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THE REACTIONS OF TRISPENTAFLUOROPHENYL-PHOSPHINE AND -ARSINE WITH HALOGENS AND INTERHALOGENS

G.S. Harris and M.F. Ali

Department of Chemistry, St. Salvator's College,
University of St. Andrews, St. Andrews.

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To-date, the only reported dihalide of type $(C_6F_5)_3MHal_2$ [M = P or As] is trispentafluorophenylphosphine dichloride, which was prepared by Emeléus and Miller (1) by the direct reaction under vacuum of the phosphine and chlorine. We have found that a simpler procedure involves the passage of chlorine gas into a methyl cyanide solution of the phosphine: in this way good yields (ca. 80%) of pure product are obtained. The analogous reactions of trispentafluorophenylphosphine with some other halogens (bromine, iodine, and iodine bromide) have also been examined, but in no case did we succeed in isolating a solid dihalide.

We have also studied the reactions of trispentafluorophenylarsine with halogens and interhalogens and, again, the only dihalide isolated was the dichloride, $(C_6F_5)_3AsCl_2$ (m.p. 214-216°: Found C, 34.3; Cl, 10.9. $C_{18}AsCl_2F_{15}$ requires C, 33.4; Cl, 11.0%). This adduct arose from the reaction of the arsine either with chlorine or a chlorine-containing interhalogen -

$$(C_6F_5)_3As + Cl_2 \longrightarrow (C_6F_5)_3AsCl_2$$

$$(C_6F_5)_3As + 2ICl \longrightarrow (C_6F_5)_3AsCl_2 + I_2$$

Like its phosphorus analogue, trispentafluorophenylarsine dichloride is readily hydrolysed, producing trispentafluorophenylarsine oxide, $(C_6F_5)_3AsO$ (m.p. 198-199°: Found, C, 36.5. $C_{18}AsF_{15}O$ requires C, 36.6%). As expected the As = O stretching vibration of $(C_6F_5)_3AsO$ occurs at a higher frequency than that of $(C_6H_5)_3AsO$ (928 $cm.^{-1}$ in the former; 881 $cm.^{-1}$ in the latter). Trispentafluorophenylarsine oxide, unlike triphenylarsine oxide (2), has no tendency to form a monohydrate.

The original aim of this work was to produce a series of dihalides, $(C_6F_5)_3MHal_2$, analogous to the well-known $(C_6H_5)_3MHal_2$ compounds [M = P or As] so that comparative conductance studies might be made. However, owing to the paucity of trispentafluorophenylphosphine (and -arsine) dihalides, this study was restricted to the dichlorides.

It was found that the trispentafluorophenylphosphine (and -arsine) dichlorides formed virtually non-conducting solutions in methyl cyanide and on account of the very low value of Λ_m they must be regarded as non-electrolytes in this solvent. A comparison of molar conductance values for 0.01M solutions of the C_6F_5- and C_6H_5- derivatives in methyl cyanide may be made from the following data:

	Λ_m		Λ_m
$(C_6F_5)_3PCl_2$	0.5	$(C_6F_5)_3AsCl_2$	0.7
$(C_6H_5)_3PCl_2$	78.1	$(C_6H_5)_3AsCl_2$	4.0

A conductimetric titration study of the $(C_6F_5)_3P$ - Br_2 system in methyl cyanide gave the graph shown in FIG. 1.

It is of interest that the configuration of this titration graph resembles that of the system $(C_6H_5)_3As$ - Br_2. The inflections at the 1:1 and 2:1 mole ratios clearly indicate the formation of the compounds $(C_6F_5)_3PBr_2$ and $(C_6F_5)_3PBr_4$ in solution. Λ_m values at the 1:1 and 2:1 inflections show that these compounds are weak and strong electrolytes respectively, and we postulate the ionisations -

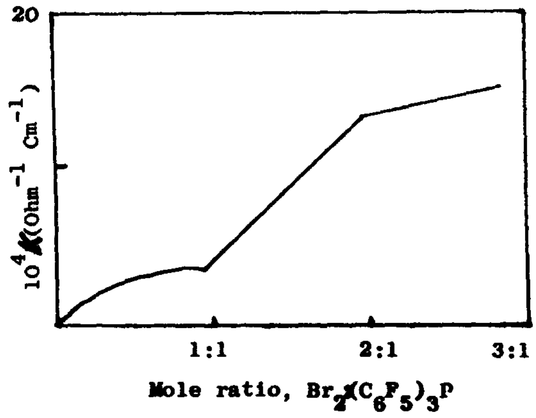

FIG. 1

Conductimetric titration of $(C_6F_5)_3P$ with Br_2.

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

$$(C_6F_5)_3PBr_4 \rightleftharpoons (C_6F_5)_3PBr^+ + Br_3^-$$

It has already been noted that the dibromide could not be isolated; the tetrabromide however was obtained as an unstable yellow solid (m.p. 190-210°. Found, Br, 38.0%. $C_{18}Br_4F_{15}P$ requires Br, 37.6%).

A vapour pressure study also has been made on the system $(C_6F_5)_3P$ - Br_2 (FIG. 2). This demonstrates

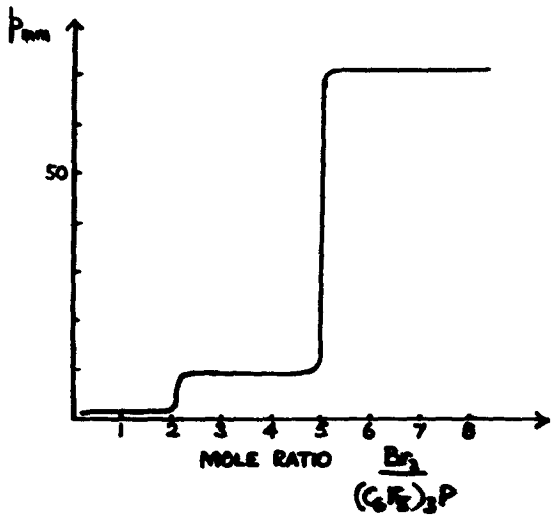

FIG. 2

The vapour pressures of mixtures of $(C_6F_5)_3P$ and Br_2 at 0°C the existence of only two solid adducts stable at 0° within the range of composition studied. These are the above mentioned tetrabromide, and a decabromide $(C_6F_5)_3PBr_{10}$. This latter can, with plausibility, be written as $(C_6F_5)_3\overset{+}{P}Br\ Br_9^{-}$; examples of compounds containing the enneabromide ion are not unknown (3).

The existence of several other tetrahalides [e.g. $(C_6F_5)_3PI_2Br_2$, $(C_6F_5)_3PIBr_3$] has been demonstrated by conductimetric titration. A full description of these studies will appear elsewhere.

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