Tertiary Phosphane-Diiodine Compounds: Are They Molcular Adducts or Iodophosphonium Iodides?

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The solid-state and solution structures of $Ph_3P \cdot I_2$ have been studied in detail by electronic, $^{31}P\{^1H\}$-NMR and Raman spectroscopy as well as conductometric measurements. When 1 : 1 ratios of triphenylphosphane and diiodine are mixed in dichloroethane, the molecular adduct is shown to exist also in solution. On the basis of the overall results, this molecular adduct is best described as a charge-transfer complex of the donor I^- with the acceptor Ph_3PI^+, rather than the charge-transfer complex of the donor Ph_3P with the acceptor I_2 or the ionic species $[Ph_3PI]I$ as previously proposed. When higher diiodine to triphenylphosphane ratios are used, the $Ph_3P \cdot I_2$ adduct dissociates to give Ph_3PI^+ and I_3^- or I_5^- depending on the diiodine excess. Previously reported solution data, which were ascribed to the ionic form of the adduct, are instead in agreement with hydrolysis products (Ph_3PO, PH_3POH^+) of the very reactive adduct, formed in the presence of traces of water.

Introduction

The nature of the diiodine adducts of tertiary phosphanes has been the subject of numerous studies for a long time[1], both for the intrinsic interest of these adducts, because alternative structures are possible, and for their applications. For example, they have been used to convert alcohols to halides[2], and are currently being extensively investigated by some of us[3] as powerful reagents for the oxidation of unactivated zero-valent metals. A large number of tertiary phosphane complexes of metals in unusual oxidation states and stereochemistries have been prepared from crude metal powders[3].

Before its relatively recent characterization by X-ray diffraction studies[4,7], conductometric[1,8] and $^{31}P\{^1H\}$-NMR[9] measurements of the adduct in solutions, and vibrational[10] and $^{31}P\{^1H\}$-NMR[11] spectroscopic studies in the solid state, suggested that it was of an ionic nature ($[Ph_3PI]I$) both in solution and in the solid state. Surprisingly, X-ray crystallographic results[6] showed instead that $Ph_3P \cdot I_2$ is a molecular four-coordinate compound in the solid state, with the linear arrangement P−I−I and with P−I and I−I bond lengths of 2.481(4) and 3.161(2) Å respectively. The $^{31}P\{^1H\}$-NMR resonances of $Ph_3P \cdot I_2$ have been reported to occur at very different fields in the solid state[12] ($\delta = -17.8$, assigned to the covalent form) and in 1,2-dichloroethane solution ($\delta = +44.8$[6], assigned to the ionic form[9,11]). This was explained by assuming that, even in less polar solvents, this compound dissociates to give the ionic form.

The linear P−I−I arrangement is also found in $tBu_3P \cdot I_2$[5], but with shorter P−I [2.461(2) Å] and longer I−I [3.326(1) Å] bond lengths. In addition, Cotton has synthesized the compounds $[Ph_3PI]I_3$ and $[(Ph_3PI)_2I_3]I_3$[4], for which alternative descriptions as molecular adducts or triaryl salts were reasonably proposed on the basis of structural results alone. Also, a recent X-ray structural analysis of $Ph_3P \cdot Br_2$[3], showing a four coordinate $Ph_3P{-}Br{-}Br$ "spoke" structure with an interbromine distance of 3.123(2) Å (shorter than the sum of the van der Waals radii, 3.9 Å), has been taken as a further example of a charge-transfer (C.T.) complex of dibromine. However Gates et al.[14] prefer the ionic formulation of $[Ph_3PBr]Br$ on the basis of the absence of the characteristic peak due to ν(Br−Br) and the simultaneous presence in the Raman spectrum of a peak assigned to ν(P−Br), in good correspondence with those of Ph_3PBr^+ salts. These authors explain the relatively long P−Br and short Br−Br distances with an ionic formulation, invoking cation-anion interactions common in halogenophosphonium compounds. However the difference between ionic and molecular C.T. complexes is not only in their P−X and X−X (X = Br, I) distances. The linear P−X−X arrangement and the presence of the characteristic C.T.

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band in the electronic spectrum of the compound should be taken into account before excluding the existence of a C.T. complex. Moreover, while molecular compounds with stoichiometry $D \cdot I_2$ are generally classified as being of C.T. type, where I_2 is assumed to be the acceptor, the increasing number of solution as well as solid-state studies of these systems clarifies the nature of this interaction and allows three main types of complexes to be distinguished: D···I−I (**1**)[15]; D−I−I (**2**)[16]; D−I···I (**3**)[17]. In **1**, long D···I and short I−I distances are found, the UV-Vis spectra show the well-known C.T. band and the blue-shifted diiodine and donor bands, and one Raman peak due to the perturbed I_2 molecule is observed [ν(I−I) in the 180−140 cm^{-1} range[18]]. In **2**, the D−I and I−I distances are comparable and correspond to a bond order of 0.5, which can be explained on the basis of a covalent three-centre, two-electron bond. Accordingly UV as well as Raman features, i.e. the presence of two peaks ascribable to antisymmetric and symmetric stretching of the D−I−I group, can be explained. In **3**, where short D−I and long I···I distances are found, the adduct may be envisaged as arising from interaction of the donor I^- with the acceptor $D-I^+$. In the Raman spectrum, only one peak ascribable to the D−I vibration is expected, as is found in the ionic form; however this peak is shifted to a lower frequency with respect to the ionic form. Moreover this interaction must be accompanied by an electronic C.T. band.

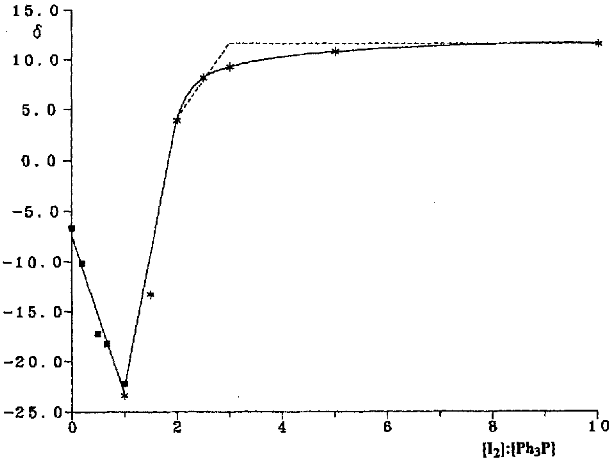
In order to better elucidate the nature of the $Ph_3P \cdot I_2$ adduct on the basis of the above criteria, we undertook a reinvestigation of the $Ph_3P + I_2$ system in 1,2-dichloroethane (DCE) solutions by means of $^{31}P\{^1H\}$-NMR, electronic and Raman spectra as well as conductometric measurements. The results are reported here.

Results

$^{31}P\{^1H\}$-NMR Measurements

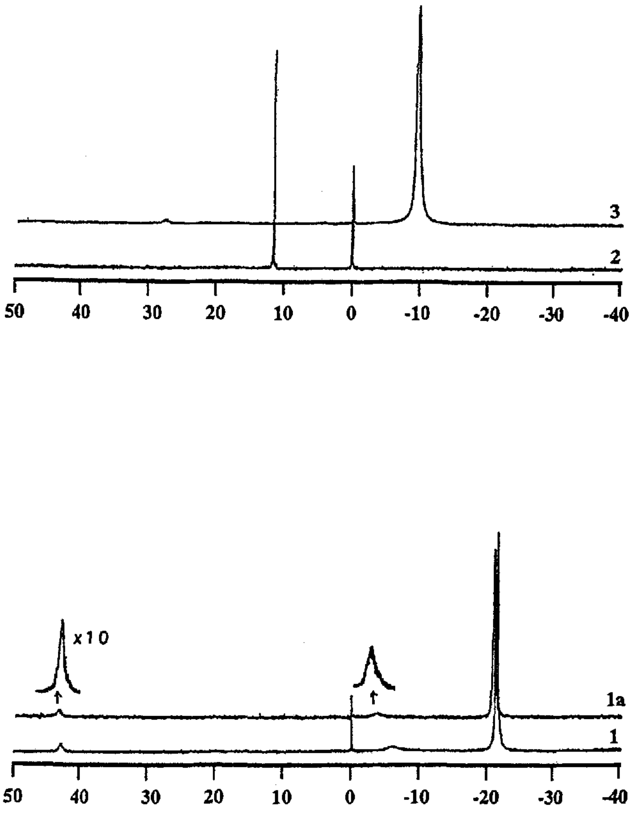
The addition of increasing amounts of I_2 to Ph_3P in DCE solutions produces continuous changes in the $^{31}P\{^1H\}$-NMR chemical shifts of the mixtures (Figure 1). The δ-value of Ph_3P is shifted upfield on coordination, and the lowest value of the chemical shift, δ = −23.4, is reached for a 1:1 ratio of the reagents. A spectrum identical to that of the 1:1 solution is obtained for a DCE solution of the X-ray-characterized $Ph_3P \cdot I_2$ (see Figure 2). This shift is assigned to the $Ph_3P \cdot I_2$ adduct. Solutions in which Ph_3P exceeds the 1:1 ratio show averaged, rather than separate, signals, indicating a rapid I_2 exchange between the adduct and the free Ph_3P. Addition of further amounts of I_2 to the adduct produces an inversion of the shift, causing continuous downfield shifts up to a limiting value of δ = +12.0. All solutions show only one peak in the examined reagent concentration ratios. Typical spectra are reported in Figure 2. The plot of the chemical shift versus the amount of diiodine added is linear until the 1:1 ratio is reached. After this "equivalence point" the plot could suggest an equilibrium reaction between two species resonating at δ = −23.4 and +12.0 (Figure 1). On the other hand FT-Raman results (see later) show that three species are involved in the explored concentration range. In fact the 1:2 solution shows the presence of a triiodide, and the 1:5 solution indicates the presence of a pentaiodide. Allowing for this, two other "equivalence points", otherwise less evident, may be inferred from the plot at ratios of 1:2 and 1:3. Table 1 contains the above data, as well as data on some characterized trisubstituted tertiary phosphane diiodine adducts; literature values are included for comparison.

Figure 1. Plot of the $^{31}P\{^1H\}$-NMR chemical shifts of Ph_3P/I_2 solutions in DCE versus the $[I_2]:[Ph_3P]$ ratio; $[I_2] = 8.3 \times 10^{-2}$ mol dm^{-3} (■); $[Ph_3P] = 1.0 \times 10^{-2}$ mol dm^{-3} (*)

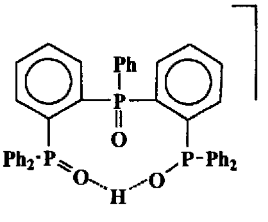


The spectrum of the 1:2 solution shows a time dependence of the peak at δ = 3.8. After a few hours a resonance appears at δ = 4.8 with an intensity more than double that of the peak at δ = 3.8. However no peaks arise in the δ = 45 region. We tentatively explain these results by suggesting that the $[Ph_3PI]I_3$ initially formed undergoes rearrangement to give partially the pentaiodide derivative or $[(Ph_3PI)_2I_3]I_3$, which has previously been isolated from solutions with this reagent ratio[4]. Solutions with an I_2 excess greater than 2 were stable. Addition of water to these solutions results in the disappearance of the original signals and the simultaneous appearance of new peaks in the δ = 25−45 range (δ = 29.2, −7.7 (Ph_3P); 31.0; 41.8; 43.0 for solutions with respectively $[Ph_3P]:[I_2]$ = 10:1; 1:1; 1:2; 1:5). This is accompanied by an instantaneous bleaching of the solutions without an excess of I_2, in accordance with the known reaction: $Ph_3P \cdot I_2 + H_2O \rightarrow Ph_3PO + 2\ HI$[21]. When a diiodine excess is present the evolution of the spectra is slower and the bleaching is not observed, because the formed HI_3 gives the solution a colour similar to that produced by the adduct with a diiodine excess. HI and HI_3 interact with Ph_3PO, giving rise to acid-base equilibria. The resonance at δ = 25 expected for Ph_3PO is therefore not observed and an averaged shift due to the protonated form, which undergoes fast hydrogen exchange with the unprotonated one, appears in the δ = 25−50 range. Spectra of solutions containing Ph_3PO (1.0×10^{-2} mol dm^{-3}), HI and I_2 in the concentration ratios 1:1:0.05, 1:2:1 and 1:2:4 show resonances at δ = 33.0, 46.0 and 48.6 respectively. At higher I_2

Figure 2. Typical $^{31}P\{^1H\}$-NMR spectra (recorded 24 h after preparation) of DCE solutions of Ph_3P ($[Ph_3P] = 1.0 \times 10^{-2}$ mol dm^{-3}) and I_2 in $[Ph_3P]$:$[I_2]$ ratios of 1:1 (1), 1:5 (2) and 5:1 (3); the spectrum of a DCE solution of the $Ph_3P \cdot I_2$ adduct characterized in the solid state ($[Ph_3P \cdot I_2] = 1.0 \times 10^{-1}$ mol dm^{-3}) (1a), is reported for comparison



concentrations the resonances are shifted increasingly downfield because, as expected, I^- forms I_3^- and I_5^-, and these species compete for the proton with Ph_3PO in decreasing order. Resonances in the range $\delta = 25-60$ have been reported earlier for Ph_3PO in various hydrogen-donating solvents ($\delta = 32$ in MeOH, 41.7 in dichloroacetic acid, and 57.2 in H_2SO_4)[22,23]. Resonances in the region of $\delta = 45$, previously assigned to the ionic form of the adduct, were not observed when working under strictly controlled anhydrous conditions. (This resonance was observed as a minor peak in some experiments, see the Experimental Section.) In addition to the $^{31}P\{^1H\}$-NMR chemical shifts of some tertiary phosphane diiodine compounds, we report in Table 1 the data for protonated Ph_3PO and tpO_3HI_3, where tpO_3H^+ (depicted below) was obtained by slow evaporation of tp and I_2 mixtures in toluene in air[24].



tpO_3H^+

Table 1. $^{31}P\{^1H\}$-NMR chemical shifts from 85% H_3PO_4 for the $Ph_3P \cdot I_2$ adduct and other related compounds

	Solution δ		Solid δ
	Present data (DCE)	Literature data	
$Ph_3P + I_2$ (1:1)	–23.4		
$Ph_3P + I_2$ (1:10)	+12.0		
$Ph_3P{\cdot}I_2$	–21.7 (–3, +43.7)[b]	+44.8 (DCE) [6] +49.7 ($CHCl_3$) [9]	–17.8[12] +42.5 [11]
$Ph_3P{\cdot}ICl$		+40.3 ($CHCl_3$) [9] +66.0, +34.7, –21.8 ($PhNO_2$) [19] [a]	+40.5 [19]
$Ph_3P{\cdot}IBr$		+44.2 ($CDCl_3$) [20] +40.5 ($PhNO_2$) [19]	+41.7[19]
$[Ph_3PI]AsF_4$		+43.3 ($CHCl_3$) [9]	
$Ph_2MeP\ I_2$	–29.8 (–3.0, +51)[b]		
$(o\text{-}MeOC_6H_4)_2PhP{\cdot}I_2$	–33.5		
$[Ph_3PO]+2HI+I_2$	+44.9		
$[tpO_3H]I_3$	+45.0 (d), +37.3 (t)		

[a] The peak at $\delta = -21.8$, observed in $PhNO_2$ and unassigned in ref.[19], can be assigned to Ph_3PI_2. – [b] Minor peaks.

Raman Spectroscopy

The Raman peaks of $Ph_3P \cdot I_2$ and related compounds in the solid state are reported in Table 2. These spectra show the presence of a peak attributable to P–I stretching[10], but no peaks could be assigned to I–I vibrations. The DCE solution spectra of the $Ph_3P + I_2$ mixtures up to a 1:1 ratio of the reagents also show a peak in the same position, providing further evidence that the adduct is in the same form in the two phases. Addition of water to the solutions causes this peak to disappear (Figure 3). When a diiodine excess is present, the formation of triiodide and the pentaiodide are recognized by their characteristic peaks at 112 and 166 cm^{-1} respectively[26]. These spectra are shown in Figure 4. The Raman spectrum of the solution where I_3^- is present does not show the peak at 159 cm^{-1}; instead it shows two peaks at 184 and 202 cm^{-1}. We suggest that at least one of these peaks is due to P–I stretching {possibly $[Ph_3PI]I_3$ or $[(Ph_3PI)_2I_3]I_3$}. Unfortunately in solutions where I_5^- is present, the P–I peak is overlaid by the stronger I_5^- (166 cm^{-1}) and free I_2 (208 cm^{-1}) bands.

Table 2. Selected Raman and structural data for some $R_3P \cdot I_2$ adducts and related compounds

	X-ray		Raman	Ref.
	d(P–I) [Å]	d(I–I) [Å]	ν(P–I) [cm^{-1}]	
$[(Bu_3PI)_2(\mu\text{-}I)]^+$	2.37(3)	3.62(1), 3.42(1)	208	25
$PhMe_2P{\cdot}I_2$	2.410(2)	3.408(2)	204	7
$Bu_3P{\cdot}I_2$			202	this work
$Ph_2Me\ P{\cdot}I_2$			185	12, this work
$Ph_3P{\cdot}I_2$	2.481(4)	3.161(2)	159	6,12, this work
$(o\text{-}MeOC_6H_4)_2PhP{\cdot}I_2$			145	7, this work

UV-Visible Spectroscopy

The spectra for the various Ph_3P/I_2 ratios are reported in Figure 5. The 1:1 solution shows a spectrum different from the summed spectra of the reagents, and two strong bands

Figure 3. FT-Raman spectra of the 1:1 Ph_3P/I_2 DCE solution (a); after addition of water (b) ($[Ph_3P] = 1.0 \times 10^{-2}$ mol dm^{-3}, cell 0.5 cm); the spectrum of the solvent is displayed (s), and the spectrum of solid $Ph_3P \cdot I_2$ (c) is reported for comparion

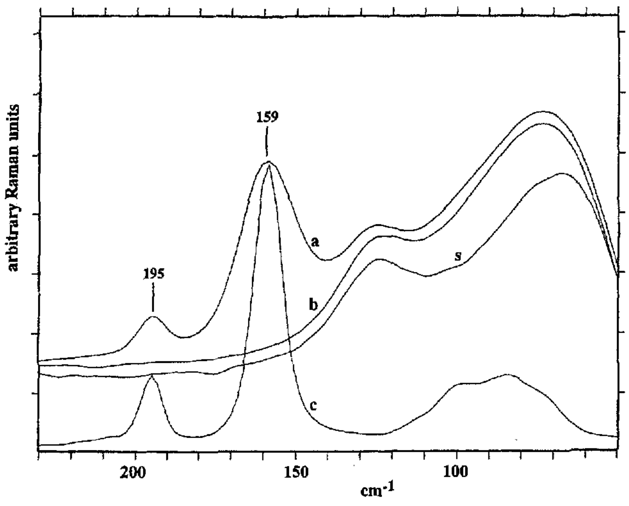
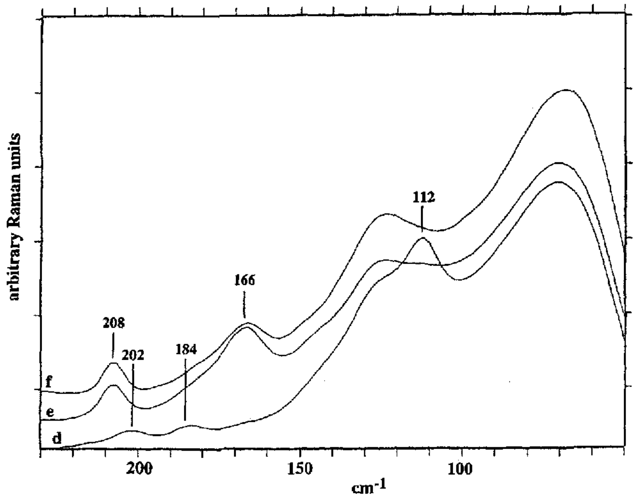


Figure 4. FT-Raman spectra of the Ph_3P/I_2 DCE solutions in the reagent ratios 1:2 (d) and 1:5 (e) ($[Ph_3P] = 1.0 \times 10^{-2}$ mol dm^{-3}, cell 0.5 cm); the spectrum of a 1:5 Bu_4NI/I_2 ($[Bu_4NI] = 1.0 \times 10^{-2}$ mol dm^{-3}) DCE solution is displayed for comparison (f)



appear at 306 (ε = 21000 dm^3 mol^{-1} cm^{-1}) and 368 (ε = 22400 dm^3 mol^{-1} cm^{-1}) nm, very near the characteristic triiodide absorptions at 294 and 364 nm[27]. Addition of I_2 over the 1:1 ratio produces a shift of these peaks to 294 and 364 nm with concomitant variation of their relative intensities, which become typical of a triiodide at a Ph_3P/I_2 ratio of 1:2. The increase in absorbance at these wavelengths due to addition of further amounts of diiodine may be ascribed to the formation of pentaiodide. Since the concentration is in the range (2.5–5.0) × 10^{-5} mol dm^{-3}, even traces of water must be excluded. The 1:1 and to a greater extent the 1:0.5 solutions show a time dependence. In Figure 6 the development of the spectra over 1 h is displayed for the 1:0.5 solution. The characteristic peaks of the adduct decrease and simultaneously the absorbance at 230 nm increases, and a band with vibrational structure in the 260–280 nm range appears together with an isosbestic point at 240 nm. The presence of these new peaks is in agreement with the formation of Ph_3PO. This time dependence has been previously observed and explained by the transformation of the outer complex ($Ph_3P \cdot I_2$) into the inner one ($[Ph_3PI]I$)[28]. However the UV-Vis spectra, reported to support the formation of the inner complex, are instead characteristic of Ph_3PO[28]. Therefore the inner- and outer-sphere mechanism proposed by Rao seems to be based on incorrect results, the $Ph_3P \cdot I_2$ adduct being hydrolyzed to Ph_3PO.

Figure 5. UV-Vis spectra of DCE solutions of Ph_3P/I_2 in reagent ratios 1:0.5 (2), 1:1 (3), 1:2 (4) and 1:5 (5); the spectrum of a DCE solution of Ph_3P (1) is also reported ($[Ph_3P] = 5.0 \times 10^{-5}$ mol dm^{-3}, cell 0.75 cm)

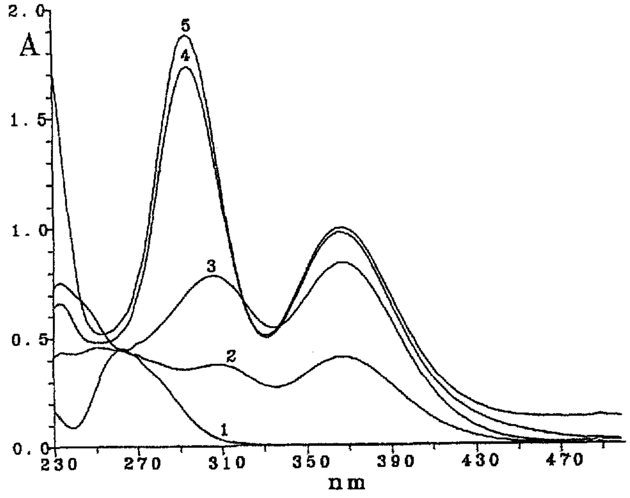
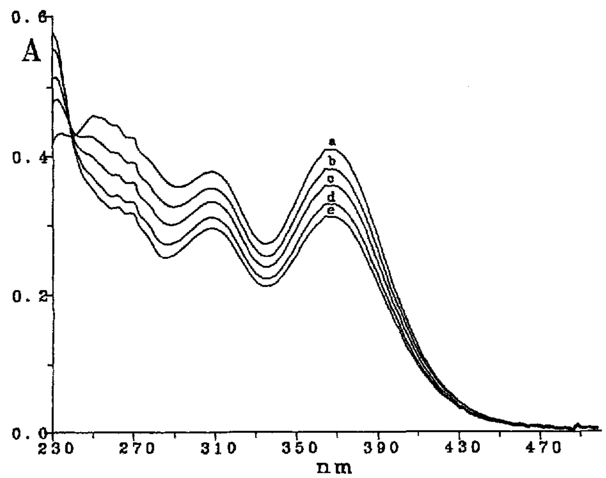


Figure 6. Time dependence of the UV-Vis spectrum of a $[Ph_3P]:[I_2]$ = 1:0.5 DCE solution ($[Ph_3P] = 5.0 \times 10^{-5}$ mol dm^{-3}, cell 0.75 cm); the spectrum was monitored every 10 min

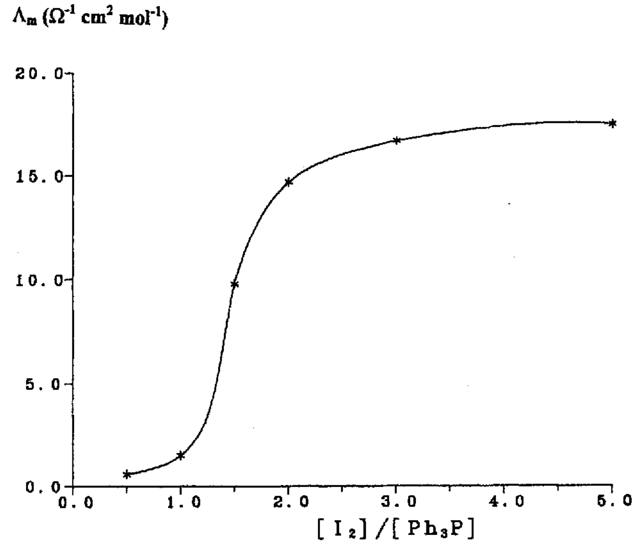


Conductometric measurements

The molar conductivity vs. mole ratio (Ph_3P/I_2) graph is displayed in Figure 7. In solutions of up to a 1:1 ratio of the reagents, a very low value of conductivity ($\Lambda_m < 1.5$ Ω^{-1} cm^2 mol^{-1}) is found; after that further additions of diiodine result in a significant increase of the conductivity, reaching a limiting value for solutions with molecular ratios higher than 1:3. The value of the limiting molar conductivity ($\Lambda_m = 17$ Ω^{-1} cm^2 mol^{-1}) falls in the range for a 1:1 electrolyte in the same DCE solvent at 25 °C. Thus the conductivity measurements further support the conclusion that the 1:1 species is a molecular adduct, and that it undergoes increasing dissociation on addition of diiodine.

Previous conductivity measurements in CH_3CN on this intriguing $Ph_3P + I_2$ system gave ambiguous results[1,8]. It has been reported that $Ph_3P \cdot I_2$ behaves like a strong 1:1 electrolyte, however the conductivity at the 1:1 break point in the conductiometric titration plot of Ph_3P with I_2 is approximately half that at the 1:2 break point[8]. This suggests that even in more strongly ionizing solvents $Ph_3P \cdot I_2$ is only partially dissociated.

Figure 7. Plot of the molar conductivity of Ph_3P/I_2 solutions in DCE vs. the $[I_2]$:$[Ph_3P]$ ratio; $[Ph_3P] = 1.0 \times 10^{-2}$ mol dm^{-3}



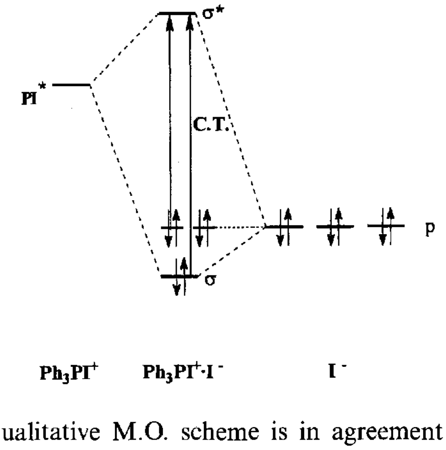
Discussion

$^{31}P\{^1H\}$-NMR, electronic, Raman spectroscopic and conductiometric results show that the molecular adduct formed between Ph_3P and I_2 with 1:1 stoichiometry exists also in DCE solutions. Its features ($^{31}P\{^1H\}$-NMR resonances shifted upfield with respect to the free ligand, two strong bands in the 300–370 nm range, the position of the Raman peak attributable to the P–I stretching, and very low molar conductivity) rule out its description as a simple ionic formulation. Moreover, the above results show that the adduct can further react with diiodine to give rise to equilibria in which the involved species undergo rapid exchange. This adduct is also very reactive towards nucleophiles, particularly water. Therefore, on the basis of the reported results, the following reaction scheme may be proposed:

1) $Ph_3P + I_2 \rightleftarrows Ph_3P \cdot I_2$; $Ph_3P^* + Ph_3P \cdot I_2 \rightleftharpoons Ph_3P^* \cdot I_2 + Ph_3P$
2) $Ph_3P \cdot I_2 + n\,I_2 \rightleftarrows Ph_3PI^+ + I_{2n+1}$ $n = 1, 2$
3) $Ph_3P \cdot I_2 + H_2O \rightarrow Ph_3PO + 2\,HI$
4) $HI + n\,I_2 \rightleftharpoons H^+ + I_{2n+1}^-$ $n = 0, 1, 2$
5) $Ph_3PO + H^+ \rightleftharpoons Ph_3POH^+$

It is noteworthy that, although the reactions described in (3) and (5) are long established[1,4,21], and although ^{31}P chemical shifts of the phosphane oxides and their significant deshielding in their conjugate acids are known[22,23], no mention has been found in the literature that $^{31}P\{^1H\}$-NMR resonances falling in their typical range could be ascribed to those oxides. We suspect that in some instances the resonances due to the conjugate acid of Ph_3PO have been wrongly assigned to Ph_3PI^+ (see Table 1). Rather confusing results regarding R_3PX_2[5,9,14,20,30] (X = Br, Cl) suggest that a reinvestigation of these similar systems, taking into account the above results, is advisable. As far as the $Ph_3P \cdot I_2$ Raman results are concerned, the agreement of our data in solution and in the solid state with those previously reported and used to provide evidence for an ionic formulation of the adduct in the solid state, seems to be in contrast with the $^{31}P\{^1H\}$-NMR and electronic spectroscopic results reported here. However, since the structural and spectroscopic features of $Ph_3P \cdot I_2$ are typical of a type-**3** C.T. complex as defined in the Introduction, the presence of one peak due to ν(P–I) and the absence of the characteristic peak due to ν(I–I) in the Raman spectrum are in accordance with such a type-**3** adduct.

We have previously found a strongly asymmetric triiodide with a similar long I–I distance, 3.141(2) Å[31]. On the basis of its structural and spectroscopic features[32] we concluded that this triiodide must be described as a donor-acceptor complex of the type $I^- \cdot I_2$ rather than as a molecular anion. Similarly, we propose that the case of $Ph_3P \cdot I_2$ can be conveniently described as a C.T. adduct of the donor I^- with the acceptor Ph_3PI^+. A qualitative M.O. scheme for the charge-transfer interaction is depicted below.



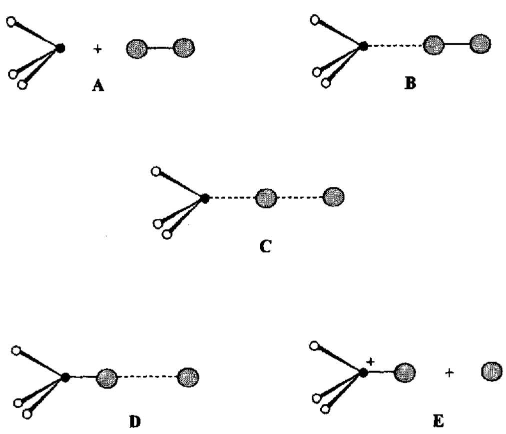
This qualitative M.O. scheme is in agreement with the reported results, and particularly with the proximity of the two electronic bands, with the higher shielding of the ^{31}P nucleus in the adduct with respect to Ph_3PI^+, the absence of the Raman peak attributable to I_2 and with the presence of a Raman peak assigned to the P–I vibration.

A similar description involving the lengthening of the P–I bonds by population of σ^*(P–I) orbitals as a consequence of the interaction with iodide, has recently been put forward by du Mont and co-workers[33] to explain iodine-iodine interactions in dialkyldiiodophosphonium iodides. The involvement of a σ^* antibonding orbital in the formation of R_3P-X (X = halogen) radicals has previously been shown by ESR spectroscopic studies[34].

Electronic and steric effects of the R substituents affect the basicity of the P atom and consequently the strength of the P–I bond, as well as the energy of the σ^* antibonding orbital. The stronger the bonding, the higher the energy of the σ^* antibonding orbital, and the lower the interaction with the donor. Lower interactions are also predicted for iodide, which can delocalize its charge on more centres as in I_3^- and I_5^-. The values of *d*(P–I) and *d*(I–I) are correlated, the lengthening of the intramolecular interaction being proportional to the shortening of the intramolecular interaction, as usually observed in molecular adducts. The limited data available give a sequence of bond distances and the position of the ν(P–I) bands in the adducts in accordance with the above (Table 2).

Conclusions

The present solution $^{31}P\{^1H\}$-NMR measurements on the triphenylphosphane-diiodine system replace the previously reported data, and suggest that other similar systems should be revised. Moreover, evidence from UV-Vis and FT-Raman spectra as well as conductometric measurements shows that the 1:1 adduct is neither an iodophosphonium iodide nor a diiodine charge-transfer adduct, but rather a charge-transfer adduct of the donor I^- with the acceptor Ph_3PI^+. This 1:1 molecular adduct undergoes increasing dissociation for further addition of diiodine to give Ph_3PI^+ and I_3^- or I_5^-. This description seems to be the most satisfactory in taking into account the features both in solution and in the solid state, and better explains the early proposal of considering the adducts under discussion as a well documented example of a "frozen transition state"[6] of the reaction of trisubstituted phosphane dihalogen to give halophosphonium halides. In the similar reaction of trialkylamine with diiodine, Bent[35] proposed describing it as a Walden inversion on a halogen atom in accordance with the scheme below.



Following this, the discussed type-**3** adduct corresponds to D. Since these adducts can be obtained in a "frozen transition state", they are valuable intermediates in many reactions, as is shown extensively in the work performed by some of us[3]. Meanwhile, in order to avoid wrong assignments their high moisture sensitivity requires strict control of the conditions during solution studies. This has been proved feasible by the present study.

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Experimental Section

General Procedure: DCE (Carlo Erba Reagent) was distilled under dry N_2 over $MgSO_4$ for 2 d in an Aldrich solvent still-head apparatus used for continuous distillation. All the solutions were prepared in a strictly controlled atmosphere of dry N_2 (atmosbags Aldrich).

$^{31}P\{^1H\}$-NMR Spectra: These spectra were recorded on a Varian FT VXR 300 spectrometer operating at 121.4 MHz in DCE solution at 20°C and referred to 85% H_3PO_4 ($\delta = 0.0$) as an external standard. NMR tubes with a PTFE valve (Aldrich) were used. The resonances of a set of solutions containing a fixed concentration of the ligand (1.0×10^{-2} mol dm^{-3}) and various I_2 concentrations (in the ratios $[Ph_3P]:[I_2]$ = 1:0, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:5 and 1:10) were measured. Another set of solutions with a fixed concentration of I_2 (8.3×10^{-2} mol dm^{-3}) and various amounts of Ph_3P (in the ratios 1:1, 1:1.5, 1:2 and 1:5) was also used (Table 1, Figure 1). The purity of the solvent and the anhydrous conditions during the experiments were crucial to obtaining the reported spectra. Before the best experimental conditions were found, the spectra of solutions where a diiodine excess was not present showed a time dependence and the production of adjunctive peaks. In particular the 1:1 solution showed a decrease in the intensity of the $\delta = -23.4$ peak and a simultaneous increase in the intensities of the peaks near $\delta = +44$ and $\delta = -3$, accompanied by a 2–3 ppm shift downfield. The latter peaks appear as minor features in the spectrum recorded 24 h after the preparation of the solution. This time dependence, varying from complete modification of the initial spectrum in half an hour to reproducible spectra after two weeks, was strongly dependent on the quality of the solvent and on the degree to which anaerobic and anhydrous conditions were maintained during the experiments. Spectra of solutions containing Ph_3PO (1.0×10^{-2} mol dm^{-3}), HI and I_2 in the concentration ratios 1:1:0.05, 1:2:1 and 1:2:4 were also recorded.

FT-Raman Spectra: These spectra (resolution ±4 cm^{-1}) were recorded on a Bruker RFS100 FTR spectrometer fitted with an indium-gallium-arsenide detector (room temp.) and operating with an excitation frequency of 1064 nm (Nd YAG laser). The same solutions prepared for NMR experiments were used to run FT-Raman spectra. The solid samples, as powders, were packed into a sealed glass capillary tube and then fitted into the compartment designed for 180°-scattering geometry. The power level of the laser source was 30 mW for solid-state measurements and 370 mW for solutions.

UV-Vis Measurements: Electronic spectra were recorded in DCE solutions with a Hewlett-Packard 8452A diode-array spectrophotometer. A set of solutions containing a fixed concentration of the ligand (5.0×10^{-5} mol dm^{-3}) and various amounts of I_2 (in the ratios $[Ph_3P]$:$[I_2]$ = 1:0.5, 1:1, 1:2 and 1:5) was reported. The two reagents were introduced into the two compartments of a silica tandem-mix cell (0.75-cm path length with a center wall opening at the top), mixed after reaching 25°C, and the absorbances monitored over the 220–550 nm range. A time dependence was observed in the 1:0.5 solution (the initial absorbance at 306 nm decreased by 7% after 10 min) and to a lesser extent in the 1:1 solution (the spectrum at 10 min almost overlays that at zero time). No time dependence was observed in the other solutions during observation for 30 min under the same experimental conditions.

Conductometric Measurements. Conductometric measurements were carried out at 25°C on DCE solutions, with a Model 120 Microprocessor Conductivity Meter "Analytical Control". The cell constant (k = 1.08 cm^{-1}) was determined by standard methods on KCl/water solutions. A set of six solutions containing a fixed concentration of Ph_3P (1×10^{-2} mol dm^{-3}) and various amounts of I_2 (in the ratios $[Ph_3P]$:$[I_2]$ = 1:0.5, 1:1, 1:2 and 1:5), was prepared and the conductivity monitored immediately after mixing the prethermostatted solutions. A slight increase in the conductivity with time was observed in the 1:0.5 and 1:1 solutions; the values of the other solutions were stable during observation for 15 min under the same experimental conditions. For comparison the conductivity of Bu_4NI (1×10^{-2} mol dm^{-3}) was also measured.

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