Iodine Adducts with Phosphine derivatives in Carbon-tetrachloride as Solvent.

ALI MOHAMMAD,[*] HABIB A. AUGHUSTEEN AND OSMAN. H. AMIN

Chemistry Department, College of Science, Sulaimaniyah University, Sulaimaniyah. Iraq.

Summary : The phosphine derivatives, $R_2R'P$ or R_3P (where R = aryl or substituted aryl group and R' = alkyl or alkoxy group) form 1:1 and 1:2 adducts with iodine. The stoichiometries of these adducts depend upon the molar ratios of the reactants. In carbon tetrachloride solutions, these adducts are present as "ion pairs". The tetraiodides are comparatively unstable and change into the more stable diiodides with time. The nature of the adducts and changes in the electronic spectra are discussed.

In a recent report[1], the formation of ions from the iodine adducts with phosphine derivatives has been detected in non-aqueous polar acetonitrile as a solvent. The present work involved conductometric and spectroscopic studies on iodine adducts with some phosphine derivatives in non-aqueous, non-polar carbon tetrachloride as a solvent. Primarily, the reactions of phosphino derivatives with iodine are a type of donor-acceptor interaction. Subsequently, the primary adducts may undergo changes and ionisation occurs in solvents of high polarity.

The nature of bonding, in iodine addition compounds, has been described[2] by the following equation :

$$\psi^0 = a\,\psi_{cov} + b\,\psi_{el} \quad \text{........(1)}$$

Where ψ_{cov} represents covalent contribution (often described as charge transfer interaction) and ψ_{el} includes electrostatic contribution. In many compounds $b > a$ in the ground state and ionic character predominates. Bhaskar et al[3] studied the interaction of triaryl derivatives of group V elements with iodine in chloroform as solvent and observed the formation of covalent (charge transfer) complex first which changed into ionic species with time. The tertiary phosphine derivatives are strongly basic[4] in nature and the formation of covalent complexes would have been expected.

The conductometric titration of diphenyl-p-tolyl phosphine with iodine (both dissolved in anhydrous carbon tetrachloride) showed little change in specific conductance (Fig. 1). The K value remained very low (ca 1.40×10^{-7} ʊ m^{-1}) during the titration performed at room temperature. The specific conductance value is too low to be taken for any
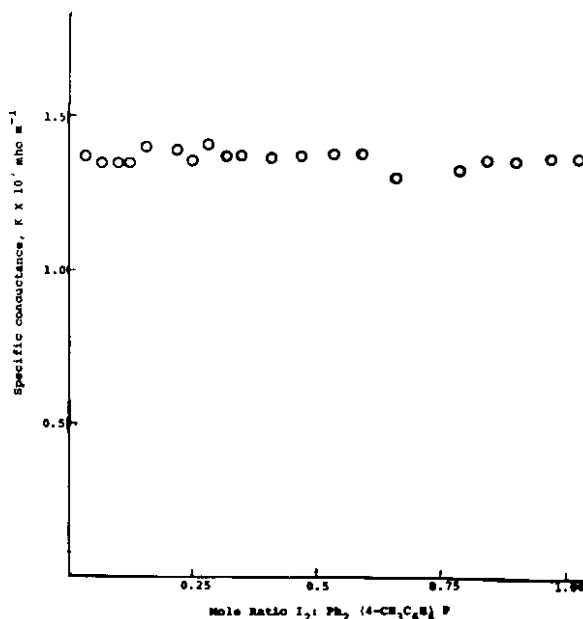

Fig.1 Conductometric titration of diphenyl-P-tolyl phosphine with iodine in carbon tetrachloride solution.

probable formation of ions in solution. Therefore, the formation of unionised molecular compound seemed more likely.

Iodine, in carbon tetrachloride solution, shows an absorption band at 520 nm (log E = 2.96). The absorption has been assigned[2] as $\pi^* \to \sigma^*$ transition. On adding phosphine derivative, charge transfer interaction is not observed but the spectral changes support the formation of ionic species, similar to base-iodine interactions reported earlier[1,5,6] in polar non-aqueous media. Unlike triaryl derivatives of arsenic and antimony, triphenyl phosphine has been known to form[3,7,8] ionic compounds with halogens, whereas arsine and stibbine derivatives from comparatively unstable molecular complexes.
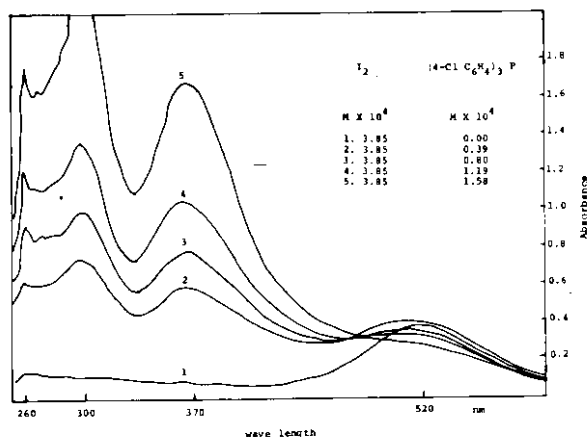
Fig.2 Electronic spectra of tris-(P—chlorophenyl) phosphine — iodine system in carbon tetrachloride solutions.

Except diphenylchlorophosphine, the other phosphine derivatives (dipheny—P—tolyl phosphine, methoxy diphenyl phosphine, ethyl diphenyl phosphine, methyl diphenyl phosphine and tris (p—chlorophenyl phosphine) show identical spectral changes. The changes in the spectrum of iodine on adding tris (p—chlorophenyl) phosphine is shown in Fig. 2 as a typical example. Iodine has negligible absorption in the UV region showing that, in carbon tetrachloride, it is almost present in the molecular form. As the phosphine derivative concentration is increased, two absorption bands are observed which are characteristic for I_3^- ion (at 365 and 295 nm). At higher concentrations of the phosphine derivative, an absorption band at 265 nm is observed coming up. This absorption is assigned [10] as charge transfer transition to solvent (CTTS). The ultravoilet spectral data are given in Table I.

Table I: Absorptions of iodine adducts with phosphine derivatives in carbon tetrachloride as solvent.
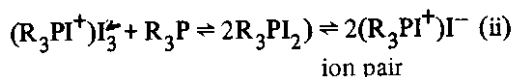
Phosphine Derivative	max in nm	
	I_3^-	I^- (CTTS)*
$Ph_2(4-CH_3C_6H_4)P$	365, 295	265
Ph_2POCH_3	368, 300	267
$Ph_2PC_2H_5$	370, 297	265
Ph_2PCH_3	377, 297	265
$(4-ClC_6H_4)_3P$	365, 295	260

* charge transfer transition to solvent.

For concentrations of iodine greater than phosphine derivatives, an isobestic point is observed which supports the presence of iodine in two forms. As the iodine concentration is in excess and the characterstic I_3^- absorptions are present, the following reaction is proposed for the formation of 1:2 adduct between the phosphine derivative and iodine :

$$R_3P + 2I_2 \rightleftharpoons R_3PI_4 \rightleftharpoons \underset{\text{ion pair}}{(R_3PI^+)I_3^-} \qquad \text{(i)}$$
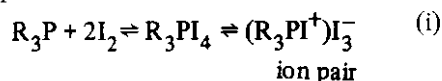
The solution being non-conducting, the adduct is present in the form of "ionpairs". Such ion pair association is observed even at low concentrations. The absorptions spectrum deviates from the isobestic point when the phosphine derivative concentration exceeds the iodine concentration and 1:1 adduct is commenced to form :

$$(R_3PI^+)I_3^- + R_3P \rightleftharpoons 2R_3PI_2) \rightleftharpoons \underset{\text{ion pair}}{2(R_3PI^+)I^-} \quad \text{(ii)}$$

The formation of $(R_3PI^+)I^-$ is supported by the appearance of absorption at 265 nm. The absorptions in the 280-250 nm range are not superimposable with the spectra of pure phosphine derivative.

The 1:2 adduct is less stable as compared with the 1:1 adduct as the spectrum of the former changes with time and ultimately the formation of 1:1 adduct is accomplished. The spectral changes with time for diphenyl methoxyphosphine — iodine system (the latter being in excess) are shown in in figure 3. The observations suggest that $R_3PI_4 \rightleftharpoons (R_3PI^+)I_3^-$ decomposes slowly, possibly, as follows

$$(R_3PI^+)I_3^-$$

II $\diagup$ $\diagdown$ I

$$R_3P + 2I_2 \rightleftharpoons (R_3PI^+)I^- + I_2 \text{ ...(iii)}$$
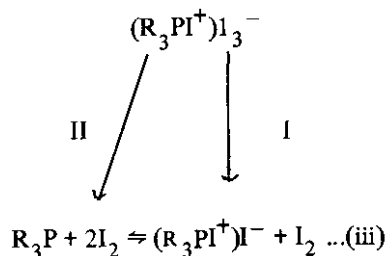
(The change via path I is concluded to be more favourable as the final solution contains molecular iodine and I^- ions.

$Ph_2PCI - I_2$ System
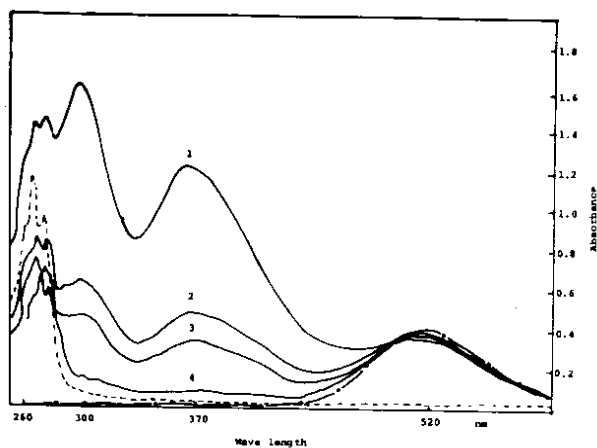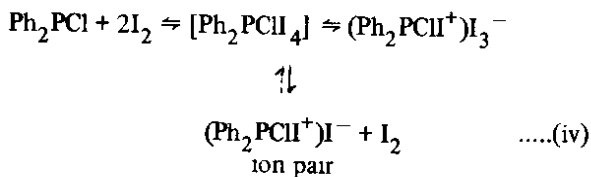
The spectral changes for this system are remarkably

Fig.3 Changes in the spectrum of diphenylmethoxyphos-phine—iodine system with time in carbon tetrachloride. Different time intervals.

1. 0.00 hr	2.29 hr	3.65 hr	4.386 hr

_ _ _ _Spectrum of disphenylmethoxyphosphine
_ _ _ _ Spectrum of iodine.

different fom the other phosphine derivative — iodine systems (see Fig. 4). As diphenylchlorophosphine is added to iodine solution., the tetraiodide is more likely to be formed. But the characteristic I_3^- ions are formed in the system. Therefore, the tetraiodide is produced in feeble concentration and simultaneouly the side reaction forming I^- ions is taking place as absorption around 260-275 nm region is enhanced extensively even at low concentration of the phosphine derivative. The CTTS absorption for I^- ions continueously increases with increasing phosphine concentration.

The diphanylochlorophosphine seems to react as follows

$$Ph_2PCl + 2I_2 \rightleftharpoons [Ph_2PClI_4] \rightleftharpoons (Ph_2PClI^+)I_3^-$$

$$\Updownarrow$$

$$(Ph_2PClI^+)I^- + I_2 \qquad .....(iv)$$
$$\text{ion pair}$$

The explanation given as above is in line with the proposed mechanism (iii). The only difference is that the tetraiodide is ionised to a much smaller extent and path I is followed to produce ion paris containing I^- ions. Further, the spectra of the other phosphine derivatives, after changing with time,
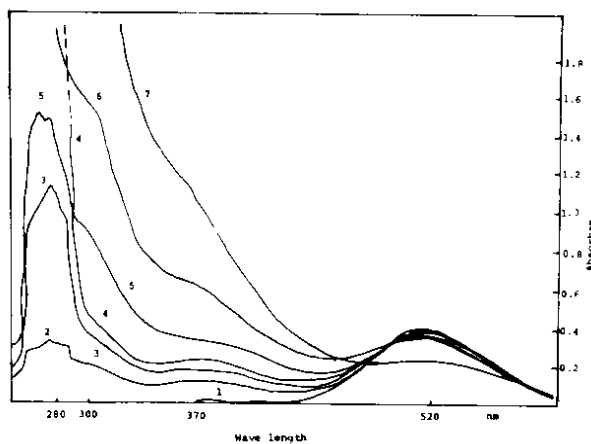

Fig.4 Electronic spectra of diphenylchorophosphine—iodine system in carbon tetrachloride.

4.15×10 iodine solutions containing phosphine derivative 3. 1.02×10^{-4} 4. 1.70×10^{-4} 5. 3.4×10^{-4} 6. 6.8×10^{-4}, 7. 12.6×10^{-4} M

become similar to the spectra of diphenylchloropho-sphine — iodine system where the tri-iodide absorp-tion for the iodide ion.

Experimental

As in previous work[1] involving similar studies in acetonitrile, strict precautions were taken to ensure a dry and an inert atmosphere. Therefore, all the apparatus and solvent were thoroughly dried and dry box having nitrogen atmosphere was used extensively.

Preparation of materials.

Carbon tetrachloride (spectroscopic grade) was obtai-ned from Fluka and was tested for the absence of moisture before use. Iodine was used after repeated vacuum sublimations. Phosphine derivatives were obtained from Fluka in leak tight packings and were used as such without any further purification. Conductometric titration was carried out in a plati-num conductance cell fitted with a small burette and a mechnical stirrer. The whole unit was worked in the dry box. The conductance values were measured by using a Wayne Kerr B642 Autobalance universal bridge. Ultraviolet and visible spectra were recorded on Perkin Elmer Spectrophotometer, Hitachi 200. The stock solutions were prepared in the dry box.

Each spectrum was recorded immediately after mixing the reactants. For observing changes in spectrum with time, the solution was wraped in black paper for excluding the effect of light.

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