

## Studies of Hydrogen Bonding

### Part II \*. Intermolecular Hydrogen Bond Association between Organophosphorus Compounds and Methanol, $\alpha$ -Naphthol and Pentachlorophenol, respectively

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The  $K_{\text{ass}}$ ,  $\Delta H$ ,  $\Delta F$  and  $\Delta S$  values of the equilibrium reaction between sixteen organophosphorus compounds and methanol,  $\alpha$ -naphthol and pentachlorophenol, respectively, have been determined. It has been found that for each system the  $\Delta H$ ,  $\Delta F$  and  $\Delta S$  values form linear relationships with the hydrogen bond frequency shift. The effect of solvent interaction on the hydrogen bond association is considered.

The ability of organophosphorus compounds to form intermolecular hydrogen bonds has been observed earlier. Gordy and Stanford<sup>2,3</sup> have shown that *n*-butyl phosphate causes a much greater O—D bond frequency shift with heavy methanol than does any other ester except *n*-butyl borate. Further it has been shown by using heat of mixing as a criterion, that organophosphorus compounds form hydrogen bonds with chloroform<sup>4-6</sup>. These results have also been confirmed by an infrared study<sup>7</sup> of the frequency shifts of the phosphoryl group and determination of the changes in the integrated absorption intensities of the C—H bond of chloroform and other solvents. However, very few systematic determinations of hydrogen bond energies have hitherto been made, and the spectroscopic evidence already available presents a somewhat confused picture. Badger and Bauer<sup>8</sup> have pointed out that there appears to be a linear relationship between the energy of the hydrogen bond and the shift in frequency of the OH-bond which accompanies the formation of the bond. More recently, Badger<sup>9</sup> reports that there exists a fairly strong indication that the relation between frequency shift and energy is not linear. Pimentel and Brown<sup>10</sup> have also reported data which do not substantiate the first proposed relation of Badger.

\* First paper in this series: Ref.<sup>1</sup>

In a previous publication<sup>1</sup> it was shown that organophosphorus compounds containing the P=O group form very strong intermolecular hydrogen bonds with phenol. Furthermore, it was shown that the  $\Delta H$ ,  $\Delta F$ ,  $\Delta S$  and the half band width of the equilibrium reaction varied linearly with the hydrogen bond O—H frequency shift. It was also shown<sup>1,11</sup> that when sufficiently low concentrations of phenol and organophosphorus compound were used, the only association complex formed is the dimeric intermolecular hydrogen bond complex. The inductive and mesomeric effects of the substituents in phosphorus compounds upon hydrogen bond association were also discussed.

Since we possessed a variety of bases which formed well defined hydrogen bonded complexes, which could be readily determined by spectroscopy, it was of interest to study the thermodynamic properties of the hydrogen bond equilibrium reaction with acidic compounds other than phenol.

### EXPERIMENTAL

*Materials.* The physical data and methods of preparation of the organophosphorus compounds used, have been published elsewhere<sup>1</sup>. However, in all cases the phosphorus compounds were purified by fractional distillation or recrystallisation just before use. The following materials were used without further purification: "Merck Guaranteed Reagent" phenol, *a*-naphthol and carbon disulphide, "Merck Spectroscopic Grade" methanol and carbon tetrachloride, "Fluka puriss." pentachlorophenol.

*Infrared measurements.* The infrared spectroscopic measurements were made with a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics. This instrument was used for the determination of the frequency shift of the ground state stretching vibration of the OH-band which accompanies the formation of hydrogen bond. The same instrument was used for the determination of the stretching frequencies of the P=O group, the half band width,  $\nu_{1/2}$ , and the intensity,  $\epsilon_{\max} \times \nu_{1/2}$  of the O—H band. Instrumental conditions were as follows: Resolution, 975; gain, 5.5; response, 1:1; speed, 3.5; suppression, 2. The cell was calibrated by the interference fringe method and was found to be of 1.00 mm thickness. For all spectra the *a*-naphthol or pentachlorophenol concentration was kept at 0.006 M, and the concentration of organophosphorus compound was, with few exceptions, 0.012 M. For the system organophosphorus compounds-methanol, the concentrations were, due to the smaller amount of hydrogen bond formation, 0.03 and 0.06 M, respectively.

The spectra were run in the following way: A solution of the organophosphorus compound in carbon tetrachloride was first run using the instrumental conditions given above, compensated with carbon tetrachloride in a reference cell of the same thickness. Secondly, the mixture of organophosphorus compound and proton donor in carbon tetrachloride was run on the same sheet and compensated with the same reference cell containing CCl<sub>4</sub>. Thirdly, still on the same sheet, the mixture was run again, but this time compensated with a reference cell containing the same concentration of organophosphorus compound as in the mixture.

*Near-infrared measurements.* The near-infrared measurements were carried out with a Beckman Ratio Recording Spectrophotometer Model DK-2. Instrumental conditions were as follows: Scanning time, full scale, 5 min; range, 0—100, sensitivity, 50; time constant, 0.6; per cent transmittance. This instrument was used for the determination of the association constants. The concentration of free proton donor was determined from the first overtone band of the stretching vibration of the hydroxyl group. These appear, with carbon tetrachloride as solvent, at 7 119 cm<sup>-1</sup>, 7 098 cm<sup>-1</sup>, and 6 860 cm<sup>-1</sup> for methanol, *a*-naphthol and pentachlorophenol, respectively.  $K_{\text{ass}}$  is calculated as shown below:

$$A-H + B \rightleftharpoons A-H \cdots B$$

$$K_{\text{ass}} = \frac{[A-H \cdots B]}{[A-H][B]} = \frac{x}{(a-x)(b-x)}$$

where  $x$  is the concentration in mole/l of the hydrogen bonded complex, calculated from the free OH-band;  $a$  and  $b$  are the formal concentrations in mole/l of proton donor and proton acceptor, respectively. The quartz absorption cell of 10 cm path length used, was the same as that described earlier. The spectra were run immediately after preparing the solutions, at temperatures of 20°C and 50°C (when carbon disulphide was used as solvent, the measurements were carried out at 20°C and 40°C). For all spectra the proton donor concentration was kept at 0.006 M to prevent self-association. The values of the association constants recorded in Table 2 are the mean values of three or four separate determinations. In Table 1 are recorded the experimental results from the determination of  $K_{\text{ass}}$  for one of the compounds studied. The concentration range shown in Table 1 was used for the systems OPC-pentachlorophenol and OPC- $\alpha$ -naphthol, whereas for the system OPC-methanol, the following concentrations of OPC were used, 0.012, 0.024, 0.036 and 0.06 mole/l.

## RESULTS

*Association constant and free energy.* In a previous publication<sup>1</sup> it was shown that, within experimental error, the logarithms of the association constants  $K_{\text{ass}}$  between organophosphorus compounds (OPC) and phenol form a linear relation with the shift in frequency,  $\Delta\nu$ , of the OH-band of phenol which accompanies the formation of the hydrogen bond. The same relation has now been found to be valid for the systems, OPC-methanol, OPC- $\alpha$ -naphthol and OPC-pentachlorophenol (see Fig. 1). It can easily be seen from this figure that it would be impossible by taking  $K_{\text{ass}}$  values from different systems to maintain the linear relationship between frequency shift and the logarithms of the association constants. Grunwald and Coburn<sup>12</sup> have collected values of

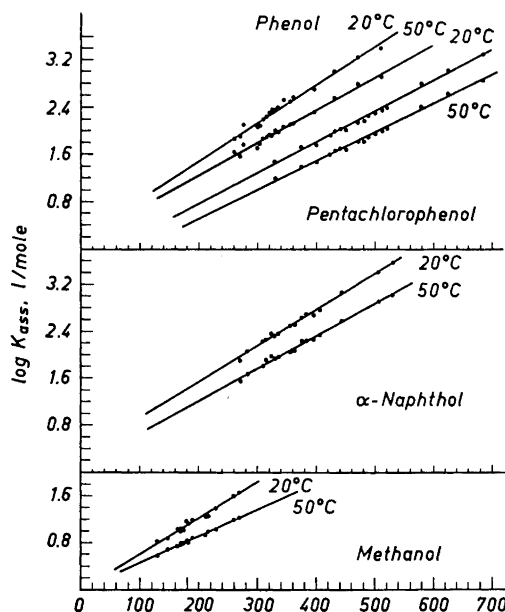


Fig. 1. The relation between the logarithms of the association constants and the frequency shifts for the hydrogen bonded complexes between organophosphorus compounds and phenol, pentachlorophenol,  $\alpha$ -naphthol and methanol, respectively.

Table 1. Determination of the association constant between pentachlorophenol and trimethylphosphate in carbon tetrachloride. Cell length, 10 cm. Temperature 20°C.

Concentration mole/l		Optical density for free O—H band	Concentration of free pentachlorophenol mole/l	Concentration of complex mole/l	$K_{\text{ass}}$ l/mole	$K_{\text{ass}}$ mean value
Pentachlorophenol	Trimethylphosphate					
0.006	0	0.1367	0.006	0	0	
0.006	0.003	0.1135	0.004983	0.001017	102.9	103.0
0.006	0.006	0.0958	0.004207	0.001793	101.4	
0.006	0.012	0.0701	0.003077	0.002923	104.7	

$\Delta\nu$  and  $K_{\text{ass}}$  for hydrogen bond association and have shown that the sequence of the  $\Delta F$  values (or  $\log K_{\text{ass}}$  values) does not follow that of  $\Delta\nu$ . However, they also indicate that there may exist a monotonic relationship between  $\Delta\nu$  and  $\Delta F$  at least for those compounds in which the hydrogen bond donors and acceptors have some common electronic feature.

In Fig. 1 our results for  $\log K_{\text{ass}}$  are plotted as a function of the frequency shift of the ground state stretching vibration of the OH-bands. The straight lines drawn through the calculated  $\log K_{\text{ass}}$  values (see Table 1) at 20°C and 50°C, are all within experimental error. For each system the two lines at 20°C and 50°C possess different slopes. The sequence, as can be seen in Fig. 1, is, in order of decreasing divergence, OPC-methanol > OPC-phenol > OPC- $\alpha$ -naphthol > OPC-pentachlorophenol. The thermodynamic significances of the observations indicated above are, a) the free energy,  $\Delta F$ , of the hydrogen bond equilibrium reaction can be fairly accurately described as a linear function of the frequency shift as shown in Fig. 2, b) as a consequence of this linear relationship together with the thermodynamic equation  $\Delta F = \Delta H - T\Delta S$ ,

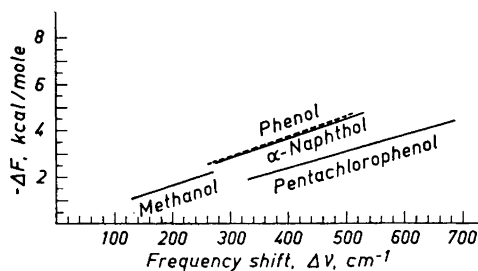


Fig. 2. Free energy,  $-\Delta F$ , at 20°C, vs. the frequency shift,  $\Delta\nu$ , for O—H bond, for hydrogen bonded systems.

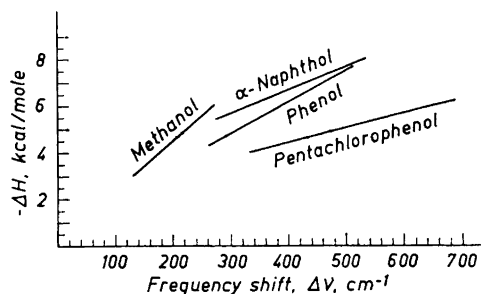


Fig. 3. Enthalpy,  $-\Delta H$ , vs. the frequency shift,  $\Delta\nu$ , for O—H bond, for hydrogen bonded systems.

Table 2. Data of dimeric hydrogen bond association between organophosphorus compounds and phenol, methanol,  $\alpha$ -naphthol and pentachlorophenol, respectively. Solvent: carbon tetrachloride.

Compound	Phenol <sup>a</sup>			Methanol			$\alpha$ -Naphthol			Pentachlorophenol		
	$\nu_{OH}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C	$\nu_{OH}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C	$\nu_{OH}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C	$\nu_{OH}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C
CCl <sub>3</sub> PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1282	73.2	44.8	130	6.8	3.8	273	81.8	36.2	330	29.7	15.7
CHCl <sub>2</sub> PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1279	133.1	60.7	148	7.5	5.0	283	117.6	47.5	374	56.3	24.7
HPO(OCH <sub>3</sub> ) <sub>2</sub>	1265	123.1	53.4	169	9.8	5.8	310	167.7	64.0	400	61.2	29.0
HPO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1258	161.9	76.8	170	10.8	6.2	316	187.7	83.3	425	85.5	40.7
CH <sub>3</sub> OPO(OCCH <sub>3</sub> ) <sub>2</sub>	1274	182.9	78.9	175	10.6	6.2	323	238.7	97.4	433	103.0	46.7
CH <sub>2</sub> ClPO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1270	239.0	84.2	165	10.9	5.6	330	217.3	88.1	440	110.3	50.3
HPO[OCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	1256	237.3	99.9	180	14.7	6.8	336	236.1	93.4	450	107.3	48.3
CH <sub>3</sub> PO(OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl) <sub>2</sub>	1245	247.0	95.7	182	13.6	6.3	356	307.8	114.2	473	145.3	67.0
C <sub>2</sub> H <sub>5</sub> OPO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1263	350.5	121.1	189	15.5	7.7	363	323.5	115.9	481	153.1	67.1
C <sub>2</sub> H <sub>5</sub> PO(OCH <sub>3</sub> ) <sub>2</sub>	1231	329.7	126.5	—	—	—	383	482.4	179.7	488	186.6	80.6
CH <sub>3</sub> PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1243	381.0	141.0	211	18.1	8.5	376	435.0	178.6	500	214.0	92.5
C <sub>2</sub> H <sub>5</sub> PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1228	—	—	211	17.5	8.4	396	476.5	180.9	511	234.8	101.0
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N—PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1254	518.2	211.8	217	17.6	9.8	406	581.9	221.8	519	257.7	111.0
C <sub>6</sub> H <sub>5</sub> PO(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1202	1055.4	365.5	231	24.3	10.6	443	1166.0	384.5	578	673.6	269.6
CH <sub>3</sub> PO(CH <sub>3</sub> ) <sub>2</sub>	1198	470	1836.0	260	40.1	15.5	506	2575.0	802.4	623	1136.0	440.7
C <sub>2</sub> H <sub>5</sub> PO(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1178	510	2522.0	270	45.9	16.7	530	3763.0	1085.0	685	2095.5	727.9

<sup>a</sup> Data from Part 1, Ref. 1

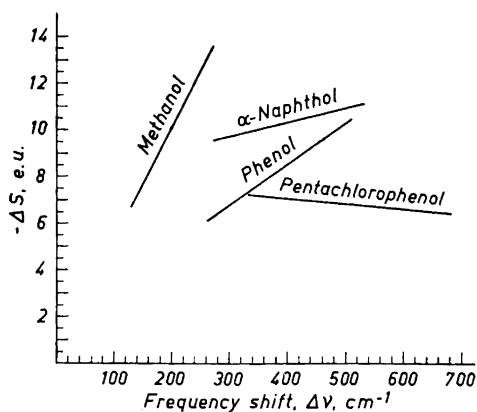


Fig. 4. Entropy,  $-\Delta S$ , vs. the frequency shift,  $\Delta\nu$ , for O-H bond, for hydrogen bonded systems.

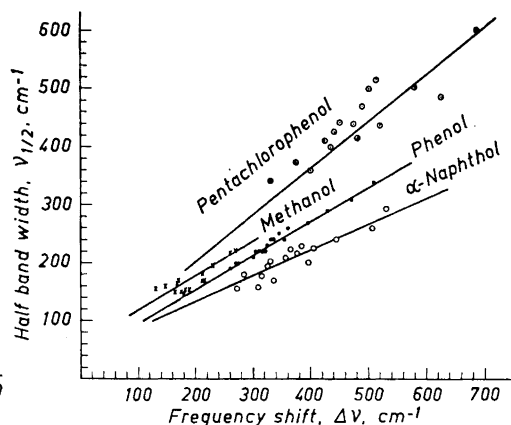


Fig. 5. Frequency shift,  $\Delta\nu$ , vs. half band width,  $\nu_{1/2}$ , of O-H bond, for hydrogen bonded systems.

both the enthalpy  $\Delta H$  and the entropy  $\Delta S$  must also vary linearly with the frequency shift  $\Delta\nu$  (see Figs. 3 and 4), c) the difference in slope between the  $K_{\text{ass}}$  vs.  $\Delta\nu$  plots for 20°C and 50°C for each system is strongly reflected in the  $\Delta H$  vs.  $\Delta\nu$  and  $\Delta S$  vs.  $\Delta\nu$  plots.

The hydrogen donors studied show an increasing tendency to form intermolecular hydrogen bonds with the organophosphorus compounds used in the order  $\alpha$ -naphthol > phenol > pentachlorophenol > methanol (see Table 2). There is a reasonable amount of evidence to suggest that the drop in association constants for pentachlorophenol compared with those for phenol and  $\alpha$ -naphthol is due to solvent interactions.

*Enthalpy and entropy.* Figs. 3 and 4 show that the displacement of the frequency of the associated band from that of the free hydroxyl band varies in an inverse linear manner with the enthalpy and entropy. The values used are calculated from the smoothed values of  $\log K_{\text{ass}}$  found from the straight lines in Fig. 1. It should be noted that the  $\Delta H$  and  $\Delta S$  curves flatten with increasing acidity of the proton donors, the sequence of decreasing slope being, methanol > phenol >  $\alpha$ -naphthol > pentachlorophenol. Table 3 shows the range of  $\Delta H$  and  $\Delta S$  values, and the slope for each system. As can be seen the increase in enthalpy is compensated by a decrease in entropy, except for the system OPC-pentachlorophenol.

*Half band width and intensity.* In Fig. 5 the displacement  $\Delta\nu$  is plotted as a function of the observed half band width  $\nu_{1/2}$  for the O-H bond. The straight lines drawn through the observed values cut the  $\nu_{1/2}$ -axis at 47, 51, 66, and 83  $\text{cm}^{-1}$ , which correspond approximately to the half band widths of the hydroxyl groups, in carbon tetrachloride, of phenol, pentachlorophenol,  $\alpha$ -naphthol and methanol, respectively. As can be seen a fairly good linear relationship is found between  $\Delta\nu$  and  $\nu_{1/2}$  for each system. Furthermore, there is for each of the proton donors studied, a systematic increase in  $\Delta\nu$  and  $\nu_{1/2}$  as the base

Table 3. Maxima and minima values of hydrogen bonding energies and entropy changes together with the slopes for different systems. Solvent, carbon tetrachloride.

System	$\Delta H$ kcal/mole		$\Delta S$ e. u.		Slope <sup>a</sup>	
	from	to	from	to	$\Delta H$ -curve	$\Delta S$ -curve
OPC *-methanol	-3.0	-6.2	-6.7	-13.6	0.91	1.97
OPC-phenol	-4.3	-7.8	-6.2	-10.5	0.55	0.70
OPC- $\alpha$ -naphthol	-5.5	-8.1	-9.6	-11.2	0.40	0.25
OPC-pentachlorophenol	-4.1	-6.4	-7.3	-6.5	0.26	-0.0086

\* OPC means the series of organophosphorus compounds shown in Table 2.

<sup>a</sup> see Figs. 3 and 4.

strength increases, while on the other hand there are deviations from a simple progression for  $\Delta\nu$  and  $\nu_{1/2}$  as the acid strength increases. This is in agreement with the results reported by Huggins and Pimentel<sup>13</sup>, although these authors found a linear relation applicable to a wide variety of systems. In this connection it should be pointed out that Huggins and Pimentel<sup>13</sup> studied binary and the present author ternary solutions. Another dependence which seems to be more empirical is the relationship between  $pK_a$  of the proton donors used and the O—H bond frequency shift, as shown in Fig. 6, where only three of sixteen systems are plotted. A linear relation between  $pK_a$  and  $\Delta\nu$  which seems to be of general validity has also been found by Henry<sup>14</sup> using a variety of alcohols.

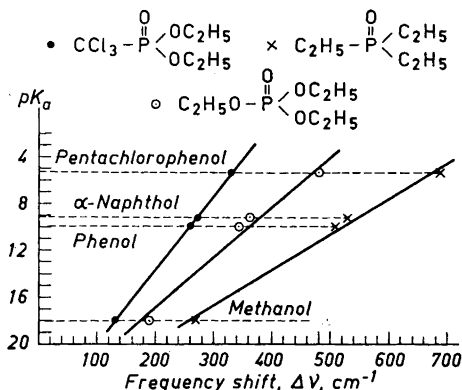


Fig. 6. The relation between  $pK_a$  values of the proton donors and the frequency shift,  $\Delta\nu$ , for some hydrogen bonded systems.

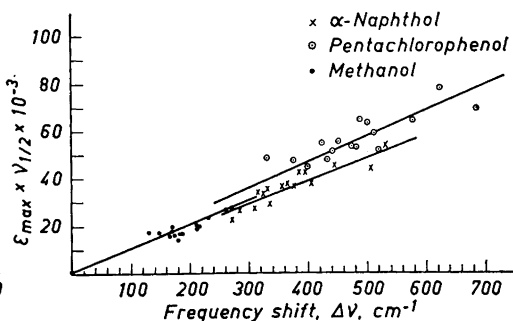


Fig. 7. IR frequency shift,  $\Delta\nu$ , vs. intensity,  $\epsilon_{\max} \times \nu_{1/2}$ , of O—H bond, for hydrogen bonded systems.

We have found as shown in Fig. 7 that the correlation between intensity expressed in terms of  $\nu_{1/2} \times \epsilon_{\max}$  and O—H bond frequency shift is surprisingly close to a linear relation. The straight lines drawn cut the ordinate at 4.00, 1.54 and 0.89 which correspond to the  $\epsilon_{\max} \times \nu_{1/2} \times 10^{-3}$  values of pentachlorophenol, *a*-naphthol and methanol, respectively.  $\epsilon_{\max}$  is the molecular extinction coefficient at the absorption maximum, and is calculated by using the association constant from the smoothed line in Fig. 1, as follows:

$$\epsilon_{\max} = \frac{D}{X \cdot l}$$

$$X = \frac{(KC + 1) - \sqrt{(KC + 1)^2 - 4K^2 ab}}{2K}$$

$X$  = concn., mole/l of hydrogen bonded complex.

$K$  = association constant, l/mole, at 20°C.

$a$  = concn., mole/l of proton donor.

$b$  = concn., mole/l of proton acceptor.

$C$  =  $a + b$ , total concn., mole/l.

$D$  = optical density.

$l$  = cell length, cm.

#### DISCUSSION OF RESULTS

When a polar molecule is placed in a polarisable medium it produces polarisation in the medium. The magnitude of this induced polarisation ( $\mu$ ) is given by the familiar equation,  $\mu = aF$ , where  $F$  is proportional to the dipole moment of the solute molecule and  $a$  is the polarisability of the medium. Now it has been shown<sup>16</sup> that the dipole moment and the shift of the absorption spectrum in near ultraviolet are anomalously large when hydrogen bond is formed. Furthermore, Sutton and collaborators<sup>17,18</sup> have shown that there appears to be an additional dipole moment about 1.0 D when trimethylamine forms complexes with weakly acidic substances in *cyclohexane* solution. From the equation above it can easily be seen that the additional dipole moment is due to an increase of  $F$ , *i.e.*, there is an increase of dipole moment from the reactants to the hydrogen bonded complex. In a previous publication<sup>1</sup> it has been pointed out that this increase of dipole moment will contribute to a negative entropy of reaction due to a greater orientation of the solvent molecules around the complex. The contribution of negative entropy difference between reactants and hydrogen bonded complex was found to be greatest for the strongest hydrogen bond.

The present investigation on ternary systems has established the following facts: Firstly, the absorption bands due to hydrogen bonding are for each system progressively lowered in frequency, broadened in contour, and enhanced in integrated intensity (or  $\epsilon_{\max} \times \nu_{1/2}$ ) as the base strength of the proton acceptor increases. The same is also the case with increasing acid strength, although deviations may occur. Secondly, the ease with which the hydrogen donors studied form hydrogen bonds in carbon tetrachloride solution with the organophosphorus compounds used is in order of decreasing association constant as follows: *a*-naphthol > phenol > pentachlorophenol > methanol.



Table 4. A comparison of thermodynamic data of hydrogen bonds in different solvents.

Compound	$\Delta\nu_{OH}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C	$\Delta H$ kcal	$\Delta F$ kcal	$\Delta S$ e.u.	$\nu_{P=O}$ cm <sup>-1</sup>	$\Delta\nu_{P=O}$ cm <sup>-1</sup>	$\nu_{1/2}$ cm <sup>-1</sup> for O-H bond	Solvent
C <sub>6</sub> H <sub>5</sub> OH...O=P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	416	1372.0	576.6*	-7.9	-4.2	-12.6	1204	27	286	CS <sub>2</sub>
	430	1055.4	356.5	-6.7	-4.1	-8.9	1202	21	290	CCl <sub>4</sub>
C <sub>6</sub> Cl <sub>5</sub> OH...O=P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	620	1071.7	453.1*	-7.8	-4.1	-12.9	1203	43	600	CS <sub>2</sub>
	578	673.6	269.6	-5.7	-3.8	-6.7	1202	42	502	CCl <sub>4</sub>
C <sub>6</sub> H <sub>5</sub> OH...O=C(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> <sup>a</sup>				-5.7		-13.7				naphtha
				-4.8		-11.9				CCl <sub>4</sub>

\* Measured at 40°C.

<sup>a</sup> Data from Ref.<sup>13</sup>

Thirdly, the sequence of the variation of  $\Delta H$  and  $\Delta S$  with  $\Delta\nu$  for each system is, in order of decreasing slope, methanol > phenol > *a*-naphthol > pentachlorophenol (see Figs. 3 and 4). The reason for these anomalies, especially with regard to pentachlorophenol, is not yet clear, but the following reasons may be taken into consideration: solvent interaction on the proton donor, on the acceptor, on the hydrogen bonded complex, and steric factors. As a consequence of the fact that a linear relation between  $K_{ass}$  and  $\Delta\nu$  exists, the conclusion has been drawn that the solvent interaction on the proton acceptors and *vice versa* is constant or nearly constant for the whole series of organophosphorus compounds studied. Steric factors are also excluded, due to the fact that  $K_{ass}$  and  $\Delta H$  for the system pentachlorophenol-triphenylphosphine oxide are increased enormously by replacing carbon tetrachloride with carbon disulphide as can be seen in Table 4. This again supports the view that the anomalies are due to interaction between the solvent molecules and the proton donor and the hydrogen-bonded complex. Nagakura<sup>15</sup> has shown that for the system phenol-ethylacetate, the enthalpy is increased by approximately 1 kcal by replacing the solvent carbon tetrachloride with naphtha. He concludes that the reason for this increase may be that the dielectric constant of carbon tetrachloride is evidently larger than that of naphtha. It has been shown in Table 4, however, that by replacing carbon tetrachloride with carbon disulphide which possesses a larger dielectric constant (2.24<sup>20°C</sup> and 2.63<sup>20°C</sup>, respectively), the reverse is the case. The association constant and enthalpy are increased, particularly with respect to pentachlorophenol. It should also be

noted that the increase in enthalpy is accompanied by a decrease in entropy. As a consequence of this we suggest that the anomalies observed are at least partly due to hydrogen bond formation between the proton donor and the

solvent, such as  $-\text{OH} \dots \text{Cl}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$ . This explanation is also in accordance with the observation that the solvent interaction becomes more pronounced with increasing acidity of the proton donor. In carbon disulphide, however, the hydrogen bond formed,  $-\text{OH} \dots \text{S}=\text{C}=\text{S}$ , is much weaker, hence the solvent interaction is less pronounced. According to this one should expect that the shape of the absorption bands in these two solvents should differ. Actually, however, the half band width as can be seen in Table 4, does not differ very much in the two solvents. A rather small tendency for the bands to broaden is found by replacing carbon tetrachloride with carbon disulphide. In the first overtone region the half band widths of phenol in carbon tetrachloride and in carbon disulphide are approximately 21  $m\mu$  and 36  $m\mu$ , and of pentachlorophenol 25  $m\mu$  and 32  $m\mu$ , respectively.

Our conclusions concerning the effect of solvent interaction on hydrogen bonding are thus that for the system OPC-methanol, the solvent interaction is predominantly due to the solvation effect around the hydrogen bonded complex. As the proton-donating power increases the solvent interaction with the proton donor becomes more pronounced. For the systems OPC-phenol and OPC-*a*-naphthol both the solvation and the solvent-proton donor effects come into play. For the system OPC-pentachlorophenol the solvent-proton donor effect predominates. These views may also explain the systematic change of the slopes for the  $\Delta H$ - and  $\Delta S$ -curves as shown in Figs. 3 and 4. Furthermore, we conclude that the linear relations between frequency shift and  $\Delta H$ ,  $\Delta F$ ,  $\Delta S$ ,  $\nu_{1/2}$  and  $\nu_{1/2} \times \epsilon_{\text{max}}$ , respectively, are only valid when kept to one system.

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