Ionic Products in Reaction between Triphenylphosphine & Tetrabromomethane

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The reaction between triphenylphosphine and tetrabromomethane has been found to be very fast and leads to the formation of ionic products, thus leading to a new method for their quantitative estimation. Various features of the conductometric titration curves of tetrabromomethane and triphenylphosphine (both forward and reverse) are explained in terms of possible ionic products.

The mixtures of phosphines with tetrahalomethanes are widely used for the conversion of alcohols\(^1,2\), hydrazines\(^3\) and S-alkylthiocarbamates into alkyl halides, hydrazonyl halides and N-phenylchlorothioformimidates respectively and as dehydrating\(^4,6\) and P\(^-\)N\(^1\) bond forming reagents. While studying the reaction between triphenylphosphine (TPP) and tetrabromomethane (TBM) in acetonitrile conductometrically it was observed that the reaction was very fast even at room temperature and the conductance of the mixture attained a constant value after a sudden jump. This observation has led us to explore the possibility of developing an analytical method for the estimation of TPP and TBM, and also to learn about the nature of the possible ionic products formed during the course of forward and reverse titrations.

Acetonitrile (IDPL) was dried over potassium hydroxide, refluxed over phosphorus pentoxide for 1 hr and the middle fraction distilling at 79-80°C was collected and stored over molecular sieves (4A). TPP (99%, Aldrich) and TBM (Aldrich) were used as such.

Tri bromomethyltriphenylphosphonium bromide was prepared as follows:

To a stirred suspension of TPP (0.5 mol) in acetonitrile was added a solution of TBM (0.5 mol) in acetonitrile. A solid separated out, which was filtered. It analysed for \([\text{Ph}_3\text{PCBr}_3]^+\ \text{Br}^-\), m.p. 227-29°C (lit.\(^3\) m.p. 230°C) (Found: C, 39.37; H, 3.2; Br, 53.0. Calc. for \(\text{C}_{19}\text{H}_{13}\text{Br}_4\text{P};\ C, 38.42; H, 2.55;\) Br, 53.9%).

Solutions of TPP and TBM in dry acetonitrile have very low conductivities \((10^{-5} \text{ S cm}^{-1})\). In the direct titrations TBM was taken in the reaction vessel which could be maintained at the desired temperature with an accuracy of \(\pm 0.1°C\), and TPP added to it. After each addition the solution was stirred vigorously at least for 2 min. It was noted that after instantaneous increase, the conductance attained a constant value after a few minutes (maximum 5 min). This was observed till the molar ratio of TPP/TBM was 2.0, after which only an increase in conductance was observed.

In the indirect titrations TPP was taken in the reaction vessel and TBM added to it, and the conductance noted after stirring the solution vigorously for a few minutes.

The titration curve of 0.03 \(M\) solution of TBM against 0.3 \(M\) solution of TPP at 55°C showed three distinct breaks at TPP/TBM molar ratios of 1.2, 2.0 and 4.0 (Fig. 1, curve-a). The curve became steeper after the first break up to the second break. After second break there was a slow rise in conductance till the third break at TPP/TBM molar ratio of 4.0. Thereafter, the conductance remained more or less constant with further addition of TPP.

The appearance of first break and the TPP/TBM molar ratio at the first break depend on the concentration of TBM (Fig. 1, curve-b, TBM conc. \(=0.01 M,\) TPP/TBM = 1.16). However, the molar ratios at the second and third breaks are always 2.0 and 4.0 respectively. Thus either of these breaks can be used to estimate the concentration of one if that of the other is known. However at TBM initial concentration of 0.005 \(M\), the first break disappeared completely (Fig. 1, curve-c). Curve-c describes the titration for TBM conc. \(\leq 0.005 M\).

Molar conductance \((58.95 \text{ S cm}^2 \text{ mol}^{-1})\) at 0.0091 \(M\) of TBM at TPP/TBM molar ratio of 1 or at the first break calculated on the basis of the starting concentration of TBM is nearly half of that of a solution of \([\text{Ph}_3\text{PCBr}_3]^+\ \text{Br}^-\) of the same concentration \((109.5 \text{ S cm}^2 \text{ mol}^{-1})\). This shows that this break does not indicate the culmination of the reaction involving the formation of \([\text{Ph}_3\text{PCBr}_3]^+\ \text{Br}^-\) but some nonconducting species like \(\text{Ph}_3\text{PCBr}_2\) and \(\text{P}_3\text{Br}_2\) are also being produced simultaneously from the very beginning by the reaction of these ionic species with TPP.

The second break at TPP/TBM molar ratio of 2.0 possibly corresponds to the reaction (1) in which one mol of TBM reacts with 2 mol of TPP to produce \([\text{Ph}_3\text{PCBr}_2\text{PPh}_3]^2+ + 2\text{Br}^-\)

\(\text{CBr}_4 + 2\text{PPh}_3 = [\text{Ph}_3\text{PCBr}_2\text{PPh}_3]^2+ + 2\text{Br}^-\) \(\ldots (1)\)

The ionic species \([\text{Ph}_3\text{PCBr}_2\text{PPh}_3]^+\) then rearranges to the above non-conducting species.

The existence of chlorine analogue of \([\text{Ph}_3\text{PCBr}_2\text{PPh}_3]^2+\) has been shown by Appel and Morbach\(^8\) and Appel et al.\(^7\). It seems that at this stage all the species \([\text{Ph}_3\text{PCBr}_2\text{PPh}_3]^2+,\) \(\text{Ph}_3\text{PCBr}_2\) and \(\text{Ph}_3\text{PBr}_2\) (which exists\(^9\) as \([\text{Ph}_3\text{PBr}]^+ + \text{Br}^-\) are
Fig. 1—Conductometric titration curves between TBM and TPP.  
[(a) TBM = 0.03 M; TPP = 0.3 M;  (b) TBM = 0.01 M; TPP = 0.1 M;  
(c) TBM = 0.005 M; TPP = 0.05 M; and (d) TBM = 0.001 M; TPP  
= 0.01 M]

Fig. 2—Conductometric titration curves between TPP and TBM.  
[(a) TPP = 0.04 M; TBM = 0.02 M;  (b) TPP = 0.01 M; TBM = 0.1 M;  
and (c) TPP = 0.005 M; TBM = 0.05 M]

Appel and Morbach\(^8\) have shown the existence of \([\text{Ph}_3\text{PCIPPh}_3]^+\) on the chemical basis and a  
symmetrical mesomeric structure for \([\text{Ph}_3\text{PCHPPPh}_3]^+\text{ Br}^-\) has been assigned by Driscoll  
et al.\(^10\). Therefore, reactions (2a) and (2b) are quite  
plausible.

The above reactions lead to a molar ratio of TPP/ 
TBM = 3.0. However the observed third break is at  
TPP/TBM molar ratio of 4.0. This means that either  
\([\text{Ph}_3\text{PCBrPPh}_3]^+\) or \(\text{Ph}_3\text{PBr}_2\) reacts with additional  
TPP. It is difficult to assign the exact structure of such  
a compound from experimental data at hand.

The reverse titration of 0.04 M TPP against 0.2 M  
TBM shows an increase in conductance till it reaches a  
maximum at TBM/TPP molar ratio of 0.5 (Fig. 2,  
curve-a). The conductance then falls till TBM/TPP  
= 0.75 ± 6.05, after which it remains constant.  
Titration curves at lower concentrations of TPP  
(≤ 0.005 M) do not show any change except that the  
maxima in the curves shift to lower values (<0.5),  
while the final break always occurs at 0.75.

The rise in conductance up to first break is probably  
due to the reactions (1) and (2). After this the fall in  
the conductance up to third break is due to the formation  
of \([\text{Ph}_3\text{PCBr}_3]^+\text{ Br}^-\). Thus the overall reaction is  
given by Eq. (3).

\[4\text{Ph}_3\text{P} + 3\text{CBr}_4 = 2[(\text{Ph}_3\text{PCBr}_3)^+\text{ Br}^-] + \text{Ph}_3\text{PBr}_2\]  
--- (3)
It is interesting to note that two mol of the phosphinium salt and one mol each of Ph₃PCBr₂ and Ph₃PBr₂ are formed. The titration curves may lead to the determination of TPP/TBM ratio for optimum use as a reagent in organic synthesis.

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References
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