BROMINE ADDUCTS WITH PHOSPHINE DERIVATIVES
IN ACETONITRILE AS SOLVENT

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ABSTRACT

The interactions of the phosphine derivatives: Et₃P, Bu₃P, (4-Cl-C₆H₄)₃P, Ph₂PCH₃, Ph₂P C₆H₅, Ph₂P OCH₃, Ph(CH₂)₂P, Ph₂P Cl and Ph P Et₂ with bromine are studied in acetonitrile as solvent. Conductance measurements of their mixtures support the formation of 2 : 1, 1 : 1 and 1 : 2 adducts in solution. These adducts are ionised and exist in equilibria with unionised species formed in polar solvents.

INTRODUCTION

The phosphine derivatives are known [1] to form addition compounds with halogens. With different halogens, the adducts do not show similar behaviour. The fluorophosphoranes, R₃ P F₃ are known to have properties, that are characteristic for covalent compounds whereas the chlorine adducts [2] lie on the borderline between the covalent fluorophosphoranes and other similar like, R₃ P X₂ compounds (where X = Br, I). The phosphine derivative adducts with iodine have recently been studied [3,4] and ionic nature of these
adducts are concluded in aprotic polar solvents like acetonitrile. In carbon tetrachloride, these adducts exist [5] as "ion-pairs". The nature of the phosphine derivative adducts with bromine is found to be dependent upon the halogen, basicity of the phosphine base and the nature of the solvent. The change of solvent from non-polar to polar can bring about a change from molecular to ionic form. However, in polar solvents, like acetonitrile, ionic species are predominantly formed [1]. The present work involves physicochemical studies of some phosphine derivative interactions with bromine. In a previous work [4], interactions of the phosphine derivatives with iodine are published. Harris and Ali [6] have reported the ionising nature of triphenylphosphine dibromide.

\[ \text{Ph}_3\text{P Br}_2 \rightleftharpoons \text{Ph}_3\text{P Br}^+ + \text{Br}^- \]  \hspace{1cm} (1)

The reactions of donor phosphine derivatives with bromine may lead to two types of products.

(I) \hspace{1cm} D: + Br-Br \rightarrow D: Br -- Br \hspace{1cm} (2)

Molecular covalent adduct

(i) \hspace{1cm} D: + Br-Br \rightarrow D: Br -- Br \rightarrow DBR^+ + Br^- \hspace{1cm} (3)

Adduct ionised

(II)

(ii) \hspace{1cm} D: + 2Br_2 \rightarrow D: Br_4 \rightarrow DBr^+ + Br_3^- \hspace{1cm} (4)

(ionised species)

Our knowledge about the nature of such adducts formed in sprotic solution has been inadequate. The reactions involve varying extents of reversibility. The reaction products formed via route (I) would be non-conducting whereas the products formed via route (II) would lead to the
formation of conducting species. Therefore, in order to distinguish between the nature of the species formed, a study of conductance measurements in an ionising non-aqueous polar solvent i.e., acetonitrile is carried out.

**EXPERIMENTAL**

The purification of materials and working conditions were the same as reported in the earlier work [4,5]. For studying interactions in solution, conductivity measurements were carried out on an Orion research conductivity meter Model 101. Strict dry and inert atmosphere was maintained in a dry box during the experiments for conductance measurements.

**RESULTS AND DISCUSSION**

**Conductance of the Reactants in Acetonitrile**

In aqueous solutions, halogens react with water and polyhalide ions are formed [7]. In a non-aqueous non-polar solvent (e.g. carbon tetrachloride), bromine is almost non-conducting showing its presence as undissociated molecular form. In non-aqueous polar solvents (e.g. acetonitrile), bromine is found to disproportionate as follows:

\[ 2 \text{Br}_2 \rightleftharpoons \text{Br}^+ + \text{Br}_3 \]  \hspace{1cm} (5)

The acetonitrile solutions of bromine show comparatively higher conductance values, suggesting the possible formation of the following equilibria:

\[ \text{CH}_3\text{CN} + \text{Br}_2 \rightleftharpoons \text{CH}_3\text{CNBr}^+ + \text{Br}^- \]  \hspace{1cm} (6)

\[ \text{Br}^- + \text{Br}_2 \rightleftharpoons \text{Br}_3 \]  \hspace{1cm} (7)

The specific conductance rises steadily with the increasing concentration of bromine. A plot of molar conductance values against square root of
concentration shows a behaviour characteristic of weak electrolytes (Fig. 1) and it conforms with the greater ionisation at higher dilutions.

The molar conductance shows marked dependence on the concentration. The value of \( \Lambda_m \) remains low until very low concentrations are reached. Then the plot sweeps up to values comparable to strong electrolytes. On dilution, the unionised form of the ionogen becomes ionised. It is found that 3.46 x 10^{-2} M bromine solution showed \( \Lambda_m = 0.26 \text{ S m}^2 \text{ mol}^{-1} \) at 25°C. These results are in agreement with the UV work as reported earliest [4]. Therefore, bromine is concluded to ionise appreciably in acetonitrile solutions.

All the phosphine derivatives used are covalent compounds and are found to be non-conducting in acetonitrile solutions.

**Conductometric Titrations**

The analogous adducts e.g. trimethylstibine dihalides are reported [8] to be covalent in nature whereas the phosphine derivative halides are ionic in the solid state and in nitrobenzene solutions [9]. In order to obtain information regarding the nature of the phosphine derivative bromides, conductance behaviour is examined in acetonitrile solutions. By using bromine solution as titrant, conductance values are obtained for the following phosphine derivatives; \( \text{Et}_3\text{P}, \text{Bu}_3\text{P}, (4-\text{Cl-C}_6\text{H}_4)\text{P}, \text{Ph}_2\text{PCH}_3, \text{Ph}_2\text{PC}_2\text{H}_5, \text{PhP(CH}_3)_2, \text{Ph}_2\text{POCH}_3, \text{Ph}_2\text{PCI} \) and \( \text{PhPEt}_2 \). In most of these cases, a maximum conductance is observed around 0.50 bromine to phosphine derivative mole ratio. This indicates the formation of \( (\text{R}_3\text{P})_2\text{Br}_2 \) (where \( \text{R} \) is alkyl or substituted aryl group) which is ionised as shown below:

\[
2 \text{R}_3\text{P} + \text{Br}_2 \rightarrow (\text{R}_3\text{P})_2\text{Br}_2 \quad \overset{\text{\( \rightarrow \)}}{\text{\( \Rightarrow \)}} \quad (\text{R}_3\text{P})_2\text{Br}^+ + \text{Br}^- \quad (8)
\]

The 1:2 mole ratio maxima in conductance values, are shown in Fig. 2 for bromine with \( \text{PhPEt}_2, \text{Ph}_2\text{PCH}_3, \text{PhP(CH}_3)_2, \text{Et}_3\text{P} \) and \( \text{Ph}_2\text{PEt} \). At this stoichiometric ratio, the solutions remain colourless. The \( (\text{R}_3\text{P})_2\text{Br}^+ \) species is assumed to have a bridged structure i.e., \( (\text{R}_3\text{P} - \text{Br}^+ - \text{PR}_3) \). Since the
1:2 adduct formed is further involved in an equilibrium with the ionic species formed in solution according to equation (8); the position of conductance maximum is delayed for the systems where the equilibrium lies more towards the unionised form. For the basic phosphine derivatives, the ionisation of the adduct is predominant and conductance maximum occurs around 1:2 bromine to phosphine derivative mole ratios.

On further increasing bromine concentration, an inflexion is observed near 1:1 mole ratio. The reaction can be represented as follows:

\[
R_3P + Br_2 \rightarrow R_3PBr_2 \rightleftharpoons R_3PBr^+ + Br^- \tag{9}
\]

At this stage, the solution starts changing to light yellow coloration. Before reaching the 1:1 mole ratio, after the first maximum, a decrease in conductance is observed. This is either due to a little change in the number of ionic species in solution probably helped by dilution effects, or a covalent character may be becoming important, inhibiting ionisation of the adducts.

After 1:1 mole ratio, the conductance rises sharply. The colour of the solution becomes brownish due to the excess of bromine in solution. In the case of PhP\text{Et}_2, PhP(CH_3)_2, Ph_2PCH_3, Et_3P (Fig.2) and for Ph_2POCH_3 (Fig.3), maximum conductance is observed around 2:1 bromine to phosphine derivative mole ratio or just after this point. In this region, where the adduct \(R_3PBr_4\) is expected to be formed.

The conducting nature of these solutions indicates the formation of the following ionic species in solution.

\[
R_3P + 2Br_2 \rightarrow R_3PBr_4 \rightleftharpoons R_3PBr^+ + Br^- \tag{10}
\]

The observed molar conductance values for the 2:1 bromine to phosphine derivative stoichiometric adducts are shown in table 1.

The molar conductance values clearly indicate the ionisation of the adducts formed in solution. All the phosphine derivatives studies form
Table 1

Observed molar conductance values for the 2:1 Br$_2$/R$_3$P mole ratio adducts in acetonitrile solutions at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stoichiometric Molarity of Base $10^4 \times M$</th>
<th>Specific Cond. $10^2 \times k_{Sm}^1$</th>
<th>Molar Conductance $10^2 \times \Lambda_m, Sm^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (4-Cl-C$_6$H$_4$)$_3$PBr$_4$</td>
<td>2.58</td>
<td>22.75</td>
<td>88.18</td>
</tr>
<tr>
<td>2. Ph$_2$EtP Br$_4$</td>
<td>5.77</td>
<td>45.00</td>
<td>77.99</td>
</tr>
<tr>
<td>3. Ph(CH$_3$)$_2$PBr$_4$</td>
<td>5.70</td>
<td>36.50</td>
<td>64.04</td>
</tr>
<tr>
<td>4. Ph$_2$CH$_3$PBr$_4$</td>
<td>7.77</td>
<td>35.00</td>
<td>45.05</td>
</tr>
<tr>
<td>5. PhEt$_2$PBr$_4$</td>
<td>10.30</td>
<td>42.88</td>
<td>41.63</td>
</tr>
<tr>
<td>6. Et$_3$PBr$_4$</td>
<td>5.80</td>
<td>21.38</td>
<td>36.85</td>
</tr>
<tr>
<td>7. Bu$_3$PBr$_4$</td>
<td>10.70</td>
<td>39.00</td>
<td>36.45</td>
</tr>
<tr>
<td>8. Ph$_2$(CH$_3$O)PBr$_4$</td>
<td>10.30</td>
<td>32.25</td>
<td>31.31</td>
</tr>
<tr>
<td>9. Ph$_2$ClPBr$_4$</td>
<td>10.60</td>
<td>28.63</td>
<td>27.00</td>
</tr>
</tbody>
</table>

conducting species in solution. However, the extent of ionization varies i.e. formation of ionic species spreads over a large range. In the case of tris (p-chlorophenyl) phosphine tetrabromide (compound 1) molar conductance is the highest because of the three electrophilic p-chlorophenyl groups which facilitate the ionization process to give ionic species. The extent to which a phosphine derivative bromine adduct is ionized seems to depend upon the nature of the R groups bonded to phosphorus atom. The alkyl derivatives form less ionized species as shown by the molar conductance values of compounds 4-7. Presence of an electron donor group is expected to yield a less ionized products (comp. 8) as compared with the derivative containing electrophilic chlorine atom (comp. 9). The higher value of molar conductance for the methoxy derivative is explained due to steric factors. The bulky alkoxy group confers instability to the adduct formed and as a result
Conductometric titration plots of phosphine derivatives against bromine in acetonitrile at 25°C

Conductometric titration of $\text{Ph}_3\text{POCH}_3$ with bromine in acetonitrile at 25°C. (Methoxy diphenyl phosphine):

(a) $0.806 \times 10^{-3}$ M  (b) $1.03 \times 10^{-3}$ M

Conductometric titration of $(4-\text{Cl-C}_6\text{H}_4)_3\text{P}$ with bromine in acetonitrile at 25°C. (tris- ($p$-chlorophenyl) phosphine)

(a) $2.58 \times 10^{-4}$ M  (b) $3.9 \times 10^{-4}$ M
formation of ionization is favoured raising the molar conductivity as compared with the chloro analog (comp.9).

Beyond 2:1 Bromine to phosphine derivative mole ratio, there is a slight decrease in specific conductance after the approach of the 2:1 addition product. This could be attributed to the dilution effects caused by further addition of bromine solutions. For the less basic phosphine derivatives, the 2:1 conductance breaks are observed to be delayed. In these cases, the donor-acceptor interactions exist in equilibrium between the ionised and unionised forms. Therefore, the 2:1 Bromine to phosphine breaks should be considered with care for establishing the stoichiometry of the adducts formed in solution. For basic phosphine derivatives e.g. (4-Cl-C₆H₄)₃P (Fig.4), the 2:1 bromine to phosphine derivative ratio break is delayed considerably. Therefore, a weaker interaction takes place and equilibrium lies in favour of the reactants.

The conductance maximum position is also observed to be dependent upon the initial concentration of the phosphine derivative taken for titration as shown in Fig.4.

Popov and Skelly [10] have drawn attention to the fact that the halide ions have a strong tendency to form polyhalide ions in acetonitrile solutions and conductance values showed variations. Further, Emeleus and Harris [11] have reported that tris-trifluoromethyl phosphine dichloride showed rise in conductance with increase in its concentration in acetonitrile solution which was attributed to show ionisation of the initially formed molecular adduct. In general, the bromine interactions with phosphine derivatives studied in the present work may be represented as follows:

\[
\begin{align*}
2R₃P & \underset{\text{1:2}}{\longrightarrow} (R₃P)₂Br \underset{\text{1:1}}{\longrightarrow} 2R₃PBr₂ \underset{\text{2:1}}{\longrightarrow} 2R₃PBr₄ \\
(R₃P)₂Br^+ + Br^- & \quad 2(R₃P)Br^+ + 2Br^- \quad 2R₃PBr^+ + 2Br_3
\end{align*}
\]
The ratios correspond to concentration ratios of bromine to phosphine derivatives.

At the conductance maxima, a greater curvature is observed with all the phosphine derivatives studied which supports [12] the reversible nature of equilibria and the equilibrium constant values are not extremely high. Nevertheless, the bromine adducts formed with most of the phosphine derivatives are appreciably ionised to varying degrees in acetonitrile solutions.

REFERENCES