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THE REACTION OF TRISPENTAFLUOROPHENYLSTIBINE WITH HALOGENS AND INTERHALOGENS

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SUMMARY

Conductometric titration studies show that the reactions of trispentafluorophenylstibine with halogens and interhalogens lead to non-conducting species. Molar conductance values of the adducts $(C_6F_5)_3SbCl_2$ and $(C_6F_5)_3SbBr_2$ in acetonitrile are very low. The reaction of trispentafluorophenylstibine with iodine chloride and iodine bromide gives $(C_6F_5)_3SbCl_2$ and $(C_6F_5)_3SbBr_2$ respectively and not the expected interhalogen adducts.

INTRODUCTION

It is known that trispentafluorophenylstibine, like its phosphorus and arsenic analogues, adds halogen, though less readily, to form dihalides, $(C_6F_5)_3SbX_2$ (X = Cl or Br) [1,2]. These dihalides are believed to have a covalent molecular structure, on the basis of their vibrational spectra [1]; the conductivity of very dilute solutions of $(C_6F_5)_3SbCl_2$ in acetone has been measured and it is suggested that partial ionisation may occur [2]. In an earlier paper [3] we have reported the results of an electrolytic conductance study of the reactions of trispentafluorophenylphosphine and trispentafluorophenylarsine with halogens in acetonitrile. We now report the findings of a conductometric titration study of the reactions of trispentafluorophenylstibine with halogens and interhalogens.

DISCUSSION

Conductometric titrations of the systems $(C_6F_5)_3Sb\text{-}X_2$ (X = Br or I) and $(C_6F_5)_3Sb\text{-}IY$ (Y = Cl or Br) were carried out in acetonitrile. In each case there was only a very slight rise in conductivity as titration proceeded;

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it is clear that the reaction occurring does not lead to ionic species. The graph of the $(C_6F_5)_3Sb-Br_2$ titration, as representative, is shown in Figure 1 (Graph A), and for comparison, the graph of the $(C_6F_5)_3P-Br_2$ system is given (Graph B) [3]. The conductivity values in the $(C_6F_5)_3Sb-Br_2$ system

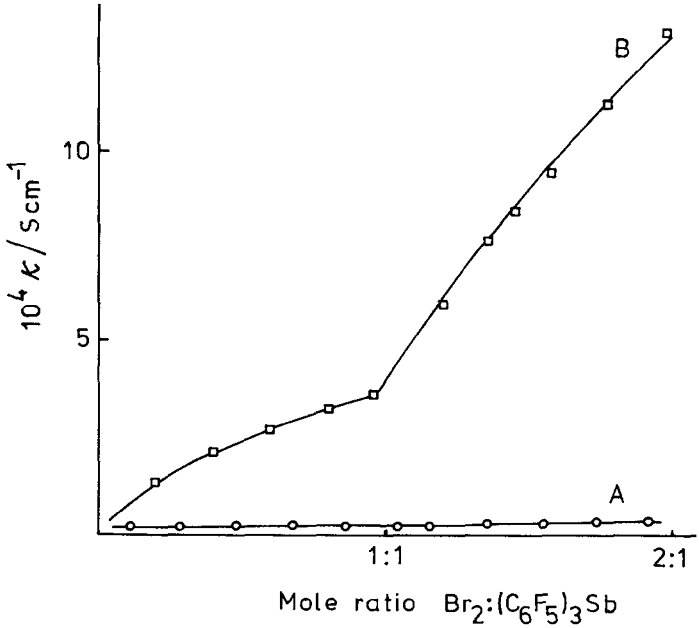

Fig.1. Conductometric Titrations: $(C_6F_5)_3Sb-Br_2$ (A), $(C_6F_5)_3P-Br_2$ (B).

are very low and do not alter significantly as titration proceeds; this contrasts markedly with the high and rising values observed in the $(C_6F_5)_3P-Br_2$ system the graph of which displays a distinct break at the 1:1 mole ratio. Although the titration graph does not provide evidence for an end-point in the $(C_6F_5)_3Sb-Br_2$ system, a visual end-point was detected at 1:1 stoichiometry; the added portions of bromine solution were instantly decolourised and the reaction mixture remained colourless as far as the 1:1 mole ratio at which point it became yellow. The 1:1 end-point so indicated and the very low molar conductivity of the solution at this point (Λ_m = 0.8 S cm^2 mol^{-1}) suggest reaction is occurring to form a covalent 1:1 adduct

$$(C_6F_5)_3Sb + Br_2 \longrightarrow (C_6F_5)_3SbBr_2 \qquad (1)$$

By contrast, in the $(C_6F_5)_3P$-Br_2 system the distinct rise in conductivity, the break at the 1:1 mole ratio and the relatively high value of molar conductivity (Λ_m = 26.2 S cm^2 mol^{-1}) at this ratio indicate the formation of a 1:1 adduct which undergoes significant ionisation in acetonitrile [3]:

$$(C_6F_5)_3PBr_2 \rightleftharpoons (C_6F_5)_3PBr^+ + Br^-$$

There was no evidence from conductometric titration for adduct formation in the $(C_6F_5)_3Sb$-I_2 or $(C_6F_5)_3Sb$-IX systems. In the $(C_6F_5)_3Sb$-IX systems (unlike the others) strong colour (dark-brown) developed in the solution from the start of titration. This is not in keeping with the formation of a 1:1 adduct,

$$(C_6F_5)_3Sb + IX \longrightarrow (C_6F_5)_3SbIX \qquad (2)$$

(X = Cl or Br)

since all known R_3MICl and R_3MIBr adducts (M = P, As, or Sb) are white or pale yellow in colour, *e.g.* Ph_3SbICl and Ph_3SbIBr are both white compounds [4,5]. Also, attempts to prepare the interhalogen adducts, $(C_6F_5)_3SbIX$, from an equimolar mixture of the reactants [Equation (2)] were unsuccessful (see later).

We believe that the reactions occurring in these systems have 2:1 stoichiometry and involve either the formation of the dichloride or dibromide of $(C_6F_5)_3Sb$ with release of iodine (acetonitrile solutions of which are brown):

$$(C_6F_5)_3Sb + 2IX \longrightarrow (C_6F_5)_3SbX_2 + I_2 \qquad (3)$$

Known crystalline halogen adducts of trispentafluorophenylstibine appear to be restricted to $(C_6F_5)_3SbCl_2$ and $(C_6F_5)_3SbBr_2$ [2,3]. Attempts to prepare $(C_6F_5)_3SbI_2$ were not successful nor were our attempts to prepare the interhalogen adducts $(C_6F_5)_3SbICl$ and $(C_6F_5)_3SbIBr$ from an equimolar mixture of $(C_6F_5)_3Sb$ and ICl or IBr; instead $(C_6F_5)_3SbCl_2$ and $(C_6F_5)_3SbBr_2$, respectively, were isolated [Equation (3)]. This latter result is at variance with a report [6] that $(C_6F_5)_3SbICl$ and $(C_6F_5)_3SbIBr$ can be obtained as brown solids. We have observed that, on removal from solution, the solid $(C_6F_5)_3SbCl_2$ and $(C_6F_5)_3SbBr_2$ obtained as above are discoloured due to contamination with iodine, the other reaction product. This is readily removed by pumping to give pure dihalide which is white. In its reactions with these interhalogens, $(C_6F_5)_3Sb$ therefore resembles $(C_6F_5)_3P$ and $(C_6F_5)_3As$ which also form dichloride or dibromide in preference to the interhalogen adduct [3,7].

The molar conductivities of acetonitrile solutions of trispentafluorophenylstibine dichloride and trispentafluorophenylstibine dibromide were measured at 25 °C over a range of concentrations. The values obtained for solutions of concentration 0.01 mol dm^{-3} were the following: $(C_6F_5)_3SbCl_2$, Λ_m = 0.3 S cm^2 mol^{-1}; $(C_6F_5)_3SbBr_2$, Λ_m = 0.1 S cm^2 mol^{-1}. These very low molar conductivity values, which are comparable with those for the corresponding phenyl compounds [5], lead to the conclusion that the trispentafluorophenylstibine dihalides, like their phenyl analogues, do not undergo any significant ionisation in acetonitrile and, accordingly, that these compounds are molecular.

EXPERIMENTAL

General Methods

The handling of moisture-sensitive compounds was carried out in a nitrogen-filled glove box. Conductances of solutions in the concentration range 7×10^{-4} - 1.2×10^{-2} mol dm^{-3}, were measured at 25 °C. For the conductometric titrations and conductance measurements, apparatus designed to exclude moisture was used [5]. Conductance was measured using a Phillips resistance bridge (type GM 4259).

Materials

Reagents and solvents were of the best grade available commercially and were purified by conventional methods. Acetonitrile for conductivity work was prepared by a special method described by Smith and Witten [9].

Trispentafluorophenylstibine was made by the method described by Fild *et al.*[8], and was recrystallised from petroleum ether (m.p. 73 - 75 °C; lit. [8], 74° C. Found: C, 34.8%. Calc. for $C_{18}F_{15}Sb$: C, 34.7%).

Trispentafluorophenylstibine dichloride and trispentafluorophenylstibine dibromide were prepared from equimolar quantities of trispentafluorophenylstibine and the appropriate halogen in a suitable solvent (methylene chloride for the dichloride and acetonitrile for the dibromide). [$(C_6F_5)_3SbCl_2$ - Found: C, 31.5; Cl, 10.4%. Calc. for $C_{18}Cl_2F_{15}Sb$: C, 31.2; Cl, 10.2%. $(C_6F_5)_3SbBr_2$ - Found: C, 27.6; Br, 20.6%. Calc. for $C_{18}Br_2F_{15}Sb$: C, 27.6; Br, 20.4%.]

Reaction between trispentafluorophenylstibine and iodine chloride [attempted preparation of $(C_6F_5)_3SbICl$]

Iodine chloride (0.244 g; 1.502 mmol) dissolved in acetonitrile (10 cm^3) was added dropwise with shaking to a solution of trispentafluorophenylstibine (0.935 g; 1.502 mmol) in the same solvent (10 cm^3). From the resulting dark-brown solution an off-white crystalline product was obtained on addition of ether. After filtration, the product was pumped on the vacuum system to remove residual solvent and a trace of iodine. This gave triphenylstibine dichloride (0.33 g; 63%) as a white crystalline solid, m.p. 240 - 242 °C (identical with an authentic sample). Found: C, 31.0%. Calc. for $C_{18}Cl_2F_{15}Sb$: C, 31.2%

Reaction between trispentafluorophenylstibine and iodine bromide [attempted preparation of $(C_6F_5)_3SbIBr$]

Iodine bromide (0.246 g; 1.19 mmol) in acetonitrile (20 cm^3) was added dropwise with shaking to trispentafluorophenylstibine (0.741 g; 1.19 mmol) in the same solvent (10 cm^3). The resultant solution was dark-brown in colour and from this a very pale yellow solid precipitated. After filtration the solid was pumped to remove a trace of iodine leaving behind white crystalline trispentafluorophenylstibine dibromide (0.28 g; 60%), m.p. 210 - 212 °C (identical with an authentic sample). Found: C, 27.7%. Calc. for $C_{18}Br_2F_{15}Sb$, 27.6%.

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