

## Intermolecular Hydrogen Bond Association between Phenol and Organophosphorus Compounds

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The intermolecular hydrogen bond association constants between phenol and eighteen organophosphorus compounds have been determined at 20°C and 50°C.

The  $\Delta F$ ,  $\Delta H$  and  $\Delta S$  values of the equilibrium reactions are found to vary linearly with the hydrogen bond shift in such a way that an increase in enthalpy is counteracted by a decrease in entropy.

The strong influence of the substituents in organophosphorus compounds on the hydrogen bond association constants is discussed in terms of the electronic properties of the phosphorus atom and the substituents.

The connection between hydrogen bond formation and proton transfer reaction is commented upon.

In a previous paper the very strong intermolecular hydrogen bond between phenol and triethylphosphate was reported<sup>1</sup>. It was shown that it is the phosphoryl group which participates in hydrogen bonding. When sufficiently low concentrations of phenol and triethylphosphate are used the only association complex formed is the dimeric intermolecular hydrogen bond complex.

This paper is devoted to the study of the influence of different substituents in the phosphorus compounds on the dimeric hydrogen bond complex. Studies of the self-association of phenol made it clear that the phenol concentration range used in the previous study<sup>1</sup> (0–0.03 M) was not quite low enough to exclude self-association of phenol. To avoid any disturbance of self-association of phenol it was found necessary to reduce the concentration range to 0–0.006 M.

We found it of special interest to evaluate the thermodynamic functions of the hydrogen bond equilibrium reaction. It was therefore necessary to determine the association constants at two different temperatures. An accurate temperature control is difficult to obtain in salt cells, and the ground state

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Table 1. Determination of the association constant between phenol and methoxyethyl-phosphoryl fluoride in carbon tetrachloride. Cell length = 10 cm. Temperature 20°C.

Concentration (moles/l)		Optical density, free OH	Conc. (moles/l) of free phenol	Conc. of complex	$K_{ass}$ (l/mole) calc.	$K_{ass}$ mean value
Phenol						
0.00600	0	0.1643	0.00600	—	—	82.5
0.00480	0.00120	0.1308	0.00447	0.000330	84.8	
0.00420	0.00180	0.1107	0.00377	0.000427	82.4	
0.00360	0.00240	0.0915	0.00312	0.000481	80.4	
0.00300	0.00300	0.0731	0.00249	0.000509	82.1	
0.00240	0.00360	0.0560	0.00191	0.000491	82.6	
0.00180	0.00420	0.0405	0.00138	0.000419	80.2	
0.00120	0.00480	0.0255	0.000869	0.000331	85.2	

stretching vibration band of phenol is therefore less suitable to use as measure of free phenol concentration. We therefore decided to employ the first overtone band of the hydroxyl group of phenol at  $7\ 052\ \text{cm}^{-1}$ . In this spectral region one can use absorption cells of quartz, and a good temperature control is therefore easily obtained.

#### EXPERIMENTAL

*Materials.* The phosphorus esters studied were synthesized from the corresponding chlorides. An equivalent amount of alcohol was added to the organophosphorus chloride in carbon tetrachloride in the presence of pyridine. The pyridine salt was filtered off and the phosphorus ester distilled under reduced pressure. The ester was purified by repeated fractionations. The organophosphorus chlorides were synthesized according to descriptions in the literature. The chlorides of the compounds Nos. 1, 3, 9, 11, 13 and 14 in Table 2 were prepared according to the method of Kinnear and Perren<sup>2</sup>, and the chloride of the compound No. 15 according to the method of Michaelis<sup>3</sup>. Compounds Nos. 4, 6, 8 and 10 were prepared according to the method of Nylien<sup>4</sup>, and the derivatives of phosphine oxide (compounds Nos. 16, 17 and 18) were synthesized according to the description of Kosolapoff<sup>5</sup>.

The fluorine-containing compounds (Nos. 2 and 5) were synthesized from the corresponding chlorides. The chloride (20 g) was added to an excess of sodium fluoride (10 g) in benzene (50 ml). The reaction mixture was rapidly stirred, and the temperature in the mixture was kept at 60°C for one hour. The sodium salts were filtered off and the fluorophosphorus compound distilled under reduced pressure.

The method used for the calculation of the association constants was the same as described previously<sup>1</sup>. The concentration of the free phenol was determined from the first overtone band of the stretching vibration of the phenolic hydroxyl group at  $7\ 052\ \text{cm}^{-1}$ .

The absorption curves were recorded on a Beckman DK 2 double beam spectrophotometer. Cylindrical quartz absorption cells of 10 cm path length were used. The absorption cell which contained the mixture of phenol and the phosphorus compound in carbon tetrachloride was jacketed with a polyethylene tube. The tube was welded to the absorption cell approximately 5 mm from the windows. A constant temperature circulating water bath maintained the polyethylene jacketed cell at  $\pm 0.1^\circ\text{C}$ . The reference cell contained carbon tetrachloride.

The frequency shifts of the ground state stretching vibration band of the associated hydroxyl group of phenol in  $\text{CCl}_4$  were measured with a Perkin Elmer infrared spectrophotometer Model 21. The same instrument was used for the determination of the stretching frequencies of the P=O group of the phosphorus compounds in  $\text{CCl}_4$ . The values of the association constants recorded in Table 2 are the mean values of seven separate determinations of each association constant. In Table 1 are recorded the experimental results from the determination of  $K_{\text{ass}}$  of one of the compounds studied.

The indexes of refraction of the phosphorus compounds were determined with a thermostated Abbe refractometer. The molar refractions (M.R.) recorded in column 5, Table 2, are calculated with the atomic refractivities of phosphorus compounds given by Jones, Davies and Dyke<sup>6</sup>, Vogel<sup>7</sup> and Holmstedt<sup>8</sup>.

## DISCUSSION

Previous findings indicate that there exists a linear relation between the logarithms of the association constants (or  $\Delta F$ ) and the frequency shift of different hydrogen bonded systems<sup>9</sup>. In Fig. 1 are plotted our results of  $\log K$  as function of the frequency shift of the ground state stretching vibration of the hydrogen bonded hydroxyl group of phenol. The straight lines drawn through the calculated  $\log K$  values at  $20^\circ\text{C}$  and  $50^\circ\text{C}$ , respectively, are both within the limits of experimental errors. The slopes of the two lines are different at the two temperatures studied. The free energy,  $\Delta F$ , of the hydrogen bond equilibrium reaction can thus be fairly accurately described as a linear function of the frequency shift. Since the enthalpy is interconnected with the free energy through the thermodynamic relation  $\Delta F = \Delta H - T\Delta S$ , it is a necessary consequence of the linear relation between  $\Delta F$  and  $\Delta\vartheta$  at different temperatures that both the enthalpy and the entropy are proportional to the frequency shift. In Figs. 2 and 3 are shown the variation of  $\Delta F$ ,  $\Delta H$  and  $\Delta S$  with  $\Delta\vartheta$  calculated from the smoothed values of  $\log K$  found from the two straight lines in Fig. 1. From the frequency shift of the hydroxyl group of phenol with the different phosphoryl compounds studied we find that in the observed series of compounds there is an increase of  $\Delta H$  from approximately 5 to 8 kcal but a decrease of  $\Delta S$  from  $-6$  to  $-11$  E.U.

We interpret this observation as due to an increase in the polarity of the hydrogen bond complex as compared with the reactants. Such increase of polarity upon hydrogen bonding has in fact been observed in dipole moment studies of hydrogen bond complexes. Thus Sutton *et al.*<sup>10,11</sup> have shown that in the O—H...N bond in the complex of phenol and trimethylamine, using cyclohexane as solvent, there appears to be an additional moment of 0.8 D. Further evidence may be found in the work of Eda and Ito<sup>12</sup> on the dipole moment of salicyl aldehyde. An increase of polarity from the reactants to the hydrogen bond complex will contribute to a negative entropy of reaction due to a greater orientation of the solvent molecules around the complex.

Table 2. Physical data of organophosphorus compounds (columns 1-6). Data of dimeric hydrogen bonding between organophosphorus compounds and phenol in carbon tetrachloride (columns 7-10).

Compound	1	2	3	4	5	6	7	8	9	10
	Bp°C/mm Hg	$n_D^{20}$	$d_4^{20}$	M.R. calc.	M.R. theory	$\nu_{P-O}$ cm <sup>-1</sup>	$\Delta\nu_{P-O}$ cm <sup>-1</sup>	$\Delta\nu_{O-H}$ cm <sup>-1</sup>	$K_{ass}$ 20°C	$K_{ass}$ 50°C
1. $\text{CCl}_3-\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	106°/3.5	1.4597	1.3568	51.54	50.40	1 280	2	260	73.2	44.8
2. $\text{F}-\text{P}(\text{O})(\text{C}_2\text{H}_5)(\text{OCH}_3)$	58°/20	1.3858	1.1710	25.25	25.73	1 296	—	270	82.5	37.5
3. $\text{CHCl}_2-\text{P}(\text{O})(\text{OC}_2\text{H}_5)(\text{CO}_2\text{H})$	89.5°/0.8	1.4537	1.2978	46.09	45.67	1 276	2	275	133.1	60.7
4. $\text{H}-\text{P}(\text{O})(\text{OCH}_3)_2$	53°/10	1.4016	1.1983	22.34	22.74	1 267	41	300	123.1	53.4
5. $\text{F}-\text{P}(\text{O})(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_5)$	72°/9	1.4134	1.0851	28.45	29.40	1 278	—	305	129.0	61.4
6. $\text{H}-\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	69°/10	1.4076	1.0728	31.73	31.66	1 260	35	310	161.9	76.8
7. $\text{CH}_3\text{O}-\text{P}(\text{O})(\text{OCH}_3)_2$	76°/10	1.3954	1.2147	27.67	27.89	1 279	31	315	182.9	78.9
8. $\text{H}-\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{CH}_3)_2$	97°/12	1.4165	1.0188	40.97	40.94	1 262	38	320	199.7	86.9
9. $\text{CH}_2\text{Cl}-\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	86°/3.5	1.4385	1.1938	41.07	40.94	1 268	1	325	239.0	84.2
10. $\text{H}-\text{P}(\text{O})(\text{OCH}(\text{CH}_3)_2)_2$	79°/13	1.4060	0.9949	40.95	40.94	1 210	34	330	237.3	99.9

Table 2, cont.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P} \\ \diagdown \\ \text{OCH}_2\text{.CH}_2\text{.CH}_2\text{.Cl} \end{array}$	131°/0.6	1.4663	1.2632	54.64	54.87	1 243	28	335	247.0	95.7
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O-P} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$	58°/0.5	1.4053	1.0690	41.79	41.83	1 271	30	345	350.5	121.1
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{-P} \\ \diagdown \\ \text{OCH}_3 \end{array}$	59°/6	1.4170	1.1134	31.19	31.56	1 228	20	355	329.7	126.5
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$	69-70°/8	1.4165	1.0520	36.33	36.20	1 237	23	360	381.0	141.0
$\begin{array}{c} \text{O} \\ \parallel \\ (\text{C}_2\text{H}_5)_2\text{N-P} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$	88°/3.5	1.4226	1.0116	52.62	52.86	1 251	28	395	518.2	211.8
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{-P} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$	215°/0.6 m.p. 157.5°	-	-	-	-	1 200	21	430	1055.4	365.5
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P} \\ \diagdown \\ \text{CH}_3 \end{array}$	m.p. 141°	-	-	-	-	1 177	9	470	1836.0	639.4
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{-P} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$	127°/20	-	-	-	-	1 176	23	510	2522.0	858.0
Pyridine	115°/760	-	-	-	-	-	-	465	64.0	19.3

The stronger the dipole in the phosphoryl group, the stronger will be the deformation of the electrons in the hydrogen bond. We find therefore that the contribution of a negative entropy difference between reactants and complex shall be greatest for the strongest hydrogen bond. Evidence for the above interpretation are also found from other hydrogen bond measurements<sup>13</sup>. Some calculated  $\Delta H$  and  $\Delta S$  values are collected in Table 3. We recognize also here the same tendency of  $\Delta H$  and  $\Delta S$  to counteract each other.

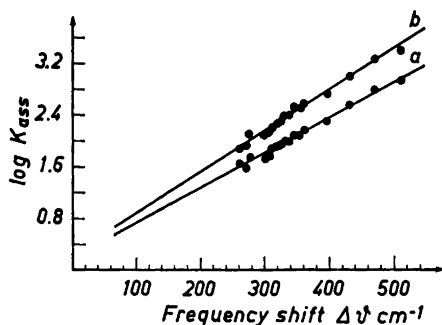


Fig. 1. The relation between the logarithms of the association constants and the frequency shift for the hydrogen bond complexes between phenol and phosphoryl compounds. *a* : 20°C, *b* : 50°C.

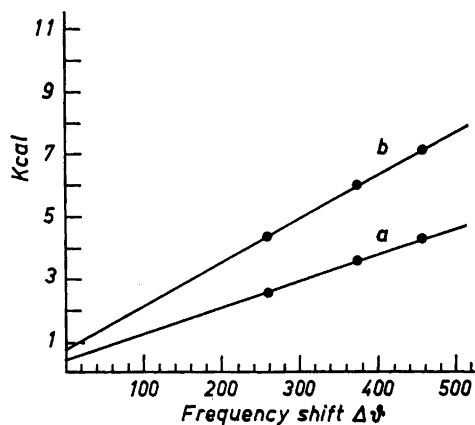


Fig. 2. The relation between  $\Delta F$  at 20°C (*a*), respectively,  $\Delta H$  (*b*) and the frequency shift for the hydrogen bond complexes between phenol and phosphoryl compounds.

It is of interest that the same opposite operating influence on the activation energy and activation entropy is found in reaction kinetic studies of phosphorus compounds <sup>14</sup>.

In Fig. 4 are plotted the observed half bond width  $\nu_{1/2}$  as function of the frequency shift  $\Delta\nu$  of the ground state stretching vibration band of phenol when it is hydrogen bonded with different phosphoryl compounds. The straight line drawn through the observed values cuts the  $\nu_{1/2}$ -axis at 35  $\text{cm}^{-1}$ . This is

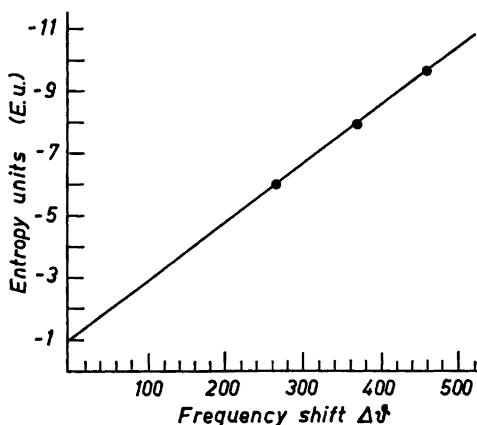


Fig. 3. The relation between  $\Delta S$  and the frequency shift for the hydrogen bond complexes between phenol and phosphoryl compounds.

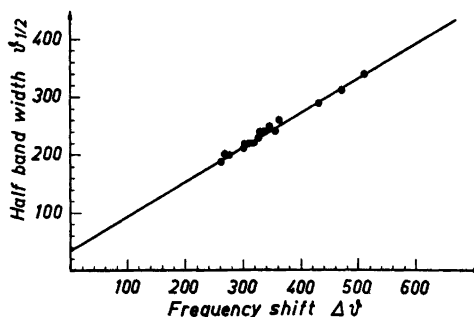


Fig. 4. The relation between the half bond width,  $\nu_{1/2}$  and the frequency shift  $\Delta\nu$  for the hydrogen bond complexes between phenol and phosphoryl compounds.

Table 3.  $\Delta H$  and  $\Delta S$  of the hydrogen bond reaction between phenolic hydroxyl and different compounds <sup>13</sup>

System	Solvent	$\Delta H$ kcal/mole	$\Delta S$ E.U.
Phenol-methylacetate <sup>10</sup>	<i>n</i> -heptane	$-5.3 \pm (0.1)$	$-12.8 \pm (0.2)$
<i>p</i> -Chlorophenol-methylacetate <sup>10</sup>	<i>n</i> -heptane	$-6.7 \pm (0.1)$	$-16.9 \pm 0.4$
<i>m</i> -Chlorophenol-methylacetate <sup>10</sup>	<i>n</i> -heptane	$-6.5 \pm (0.3)$	$-15.2 \pm (1.0)$
<i>o</i> -Chlorophenol-methylacetate <sup>10</sup>	<i>n</i> -heptane	$-1.4 \pm (0.3)$	$-3.5 \pm (1.0)$
Phenol-pyridine *	carbon tetrachloride	$-7.5$	$-17.4$

\* Data from this work.

approximately the half band width of the hydroxyl group of phenol in carbon tetrachloride. It is very interesting that the linear relation between  $\nu_{\frac{1}{2}}$  and  $\Delta\theta$  seems to be independent of the hydrogen bonded species involved. This conclusion is reached by comparing our results with the observations made by Huggins *et al.*<sup>15</sup> They find for quite different hydrogen bonding species not only the same linear relation between  $\nu_{\frac{1}{2}}$  and  $\Delta\theta$ , but also approximately the same slope of the line. The empirical relation seems to be of such general validity that we may suppose that it is connected with some fundamental properties of the hydrogen bond.

To shed further light on this problem we have tried to determine the intensity of the hydrogen bonded hydroxyl groups. Due to the experimental difficulties in the determination of this quantity we have used the product  $\nu_{\frac{1}{2}} \times \epsilon_{\max}$  (where  $\epsilon_{\max}$  is the absorption coefficient of the band at the band maximum) as a relative measure of the intensity. The  $\epsilon_{\max}$  is determined by using so great excess of phosphoryl compound that all of the free phenol has disappeared (0.003 M phenol + 0.2 M phosphoryl compound). The results of the determination of  $\epsilon_{\max}$  is plotted in Fig. 5. We find in this case a nearly linear relation between  $\epsilon_{\max}$  and  $\Delta\theta$  up to frequency shift of approximately 400  $\text{cm}^{-1}$ . The  $\epsilon_{\max}$  of the two last compounds have decreased very markedly. The  $\epsilon_{\max}$  seems therefore to increase to a maximum value in the neighbourhood of 400  $\text{cm}^{-1}$ . The same variation of  $\epsilon_{\max}$  was also observed by Gordy<sup>16</sup> in his study of hydrogen bond between amines and deuterium oxide. If we consider only the phosphorus compounds which cause frequency shifts of less than 400  $\text{cm}^{-1}$  it seems that the intensity as function of the frequency shift can be approximately described by the following equation:

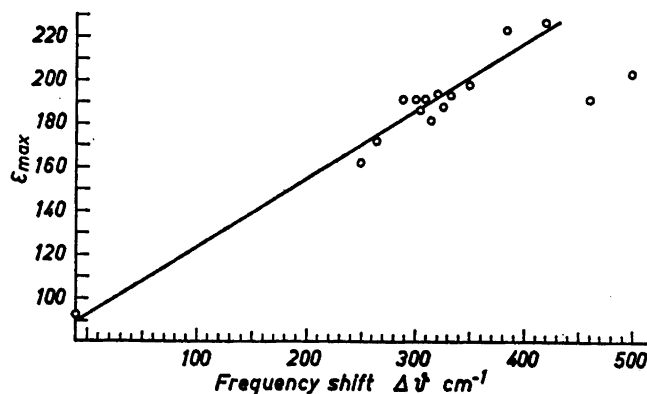


Fig. 5. The relation between  $\epsilon_{\max}$  and  $\Delta\nu$  for the hydrogen bond complexes between phenol and phosphoryl compounds.

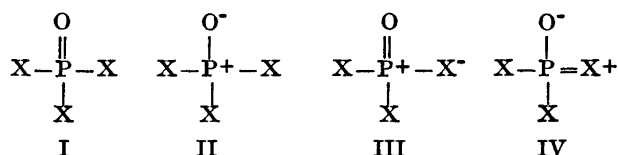
$$\text{Intensity} \approx \nu_{\frac{1}{2}} \times \epsilon_{\max} \approx$$

$(\text{const}_1 + f_1 \Delta\nu) (\text{const}_2 + f_2 \Delta\nu) = a + b \Delta\nu + c(\Delta\nu)^2$  where  $a$ ,  $b$  and  $c$  are constants.

That the variation of the intensity as function of the frequency shift is better described by a parabolic equation than by a linear one, is also clearly observed from the intensity data collected by Huggins and *et al.*<sup>15</sup>

An interesting result of the present study is the observed strong influence of the substituents in the phosphorus compounds on the equilibrium constants of the hydrogen bonded complexes. This must be connected with an easy deformation of the electronic atmosphere around the phosphorus atom. The influence of the substituents upon the polarity of the P=O bond is shown in Table 2, column 6, where the frequencies of the stretching vibration band of the phosphoryl group in carbon tetrachloride are recorded. The general tendency is that electron withdrawing substituents on the phosphorus atom strongly reduce the polarity of the P=O bond. The displacement of the stretching vibration frequency of the P=O group upon hydrogen bonding will be a measure of the polarisability of the phosphorus compound involved. The observed frequency shifts are seen in Table 2, column 7. We recognize that the most strongly polarisable substituents, amino and alkoxy groups, give rise to the greatest frequency shifts of the P=O bond. The chlorine substituted phosphorus compounds are seen to stabilize the electronic constitution of the compounds to such a degree that the formation of the hydrogen bond complex occurs almost without any electronic deformation of the phosphorus compounds. The present findings provide further evidence for the view that the phosphorus atom has a marked tendency to expand its valence shell by utilization of its  $3d$  orbitals in the formation of a double bond<sup>17,18</sup>. It seems reasonable that the main contributing structures of the resonance hybrid of phosphorus compounds are as follows<sup>18</sup>:





The frequencies of the stretching vibrations of the different phosphorus compounds in carbon tetrachloride summarized in Table 2 indicate that both the inductive and mesomeric effects of the substituents contribute to the observed polarity of the phosphoryl bond. We suppose that the structures I and II will be the main contributing structures of trialkylphosphine oxides. When strongly negative substituents as fluorine and chlorine are present in the molecule, structure III may be expected to contribute to a larger degree due to the strong  $-I$  effect. The mesomeric effect ( $+M$ ) of alkoxy and amino substituents should be characterized by an increasing contribution from structure IV. The observed strong frequency shifts of the phosphoryl group in the alkoxy and amino substituted phosphorus compounds upon hydrogen bonding with phenol points to the conclusion that also the electromeric effect of these substituents are considerable. This effect requires a phosphorus  $\pi$ -orbital capable of interacting with the unshared pair of electrons on the oxygen and nitrogen atoms. The above conclusions are in accordance with the interpretation of Larsson summarized in a recent review<sup>18</sup>.

In the previous paper<sup>1</sup> it was shown that the carbonyl group of N-diethylacetamide participated in the hydrogen bonding with phenol. When sufficiently strong acid was used (HCl) a proton transfer reaction occurred, but in this case the proton was attached to the nitrogen. It was mentioned that there seems to exist a principal difference between groups which are involved in hydrogen bonding and proton transfer reaction. We have therefore in this paper included the results of the measurements of the association constants of the complex between phenol and pyridine at 20° and 50°C (Table 2). From Table 3 we observe that the calculated  $\Delta H$  value of 7.5 kcal of the pyridine-phenol reaction is approximately identical with the  $\Delta H$  value expected from the frequency shift of 465  $\text{cm}^{-1}$  (Fig. 5 b). The reason for the low association constant of the phenol-pyridine complex must therefore be found in an unfavorable entropy of reaction.

The calculated value  $-17.4$  E.U. is in fact approximately 7 E.U. lower than the entropy of the phosphoryl complex with the same  $\Delta H$ . The more unfavorable entropy of the formation of the pyridine-phenol complex as compared with the phosphate-phenol complex may depend on different steric properties of the complexes. Another reasonable explanation may be found in a difference of polarity of the two types of hydrogen bonds.

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