Tetrahedron Letters No.1, pp. 37-38, 1968. Pergamon Press Ltd. Printed in Great Britain.

THE STRUCTURE OF TRIPHENYLPHOSPHINE DIHALIDES IN SOLUTION

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(Received in UK 1 September 1967)

A recent note to this journal, by Wiley and Stine (1), on the nature of tertiary phosphine dihalides in solution, prompts us to make some comments and to report briefly an extension of our earlier work on this topic (2).

From the ^{31}P N.M.R. data for triphenylphosphine dichloride in methyl cyanide Wiley and Stine show beyond reasonable doubt that in this solvent the dihalide is completely ionised in the sense

$$Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Cl^- \quad \text{....................(i);}$$

and not in the sense

$$2Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Ph_3PCl_3^- \quad \text{....................(ii),}$$

which, by analogy with the behaviour of phosphorus pentachloride in methyl cyanide (3) seemed to be not unlikely. It is of interest that this result is the reverse of the conclusion reached by us earlier (2) from the results of the determination of the transport numbers of the ions in solution. These determinations are, however, fraught with sources of experimental error (these being enhanced when the compounds, like the one being considered, are hydrolytically unstable), and numerous assumptions have to be made in the interpretation of the results. Never-the-less, the results of a number of experiments favoured ionisation (ii) for triphenylphosphine dichloride; and, interestingly for the corresponding dibromide, ionisation of type (i), namely,

$$Ph_3PBr_2 \rightleftharpoons Ph_3PBr^+ + Br^- \quad \text{....................(iii)}$$

was indicated.

The formation of $Ph_3PCl_3^-$ in the ionisation of triphenylphosphine dichloride implies the acceptance of a chloride ion by Ph_3PCl_2. Thus to gain further support for the existence of the ion $Ph_3PCl_3^-$ we examined the reaction of triphenylphosphine dichloride with the strong chloride ion donor, tetraethylammonium chloride; if Ph_3PCl_2 has indeed a tendency to accept a chloride ion in methyl cyanide solution the following overall process should occur -

$$Et_4N^+Cl^- + Ph_3PCl_2 \longrightarrow Et_4N^+Ph_3PCl_3^- \qquad \text{.............(iv).}$$

The reaction was carried out by stepwise addition of Et_4NCl to Ph_3PCl_2 and was followed conductimetrically. The conductance of the solution rose uniformly with the addition of Et_4NCl but there was no suggestion of an inflection in the titration graph at the 1:1 ratio as would be expected if reaction (iv) had in fact, occurred. Also, we were not able to isolate an adduct containing the $Ph_3PCl_3^-$ ion. These observations therefore, in failing to confirm the existence of the $Ph_3PCl_3^-$ ion, lend support to the structure $Ph_3PCl^+Cl^-$ for triphenylphosphine dichloride in solution as proposed by Wiley and Stine.

These authors conclude also that in nitrobenzene solutions of triphenylphosphine dichloride "the pentavalent form prevails". We have found that the molar conductance of these solutions is about 3 ohm^{-1} cm^2 $mole^{-1}$ (0.01M solution) which implies weak electrolyte behaviour (i.e. partial ionisation). The observed molecular weight (freezing point determination) of the solute was found to be 272.0, which suggests that the ionisation

$$Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Cl^-$$

occurs to an extent of almost 25% in nitrobenzene at its freezing point.

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