Studies of Hydrogen Bonding

Part IV. A Comparison between the Ability of Organophosporus Compounds to Form Addition Compounds with Iodine and their Ability to Take Part in Hydrogen Bonding

THOR GRAMSTAD and SVEIN IVAR SNAPRUD

Norwegian Defence Research Establishment, Division for Toxicology, Kjeller, Norway

The K_{ass}, ΔH, ΔF and ΔS values for the formation of 1:1 addition compounds between eight organophosphorus compounds and iodine in carbon tetrachloride solution have been determined. The logarithms of the association constants are linearly related to the blue shifts, $\Delta \lambda_{I-I}$, of the visible iodine band which accompany the formation of the complexes. A linear relationship also exists between the ability of these organophosphorus compounds to form hydrogen bonds with proton donors and addition compounds with iodine. The ultraviolet absorption in the addition compounds which could be attributed to a charge-transfer band is considered to lie at wavelengths shorter than 220 mμ. In the infrared region, addition compound formation with iodine causes a large shift in the P=O stretching frequency of the organophosphorus compounds. The self-association of organophosphorus compounds is also discussed.

It was shown in two previous publications [1,2] that organophosphorus compounds containing the P=O group form very strong intermolecular hydrogen bonds with phenol, methanol, α-naphthol, and pentachlorophenol. It was now of interest to extend our work to see if there was any relation between the ability of organophosphorus compounds to form hydrogen bonds in this way and their ability to form intermolecular addition compounds with halogens, interhalogens and cyanogen halides, respectively. To our knowledge there is only one previous paper on the equilibrium reaction between halogens and organophosphorus compounds, namely by Tsubomura and Kliegman [3] who describe the interaction of iodine and tributyl phosphate. The present paper presents the results of a spectrophotometric investigation of the interaction of iodine with twelve organophosphorus compounds.

Numerous investigators have studied the addition compounds of the halogens and interhalogens with various nitrogen- and oxygen-containing compounds by various methods including X-ray crystallography, thermodynamic

measurements and ultraviolet, visible and infrared spectroscopy. Two theories on the nature of the chemical bond between the two components of these addition compounds have been advanced; the Benesi-Hildebrand donor-acceptor theory [4] in which one of the two reactants acts as an electron donor (Lewis base) and the other as an electron acceptor (Lewis acid), and Mulliken's charge-transfer resonance theory [5] which postulates resonance between so-called "no-bond" and "dative" structures. Hassel *et al.*[6],[7] have made a series of X-ray crystallographic studies of the molecular structure of solid addition compounds. In some of the addition compounds studied they found that the electron-donating property was localised on atoms possessing unshared electron pairs, *e.g.*, O, N and S. Furthermore, they found that the electron donor atom was directly linked to one of the halogen atoms to form a co-linear structure. The bond between the donor and acceptor atoms tends to extend or complete a tetrahedral arrangement around the donor atom; sometimes, however, planar structures were found as in the atom complexes of acetone and pyridine. The interatomic distances in addition compounds found by Hassel *et al.* will be compared with spectrophotometric data on hydrogen bonds and addition compounds in the discussion below. Person *et al.*[8] have studied the X—Y stretching vibration of the electron-acceptor molecule by infrared spectroscopy and found a linear relationship between ε_a, the added effective charge, and $\Delta k/k$, the relative change in force constant, due to complex formation. They also found that hydrogen bonded complexes fit this relationship. They interpreted their results in terms of resonance between the structures: D...X—Y $\leftrightarrow$ (D—X)$^+$...Y$^-$, the latter being a modification of Mulliken's "dative" structure D$^+$...(XY)$^-$.

de Maine [9] has reported thermodynamic data for complexes of methanol, ethanol and diethyl ether with iodine in carbon tetrachloride and shown that the linear relationships between ΔF and ΔH or ΔS for aromatic complexes of iodine found by Andrews and Keefer [10] do not hold for all iodine complexes. These linear relations appear to hold only for donor molecules of similar geometrical form. Schmulbach and Drago [11] have shown by infrared spectroscopy that for dimethyl acetamide and iodine in carbon tetrachloride solution complex formation occurs through the oxygen atom. They obtained some thermodynamic data by following the changes in the carbonyl absorption on complex formation. A recent paper by Tsubomura and Lang [12] describes a spectrophotometric study of solutions of iodine in acetamide, N,N-dimethylformamide, diethyl sulphide, and diethyl disulphide, and discusses the general features of the spectra of iodine-donor complexes.

EXPERIMENTAL

Materials. The methods of preparation and physical data on the organophosphorus compounds used have, with one exception, [$(C_2H_5)_2N]_2P(O)C_2H_5$, b.p. 100°C/0.7 mm, been published earlier [1]. The phosphorus compounds were purified by fractional distillation or recrystallisation just before use. The iodine was resublimed and dried in a desiccator over phosphorus pentoxide. "Merck Spectroscopic Grade" carbon tetrachloride was used without further purification.

Infared measurements. The infrared spectroscopic measurements were made with a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics. This instrument
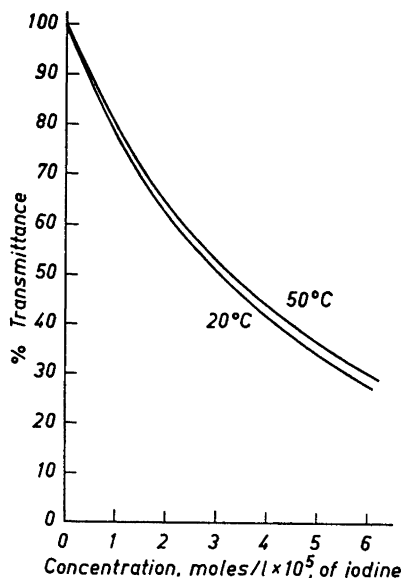
Fig. 1. The relation between percent transmittance and various concentrations of iodine, measured at 518 mμ. Solvent, carbon tetrachloride. Cell length, 10.0 cm.

was also used for the determination of the frequency shift of the ground state stretching vibration of the P=O band which accompanies complex formation with iodine. The association constants of the equilibrium reaction were determined from the decrease in intensity of the free P=O band upon complex formation. These measurements were carried out as a check of the association constants obtained from the decrease in intensity of the iodine visible band upon complexation. The instrumental conditions and the method of running the spectra were the same as described earlier [2]. The concentrations of iodine and phosphorus compounds were, with few exceptions, 0.03 moles/l each for all spectra. For $(CH_3)_3PO$, $(C_2H_5)_3PO$ and $[(C_2H_5)_2N]_2P(O)C_2H_5$ the concentrations were reduced to 0.015 moles/l because of their greater complexing ability. The cell was of 1.00 mm thickness and the temperature was about 30°C.

Visible and ultraviolet measurements. The visible and ultraviolet measurements were carried out with a Beckman Ratio Recording Spectrophotometer Model DK-2. Instrumental conditions were as follows: Scanning time, full scale, 20 min; range, 0−100; sensitivity, 50; time constant, 0.6; percent transmittance. The cell used was the same as described earlier [1]. This instrument was used for the determination of the association constants and the blue shift of the iodine visible band upon complexation with the phosphorus compounds. The concentration of free iodine was determined from the iodine visible band at 518 mμ by using the calibration curves shown in Fig. 1. K_{ass} was calculated as shown below:

$$D + X-X \rightleftharpoons D...X-X$$

$$K_{ass} = \frac{(D...X-X)}{(D)(X-X)} = \frac{c}{(a-c)(b-c)}$$

where c is the concentration in moles/l of the addition compound calculated from the decrease of the free iodine band, and a and b are the initial concentrations in moles/l of electron donor and acceptor, respectively. The spectra were run immediately after preparing the solutions because of the reaction of iodine with carbon tetrachloride and with some of the electron donors. These reactions, however, were sufficiently slow at the low concentrations used to permit exact measurements. The temperatures were kept at 20 and 50°C. The concentration of iodine was kept at 6 × 10⁻⁵ moles/l for all spectra and the concentrations of the organophosphorus compounds used are recorded in Table 1.
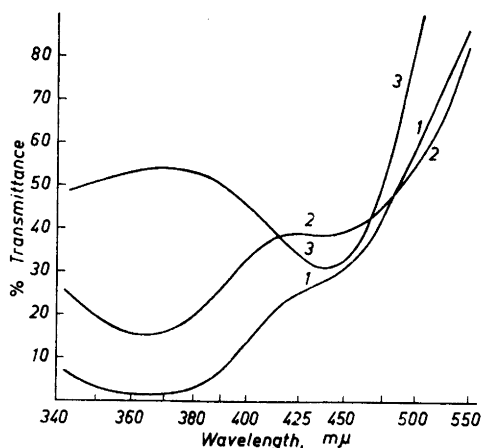
Fig. 2. The visible absorption spectra of $(C_2H_5)_2NP(O)(OC_2H_5)_2-I_2$. Curve 1, 0.27 moles/l of $(C_2H_5)_2NP(O)(OC_2H_5)_2$ and 6×10^{-5} moles/l of I_2, temperature 20°C; curve 2, the same concentration as in curve 1, but the temperature was 50°C; curve 3, 0.20 moles/l of $(C_2H_5)_2NP(O)(OC_2H_5)_2$ and 6×10^{-5} moles/l of I_2, compensated with a reference cell containing 6×10^{-5} moles/l of I_2, temperature 20°C. Solvent, carbon tetrachloride. Cell length, 10.0 cm.

As can be seen, the values of the association constants are the mean values of two or three separate determinations. Table 2 shows the experimental results obtained from the determination of K_{ass} for one of the compounds studied.

RESULTS

Visible absorption spectra. In Fig. 2 are shown the spectra of $(C_2H_5)_2NP(O)(OC_2H_5)_2$ with iodine in carbon tetrachloride solution. These visible absorption spectra are typical for such solutions containing iodine and an organophosphorus compound with a P=O group. Since such phosphorus compounds have no absorption in this region the new absorption band at 438 mμ is assigned to the iodine visible band which has undergone a blue shift upon complex formation. The corresponding free iodine band in carbon tetrachloride solution has its peak at 518 mμ. The assignment for the new absorption band at 364 mμ is not yet clear, but it appears that the intensity of this band is very sensitive to variation in the concentrations of the reactants. As can be seen in Fig. 2, when the concentration of the electron donor is decreased from 0.27 moles/l (curve 1) to 0.20 moles/l (curve 3), the absorption peak at 364 mμ is markedly decreased. Furthermore, comparison of curve 1 with curve 2 (in Fig. 2) shows that both peaks (438 and 364 mμ) are temperature dependent. Tsubomura and Lang [12] also observed a peak at 360 mμ for iodine with amides in methylene chloride solution. The peak, however, disappeared on purification of the amides. The same was also the case with tributyl phosphate and iodine in heptane solution [3]. The observed peak, in this case at 366 mμ, was concluded to be caused either by impurities or by reaction products. We have found, however, in our investigations a strong absorption band at about 364—368 mμ with all the organophosphorus compound-iodine complexes studied. Further-

Table 1. Data of intermolecular addition compounds between organophosphorus compounds and iodine. Solvent, carbon tetrachloride.

Compound	Measurements in infrared region.				
	I $\nu_{P=O}$ cm^{-1}	II $\nu_{P=O}$ cm^{-1}	III $\Delta\nu_{P=O}$ cm^{-1}	IV $\nu_{1/2}$ cm^{-1}	K_{ass} l/mole *ca.* 30°C
$CCl_3PO(OC_2H_5)_2$	1278	1282	32	36	0.69
$CHCl_2PO(OC_2H_5)_2$	1272	1279	38	40	0.82
$CH_3OPO(OCH_3)_2$	1285	1274 1295			
$CH_2ClPO(OC_2H_5)_2$	1267	1270	32	24	1.10
$C_2H_5OPO(OC_2H_5)_2$	1276	1263 1279	36 52	28	5.09
$CH_3PO(OC_2H_5)_2$	1244	1243	35	40	
$C_2H_5PO(OC_2H_5)_2$	1228 1252	1228 1245	28 45	20	4.74
$(C_2H_5)_2NPO(OC_2H_5)_2$	1258	1254	36	28	5.76
$C_6H_5PO(C_6H_5)_2$	1188	1202	40	40	17.48
$C_2H_5PO[N(C_2H_5)_2]_2$	1210 1190	1206 1190	70 54	74	60.21
$CH_3PO(CH_3)_2$	1177	1198	47		
$C_2H_5PO(C_2H_5)_2$	1160	1178	46	52	71.66

more, we observed that this absorption, besides being very concentration dependent, was more enhanced the more the P=O group was polarised. Since this absorption is found at almost the same wavelength for different addition compounds and in different solvents, and is only formed upon complexation, we believe that it may be due to the I_3^- ion. This is in accordance with the results reported by Autrey and Connick[13] and by Buckles et al.[14] who found that the I_3^- ion has an absorption peak at 365 mμ.

An attempt to find a charge-transfer absorption band (CT band) between 220 and 300 mμ corresponding to that found for iodine complexes with ether[9], alcohols[9], amines[15], *etc.* was unsuccesful. This result is consistent with the observation by Tsubomura and Kliegman[3] who were unable to find the CT band of the iodine-tributylphosphate complex in heptane solution. However, by using a perfluorocarbon as solvent they did find an absorption tail at about 220 mμ which they considered to be a part of the CT absorption band, and hence concluded that the peak lies at a wavelength shorter than 220 mμ.

Usually the association constants for iodine with electron donors have been evaluated either form the CT band or from the displaced iodine visible band by using the method of Benesi-Hildebrand[17] or a modification thereof[16]. In this work we have evaluated the association constants by measuring the decrease in intensity of the free iodine band upon complex formation. The superposition of the complexed iodine and free iodine bands seems not, at

Table 1, cont.

Compound	Measurements in visible region.								
	$C_p \times 10^2$	$C_i \times 10^5$		$C_c \times 10^5$		K_{ass} l/mole		K_{ass} l/mole	$\Delta\lambda_{I\text{-}I}$ (mμ)shifted.vis. iodine band
		20°	50°	20°	50°	20°	Av.	50°	Av.	
CCl$_3$PO(OC$_2$H$_5$)$_2$										
CHCl$_2$PO(OC$_2$H$_5$)$_2$	10	5.30	5.50	0.70	0.50	1.32		0.91		
	13	5.15	—	0.85	—	1.27	*1.33*	—	*0.96*	65
	15	4.95	5.30	1.05	0.70	1.41		1.00		
CH$_3$OPO(OCH$_3$)$_2$	5	5.35	—	0.65	—	2.43		—		
	7	5.00	5.30	1.00	0.70	2.86	*2.64*	1.85	*1.85*	68
	10	4.75	5.07	1.25	0.93	2.63		1.84		
CH$_2$ClPO(OC$_2$H$_5$)$_2$	7	4.95	5.45	1.05	0.55	3.03		1.44		
	10	4.65	5.15	1.35	0.85	2.90	*2.83*	1.65	*1.60*	68
	13	4.50	4.90	1.50	1.10	2.56		1.72		
C$_2$H$_5$OPO(OC$_2$H$_5$)$_2$	2	5.35	5.60	0.65	0.40	6.08		3.67		
	3	5.10	—	0.90	—	5.90	*6.18*	—	*3.74*	72
	4	4.75	5.20	1.25	0.80	6.57		3.85		
(C$_2$H$_5$)$_2$NPO(OC$_2$H$_5$)$_2$	2	5.20	5.45	0.80	0.55	7.70		4.60		
	3	5.00	5.20	1.00	0.80	6.67	*7.19*	5.13	*4.85*	73
	—	—	—	—	—	—		—		
C$_6$H$_5$PO(C$_6$H$_5$)$_2$	0.8	5.20	5.55	0.80	0.45	19.20		10.15		
	1.0	4.95	5.45	1.05	0.55	21.22	*22.27*	10.10	*10.92*	78
	1.5	4.30	5.05	1.70	0.95	26.40		12.15		
C$_2$H$_5$PO[N(C$_2$H$_5$)$_2$]$_2$	0.2	5.25	5.65	0.75	0.35	71.40		31.00		
	0.3	4.90	—	1.10	—	74.80	*75.07*	—	*35.50*	84
	0.5	4.30	5.00	1.70	1.00	79.10		40.00		
CH$_3$PO(CH$_3$)$_2$										
C$_2$H$_5$PO(C$_2$H$_5$)$_2$	0.08	5.60	—	0.40	—	85.30		—		
	0.17	5.30	5.65	0.70	0.35	79.30	*83.17*	37.30	*38.75*	86
	0.25	4.95	5.45	1.05	0.55	84.90		40.20		

I the frequency of pure liquid film or as KBr-disk.
II the frequency of solution in carbon tetrachloride, 0.012 moles/l.
III the frequency shift due to complexation with iodine.
IV the half band width of P=O band when complexed with iodine.
   C_p means initial concentration, moles/l, of organophosphours compound
   C_i means concentration, moles/l, of free iodine after complex formation
   C_c means concentration, moles/l, of complex.

low concentrations, to interfere seriously except in the case of $CCl_3P(O)(OC_2H_5)_2$, where the two bands overlap to such an extent that the K_{ass} value obtained is not very reliable. The agreement of the K_{ass} values determined at various concentrations (Table 1) indicates that 1:1 complexes are formed, and that the superposition of the bands does not in these cases interfere seriously. The K_{ass} values have also been checked by infrared spectroscopy and, as can be seen in Table 1, the association constants evaluated by both methods agree very well. Table 1 also shows the concentrations of reactants, of free iodine after
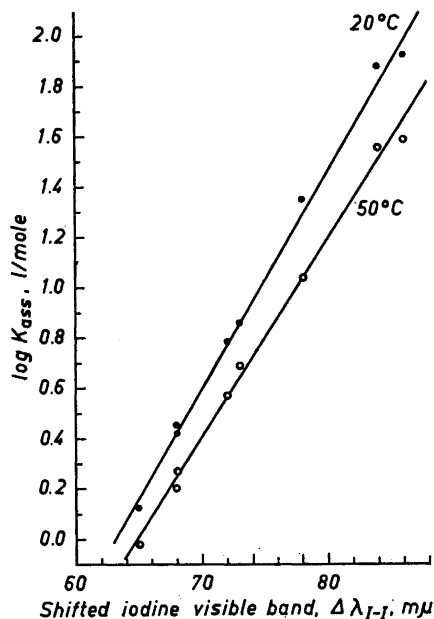
Fig. 3. The relation between the logarithms of the association constants and the shifts in wavelength, $\Delta\lambda_{I\text{-}I}$, of visible iodine band for addition compounds between various organophosphorus compounds and iodine.

complex formation, and of the complexes formed. The association constant of 20.9 l/mole at 20°C for tributyl phosphate and iodine in heptane solution reported by Tsubomura and Kliegman [3] seems very large in comparison with our results, *e.g.*, the association constant of 6.18 l/mole for iodine and triethyl phosphate in carbon tetrachloride solution. The reason for this disagreement may lie either in a difference in the effect of solvent interaction on the complex (or on the reactants) for the two solvents used or in the method of evaluation of the K_{ass} values. (The greater electron release by the butyl group as compared with the ethyl group will also be a factor). On the other hand, their ΔH value of -2.94 kcal/mole is consistent with our result of -3.15 kcal whereas the ΔS values differ greatly, being -3.99 and -7.13 e.u., respectively.

In two previous publications [1,2] it was shown that with experimental error, the logarithms of the association constants, K_{ass}, between organophosphorus compounds (OPC) and phenol, methanol, α-naphthol, and pentachlorophenol, respectively, form a linear relationship with the frequency shift, $\Delta\nu_{\text{O-H}}$, of the O—H band which accompanies the formation of the hydrogen bond. A similar relationship has now been found to be valid for the complexation of organophosphorus compounds with iodine. In Fig. 3 the log K_{ass} values between OPC and iodine are plotted as a function of the blueshift in wavelength, $\Delta\lambda_{I\text{-}I}$, of the iodine visible band upon complex formation. The straight lines drawn through the calculated log K_{ass} values (see Table 1) at 20 and 50°C, are all within experimental error. The smoothed values of log K_{ass} evaluated from the two straight lines in Fig. 3, have been used to determine the corresponding values of ΔH, ΔF, and ΔS. The variation of these with $\Delta\lambda_{I\text{-}I}$ are shown
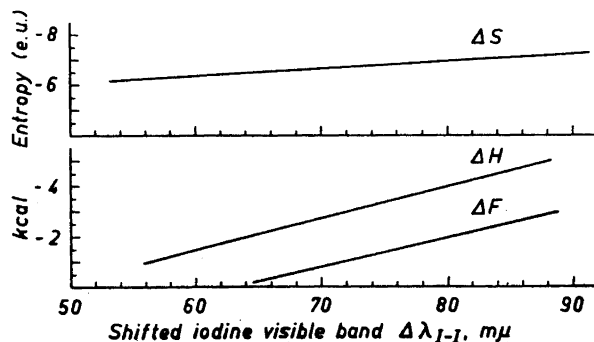
Fig. 4. Enthalpy, $-\Delta H$, free energy, $-\Delta F$, and entropy, $-\Delta S$, *vs.* the blue shifted wavelength, $\Delta\lambda_\text{I-I}$, of the iodine visible band upon complexation with various organophosphorus compounds.

in Fig. 4. As can be seen a decrease in enthalpy is compensated by a decrease in the entropy of the system. In the series of OPC studied there is upon complexation with iodine, a decrease of ΔH from approximately -2.1 to -4.8 kcal/mole which is compensated by a decrease of ΔS from -6.6 to -7.1 e.u. Similar results were found for hydrogen bonded complexes of OPC with various proton donors [2], except with pentachlorophenol. The most striking result is perhaps the observation of a linear relationship between the ability of OPC to form hydrogen bonds with phenol and to form addition compounds with iodine, as shown in Fig. 5. The straight lines drawn through the calculated log K_ass values at 20 and 50°C for the systems OPC-phenol (see [Part II)[2] and
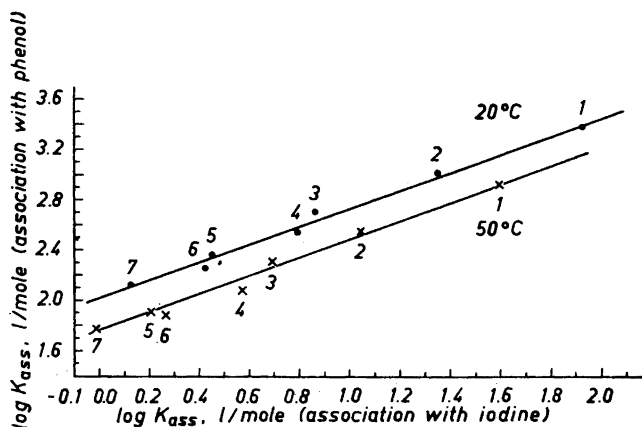

Fig. 5. The relation between the logarithms of the association constants for hydrogen bonded complexes between various organophosphorus compounds and phenol and the logarithms of the association constants of the same phosphorus compounds with iodine, (1) $(C_2H_5)_3PO$, (2) $(C_6H_5)_3PO$, (3) $(C_2H_5)_2NP(O)(OC_2H_5)_2$, (4) $(C_2H_5O)_3PO$, (5) $CH_2ClPO(OC_2H_5)_2$, (6)$(CH_3O)_3PO$, (7) $CHCl_2P(O)(OC_2H_5)_2$. Temperatures, 20 and 50°C.
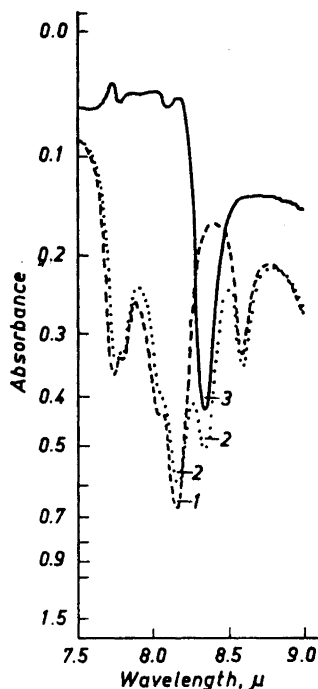
Fig. 6. The infrared absorption spectra of (1) 0.03 moles/l of $C_2H_5P(O)(OC_2H_5)_2$; (2) 0.03 moles/l of $C_2H_5PO(OC_2H_5)_2$ and 0.03 moles/l of I_2; (3) the same concentration as in (2), but compensated with a reference cell containing 0.03 moles/l of $C_2H_5P(O)$-$(OC_2H_5)_2$. Solvent, carbon tetrachloride. Cell length, 1.00 mm. Temperature, *ca.* 30°C.

OPC-iodine are all within experimental error. It should also be noted that the two curves are nearly parallel. This figure demonstrates very clearly that there is a close connection between hydrogen bonding and the bonding in the addition complexes.

Infrared absorption spectra. Fig. 6 shows the effect of iodine on the P=O ground state stretching vibration in a typical case, $C_2H_5P(O)(OC_2H_5)_2$-iodine. The solid curve shows the complexed P=O band when compensated with a reference cell containing the same concentration of organophosphorus compound as in the mixture. As can be seen the complexed P=O band is not very enhanced in broadness in comparison with the free P=O band. This implies that the superposition of the bands does not interfere seriously in the evaluation of the K_{ass} values, which were also found to be consistent with those obtained from the free iodine band. The half band widths of the complexed P=O bands are shown in Table 1. The displacement of the stretching-vibration frequency of the P=O group upon complex formation which should be a measure of the polarisability of the phosphorus compound seems to be larger for the iodine complexes than for the hydrogen bonded complexes, although the K_{ass} and $-\Delta H$ values are larger for the latter. Furthermore, it seems as if the frequency shift of the phosphoryl group is greatest for those compounds containing substituents which contribute to the $+ I$ effect and to the $+ M$ effect. The strong $-I$ effect of chlorine seems to stabilise the electronic constitution of the P=O group whereas the electromeric effect of particularly the amino group, comes into play upon complexation. These observations are in accordance with

Table 2. Determination of the association constants between iodine and triethylphosphine oxide in carbon tetrachloride. Cell length, 10 cm. Temperature, 20° and 50°C

Concentration (initial)		Percent trans-mittance	Concentra-tion of free iodine * $M \times 10^5$	Concentra-tion of complex $M \times 10^5$	K_{ass} l/mole	K_{ass} mean value	Tem-pera-ture
Iodine $M \times 10^5$	Triethyl-phosphine oxide $M \times 10^3$						
6.00	0	26.6	6.00	0	0		
6.00	0.83	29.0	5.60	0.40	85.30		
6.00	1.87	31.0	5.30	0.70	79.30	*83.17*	20°C
6.00	2.50	33.2	4.95	1.05	84.90		
6.00	0	28.8	6.00	0	0		
6.00	1.67	30.6	5.65	0.35	37.30	*38.75*	50°C
6.00	2.50	32.0	5.45	0.55	40.20		

* The concentration of free iodine in this column has been determined by using the calibration curves in Fig. 1.

those predicted in a previous publication [1]. We have also observed that some of the organophosphorus compounds give two new absorption bands upon complexation with iodine, e.g., $CH_2ClP(O)(OC_2H_5)_2$ at 1238 and 1200 cm^{-1}, $(C_2H_5)_2NP(O)(OC_2H_5)_2$ at 1218 and 1207 cm^{-1}, and $(C_6H_5)_3PO$ at 1162 and 1089 cm^{-1}. One of the peaks in the double band is assigned to the complexed P=O stretching vibration band, but the assignment of the other is not quite clear. With regard to the self-association of organophosphorus compounds, we have made some comparisons between the P=O ground state stretching vibration of various phosphorus compounds in pure liquid state (or as a KBr-disk) and in carbon tetrachloride solution. The results are recorded in Table 1.

DISCUSSION OF RESULTS

The present investigation on ternary solutions of iodine with various organo-phosphorus compounds in carbon tetrachloride has established the following facts: Firstly, the ΔH, ΔF and ΔS values form linear relationships with the blue shift of the wavelength, $\Delta\lambda_{I-I}$, of the iodine visible band which accompanies the formation of the complex (see Figs. 3 and 4). Secondly, the ability of organophosphorus compounds to form addition compounds with iodine and to form hydrogen bonds with proton donors is related by a linear rela-tionship (see Fig. 5). Thirdly, the frequency shift of the ground state stretching vibration of the P=O band is much larger on complexation with iodine than on hydrogen bonding in relation to the respective association constants; e.g., the K_{ass} and $\Delta\nu_{P=O}$ values for the association of triethylphosphine oxide with pentachlorophenol, α-naphthol, phenol, methanol and iodine are, 2 095.5, 35; 3 763, 20; 2 522, 23; 45.9, 12; and 83.17 l/mole, 46 cm^{-1}, respectively. The extre-mely large $\Delta\nu_{P=O}$ value for iodine complexation in relation to the low asso-

Table 3. A comparison of data between various hydrogen bonded complexes and the corresponding addition compounds with iodine.

Compound	Iodine				Pentachlorophenol			**Solvent for the addition compounds
	K_{ass} 1/mole 20°C	ΔH kcal	$\Delta \lambda_{I-I}$ $m\mu$	CT λ $m\mu$	K_{ass} 1/mole 20°C	ΔH kcal	$\Delta \nu_{O-H}$ cm^{-1}	
$(C_2H_5)_3N$ [15]	6460	−12.0	108	278			1155	heptane
CH:CHCH:CHCH:N [21]	269	−7.8	100	235	111.4	−5.8	805	»
$HC(O)N(CH_3)_2$ [12]	1.13	−4.0	61	<255	54.1 [26]	−4.6	364	CH_2Cl_2
$C_2H_5OC_2H_5$ [9]	0.97	−4.3	44	249				CCl_4
$C_2H_5OC_2H_5$ [22,23]	1.16	−4.2	60	252				heptane
$CH_3C(O)CH_3$ [24]	0.29*							CS_2
$CH_3(CH_2)_4CO$ [24]	0.56*							»
$CH_3C(O)OCH_3$ [24]	0.34*							»
CH_3OH [9]	0.47	−1.9	72	242.8				CCl_4
C_2H_5OH [9]	0.45	−2.1	69	243.3				»
$CHCl_2P(O)(OC_2H_5)_2$	1.33	−2.1	65	<220	56.3	−5.2	374	»
$(C_2H_5)_3PO$	83.17	−4.9	86	<220	209.5	−6.6	685	»

ciation constant may indicate that we have to differentiate between these addition compounds and hydrogen bonded complexes with regard to the mode of formation of the chemical bond in spite of the linear relationship shown in Fig. 5.

As concluded in a previous publication [2], the relationships between frequency shift, $\Delta \nu_{O-H}$, and ΔH, ΔF and ΔS are only valid when kept to one system, *e.g.*, OPC-phenol, OPC-methanol, *etc.* Furthermore, it has been shown [18] that there exists for the system phenol-pyridines a linear relationship between the logarithms of the association constants and the pK_a values of the proton acceptors, and that this relationship was not applicable to tertiary aliphatic amines. Similar conclusions can now be drawn with respect to addition compounds with iodine. The data for the iodine complexes of triethylamine, pyridine, ether, *etc.*, as shown in Table 3, do not fit with those obtained for the system OPC-iodine. Table 3 also contains a comparison of data obtained by the present authors and by others for various hydrogen bonded complexes with those for the corresponding addition compounds with iodine. If we compare the abilities of triethylamine and pyridine to form addition compounds with iodine and to form hydrogen bonds we see that both nitrogen compounds form addition compounds more readily than hydrogen bonds, whereas for all the other compounds studied the reverse is the case. This supports the view indicated earlier [18], that a difference exists between hydrogen bonded complexes (and addition compounds) containing nitrogen and those containing oxygen. We there [18] put forward the idea that for the system OPC-hydroxy compounds

Table 3, cont.

Compound	α-Naphthol			Phenol			Methanol			**Solvent for the addition compounds
	K_{ass} l/mole 20°C	ΔH kcal/mole	$\Delta\nu_{O-H}$ cm^{-1}	K_{ass} l/mole 20°C	ΔH kcal/mole	$\Delta\nu_{O-H}$ cm^{-1}	K_{ass} l/mole 20°C	ΔH kcal/mole	$\Delta\nu_{O-H}$ cm^{-1}	
$(C_2H_5)_3N$ [18]	108.9	−6.6		90.9	−7.8	380	6.4	−3.8	427	heptane
$CH{:}CHCH{:}CHCH_2N$ [18]	82.5	−5.7	530	59.8	7.0	492	6.0	−3.2	300	»
$HC(O)N(CH_3)_2$ [26]				78.6 [26]	−5.4	292				CH_2Cl_2
$C_2H_5OC_2H_5$ [25]				9.6	−4.6	270				CCl_4
$CH_3C(O)CH_3$ [25]				12.3	−4.5	225				CS_2
$CH_2(CH_2)_4CO$ [25]				14.8	4.2	241				»
$CH_3C(O)OCH_3$ [25]				9.5	−5.3	165				»
$CHCl_2P(O)(OC_2H_5)_2$	117.6	−5.7	283	133.1	−5.0	275	7.5	−2.5	148	»
$(C_2H_5)_3PO$	3763	−7.8	530	2522	−6.8	510	45.9	−6.3	270	»

* Association constants at about 30°C.

** Solvent for all hydrogen bonded complexes was carbon tetrachloride (see Refs [2,18])

CT means charge-transfer band.

$\Delta\nu_I$ means shift of visible iodine band.

proton transfer does not occur on hydrogen bonding, whereas for nitrogen compounds two types of hydrogen bonds were possible in which the above type (I) or the proton-transfer structure (II) predominates, depending on the nature of the proton donor and acceptor.

$$\overset{\delta-}{R}O-H \ldots \overset{\delta+}{N} \qquad\qquad \overset{-}{R}O \ldots H-\overset{+}{N}$$

$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

We also gave strong support for the view that for the system tertiary aliphatic amines-pentachlorophenol the structure (II) predominates, whereas for pyridines the structure (I) or (II) is most pronounced depending on the pK_a value of the proton donor. Furthermore, we have found, as pointed out above, that iodine forms addition compounds more readily with nitrogen than with oxygen compounds, whereas the reverse is the case with hydrogen bonding (see Table 3). From these observations the conclusion may be drawn that the ability to form hydrogen bonds is a function of the electron density around the proton acceptor atom, whereas the ability to form addition compounds with iodine is more likely a function of the basicity of the electron donor atom. Thus the ease with which an addition compound with a halogen or interhalogen is formed depends on the ease with which either an electron is transferred to the acceptor atom to give Mulliken's "dative" structure, $D^+ \ldots (XY)^-$, or the donor atom can form a covalent bond with the acceptor atom to give the halogen-transfer structure, $(D-X)^+ \ldots Y^-$. The former should be function of the ionisation potential of the donor atom, the latter of its basicity.

The reaction mechanism of the complexing of iodine with triethylamine (and pyridine) could thus be described as follows:

$$(C_2H_5)_3N: + \overset{\delta+}{I} \overset{\delta-}{\frown} I \rightleftharpoons [(C_2H_5)_3N:I]^+ \ldots I^-$$

$$\text{(III)}$$
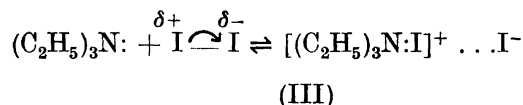
On approach of the strongly basic amine, a halogen-transfer structure (III) results. This mechanism is consistent with the large shift in wavelength, $\Delta\lambda_{I-I}$, of the iodine visible band, the enhanced broadness of the contour of the blue shifted iodine band ($\nu_{\frac{1}{2}}$, 5 700 cm^{-1}), and the very large enthalpy value (ΔH, -12 kcal/mole) found for the system iodine triethylamine-iodine [12,15]. Complex formation between triethylamine and iodine would thus be analogous to that between amines and pentachlorophenol [18] where the proton-transfer structure (II) was found to predominate.

With electron donors containing oxygen ($=C=O$, $\diagdown{P}=O$, $=O$), we propose that the electrostatic structure (IV) predominates, and that the association scheme may be written as, for example:

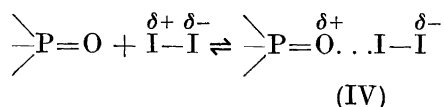$$\diagdown\overset{}{P}=O + \overset{\delta+}{I}-\overset{\delta-}{I} \rightleftharpoons \diagdown\overset{}{P}=\overset{\delta+}{O} \ldots \overset{\delta-}{I}-I$$

$$\text{(IV)}$$

Table 4. Interatomic distances in some solid addition compounds in Å units, as determined by Hassel and co-workers[6].

Compound	Bond	Length obs.	Sum of covalent radii	Δl*	Bond	Length obs.	Sum of covalent radii	Sum of van der Waals' radii	Δl*	Δw*
Trimethylamine-I₂	I–I	2.84	2.66	0.18	N–I	2.27	2.03	3.65	0.24	1.38
Trimethylamine-ICl	I–Cl	2.53	2.32	0.21	N–I	2.30	2.03	3.65	0.27	1.35
Pyridine-ICl	I–Cl	2.54	2.32	0.22	N–I	2.30	2.03	3.65	0.27	1.35
Acetone-Br₂	Br–Br	2.28	2.28	0.00	O–Br	2.82	1.80	3.35	1.02	.053
1,4-Dioxane-Br₂	Br–Br	2.31	2.28	0.03	O–Br	2.71	1.80	3.35	0.91	0.64
1,4-Dioxane-ICl	I–Cl	2.33	2.32	0.01	O–I	2.57	1.99	3.55	0.58	0.98

* Δl, Δw, means the difference between the interatomic distance observed and the sum of covalent radii, and the sum of van der Waals' radii, respectively.

This mechanism is consistent with the small association constants, the low enthalpies, and the relatively small shift of the iodine visible band found for such complexes.

If we assume that there is some relation between interatomic distances in solid addition compounds and in the corresponding addition compounds in solution our reasoning above is in accordance with X-ray work of Hassel *et al.*[5,7] Some examples are given in Table 4, where the observed distances are compared with the sums of covalent radii and van der Waals' radii of the atoms concerned in the bonding. The observed interhalogen distances are not very much different from those of the free molecules, however Δl (Table 4) is largest for triethylamine and pyridine which indicates a halogen-transfer structure (III), whereas Δl for acetone-Br_2 is nil which indicates an electrostatic structure (IV). The same conclusions may be drawn from the distances between the donor and acceptor atoms. The observed N—I distance in triethylamine and pyridine addition compounds suggests that there is more covalent than electrostatic bonding, whereas for acetone the reverse is the case. Unfortunately no solid addition compounds between organophosphorus compounds and halogens or interhalogens are known since it would be of considerable interest to compare the interatomic distances in these with our results.

Self-association of organophosphorus compounds. Miller, Miller and Rogers[19] have recently shown that organophosphorus compounds have a tendency to form intermolecular association complexes in the pure state. With disubstituted phosphine oxides, $R_2P(O)H$, they found a P=O frequency shift from $1150-1155$ cm^{-1} in the solid state to 1190 cm^{-1} in carbon disulphide solution which was attributed to intermolecular association. Furthermore, they found a decrease in the P—H frequency upon solution which is not consistent with bonds of the type $R_2P(O)H...OP(H)R_2$ in the solid state. These results should be compared with those obtained by us for some disubstituted phosphites as shown below.

	$\nu_{P=O}$ (cm^{-1})		ν_{P-H} (cm^{-1})	
	Pure State	Solution in CCl_4 0.012 moles/l	Pure state	Solution in CCl_4 0.012 moles/l
$HP(O)(OCH_3)_2$	1267	1265	2420	2432
$HP(O)(OC_2H_5)_2$	1263	1258	2416	2428
$HP(O)[OCH(CH)_2]_2$	1260	1252	2410	2428

As can be seen we have found no increase in the P=O stretching vibration of the phosphites upon solution, rather a small decrease. However, an increase in the P—H frequency was observed upon solution. These results are just the reverse of those reported for disubstituted phosphine oxides [19]. From these observations the conclusion may be drawn that the P=O group in phosphites is not involved in the formation of self-association complexes, whereas in the disubstituted phosphine oxides the P=O group participates. This explanation is consistent with the relative polarity of the P=O bond in the two types of compounds. However, most phosphorus compounds other than the disubstituted phosphites (see Table 1) show an increase in the P=O stretching vibra-

tion frequency upon solution. Furthermore, the shift is greatest for the most polarised phosphine oxides, *e.g.*, the frequency of triethylphosphine oxide is shifted from 1160 cm^{-1} in solid state to 1178 cm^{-1} in carbon tetrachloride solution. This strongly indicates an intermolecular association which may be attributed to a dipole-dipole association, $\overset{\delta+}{\equiv}\overset{\delta-}{P}=\overset{}{O}\ldots\overset{\delta+}{P}=\overset{\delta-}{O}$. Hyperconjugation, *e.g.*, $\equiv\overset{\delta+}{P}(O)CH_2-\overset{\delta-}{H}\ldots O=\overset{|||}{P}-CH_3$, however, should also be taken into

account when considering the association since the shift is largest for trimethylphosphine oxide. The observed reactivity of iodine with all compounds containing the P—CH$_3$ group may also be explained by this methyl hyperconjugation effect. Thus, whereas the triethylphosphine oxide-iodine complex is stable in carbon tetrachloride, trimethylphosphine oxide reacts with iodine. Further evidence for hyperconjugation in the methylphosphines is provided by the fact [20] that they are much stronger bases than other phosphines.

REFERENCES

1. Aksnes, G. and Gramstad, T. *Acta Chem. Scand.* **14** (1960) 1485.
2. Gramstad, T. *Acta Chem. Scand.* **15** (1961) 1337.
3. Tsubomura, H. and Kliegman, J. H. *J. Am. Chem. Soc.* **82** (1960) 1314.
4. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* **70** (1948) 2832; **71** (1949) 2703.
5. Mulliken, R. S. *J. Am. Chem. Soc.* **72** (1950) 600, **74** (1952) 811; *J. Phys. Chem.* **56** (1952) 801, **23** (1955) 397; *Rec. trav. chim.* **75** (1956) 845.
6. Hassel, O. and Hvoslef, J. *Acta Chem. Scand.* **8** (1954) 873; **10** (1956) 138.
   Hassel, O. and Römming, C. *Acta Chem. Scand.* **10** (1956) 696; **11** (1957) 195.
   Hassel, O. *Proc. Chem. Soc.* **1957** 250.
   Hassel, O. and Strömme, K. O. *Acta Chem. Scand.* **13** (1959) 275.
   Hassel, O. and Hope, H. *Acta Chem. Scand.* **14** (1960) 391.
7. Strömme, K. O. *Acta Chem. Scand.* **13** (1959) 268.
8. Person, W. B., Humphrey, R. E., Deskin, W. A. and Popov, A. J. *J. Am. Chem. Soc.* **80** (1958) 2049; **81** (1959) 273.
   Person, W. B., Erickson, R. E. and Buckles, R. E. *J. Am. Chem. Soc.* **82** (1960) 29.
9. de Maine, P. A. D. *J. Chem. Phys.* **26** (1957) 1189, 1192, 1199.
10. Andrews, L. J. and Keefer, R. M. *J. Am. Chem. Soc.* **77** (1955) 2164.
11. Schmulbach, C. D. and Drago, R. S. *J. Am. Chem. Soc.* **82** (1960) 4484.
12. Tsubomura, H. and Lang, R. P. *J. Am. Chem. Soc.* **83** (1961) 2085.
13. Autrey, A. D. and Connick, R. E. *J. Am. Chem. Soc.* **73** (1951) 1842.
14. Buckles, R. E., Yuk, J. P. and Popov, A. I. *J. Am. Chem. Soc.* **74** (1952) 4379.
15. Nagakura, S. *J. Am. Chem. Soc.* **80** (1958) 520.
16. Tsubomura, H. *J. Am. Chem. Soc.* **82** (1960) 40.
17. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* **71** (1949) 2703.
18. Gramstad, T. *Acta Chem. Scand.* **16** (1962) 807.
19. Miller, C. D., Miller, R. C. and Rogers, W. *J. Am. Chem. Soc.* **80** (1958) 1562.
20. Kaesz, H. D. and Stone, F. C. A. *J. Am. Chem. Soc.* **82** (1960) 6213.
21. Reid, C. and Mulliken, R. S. *J. Am. Chem. Soc.* **76** (1954) 3869.
22. Brandon, M., Tamres, M. and Searles, S. *J. Am. Chem. Soc.* **82** (1960) 2129.
23. Tamres, M. and Brandon, M. *J. Am. Chem. Soc.* **82** (1960) 2134.
24. Yamada, H. and Kozima, K. *J. Am. Chem. Soc.* **82** (1960) 1543.
25. Gramstad, T. *To be published.*
26. Gramstad, T. and Fuglevik, W. *To be pubslihed.*