac{1}{3}ICl_3 \longrightarrow AsPh_3Cl_3I \quad (10)$$
$$(\equiv AsPh_3Cl^+ICl_2^-)$$



SCHEME 2

The $SbPh_3$–ICl_3 *System*.—In the conductance against composition plot for this reaction (I, Figure 3) a hump appears between the 0.5 : 1 and 1 : 1 ($ICl_3 : SbPh_3$) mole ratios. The low conductance values at the 0.5 : 1 and 1 : 1 breaks suggest dihalide formation at these ratios and the following reactions and stoicheiometries are indicated (Scheme 3). Between the 0.5 : 1 and 1 : 1 ratios the solution was dark red in colour and the u.v. spectrum showed I_3^- to be present. The maximum in the graph can again be accounted for by the temporary



SCHEME 3

formation of the tetrahalide $SbPh_3ClI_3$ ($\equiv SbPh_3Cl^+I_3^-$), since $SbPh_3ClI$ and I_2 are both present in solution between ratio 0.5 : 1 and ratio 1 : 1. As with other triphenylstibine–halogen systems the only adducts obtained as crystalline solids were dihalides. The compounds $SbPh_3ClI$ and $SbPh_3Cl_2$ were isolated at the mole ratios 0.5 : 1 and 1 : 1 respectively.

EXPERIMENTAL

Since many of the compounds involved in this work were moisture-sensitive, manipulations were carried out in a dry nitrogen atmosphere in a glove box. A vacuum system was used in the handling and purification of volatile compounds. All apparatus and solvents were carefully dried before use.

TABLE 2

Elemental analysis and properties of the adducts

Compound	Colour	M.p.[a] (θ_c/°C)	Analysis (%)[b] C	H	Cl	Br	I	Λ_M[c] (S cm^2 mol^{-1})
PPh_3Cl_3I	Yellow	94—95	44.2	3.3	21.7		24.8	114.0
			(43.6)	(3.0)	(21.5)		(25.6)	
$AsPh_3Cl_3I$	Yellow	80—81	40.2	2.9	19.6		23.4	108.0
			(40.2)	(2.8)	(19.8)		(23.6)	
$AsPh_3Cl_5I$	Yellow	122—124	35.3	2.5	28.1		19.9	117.5
			(35.4)	(2.4)	(29.1)		(20.8)	
$AsBr_2Ph_3ClI$	Red	92—94	35.4	2.5	5.6	26.0	19.7	107.4
			(34.4)	(2.4)	(5.6)	(25.4)	(20.2)	
PPh_3ClI	Yellow	122—124	50.0	3.6	8.2		29.3	68.0
			(50.9)	(3.5)	(8.3)		(29.9)	
$SbPh_3ClI$	White	159—161	41.6	2.9	6.1		25.4	1.5
			(41.8)	(2.9)	(6.9)		(24.5)	

[a] With decomposition. [b] Calculated values are given in parentheses. [c] In 0.01 mol dm^{-3} acetonitrile solution.

Standard reagents of the best commercial grade available were used and these were purified by conventional methods. The dichlorides MPh_3Cl_2 (M = P, As, or Sb) were prepared by passing dry chlorine gas in a stream of nitrogen into a solution of MPh_3 in a suitable solvent (light petroleum or carbon tetrachloride). Cooling was necessary. White crystals of the dichlorides were precipitated, filtered off, and washed with anhydrous diethyl ether (Found: Cl, 20.9. Calc. for $C_{18}H_{15}Cl_2P$: Cl, 21.2%. Found: Cl, 19.0. Calc. for $C_{18}H_{15}AsCl_2$: Cl, 18.8%. Found: Cl, 16.4. Calc. for $C_{18}H_{15}Cl_2Sb$: 16.6%). Purification of acetonitrile for the conductance studies was achieved by the method described by Smith and Witten.[12] Nitrobenzene for the cryoscopic measurements was purified by repeated distillation at reduced pressure of AnalaR grade material.

Preparation of Adducts.—The following adducts were obtained as crystalline solids on adding diethyl ether to acetonitrile containing a 1 : 1 molar mixture of the reactants indicated in parentheses: PPh_3Cl_3I (from PPh_3 and ICl_3 or PPh_3Cl_2 and ICl); $AsPh_3Cl_3I$ (from $AsPh_3$ and ICl_3 or $AsPh_3Cl_2$ and ICl); $AsPh_3Cl_5I$ (from $AsPh_3Cl_2$ and ICl_3); $AsBr_2Ph_3ClI$ (from $AsBr_2Ph_3$ and ICl). The compound PPh_3ClI was obtained as a yellow crystalline solid on adding anhydrous diethyl ether to a 1 : 0.5 molar mixture of PPh_3 and ICl_3 in acetonitrile. The compound $SbPh_3ClI$ was obtained as a white solid on addition of diethyl ether to acetonitrile containing a 1 : 1 molar mixture of $SbPh_3$ and ICl or a 1 : 0.5 molar mixture of $SbPh_3$ and ICl_3. Elemental analysis and properties of the adducts are given in Table 2. Carbon and hydrogen were determined microanalytically: halogens were determined potentiometrically as silver halide after hydrolysis of the adducts.

The apparatus and techniques used for the conductometric titrations and for conductance measurements on solutions of moisture sensitive compounds have already been described.[6,13] Conductance was measured using a Phillips resistance bridge (type GM 4249). Ultraviolet spectra were recorded on a Unicam SP 800 u.v.–visible recording spectrophotometer; the solutions were contained in stoppered cells. Cryoscopic measurements were made using a Normag depression of freezing point apparatus.

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REFERENCES

[1] A. Michaelis, *Annalen*, 1902, 321, 141.

[2] W. Steinkopf and G. Schwen, *Ber. Bunsengesellschaft Phys. Chem.*, 1921, **54**, 1437.

[3] A. Augustine, G. Ferguson, and F. C. March, *Canad. J. Chem.*, 1975, 1647.

[4] K. B. Dillon and T. C. Waddington, *Nature Phys. Sci.*, 1971, **230**, 158.

[5] K. B. Dillon, R. J. Lynch, and T. C. Waddington, *J.C.S. Dalton*, 1976, 1478.

[6] A. D. Beveridge, G. S. Harris, and F. Inglis, *J. Chem. Soc.* (*A*), 1966, 520.

[7] A. D. Beveridge and G. S. Harris, *J. Chem. Soc.*, 1964, 6076.

[8] G. S. Harris, I. M. Mack, and J. S. McKechnie, *J. Fluorine Chem.*, 1978, **11**, 481.

[9] A. I. Popov and R. F. Swensen, *J. Amer. Chem. Soc.*, 1955, **77**, 3724.

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

[11] M. F. Ali and G. S. Harris, *Chem. Comm.*, 1966, 819.

[12] J. W. Smith and L. B. Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.

[13] G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 1956, 3033.