

Studies of Hydrogen Bonding

Part VI*. A Comparison between the Ability of the $\equiv\text{P}=\text{O}$ and the $\equiv\text{P}=\text{S}$ Groups to Form Addition Compounds with Iodine and to Take Part in Hydrogen Bonding

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It has been found that $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ takes part in hydrogen bonding more readily than $(\text{C}_2\text{H}_5\text{O})_3\text{PS}$ but that the reverse is the case for complex formation with iodine. These, and earlier results, are discussed in terms of the mechanism of association of proton donors and iodine with compounds containing oxygen, sulphur, and nitrogen.

In a previous publication¹, the ability of organophosphorus compounds containing the $\equiv\text{P}=\text{O}$ group to form hydrogen bonds was compared with their ability to take part in complex formation with iodine. It was found that the $\equiv\text{P}=\text{O}$ group forms hydrogen bonds readily, whereas its ability to form addition compounds with iodine is considerably smaller. It was therefore of interest to extend these measurements to compounds containing the $\equiv\text{P}=\text{S}$ group.

RESULTS AND DISCUSSION

In a recent paper Zingaro and Hedges⁵ describe a spectrophotometric study of the interaction of the halogens and interhalogens with organophosphorus compounds containing the $\equiv\text{P}=\text{O}$ or $\equiv\text{P}=\text{S}$ group. They found that the infrared frequency shifts upon complex formation, $\Delta\nu_{\text{P}=\text{O}}$ and $\Delta\nu_{\text{P}=\text{S}}$, are related to the polarity of acceptor molecule according to the sequence $\text{ICl} > \text{IBr} > \text{I}_2 > \text{Br}_2$. The frequency shift for a $\equiv\text{P}=\text{S}$ compound is smaller than that observed for the $\equiv\text{P}=\text{O}$ compound. The factors which affect the $\equiv\text{P}=\text{O}$ and $\equiv\text{P}=\text{S}$ frequency shifts were discussed, and it was pointed out that special importance must be attached to π bonding between the p and d orbitals of the oxygen or sulphur and the phosphorus, and back-bonding

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from the p orbitals of the halogens to the d orbitals of the sulphur atom. This latter effect is impossible in the phosphoryl complexes owing to the lack of a suitable d orbital on the oxygen.

As has been shown previously^{1,2,8}, the K_{ass} values for the association of organophosphorus compounds with hydroxy compounds and iodine depend upon the electron density on the phosphoryl oxygen atom which in turn is controlled by the inductive and mesomeric effects of the substituents attached to the phosphorus atom. K_{ass} is largest for the most polarised $\equiv\text{P}=\text{O}$ group. Furthermore, it has been shown¹ that the $\equiv\text{P}=\text{O}$ frequency shift, $\Delta\nu_{\text{P}=\text{O}}$, is much larger upon complexation with iodine than upon formation of a hydrogen bond, *i.e.*, that $\Delta\nu_{\text{P}=\text{O}}$ depends both on the substituents on the phosphorus atom and those on the complexing agent. Some examples are given below:

	$K_{\text{ass}}^{20^\circ}$ l/mole	$\Delta\nu_{\text{PO}}$ cm^{-1}	Ref.
$(\text{C}_2\text{H}_5)_3\text{PO}-\text{HOC}_6\text{H}_5$	2522.0	23	2
$(\text{C}_2\text{H}_5)_3\text{PO}-\text{I}_2$	83.2	46	1
$(\text{C}_2\text{H}_5\text{O})_3\text{PO}-\text{HOC}_6\text{H}_5$	350.5	30	2
$(\text{C}_2\text{H}_5\text{O})_3\text{PO}-\text{I}_2$	6.2	36	1

The sequence of decreasing $\equiv\text{P}=\text{O}$ frequency shift upon complex formation is, iodine monochloride > iodine monobromide > iodine > bromine⁵ > pentachlorophenol > α -naphthol and phenol > methanol, although the enthalpies of formation ($-\Delta H$) of the hydrogen bonds are larger than those of the analogous iodine complexes (Table 1 and Ref.¹). The observations on the $\equiv\text{P}=\text{O}$ frequency shifts in iodine complexes may be interpreted as indicating that the structure $\overset{\delta+}{\equiv}\text{P}=\overset{\delta-}{\text{O}}\dots\overset{\delta+}{\text{I}}-\overset{\delta-}{\text{I}}$ (or perhaps $\overset{\delta+}{\equiv}\text{P}=\overset{\delta-}{\text{O}}\overset{\delta+}{\text{I}}\dots\overset{\delta-}{\text{I}}$) is of major importance, whereas in the hydrogen bond complexes the structure $\overset{\delta-}{\equiv}\text{P}=\overset{\delta+}{\text{O}}\dots\overset{\delta-}{\text{H}}-\overset{\delta+}{\text{OR}}$ makes the largest contribution. In Table 1 results are tabulated which show that triethyl phosphorothionate forms more stable iodine complexes than hydrogen bond complexes, these observations being the reverse of those found for phosphoryl derivatives. The values of K_{ass} and $-\Delta H$ are larger for the system $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{S}-\text{I}_2$ than for $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{O}-\text{I}_2$, being 10.0 and 6.2 l/mole, 5.9 and 3.2 kcal/mole, respectively. Similar results have been reported by Tsubomura and Lang⁶ for $(\text{C}_2\text{H}_5)_2\text{S}-\text{I}_2$ and $(\text{C}_2\text{H}_5)_2\text{O}-\text{I}_2$ (see Table 2). Spectrophotometric measurements on the $\equiv\text{P}=\text{S}$ and $\equiv\text{P}=\text{O}$ complexes thus show that the sulphur compound is more strongly complexed to iodine than is the $\equiv\text{P}=\text{O}$ compound; the relative stability of these complexes is related to the shift in the iodine peak (72 and 77 $\text{m}\mu$, respectively, for the $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{O}$ and $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{S}$ complexes, see Table 1). In contrast, the $\equiv\text{P}=\text{O}$ stretching frequency shift, $\Delta\nu_{\text{P}=\text{O}}$ in the infrared is larger than the $\equiv\text{P}=\text{S}$ frequency shift, $\Delta\nu_{\text{P}=\text{S}}$ on complexing with iodine, in spite of the fact that a larger enthalpy ($-\Delta H$) value is found for the phosphorothionate complex (Table 1). Following Zingaro and Hedges⁵, this discrepancy may be due to greater $\text{S} \rightarrow \text{P}$ π bonding in the phosphorothionate complex than $\text{O} \rightarrow \text{P}$ π bonding

Table 1. A comparison of the abilities of triethyl phosphate and triethyl phosphorothionate to form hydrogen bonds and to form addition compounds with iodine.

Electron donor / Electron acceptor	$(C_2H_5O)_3P=O^a$						$(C_2H_5O)_3P=S$								
	$\Delta\nu_{O-H}$ cm ⁻¹	$K_{ass}^{20^\circ}$ l/mole	$K_{ass}^{50^\circ}$ l/mole	ΔH kcal/mole	ΔF kcal/mole	ΔS e.u.	$\Delta\nu_{P-O}$ cm ⁻¹	$\Delta\nu_{O-H}$ cm ⁻¹	$K_{ass}^{20^\circ}$ l/mole	$K_{ass}^{50^\circ}$ l/mole	ΔH kcal/mole	ΔF kcal/mole	ΔS e.u.	$\Delta\nu_{P-S}$ cm ⁻¹	Solvent
Phenol	345	350.5	121.1	-6.7	-3.4	-11.1	30	157	5.5	4.0 ^c	-2.9	-1.0	-9.7	16	CS ₂
Pentachloro-phenol	481	153.1	67.1	-5.2	-2.9	-7.7	33	181	2.3	1.7 ^c	-2.8	-0.5	-8.3	27	CS ₂
Iodine	72 ^b	6.2	3.7	-3.2	-1.1	-7.9	36	77 ^b	4.0	2.1 ^c	-5.9	-0.8	-18.7	22	CS ₂
								77 ^b	10.0	3.9	-5.9	-1.3	-16.7		CCl ₄

^a Corrected data from Part II, Ref.²

^b Means shifted iodine visible band (m μ), see Part IV, Ref.¹

^c Measured at 40°C.

Table 2. A comparison of thermodynamic data for hydrogen bonds and iodine complexes for various oxygen, nitrogen and sulphur compounds. Solvents were carbon tetrachloride and n-heptane respectively for hydrogen bonded complexes and iodine complexes.

Electron acceptor Electron donor	Iodine ⁶			Phenol		
	$\Delta\lambda_{I-I}$ m μ	$K_{\text{ass}}^{20^\circ}$ l/mole	ΔH kcal/mole	$\Delta\nu_{O-H}$ cm ⁻¹	$K_{\text{ass}}^{20^\circ}$ l/mole	ΔH kcal/mole
(C ₂ H ₅) ₂ S	87	210	- 7.82	165	4.7	-3.4
(C ₂ H ₅) ₂ O	60	1.16	- 4.2	270 ^a	9.6	-4.6
CH:CHCH:CHCH:N	100	269	- 7.8	492 ^b	59.8	-7.0
(C ₂ H ₅) ₃ N	108	6460	-12.0	380 ^b	90.9	-7.8

^a see Ref. ⁹ ^b see Ref. ³

in the phosphate complex, which will give greater stability to the former. The frequency shift $\Delta\nu_{P=O}$ is also larger than $\Delta\nu_{P=S}$ on hydrogen bonding, but here as distinct from complexation with iodine, the enthalpy ($-\Delta H$) of complex formation is largest for the phosphate-phenol complex (Table 1). We consider, however, that the lower K_{ass} value for the system $\equiv P=S-HOR$ as compared with $\equiv P=O-HOR$ is due to a lower electron density around the sulphur than around the oxygen atom consistent with their relative electronegativities (2.5 and 3.5, respectively). The smaller frequency shift, $\Delta\nu_{O-H}$, for the association of phenol with triethyl phosphorothionate as compared with triethyl phosphate (172 and 345 cm⁻¹, respectively, Table 1) is also consistent with the lower electronegativity of sulphur. If we compare (C₂H₅)₃PO and (C₂H₅)₂O with (C₂H₅)₃PS and (C₂H₅)₂S with respect to their ability to form a complex with iodine, we see that while the ability of (C₂H₅)₃PS is smaller than that of (C₂H₅)₂S the reverse is the case for the oxygen analogues (Tables 1 and 2). However, (C₂H₅)₂S has no back-bonding from the sulphur and hence has a higher electron density on the sulphur than has $\equiv P=S$. The most probable contributing structures are thus (C₂H₅)₂S⁺I⁻ and (C₂H₅)₂S^{δ+} . . . I^{δ-}-I. These structures are favoured by the strong +I effect of the ethyl groups. Further, as shown earlier ¹, iodine forms more stable addition compounds with nitrogen bases than with oxygen bases, whereas the reverse is the case with hydrogen bonding. It seems therefore, that the nitrogen bases resemble the sulphur bases when abilities to form hydrogen bonds and addition compounds with iodine are compared. The unshared electron pair on nitrogen has a greater tendency to form a covalent bond with the acceptor and hence $\equiv N^+-I \dots \bar{I}$ should predominate ^{1,3}. This is in accordance with the X-ray

work of Hassel *et al.*⁷ whose observed N—I distance in the triethylamine and pyridine addition compounds with iodine indicates that the N—I bond is more covalent than electrostatic in nature. Thermodynamic data for some typical systems are given in Table 2.

Solvent interaction. As shown earlier^{2,3} the thermodynamic properties of hydrogen bonds are greatly affected by solvent interaction. The lower association constants found for the systems OPC-pentachlorophenol and amides-pentachlorophenol⁹ compared with those for OPC-phenol and amides-phenol was suggested as being due, at least partly, to hydrogen bond formation between the proton donor and the solvent. When carbon tetrachloride was replaced by carbon disulphide as the solvent a marked increase in the association constant was observed for most systems. With regard to complex formation with iodine, however, the effect of these solvents on complexing ability appears to be reversed. As can be seen in Table 1, a decrease in the association constant for triethyl phosphorothionate and iodine was found when carbon tetrachloride was replaced by carbon disulphide. An explanation for this reversal in the effect of these two solvents may be that iodine interacts more strongly with CS₂ (to form S=C=S . . I—I) than it does with CCl₄.

EXPERIMENTAL

The instruments, the instrumental conditions, the methods of determining the spectra, the method of calculation of the association constants, and the solvents used were the same as described elsewhere⁹. Triethyl phosphorothionate was purchased from Aldrich Chemical Co., Inc.

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