Iodine Adducts with Phosphine Derivatives in Acetonitrile as Solvent

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Summary: The phosphine derivatives having general formulae; R_3P, $R_2\acute{R}P$ and R_2PX (where R = aryl or substituted aryl group, $\acute{R}$ = alkyl or alkoxy group and X = halogen) react with iodine to form 2:1, 1:1 and 1:2 addition compounds in solution. The solvent acetonitrile, exerts an ionising affect on the adducts formed. The interactions are studied by conductometric and spectroscopic methods. In presence of excess of phosphine derivative concentration, formation of iodide ions takes place.

$2\ R_2\acute{R}P + I_2 \quad (R_2\acute{R}P)_2I_2 \quad (R_2RP)_2I^+ + I^-$ and $R_2\acute{R}P + I_2 \quad R_2\acute{R}PI_2 \quad R_2\acute{R}PI^+ + I^-$. The reaction involves the formation of an equilibrium system predominantly lying towards the right side. When excess of iodine is present, triiodide ions are formed:

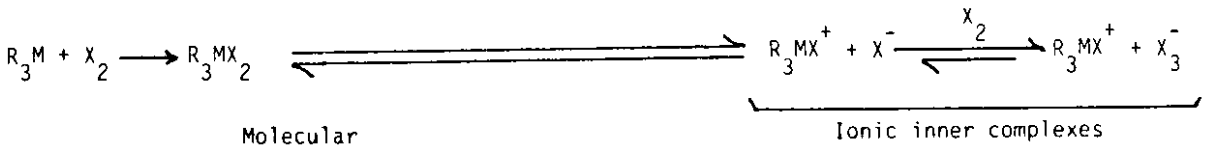
$$R_2\acute{R}P + 2I_2 \quad R_2\acute{R}PI_4 \quad R_2\acute{R}PI^+ + I^-_3$$

The spectroscopic results complement the results obtained by conductometric measurements.

Introduction

Some phosphine derivatives are known [1] to react with halogens to form 1:1 and 1:2 adducts. The tertiary organophosphorous dihalides of the type R_3PHal_2 (R = alkyl or aryl group) have well established 1:1 stoichiometric ratios. Beveridge and Harris [1] reported conductance measurements on some R_3PHal_2 compounds in solvents such as nitrobenzene and acetonitrile. The formation of 1:2 adducts having general formula, R_3PHal_4 were also reported as the concentration of the halogen becomes greater than that of the phosphine derivative concentration. The studies on the nature of such addition compounds have been inadequate.

The complexes produced have been thought to be differing [2] strongly in the extent of charge-transfer (between the phosphine derivative and the halogen) and often at the same time to be present in the molecular form as well. The environmental conditions effect the nature of the products obtained. Thus on changing the solvent from non-polar to polar, the species formed may change from molecular to ionic. Such isomeric forms have been designated [3] as "outer complex" (usually bound with little charge-transfer) and "inner complex" (with more or less complete charge-transfer). In general, the possiblities for the formation of various species can be shown as follows:



$R = CH_3, C_6H_5$

M = P, As;

The ionisation is favoured [4] by a solvent having high dielectric constant. In less polar solvents, like nitrobenzene, the molecular pentavalent form prevails. A study of iodine adducts with phosphine derivatives, in carbon tetrachloride as solvent, has shown [5] the formation of 1:1 and 2:1 adducts which are present as "ion-pairs".

The formation of ionic species, for the Ph_3PCl_2 complex, is shown [6] to exist as Ph_3PCl^+ and Cl^- ions in acetonitrile. Since acetonitrile has polar and ionising properties, the interaction of a number of phosphine derivatives, having different basicities, with iodine as Lewis acceptor in acetonitrile as solvent is reported here. The results are found to support the ionised nature of the adducts similar to the triphenylphosphine dichloride [6] and triphenylphosphine dibromide [7] compounds.

Experimental

Purification of Materials

Acetonitrile (Fluka, Puriss. p.a.) was purified by somewhat modified method as described by Coetzee et al. [8]. The solvent was successively treated with sodium hydroxide, calcium chloride and phosphorous pentaoxide. After refluxing, the solvent was distilled to collect the middle cut during each distillation. The dried solvent was further distilled on the vacuum line so as to remove traces of any drying agent left over. The purified solvent had little absorption above 200 nm. This solvent was used for conductance measurements. For spectroscopic measurements, Fluka spectroscopic grade acetonitrile was used after drying over molecular sieve. The solvent samples were tested for the absence of moisture by running the infrared spectra.

Iodine was used after purifying under vacuum in a sublimer. The purified iodine was stored in a desiccator over phosphorous pentaoxide.

Phosphine derivatives were received from Fluka. The samples were sealed and were kept under refrigiration.

Handling of Materials

In order to avoid contact with moisture, all the work was carried out in a dry box which was kept dry by using phosphorous pentaoxide. Dry nitrogen was flushed frequently so as to maintain an inert atmosphere.

Conductometric titrations

A conductometric cell was placed in the dry box on a magnetic stirrer, and was fitted with a dropping burette. The conductance of the solution, placed in the cell, was measured by using Orion Research conductivity meter model 101. The bridge was

placed outside the dry box. The titrations were performed by taking suitable concentrations in the 10^{-4} --- 10^{-3}M range and iodine concentration was taken ten times greater. In reverse titrations the iodine concentration ($\sim 10^{-4}$M) was kept constant and the phosphine derivative concentrations were increased.

Spectroscopic measurements:

Ultraviolet spectra were recorded on a Pye-Unicam SP8-400 UV/VIS spectrophotometer. Pure solvent was used as reference. The absorbance scale was kept from 0-1. Mixtures of the reactants containing varying molar ratios were prepared in 10 cm^3 flasks and their spectra were scanned between 450 - 200 nm. Quartz cells having one cm path length were used.

Results and Discussion

Conductance measurements are carried out with the following phospine derivatives in acetonitrile solutions Ph_2PCH_3, $Ph_2PC_2H_5$, Ph_2POCH_3, $Ph_2(4\text{-}CH_3C_6H_4)P$, $(But)_3P$, $(4\text{-}ClC_6H_4)_3P$ and Ph_2PCl.

At first, the phosphine derivative concentration is kept constant (i.e. the stoichiometric conc.) and the iodine concentrations are varied. The conductance plots obtained for the various phosphine derivatives are shown in fig.1. The conductance plots show breaks around 0.50: 1, 1:1 and 2:1 mole ratios of iodine/phosphine derivative; corresponding to the formation of bis-phosphine derivative iodide di-iodides and tetra iodides (plots 1,2,4). The rise in specific conductance indicates that ionic nature of the species produced in solution. At the beginning of titration when the concentration of iodine is less than that of the phosphine derivative, the addition compounds having 0.5:1.0 s toichiometry is detected.

$$2R_3P + I_2 \rightleftharpoons (R_3P)_2\ I_2 \quad (R_3P)_2I^+ + I^- \text{ -- (i)}$$

On further increasing iodine concentration, inflextion observed near 1:1 mole ratio indicates the following reaction.

$$R_2RP + I_2 \longrightarrow (R_2RPI_2) \rightleftharpoons R_2RI^+ + I^- \quad \text{(ii)}$$

The breaks around 1:1 mole ratios are not sharp but are somewhat curved which means the presence of an equilibrium between the ionic and molecular species. The curvature [9] observed in these plots indicates the equilibrium constant values are not extremely high. The formation of I^- ions, in equation (i) and (ii) is supported by the appearance of a characteristic absorption band at 246 nm in the UV region. The equilibrium lies predominantly towards the ionic species. The conductance is increased sharply as the concentration of iodine exceeds 1:1 mole ratio. At this region, formation of tetraiodide is indicated which is suggested to be ionised according to the following process:

$$R_2RP + 2I_2 \longrightarrow (R_2RPI_4) \longrightarrow R_2RPI^+ + I_3^- \quad \text{(iii)}$$

The 2:1 break, in the case of diphenylethylphosphine and tris p-chlorophenyl phosphine, appear to be lagging behind the expected ratios (plots 3,5). This may be explained in terms of the more reversible nature of the equilirbium. However, the overall reaction for these titrations may be explained by the stepwise reactions that are responsible for the

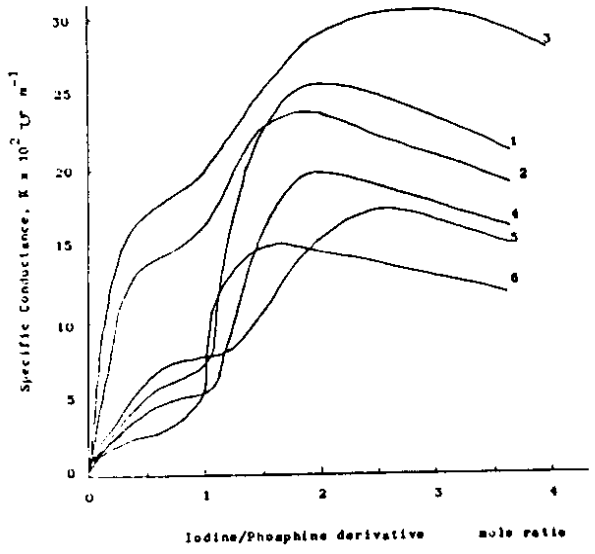


Fig.1: Conductometric titration plots of phosphine derivatives with iodine in acetonitrile at 25°C.
1. Ph_2PCH_3 2. Ph_2POCH_3 3. $Ph_2PC_2H_5$
4. $Ph_2(4\text{-}CH_3C_6H_4)P$ 5. $(4\text{-}Cl\ C_6H_4)_3P$
6. Ph_2PCl

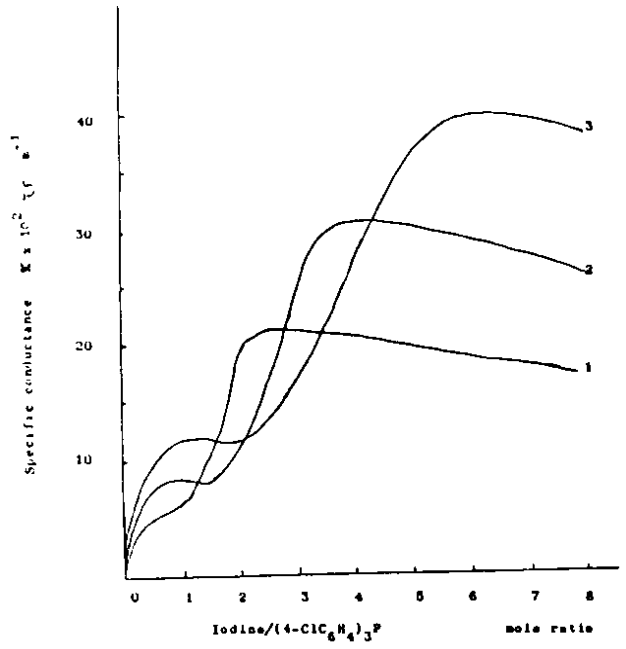


Fig.2: Conductometric titration plots of tris p-chlorophosphine (1, 0.15 x 10^{-3} 2. 0.30 x 10^{-3} and 3, 0.50 x 10^{-3}M) with iodine in acetonitrile at 25°C.

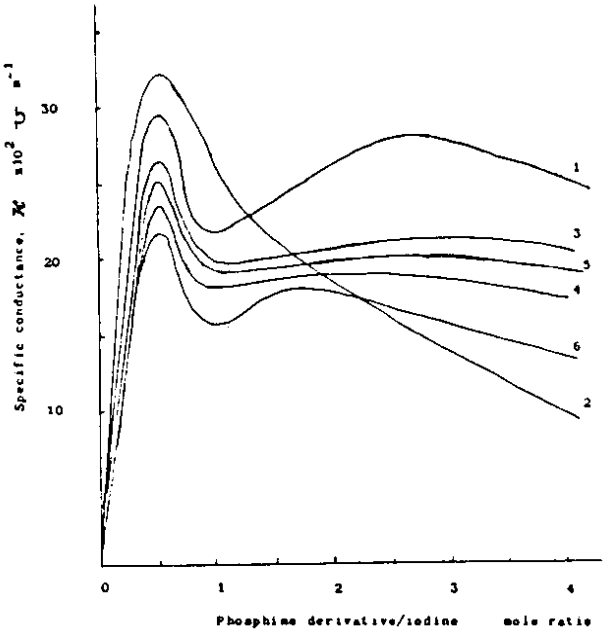


Fig.3: Conductometric titration plots of iodine solution with phosphine derivatives ion acetonitrile at 25°C.

1. Ph_2PCH_3 2. Ph_2POCH_3 3. $Ph_2PC_2H_5$
4. $Ph_2(4\text{-}CH_3C_6H_4)P$ 5. $(4\text{-}ClC_6H_4)_3P$
5. Ph_2PCl. (Iodine) = 10^{-4}M

breaks in the conductance plots (after the formation of 2:1 phosphine derivative to iodine mole ratio as represented by eq (i)).

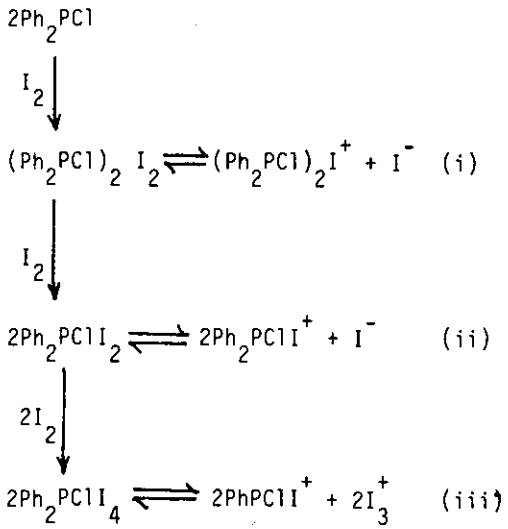
$$R_2RP + I_2 \longrightarrow R_2RPI^+ + I^-$$

$$I^- + I_2 \longrightarrow I_3^-$$

$$R_2RP + 2I_2 \longrightarrow R_2RPI^+ + I_3^-$$

The conductance plot (6) for diphenylchlorophosphine-iodine system shows a weaker interaction as compared with the other phosphine derivatives. In this case, the conductance plot is similar to other phosphine derivatives except the breaks appear

earlier than expected. However, the breaks can be interpretted as involving the following equilibria,



From the present results and previously reported [1,4,9, 14] conductance plots, it may be concluded that the conductometric titration graphs could be of four types. (1) For stoihciometric formation or removal of ionic species results in a sharp inflexion/break [1,4,14] in conductance plot. (2) For a system involving equilibria, that lie predominantly towards the products side, show curved [9] change over in conductance around the stoichiometric ratios. (3) For systems involving weak interactions leading to the establishment of equilibria where large quantity of one of the reactants is needed to shift the equilibrium substantially towards the products side, the conductance breaks are curved and delayed. (4) The quilibrium involves a much weaker interaction and no information could be obtained from such conductometric titrations. The type (3) conductance plot would lead erronious stoichiometrics. In order to check this type of system, the base (e.g. (4-Cl $C_6H_4)_3P$) concentration is varied while titrating against iodine. The conductance breaks shift their positions (Fig. 2). The systems of the type (1) and (2) give reproducible conductance plots irrespective of the concentration of the base used for the titration.

Reverse titrations

In order to check the stoichiometry of the adducts produced, the method of reverse titration is adopted. The phosphine derivative concentrations are varied for a fixed amount of iodine. Under these experimental conditions, when iodine is in large excess, at the beginning of the titration, tetraiodides are more likely to be produced eq. (iii) as shown by the first break around 0.50 phosphine to iodine molar ratio (Fig. 3).

The conductance plots 3,4,5, after 0.5:1.0 phosphine derivative to iodine mole ratio, show a drop and then there is an increase with increasing concentration of the phosphine derivative. The drop in conductance suggests the formation of an adduct that is less conducting than the tetraiodide, R_2RPI_4 along with minor dilution effects. Where the concentration of the phosphine derivative is in excess of iodine concentration, the conducting species likely to be formed is the diiodide, eq. (ii) and the product represented by equation (i). The complete formation of 1:1 or 2:1 adduct is not accomplished except for diphenylmethylphosphine (plot 1) which shows a second maximum around 2.75 mole ratio (phosphine/iodine). The other phosphine derivatives do not seem to approach the second maximum position under the experimental conditions used. The 1:1 break is either delayed (type (3) equilibrium) or the titration gives inconclusive result of the type (4).

The conductance plot 2 for diphenylmethoxyphosphine-iodine system shows that the specific conductance decreases continuously, after the 0.5:1.0 mole ratio, as the concentration of the phosphine derivative is increased. While there is a continuous fall in conductance, precipitation is observed and the 1:1 adduct formed is thrown out as soon as it is formed. The oxygen to iodine coordination is likely in this case. For the diphenylchlorphosphine-iodine system (plot 6) the formation of the tetraiodide is evident from the break at 0.5:1.0. The second maximum beyond 1:1 molar ratio indicates the presence of an equilibrium existing between the species present in solution. The reactions involved are like the one encountered during direct titration of the base with iodine solution. The base being weaker, the formation of less stable $(Ph_2PCl)_2I_2$ adduct produces I^-_3 ions according to eq. (v).

Electronic spectrum of iodine in acetonitrile solution

Iodine is readily soluble in acetonitrile and it shows two absorption bands at λ_{max} = 360 and 290 nm. The absorption bands are characteristic [3] for the triiodide ion present in acetonitrile. The two bands show lower values of molar absorbances as compared with the reported values (log ε_{360} = 4.49 and log ε_{290} = 4.76). Therefore, disproportionation of iodine is suggested when dissolved in acetonitrile:

$$2I_2 \rightleftharpoons I^+ + I_3^- \quad ---- \text{(iv)}$$

The disproportionation is further supported by observing an absorption band at 462 nm (characteristic [15] of molecular iodine) at higher concentrations.

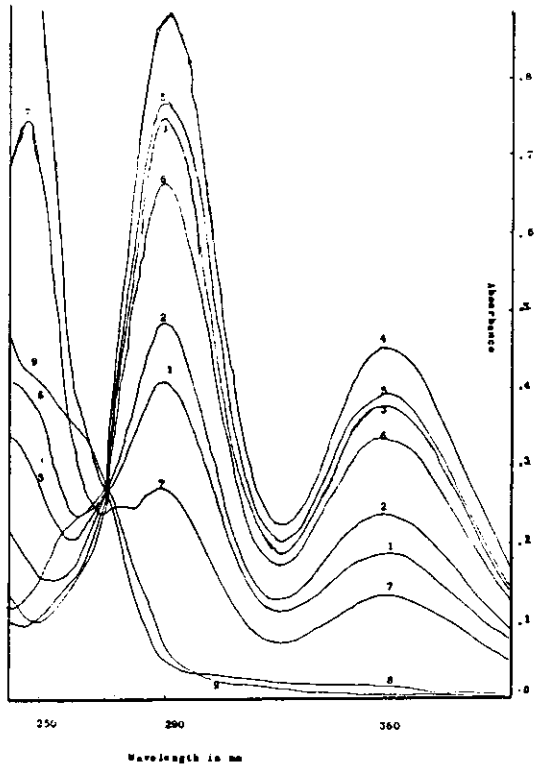


Fig.4: Electronic spectra of $Ph_2PC_2H_5$-I_2 system in acedtonitrile. The spectra of iodine (2.45×10^{-5}M) containing varying concentrations ($\times 10^5$) of diphenylethylphosphine (1) 0.00 (2) 0.48 (3) 0.96 (4) 1.12 (5) 1.79 (6) 2.24 (7) 3.35 (8) 4.45 M; spectrum 9. $Ph_2PC_2H_5$ (4.45×10^{-5}) without iodine.

Spectroscopic study of iodine reactions with the following phosphine derivatives is carried out: Ph_2PCH_3, $Ph_2PC_2H_5$, Ph_2POCH_3, $Ph_2(4\text{-}CH_3C_6H_4)P$, $(4\text{-}ClC_6H_4)_3P$.

The iodine concentration is kept constant (ca 2.45×10^{-5} M) and the phosphine derivative concentration is varied over a range, as far as practically possible. In mixtures containing phosphine derivative concentrations less than that of iodine, enhancement in the I_3^- absorption bands is observed at 360 and 290 nm (characteristic

Table-1: Absorbance changes at 360 nm band for diphenylethylphosphine-iodine system in acetonitrile at 25°. $[Iodine]_{stoich} = 2.45 \times 10^{-5}$ M

$[Ph_2PC_2H_5]_{stioch}$ x10^5 M	$Ph_2PC_2H_5 : I_2$	$A_{360\ nm}$
0.000	0.000	0.188
0.480	0.196	0.238
0.960	0.392	0.387
1.120	0.457	0.456
1.225	0.500	0.480
1.790	0.731	0.394
2.240	0.914	0.337
3.350	1.367	0.131
4.450	1.816	0.020

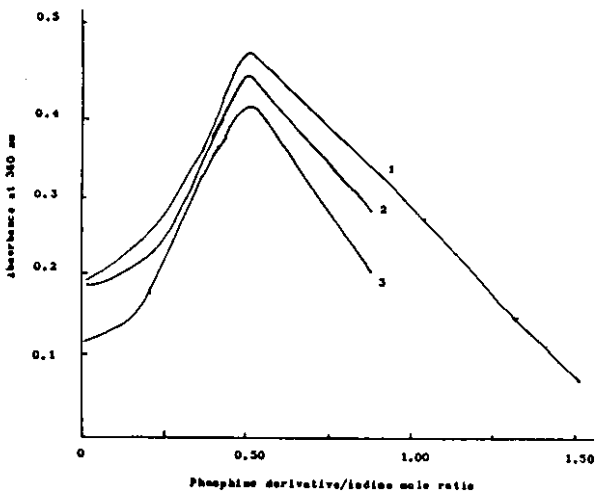


Fig.5: Graphs between absorbance at 360 nm vs phosphine/iodine solar ratios.
1. $Ph_2PC_2H_5$ 2. Ph_2PCH_3 and 3. Ph_2POCH_3

[3] bands for the triiodide ion). The formation of tetraiodide (R_2RPI_4 = $R_2RPI^+ + I_3^-$) is most favourable under these experimental conditions. The concentration of I_3^- ions is increased as the absorbance reaches to a maximum at the two absorption maxima. All these phosphine derivatives show a similar behaviour. In general, the spectral changes, as observed for diphenylethylphosphine-iodine system, are shown in Fig.4. For varying concentrations of the phosphine derivative, the absorbance values, at different molar ratios, are shown in Table 1. The results show almost stoichiometric 1:2 phosphine/iodine adduct formation which is completely ionised in solution.

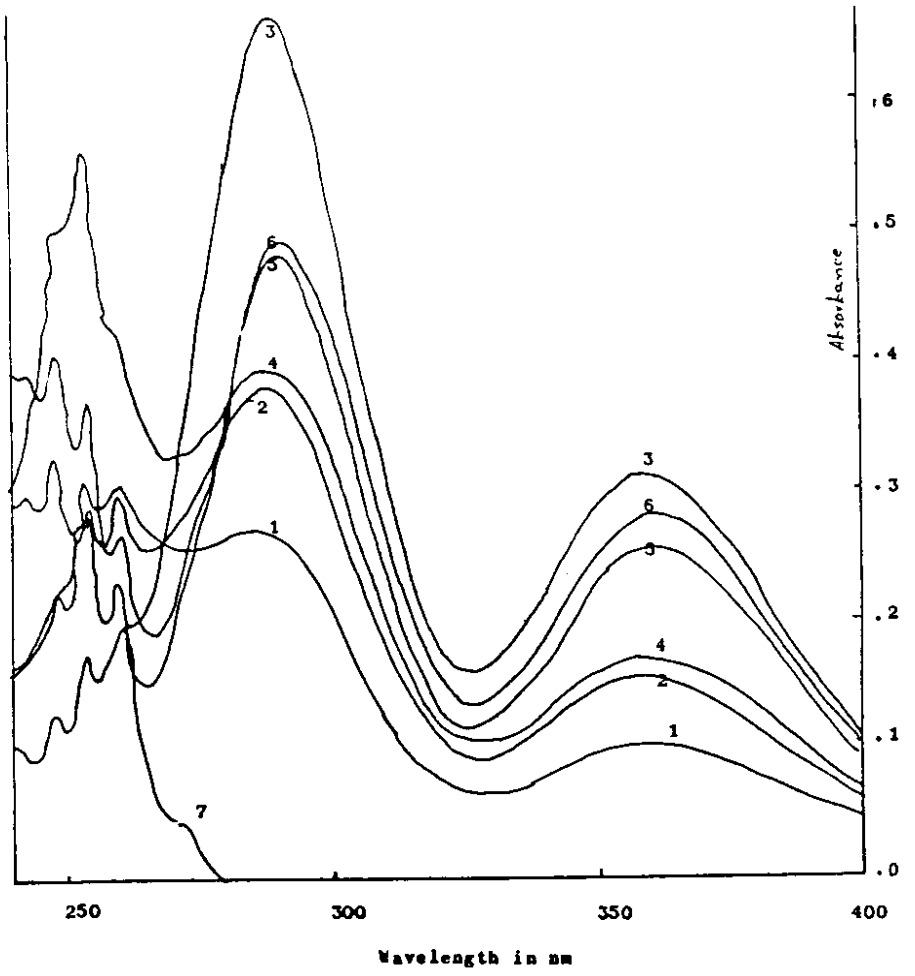


Fig.6: Electronic spectra of Ph_2PCl - I_2 system in acetonitrile. The spectra of iodine (2.08×10^{-5}) containing varying concentrations ($\times 10^{5}$) of diphenylchlorphosphine. (1) 0.00 (2) 0.713 (3) 1.426 (4) 2.121 (5) 3.535 (6) 4.424 M; spectrum 7. Ph_2PCl (4.242×10^{-5}M) without iodine.

The phosphine derivatives studied possess enough basic properties and show almost complete interactions with iodine. Plots of absorbance at 360 nm vs phosphine derivative to iodine molar ratios are shown in Fig. 5 for diphenylethylphosphine, diphenylmethylphosphine and diphenylmethoxyphosphine. In each case, a break at 0.50 phosphine to iodine molar ratio is observed. On further increase of molar ratio, I_3^- absorption bands decrease whereas absorptions for the formation of I^- ions is observed in the range 240-245 nm. This is one of the CTTS transitions reported [10,15] for the I^- ions in acetonitrile. For phosphine derivative concentrations greater than iodine, an equilibrium system is established as excessive amount of phosphine derivative is required for completely diminishing the triodide absorption bands. In general, these systems may be represented by equations (iii) and (ii).

The reversible nature of the equation (ii) is in line with the suggested greater stability (11,12) for the I_3^- ions.

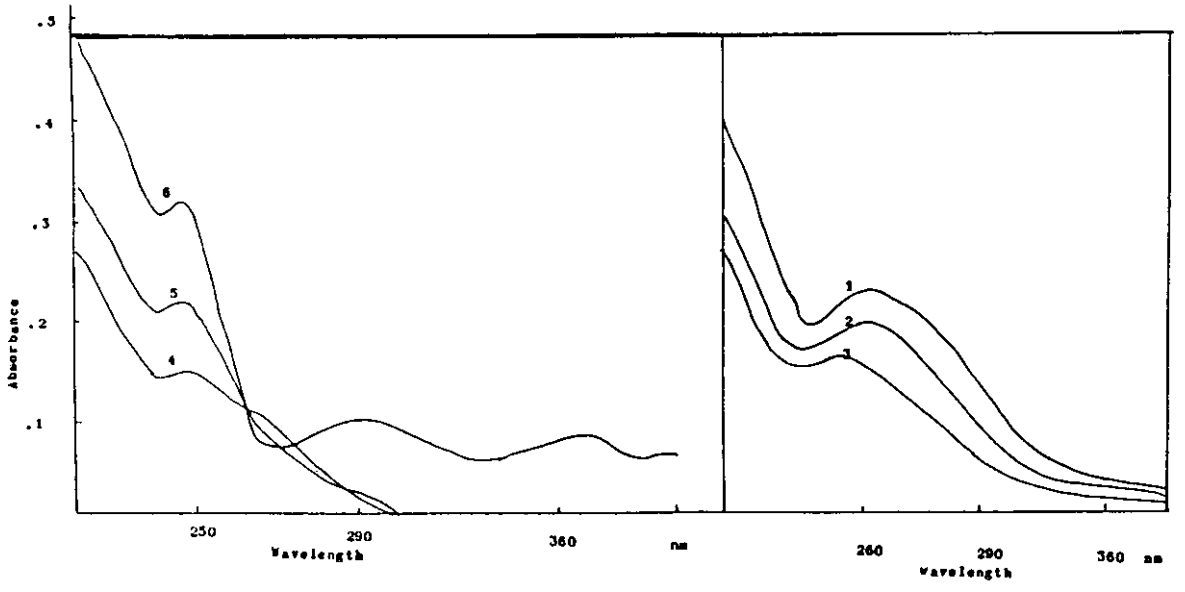


Fig.7: Electronic spsectra of $Ph_2(4\text{-}CH_3C_6H_4)P\text{-}I_1$ system in acetonitrile. The spectra of 1.08×10^{-5} solution of $Ph_2P(4\text{-}CH_3C_6H_4)$ containing varying concentrations ($\times 10^5$) of iodine: (1) 0.00 (2) 0.056 (3) 0.14 (4) 0.28 (5) 0.56 (6) 1.10 M.

The dipehnylchlorophosphine-iodine system

For this system, as the concentration of the phosphine is increased, the absorption bands at 360 and 290 nm are enhanced (fig. 6). This is due to the formation of 1:2 adduct ($Ph_2PClI^+ + I_3^-$). After reaching a maximum, the absorbance decreases according to the equilibria represented by equation (ii) Here I^- absorption at 245 nm is maximum. Thereafter, on approaching 2:1 mole ratio, the I_3^- absorption bands become enhanced, unlike other phosphine interactions with iodine, most probably due to the presence of the following equilibrium:

$$2(Ph_2PCI)_2I_2 \rightleftharpoons Ph_2PCl + Ph_2PClI^+ + I_3^- \quad (v)$$

This is, of course in agreement with the conductometric titration results reported in this paper.

In order to observe the effects of changing concentrations of the diphenyl, p-methylbenzyl-phosphine, the phosphine derivative concentration is kept constant and iodine concentration is varied. The phosphine derivatives absorb at 260 nm for the n π transition [13]. The absorption decreases on increasing iodine concentration (Fig. 7). The results support the formation of I^- ions.

$$2Ph_2(4\text{-}CH_3C_6H_4)P + I_2 \longrightarrow [Ph_2(4\text{-}CH_3C_6H_4)P]_2I_2$$

$$\rightleftharpoons [Ph_2(4\text{-}CH_3C_6H_4)P]_2^+ + I^- \text{ ------- (vi)}$$

$$Ph_2(4\text{-}CH_3H_6H_4)P + I_2 \longrightarrow Ph_2(4\text{-}CH_3C_6H_4)PI_2$$

$$Ph_2(4\text{-}CH_3C_6H_4)PI^+ + I_3^- \quad \text{(vii)}$$

The increase in absorption around 245 nm shows the formation of I^- ions. A further increase in iodine concentration leads to the formation of I_3^- ions as characteristic absorption bands

at 360 and 290 nm are noticed (spectrum 6). This is found to be in agreement with the formation of ionised 1:2 phosphine derivative to iodine adduct, alongwith the adducts represented by equations (vi) and (vii).

$$Ph_2(4\text{-}CH_3C_6H_4)P + 2I_2 \rightleftharpoons Ph_2(4\text{-}CH_3C_6H_4)PI^+ + I_3^- \qquad \text{(viii)}$$

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