

Reaction of Triarylantimony Dihalides with Interhalogens and Antimonypentachloride

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Summary: The formation of chlorotriaryl, and bromotriaryl antimony cations by the reactions of various triarylantimony dichlorides and triarylantimony dibromides with the halide ion acceptors, iodine chloride, iodine bromide and antimonypentachloride, have been studied by conductometric titrations in acetonitrile.

Formation of cations of type R_3SbX^+ are not very common. R_3SbCl^+ can only be formed when the halide acceptor is $SbCl_5$ and the complexes have the composition $R_3SbCl_2 \cdot 2SbCl_5$ ($\equiv R_3SbCl^+Sb_2Cl_{11}^-$). Evidence for the R_3SbBr^+ cation is obtained from the conductometric titration of $[(CH_3)_2C_6H_3]_3SbBr_2 - IBr$ and from the formation of the solid adduct $[(CH_3)_2C_6H_3]_3SbBr_3I$ ($\equiv [(CH_3)_2C_6H_3]_3SbBr^+IBr_2^-$).

Introduction

Triphenylphosphine dichloride and triphenylarsine dichloride react with iodine chloride and iodine bromide to give 1:1 adducts in acetonitrile, thus showing a clear indication of tetrahalide MPh_3X_4 ($M=P,As$) formation in these systems [1]. All these tetrahalides showed a strong 1:1 electrolyte behaviour in acetonitrile. The Ultra-violet spectra of the solution in these systems showed that chloro-phosphonium and chloro-arsonium cations were formed rather than the possible bromo or iodo alternatives [2,3]. Ph_3PCl_3I and Ph_3AsCl_3I have been isolated as crystalline compounds, and their molar conductance showed that they are ionic in nature: $Ph_3PCl^+ICl_2^-$ and $Ph_3AsCl^+ICl_2^-$ [1]. This confirms the presence of

the halogen of lowest atomic number in chloro-phosphonium and chloro-arsonium cations [4].

The analogous reactions of Ph_3SbCl_2 with halogens and interhalogens indicated that no compound formation takes place in solution [1]. However, a temporary ionic tetrahalide Ph_3SbClI_3 ($\equiv Ph_3SbCl^+I_3^-$) does exist and has also been confirmed from the conductometric titration of Ph_3SbClI_2 with I_2 [5]. Other tetrahalides, Ph_3SbI_4 ($\equiv Ph_3SbI^+I_3^-$) and Ph_3SbBrI_3 have been indicated from the conductometric titration study [2,5] of $Ph_3SbI_2-I_2$ and $Ph_3SbIBr-I_2$ respectively. However, previous attempts to prepare a tetrahalide as a crystalline solid were not successful [2]. Sowerby *et*

al [6] have suggested that antimonypentachloride may accept the chloride ion from Ph_3SbCl_2 , and in fact a 1:1 addition solid was obtained when equimolar quantities of SbCl_5 and Ph_3SbCl_2 in carbon tetra-chloride were reacted. X-ray studies [6] showed that the compound is best represented in the form of $[\text{Ph}_3\text{SbCl}]^+$ and $[\text{SbCl}_6]^-$ ions.

The formation of Ph_3SbBr^+ and Ph_3SbI^+ were not observed from the reactions of either Ph_3SbBr_2 or Ph_3SbI_2 with antimonypentachloride [6]: rather $\text{Ph}_3\text{SbCl}_2 \cdot \text{SbCl}_5$ was formed, with the liberation of free bromine and iodine respectively. With Ph_3SbF_2 , the product obtained is suggested to be $\text{Ph}_3\text{SbFCl} \cdot \text{SbCl}_5$ rather than the expected $\text{Ph}_3\text{SbF}_2 \cdot \text{SbCl}_5$. A solid adduct with the composition $\text{Ph}_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$ has been prepared when two moles of SbCl_5 reaction with one mole of Ph_3SbCl_2 in chloroform. Of the two possible ionic structures, $(\text{Ph}_3\text{Sb})^{2+} 2(\text{SbCl}_6)^-$ and $(\text{Ph}_3\text{SbCl})^+ (\text{Sb}_2\text{Cl}_{11})^-$, the latter is suggested to be the more favourable formation [6].

To investigate further the possible formation of the halotriarylantimony cation, the reactions of various triarylantimony dichlorides with iodine chloride and antimonypentachloride have been studied by conductometric titration in acetonitrile. Antimonypentachloride was chosen because of its strong chloride ion acceptor behaviour. Also, the presence of the bromotriarylantimony cation, R_3SbBr^+ , was indicated by the conductometric titrations of the $\text{R}_3\text{Sb} - \text{IBr}$ systems [7], the direct reactions of R_3SbBr_2 [$\text{R} = 2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3$ and $2\text{-CF}_3\text{C}_6\text{H}_4$] with IBr were studied with a view to confirming the existence of bromotriarylantimony cation, R_3SbBr^+ .

Results and Discussion

Reaction with iodine chloride

The results of the conductometric titrations of R_3SbCl_2 [$\text{R} = \text{Ph}$, 2-, 3-, 4- $\text{CH}_3\text{C}_6\text{H}_4$, $(\text{CH}_3)_2\text{C}_6\text{H}_3$, 2-, or 4- $\text{CF}_3\text{C}_6\text{H}_4$] with ICl in acetonitrile are all very similar, and they are exemplified by curve A ($\text{ICl} : \text{Ph}_3\text{SbCl}_2$) and curve B [$\text{ICl} : (2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2$] in Fig. 1.

The main features of all of these reactions is the small rise in conductivity and in this respect these systems are unlike the triarylsarsine dichloride - iodine chloride system [1]. The slight increase in

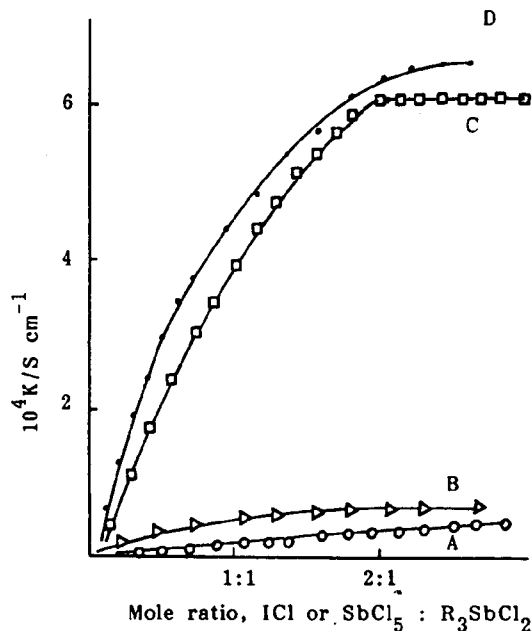


Fig. 1: Conductometric titration of triarylantimony dichloride with ICl or SbCl_5 . (A) $\text{Ph}_3\text{SbCl}_2\text{-ICl}$ (B) $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2\text{-ICl}$ (C) $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2\text{-SbCl}_5$ (D) $(4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2\text{-SbCl}_5$

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

Reactions of antimonypentachloride with triarylantimony dichlorides

Conductometric titrations of SbCl_5 with R_3SbCl_2 in acetonitrile gave two types of graphs which are shown in Fig. 1, curves C and D.

Curve C

The $(3\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2\text{-SbCl}_5$ system exemplifies the graphs obtained in the conductometric titrations of R_3SbCl_2 with SbCl_5 [$\text{R} = \text{Ph}$, 3-, 4- $\text{CH}_3\text{C}_6\text{H}_4$ or $(\text{CH}_3)_2\text{C}_6\text{H}_3$]. All these systems are similar to each other. The conductivity rose sharply up to the 2:1 mole ratio when SbCl_5 was added to the R_3SbCl_2 . Further addition of SbCl_5 to the

solution did not increase the conductivity, thus giving a distinct break in the graph at the 2:1 ratio.

Curve D

The [(4-CF₃C₆H₄)₃SbCl₂-SbCl₅] system is an example of the type of graph obtained in the conductometric titrations of R₃SbCl₂ (where R = 2-CH₃C₆H₄, 2-, or 4-CF₃C₆H₄) with SbCl₅ in acetonitrile. All the reactions are similar to each other but different from those mentioned above (curve C case), in the sense that there was no sharp break at the 2:1 mole ratio. Thus, if there is a 2:1 reaction occurring in these cases, it does not go to completion at the stoichiometric point. None of the graphs show a break at the 1:1 mole ratio, thus suggesting that no adduct of composition R₃SbCl₂·SbCl₅ (≡R₃SbCl⁺·SbCl₆⁻) is forming in the solution. However, the breaks at 2:1 ratio suggest the formation of an adduct R₃SbCl₂·2SbCl₅.

The molar conductivity values at the 2:1 (SbCl₅: R₃SbCl₂) ratio are given in Table-1.

Table-1: Molar conductivity of the 2:1 breaks in the system R₃SbCl₂:SbCl₅.

System	$\Lambda_m(2:1)/\text{Scm}^2\text{mol}^{-1}$	$C_m = \text{mol dm}^{-3}$
Ph ₃ SbCl ₂ -SbCl ₅	192.1	0.003019
(2-CH ₃ C ₆ H ₄) ₃ SbCl ₂ -SbCl ₅	189.4	0.003378
(3-ClH ₃ C ₆ H ₄) ₃ SbCl ₂ -SbCl ₅	196.4	0.003121
(4-CH ₃ C ₆ H ₄) ₃ SbCl ₂ -SbCl ₅	189.8	0.004110
[(CH ₃) ₂ C ₆ H ₃] ₃ SbCl ₂ -SbCl ₅	205.4	0.003066
(2-CF ₃ C ₆ H ₄) ₃ SbCl ₂ -SbCl ₅	172.6	0.00292
(4-CF ₃ C ₆ H ₄) ₃ SbCl ₂ -SbCl ₅	192.8	0.00300

To confirm the absence of a 1:1 break in the system R₃SbCl₂-SbCl₅ and to make sure that the presence of any break at this ratio is not being obscured by the high conductivity of the titrant [SbCl₅ (2SbCl₅=SbCl₄⁺SbCl₆⁻) is a strong conductor in acetonitrile and its conductivity increases with dilution], the above reactions were studied conductometrically the other way round using the non-conducting (or weakly conducting) R₃SbCl₂ solution as titrant, and adding this to the SbCl₅ solution in the reaction vessel. The results are as follows.

Reactions of triarylantimony dichlorides with antimonypentachloride

The conductometric titrations of the R₃SbCl₂ with SbCl₅ in acetonitrile are all similar (the only exception is the SbCl₅-[(CH₃)₂C₆H₃]₃SbCl₂ which

will be discussed later); the titration graphs are exemplified by curve E and F in Fig. 2.

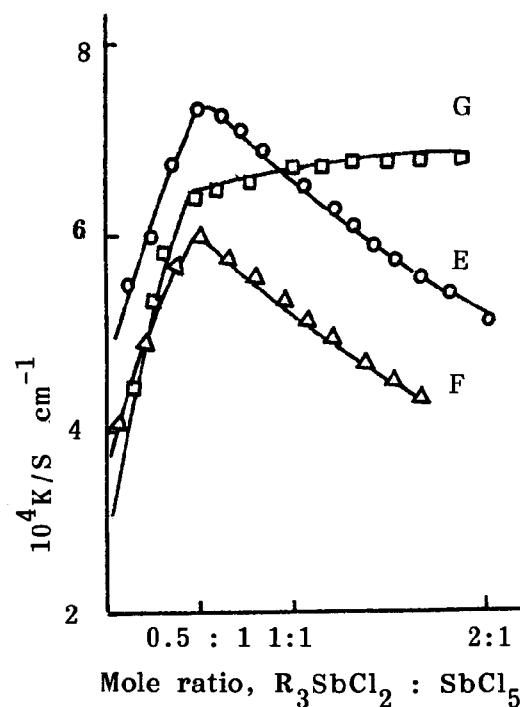


Fig.2: Conductometric titration of SbCl₅ with triarylantimony dichloride (E) SbCl₅-(2-CH₃C₆H₄)₃SbCl₂ (F) SbCl₅-Ph₃SbCl₂ (G) SbCl₅-[2,6-(CH₃)₂C₆H₃]₃SbCl₂

The conductivity rose sharply up to the 0.5:1* (R₃SbCl₂: SbCl₅) mole ratio when R₃SbCl₂ was added to the SbCl₅ solution. On further addition of R₃SbCl₂ to the solution, the conductivity dropped sharply (probably due to the dilution effect of the poorly conducting R₃SbCl₂ solution). Thus a distinct break at the 0.5:1 mole ratio was indicated in each titration graph.

SbCl₅-[2,6-(CH₃)₂C₆H₃]₃SbCl₂ system

Because of the low solubility of [2,6-(CH₃)₂C₆H₃]₃SbCl₂ in acetonitrile, this titration was performed by adding small, weighed quantities of the [2,6-(CH₃)₂C₆H₃]₃SbCl₂ to the SbCl₅ solution (Fig. 2, curve C). As in the other SbCl₅-R₃SbCl₂ titrations the conductivity increased sharply upto the 2:1 mole ratio, then stayed steady on further

*The 0.5:1 ratio in the titration is equivalent to the 2:1 break in the previous titration in which the SbCl₅ solution was added to the R₃SbCl₂ solution

addition of tri(2,6-dimethylphenyl)antimony dichloride to the solution. Thus, again, a distinct break at the 0.5 : 1 ratio was observed in the graph.

Again there was no break observed at the 1:1 mole ratio in any of the system's graphs, confirming the absence of the formation of a 1:1 adduct ($R_3SbCl_2 \cdot SbCl_5$) in solution: 0.5 : 1 break represents the formation of adducts of stoichiometry $(SbCl_5)_2R_3SbCl_2$ and these titrations confirm the formation of these adducts by every system studied. Thus, it is clear that in the previous titrations ($SbCl_5$ added to R_3SbCl_2) the 2:1 break was less sharp in some cases (graph D, Fig. 1) due to the highly conducting nature of the titrant solution.

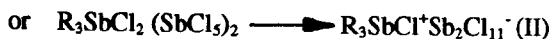
The molar conductivity values at 0.5 : 1 break are given in Table-2.

Table-2: Λ_m values at 0.5:1 ratio break in the system $SbCl_5-R_3SbCl_2$

System	$\Lambda_m(2:1)/Scm^2mol^{-1}$	$C_m = mol dm^{-3}$
$SbCl_5 \cdot Ph_3SbCl_2$	218.0	0.0037
$SbCl_5 \cdot (2-CH_3C_6H_4)_3SbCl_2$	211.0	0.0028
$SbCl_5 \cdot (3-CH_3C_6H_4)_3SbCl_2$	206.1	0.0028
$SbCl_5 \cdot (4-CH_3C_6H_4)_3SbCl_2$	198.7	0.0031
$SbCl_5 \cdot [2,6-(CH_3)_2C_6H_3]_3SbCl_2$	235.9	0.0027
$SbCl_5 \cdot (2-CF_3C_6H_4)_3SbCl_2$	203.5	0.0028
$SbCl_5 \cdot (4-CF_3C_6H_4)_3SbCl_2$	193.2	0.0021

Although 1:1 adducts $R_3SbCl_2 \cdot SbCl_5$ appear not to exist in acetonitrile solution, they have been prepared as solids from acetonitrile solutions containing stoichiometric quantities of R_3SbCl_2 and $SbCl_5$. A solvated adduct, $Ph_3SbCl_2 \cdot SbCl_5 \cdot CH_3CN$ was obtained. It is an off-white solid, extremely moisture sensitive, and melts at 40°C.

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



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

$[Ph_3SbCl_2(SbCl_5)_2: \Lambda_m = 116 S cm^2mol^{-1}; (2-CH_3C_6H_4)_3SbCl_2 (SbCl_5)_2: \Lambda_m = 168 S cm^2mol^{-1}]$.

These values are more in keeping with strong 1:1 rather than 2:1 electrolyte behaviour and hence favour ionisation mode II. Also it is noted that Sowerby *et al.* [6], from an infra-red spectral study of $Ph_3SbCl_2(SbCl_5)_2$, suggested that $Ph_3SbCl^+Sb_2Cl_{11}^-$ was more likely than $Ph_3Sb^{2+}(SbCl_6)^-$. There is in fact no previous report of any compound containing the Ph_3Sb^{2+} ion, but it should be mentioned that the Raman spectrum of an aqueous trimethyl-antimony dinitrate $[Me_3Sb(NO_3)_2]$ has been interpreted in terms of the presence of either the solvated Me_3Sb^{2+} ion, $[Me_3Sb(OH_2)_2]^{2+}$, or the unipositive ion $[Me_3Sb(OH)OH_2]^+$ [8].

Reactions of triarylantimony dibromides with iodine bromide

The results of the conductometric titrations of tri(2,6-dimethyl-phenyl)antimony-dibromide and tris(2-trifluoromethylphenyl) antimony-di-bromide with iodine bromide in acetonitrile are illustrated graphically in Fig. 3 (curves A and B respectively).

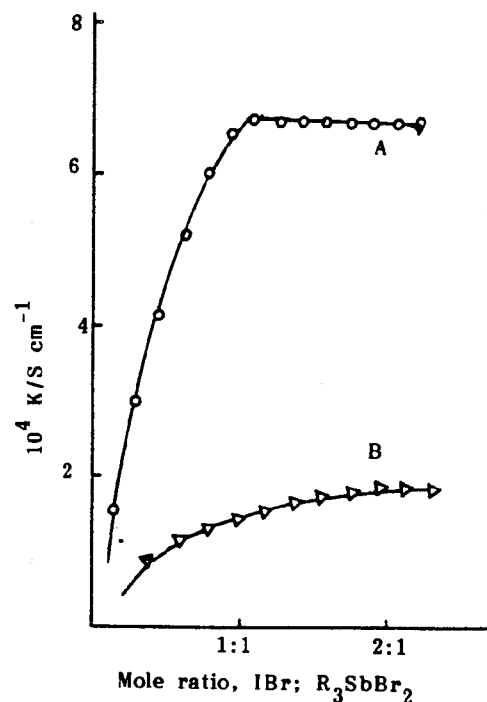


Fig. 3: Conductometric titration of triarylantimony dibromide with iodine bromide (A) $[2,6-(CH_3)_2C_6H_3]_3SbBr_2-IBr$ (B) $[2-CF_3C_6H_4]_3SbBr_2-IBr$

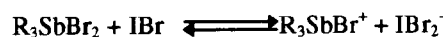
In the $[(\text{CH}_3)_2\text{C}_6\text{H}_3]_3\text{SbBr}_2\text{-IBr}$ system, the conductivity increased sharply up to the 1:1 mole ratio, but thereafter it remained steady when further IBr was added to the solution. A definite 1:1 break in the titration graph was thus obtained. The solution became yellow in colour from the start of the titration and the Ultraviolet spectrum of the solution showed absorption due to the IBr_2^- ion ($\lambda_{\text{max}} = 257 \text{ m}\mu$).

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



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

The other $\text{R}_3\text{SbBr}_2\text{-IBr}$ systems (R= 2-, 3-, 4- $\text{CH}_3\text{C}_6\text{H}_4$, 2- and 4- $\text{CF}_3\text{C}_6\text{H}_4$) are similar to each other and they are exemplified by the reaction of $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{SbBr}_2\text{-IBr}$. In the $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{SbBr}_2\text{-IBr}$ system (curve B, Fig. 3) the conductivity rose as IBr was added to the $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{SbBr}_2$, but the titration graph did not give a distinct break at any mole ratio. The reaction is obviously not complete at the 1:1 stoichiometric point. The solution was yellow from the start of the titration and its ultraviolet spectrum showed absorption due to the IBr_2^- ion. The Λ_m values at the 1:1 mole ratio was $42.2 \text{ S cm}^2\text{mol}^{-1}$ ($C_m = 0.00003508 \text{ mol dm}^{-3}$). The reaction occurring may be represented as



$[(\text{CH}_3)_2\text{C}_6\text{H}_3]_3\text{SbIBr}_3$ is the only solid adduct of such composition (R_3SbX_4) of the triarylstibine tetrahalide.

Adducts of composition $\text{R}_3\text{SbCl}_2 \cdot \text{SbCl}_5$

Although conductometric titrations of R_3SbCl_2 with SbCl_5 do not give any indication of the formation of a 1:1 adduct, yet the solvated adduct, $\text{Ph}_3\text{SbCl}_2 \cdot \text{SbCl}_5 \cdot \text{CH}_3\text{CN}$, was obtained as a crystalline solid from the mixture (1:1) of Ph_3SbCl_2 and SbCl_5 in acetonitrile. It is an off-white solid, extremely moisture sensitive, and melts at 40°C .

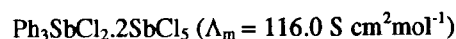
Adducts of composition of $\text{R}_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$

The existence of these 2:1 adducts was shown by the conductometric titration of R_3SbCl_2 with SbCl_5 and vice versa. The preparation of two adducts of this type was attempted. These were $\text{Ph}_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$ and $(2\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$. $2\text{CH}_3\text{CN}$, and they were obtained readily from the mixture of one mole of R_3SbCl_2 and two moles of SbCl_5 in acetonitrile. Both the compounds are light yellow in colour. $(\text{C}_6\text{H}_5)_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$ melts at room temperature, while the solvated $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SbCl}_2 \cdot 2\text{SbCl}_5 \cdot 2\text{CH}_3\text{CN}$ melts at $84\text{-}86^\circ\text{C}$.

Conductivity study of 1:1 and 2:1 adducts (SbCl_5 : R_3SbCl_2)

To gain information on the behaviour of $\text{Ph}_3\text{SbCl}_2 \cdot \text{SbCl}_5$ in solution, conductivity measurements were made on the acetonitrile solution of the compound at different concentrations. The molar conductivity Λ_m at $C_m=0.01$ was found to be $113.0 \text{ S cm}^2\text{mol}^{-1}$. This high value suggests that the adduct is a strong electrolyte in acetonitrile. Its solution behaviour is therefore in keeping with its solid state structure [6].

The molar conductivity Λ_m of the compounds of type $\text{R}_3\text{SbCl}_2 \cdot 2\text{SbCl}_5$ (R=Ph and 2- $\text{CH}_3\text{C}_6\text{H}_4$) was measured in acetonitrile and values at $C_m=0.01 \text{ mol dm}^{-3}$ were found to be:



The molar conductivity values suggest that the adducts are strong electrolytes in acetonitrile and again this accords with Sowerby's suggestion [6] that compounds of this type are ionic in the solid state [$\text{R}_3\text{SbCl}^+ \cdot \text{Sb}_2\text{Cl}_{11}^-$].

Experimental

Most of the compounds involved in this work are moisture sensitive; all operation were carried out in a dry nitrogen atmosphere in a dry box. Apparatus and solvents were thoroughly dried before use.

Standard reagents were purified by conventional methods. Acetonitrile suitable for conducti-

Conductivity studies were obtained using the method described by Smith and Witten [9]. Antimonypentachloride was distilled under nitrogen atmosphere. Triarylantimony dichlorides were prepared by passing chlorine gas through the chloroform solution of triarylantimony and the crystalline solids were obtained by freeze-drying the mixture solutions or by adding dry ether to the solution. Triarylantimony dibromides were obtained by mixing stoichiometric quantities of triarylantimony and bromine in acetonitrile. $[(CH_3)_2C_6H_3]_3SbBr_2I$ was prepared by freeze-drying the 1:1 molar mixture of R_3SbBr_2 with I_2 in acetonitrile. $Ph_3SbCl_2 \cdot SbCl_5$ was prepared by mixing 1:1 molar solution of R_3SbCl_2 with $SbCl_5$ while $Ph_3SbCl_2 \cdot 2SbCl_5$ and $(2-CH_3C_6H_4)_3SbCl_2 \cdot 2SbCl_5$ were obtained by freeze-drying 2:1 ($SbCl_5 : R_3SbCl_2$) mole ratio of the reactants. Satisfactory analytical data were obtained for these compounds. The apparatus and techniques used for the conductometric titrations were the same as those illustrated and described elsewhere [2,10].

Conductivity measurements were made in a cell of the dipping electrode type. The electrode supports passed through a standard ground-glass cone which fitted a vessel for the solution which

was prepared in situ in the dry box. Conductivity was measured by means of a Phillips resistance bridge (Type PR 9500). Ultra-violet spectra were recorded on a Unicam SP-800 UV/visible recording spectrophotometer. The solutions were contained in a stoppered quartz cell.

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