Intermolecular Hydrogen Bond Association between Phenol and Compounds which Contain the Phosphoryl and Carbonyl Groups

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The intermolecular hydrogen bond association between phenol and triethylphosphate respectively N-diethylacetamide gives 1:1 association complexes, where the P=O respectively the C=O group participates in the hydrogen bond. The association constants and molar extinction coefficients of the hydrogen bond complexes have been determined. The salt-like addition compounds between tertiary amides and strong acids (HCl) give proton transfer bond where the hydrogen is attached to the amide nitrogen. By using triethylphosphate it has been possible to locate 6 bands in the infrared spectrum of phenol which are due to vibrations of the free hydroxyl group. Two of the bands are interpreted as bands due to bending vibrations and four as bands due to combination between stretching and bending of the hydroxyl group. The vibrations of the hydroxyl group in alcohols are also discussed.

It has long been recognized that hydroxylic compounds show a strong tendency for hydrogen bond association. In the infrared spectral region the ground state stretching vibration of the free O−H bond will be displaced towards lower frequencies upon association [1-6]. Alcohols and phenols give rise to both dimeric and polymeric association [7-8]. The degree of association is very sensitive to changes in concentration and temperature [8].

It is known that the hydrogen bond association between compounds which contain the hydroxyl and carbonyl groups gives rise to displacement of the stretching frequencies of both the OH and C=O band. This is explained by assuming hydrogen bond between the two groups: ROH...O=C. Examples are dimeric carboxylic acids [9-13] and intramolecular association in hydroxy keto compounds [14-17], but intermolecular associations between unlike species are also known [8,18-20,24].

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THEORETICAL

The strong hydrogen bond association between phenol and N-dialkyl-acetamide respectively orthophosphate esters makes it possible to study the bond formation with sufficiently low concentration of phenol to avoid dimeric and polymeric phenol association. The hydrogen bond must therefore be due to association between unlike species. If we assume the molar ratio of phenol and substrate in the complex to be 1:1 we have for the equilibrium condition:

$$ROH + S \rightleftarrows RO-H \cdots S$$
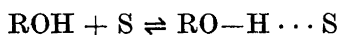
When the total concentration of phenol and substrate is constant $= c$, and α and $1 - \alpha$ are the mole fractions of phenol and substrate, respectively, and X = concentration of complex we have:

$$K = \frac{X}{[a \cdot c - x][(1 - a)c - X]} \tag{1}$$

where K = association constant.

The solution of the equation gives:

$$X = \frac{(K \cdot c + 1) \pm \sqrt{(K \cdot c + 1)^2 - 4K^2 a \cdot c^2 (1-\alpha)}}{2K} \tag{2}$$

where the sign $-$ is the only valid.

Upon derivation we find:

$$X_{\text{max}} = \frac{(Kc - 1) - \sqrt{2Kc + 1}}{2K} \tag{3}$$

when $\alpha = \frac{1}{2}$.

The concentration of phenol or substrate is $\dfrac{c}{2} - X_{\text{max}}$ when $\alpha = \frac{1}{2}$. The complex is therefore 1:1 if X has maximum at $\alpha = \frac{1}{2}$. A plot of the concentration of X as function of α is symmetrical on both sides of $\alpha = \frac{1}{2}$.

The concentration of phenol and substrates (N-diethylacetamide and tri-ethylphosphate) can be determined from the optical density of the free O-H stretching band, and from the C=O or P=O bands of the substrates when the molar extinction coefficients are known and as a first approximation we assume the Lambert-Beer's law to be valid. The molar extinction of the complex, ε_{max}, can be calculated from two different sets of values of phenol and substrate.

If we use equimolecular amounts of phenol and substrate we have:

$$K = \frac{X_1}{(A_1 - X_1)^2} = \frac{X_2}{(A_2 - X_2)^2} \tag{4}$$

where: X_1 and X_2 = concentration of complex
A_1 and A_2 = concentration of phenol and substrate.

If we assume Lambert-Beer's law to be valid we get:

$$K = \frac{f \cdot E_1}{(A_1 - f \cdot E_1)^2} = \frac{f \cdot E_2}{(A_2 - f \cdot E_2)^2} \tag{5}$$

$$\text{where } f = \frac{1}{\varepsilon_{\max} \cdot l} \text{ and } E = \log \frac{I_0}{I}.$$

The equation gives for f:

$$f = \frac{1}{\varepsilon_{\max} \cdot l} = \frac{(A_2 - A_1) \pm \sqrt{A_2^2 \dfrac{E_1}{E_2} + A_1^2 \dfrac{E_2}{E_1} - 2A_2 \cdot A_1}}{E_2 - E_1} \tag{6}$$

where the sign $-$ is the only valid when $A_2 - A_1 > 0$.

Table 1. Calculation of the association constant between phenol and triethylphosphate from the hydroxyl stretching vibration band.

Conc. of phenol (moles/l)	Conc. of triethyl-phosphate	Optical density, free OH	Optical density, ass. OH	Conc. of complex	K	Temperature 30°C $\varepsilon_{\max}$ of ass. OH bond calculated	
						From free OH-bond	From eqn. (6)
0.03	0	0.160	—	—			
0.02625	0.00375	0.122	0.057	0.00340	(431)	167	164
0.0225	0.00775	0.083	0.115	0.00694	550	166	
0.01875	0.01125	0.050	0.153	0.00937	532	163	
0.0150	0.0150	0.025	0.170	0.01031	468	165	
0.01125	0.01875	—	0.153	0.00933	516*	164*	
0.00775	0.0225	—	0.115	0.00700	591*	164*	
0.00375	0.02625	—	0.057	0.00347	544*	164*	
0	0.03	—	—	—			

* Calculated from the associated OH-band.

Table 2. Calculation of the association constant between phenol and N-diethylacetamide from the hydroxyl stretching vibration band.

Temperature 30°C

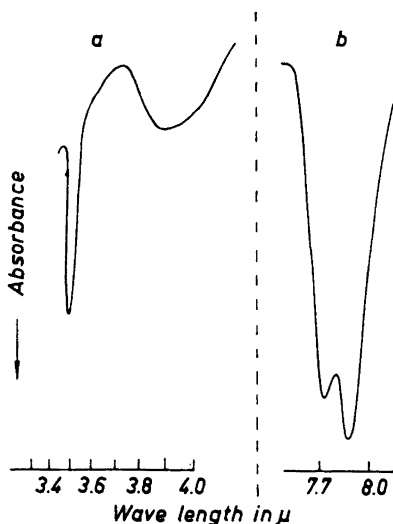| Conc. of phenol (moles/l)	Conc. of N-diethyl-acetamide	Optical density, free OH	Optical density, ass. OH	Conc. of complex	K	$\varepsilon_{\max}$ ass. OH
0.03	0	0.160	—	—	—	
0.02625	0.00375	0.123	0.040	0.00319	(246)	122
0.0225	0.00775	0.090	0.075	0.00562	156	134
0.01875	0.01125	0.060	0.095	0.00750	178	127
0.0150	0.0150	0.035	0.102	0.00844	196	121
0.01125	0.01875	0.020	0.098	0.00750	178	131
0.00775	0.0225	—	0.080	—	—	—
0.00375	0.02625	—	0.040	—	—	—
0	0.03	—	—	—	—	—

Fig. 1. a). Free and associated stretching bands of HCl (0.03 M) in CCl$_4$ in the presence of di*iso*propylfluorophosphate (0.03 M). *b)* Free and associated stretching bands of the P = O group of di*iso*propylfluorophosphate (0.03 M) in CCl$_4$ in the presence of HCl (0.03 M).

RESULTS OF THE MEASUREMENTS

The results of the measurements are collected in Tables 1 and 2. From the approximate constancy of the association constant at different concentrations of phenol and substrate we conclude that the complexes between phenol and diethylacetamide and between phenol and triethylphosphate are 1:1. The same results is also reached by comparing the optical densities of the associated hydroxyl stretching vibration band at different concentrations of phenol and substrate recorded in column 4, Tables 1 and 2. The expected maximum in optical density at $\alpha = \frac{1}{2}$ and the symmetrical distribution of the complex concentration on both sides of $\alpha = \frac{1}{2}$ give a convincing picture of the 1:1 association. In column 7, Tables 1 and 2, are recorded the calculated molar extinction coefficients of the two different complexes. The complex with the highest association constant shows the greatest molar extinction coefficient. A reasonable interpretation of this behaviour is that the complex with the highest association constant gives rise to the strongest change in dipole moment of the hydroxyl group during the vibration and in this way contributes to a greater intensity of absorption.

The stretching vibration band of the free and associated phosphoryl- and carbonyl group at 1 271 cm^{-1} and 1 655 cm^{-1} vary with the mole fraction of phenol in the same manner as the free and associated hydroxyl group. The displacements of the C=O and P=O bands upon hydrogen bonding are approximately 18 cm^{-1} and 30 cm^{-1}, respectively. For quantitative study of the hydrogen bond formation the use of the C=O and P=O bands are less suitable due to the small displacements of the associated bands.
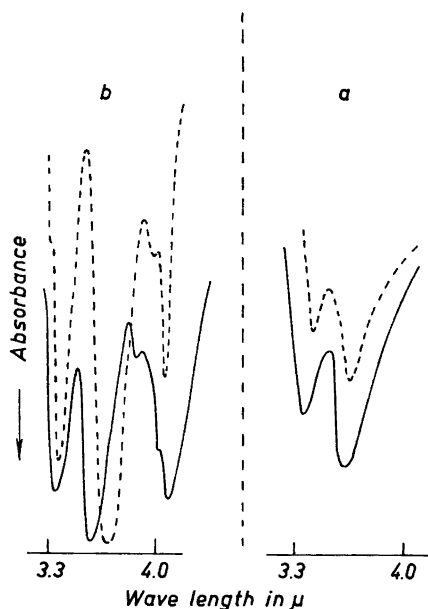
Fig. 2. a). Solid curve: Spectrum of N-dimethylacetamide hydrochloride (0.1 M) in CHCl₃; Dotted curve: Spectrum of trimethylamine hydrochloride (0.1 M) in CHCl₃. *b*) Solid curve: Spectrum of N-dimethylacetamide (0.5 %) in solid phase (KBr-briquet); Dotted curve: Spectrum of trimethylamine hydrochloride (0.5 %) in solid phase (KBr-briquet).

THE BEHAVIOUR OF ESTERS OF PHOSPHORIC ACID AND TERTIARY AMIDES UPON ASSOCIATION WITH HYDROCHLORIC ACID

Hydrochloric acid gives with esters of phosphoric acid in carbon tetrachloride the normal hydrogen bond association product where the phosphoryl oxygen participates in the hydrogen bond. Fig. 1 shows the free and associated stretching frequencies of the HCl-bond at 2 825 cm⁻¹ and 2 440 cm⁻¹. The displacement is practically identical with the displacement of the H—Cl bond which is observed when hydrochloric acid is associated with ethyl ether [22]. The free and the associated P=O stretching frequencies are observed at 1 295 cm⁻¹ and 1 268 cm⁻¹ (Fig. 1). With tertiary amides the picture is quite different. The salt-like compounds which are formed between hydrochloric acid and tertiary amides were studied both in solid phase (KBr-briquet) and in chloroform solution. The solution showed no free or associated H—Cl stretching vibration and the frequencies of the vibration of the C=O bond were slightly higher than for the vibration of the C=O group in the pure amide solution. The spectrum between 2 300 cm⁻¹ and 3 000 cm⁻¹ showed the typical character of quaternary ammonium compounds with 3 carbon and 1 hydrogen atom attached to the nitrogen. In Fig. 2 are compared the spectra of trimethylamine hydrochloride with N-dimethyl acetamide hydrochloride in chloroform solution (a) and in solid phase (b). The very similar form of these spectra gives strong support to the quaternary nitrogen structure of the addition compounds between tertiary amides and strong acids. The above observations give evidence that there exist principal differences
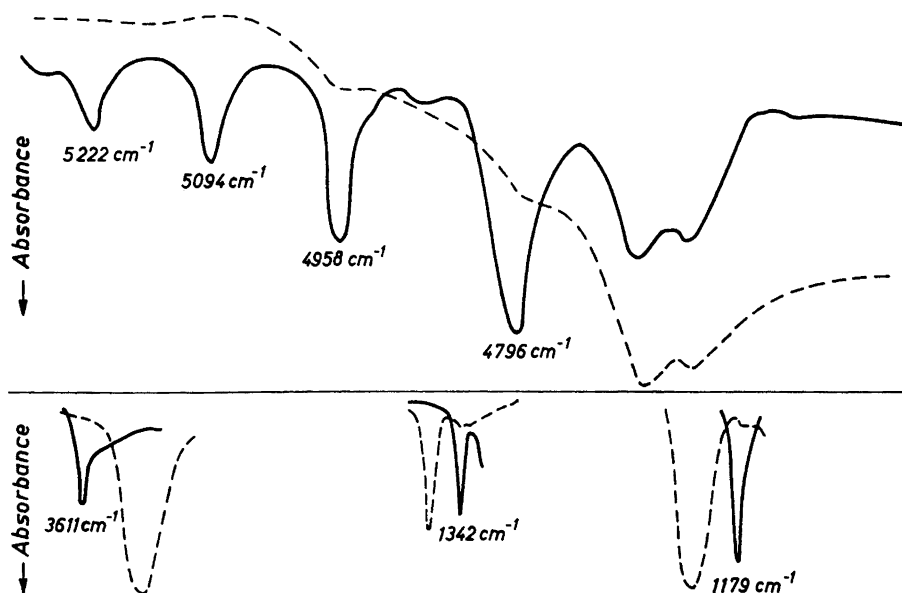
Fig. 3. Solid lines: Absorption bands of the free hydroxyl group of phenol (0.2 M) in CCl₄; Dotted lines: The disappearance of the free hydroxyl group of phenol (0.02 M) in CCl₄ in the presence of triethylphosphate (0.02 M).

between the formation of hydrogen bonds and proton transfer bonds. The explanation may be that the semi-polar oxygen is favoured in hydrogen bonding due to a great polarity of the bond but the nitrogen is favoured in proton transfer due to a greater tendency to share an electron pair with hydrogen.

THE APPLICATION OF TRIETHYLPHOSPHATE FOR THE IDENTIFICATION OF BANDS WHICH ARE DUE TO VIBRATIONS OF THE HYDROXYL GROUP

The very strong hydrogen bond between phenol and triethylphosphate makes the latter compound suitable for identification of the different vibrations of the hydroxyl group. When the hydroxyl group participates in hydrogen bond formation the bands due to the free hydroxyl disappear. The association constant between phenol and triethylphosphate in CCl₄ was found to be approximately 500. By using equimolecular amounts of phenol and triethylphosphate, concentrations of 0.2 M will reduce the concentration of free phenol to about 10 % of its original value. By using a double beam infrared instrument it is easy to compensate for the added triethylphosphate. In this way the disappearance of bands due to vibration of the free hydroxyl group is easily detected. Six hydroxyl bands were found at the following wave numbers: 1 178 cm⁻¹, 1 342 cm⁻¹, 4 796 cm⁻¹, 4 958 cm⁻¹, 5 094 cm⁻¹ and 5 222 cm⁻¹. In Fig. 3 are recorded the spectra of the vibrations of the hydroxyl group in the above mentioned regions before and after addition of triethylphosphate.

Table 3. Optical densities of hydroxyl vibration bands of phenol in carbon tetrachloride (Measured at bond maximum).

Conc. of phenol (moles/l)	Optical density (cell length 10 mm)				Optical density (cell length 1 mm)					
	free OH 5 222 cm^{-1}	free OH 5 094 cm^{-1}	free OH 4 958 cm^{-1}	free OH 4 796 cm^{-1}	free OH 3 611 cm^{-1}	ass. OH 3 300 cm^{-1}	free OH 1 342 cm^{-1}	ass. OH 1 358 cm^{-1}	free OH 1 178 cm^{-1}	ass. OH 1 215 cm^{-1}
0.1	0.022	0.032	0.062	0.090	0.03	0.03	0.155	0.02	0.46	0.05
0.2	0.040	0.061	0.108	0.168	0.04	0.08	0.275	0.07	0.81	0.19
0.3	—	—	—	—	0.06	0.17	0.385	0.135	1.15	0.39
0.4	0.060	0.088	0.160	0.256	0.09	0.28	0.455	0.205	1.30	0.62
0.5	—	—	—	—	0.011	0.39	0.535	0.280	1.60	0.89
0.6	0.080	0.120	0.220	0.360	0.014	0.51	0.620	0.365	1.80	1.07

To prove that the six hydroxyl bands which were located with triethyl-phosphate are free hydroxyl bands their optical densities were studied as function of phenol concentration. The results are recorded in Table 3. Due to the increasing association of phenol the optical densities of the free hydroxyl bands shall increase less than proportional to the concentration of phenol. It is seen that the absorbance of the six hydroxyl bands vary with the concentrations of phenol in exactly the same way. The observed variations are just the same as the variation of the free stretching vibration band at 3 611 cm^{-1}.

It is observed that upon increasing the concentration of phenol two new bands appear displaced to higher frequencies of the free hydroxyl bands. These two association bands are located at 1 358 cm^{-1} and 1 215 cm^{-1}. The optical densities of the bands increase more rapidly than proportional to the concentration of phenol. From Table 3 we observe that the increase in optical densities are exactly parallel to the increase of absorbance of the association band at 3 300 cm^{-1} which is due to the hydroxyl stretching vibration of associated phenol.

INTERPRETATION OF THE LOCATED HYDROXYL BONDS

1. Bending vibrations of the hydroxyl group

There has for a long time been disagreement about the location of the bending vibrations of the hydroxyl group. Of the two bending vibrations, δ-OH (in-plane bending) and γ-OH (out-of-plane bending) one has expected to find the δ-OH in the region 1 300—1 200 cm^{-1} and the γ-OH in the region 1 000—600 cm^{-1} [22]. The present findings suggest that the δ-OH and γ-OH vibration bands of phenol are the absorption bands which are found at 1 342 cm^{-1} and 1 178 cm^{-1}.

The arguments for this interpretation are:

a) The bending vibrations of the hydroxyl group are perpendicular to the hydrogen bond. The hydrogen bond should therefore contribute to a stronger restoring force of the bending vibrations. The frequency of the hydroxyl bending vibrations should therefore be expected to increase upon formation of the hydrogen bond. This is also the situation of the two bands which are located at 1 342 cm^{-1} and 1 178 cm^{-1}. Their association bands are found at 1 358 cm^{-1} and 1 215 cm^{-1}, respectively.

b) The hydrogen bond should be expected to decrease the amplitude of the bending vibration. The change in dipole moment during vibration will therefore be smaller, which is tantamount to a lower intensity of the bending vibration of the associated hydroxyl bond. If we compare the absorbance of the free and the associated vibration bands with the free and the associated stretching bands at corresponding phenol concentrations in Table 3 it is seen that the ratios between the absorbances of the free and the associated vibration bands are opposite to the ratio observed for the stretching band. If the breadth of the bands are also considered which must be done when intensities are to be compared, the inverse relationship is still greater than when only the absorbances are compared.

2. Combination between stretching and bending vibrations

The most reasonable interpretation of the 4 hydroxyl bands located in near infrared at 5 222 cm^{-1}, 5 094 cm^{-1}, 4 958 cm^{-1} and 4 796 cm^{-1} seems to be that the two bands of highest frequencies are bands due to combination between the free stretching vibration and the in-plane bending vibration and the two bands at the lowest frequencies are combination bands between the free stretching vibration and the free out-of-plane bending vibration.

The arguments for this view are:

a) From the experiment with phenol and triethylphosphate it was found that the four bands were all due to free hydroxyl groups. The same result was also found in the study of the concentration dependence of the bands.

b) If the two bending vibrations combine with the same stretching vibration to give combination vibrations it is reasonable to expect that the ratio between the absorbance of the two bending vibrations should be identical with the ratio between the corresponding combination vibrations.

Table 4. Bands due to bending of the hydroxyl group in alcohols.

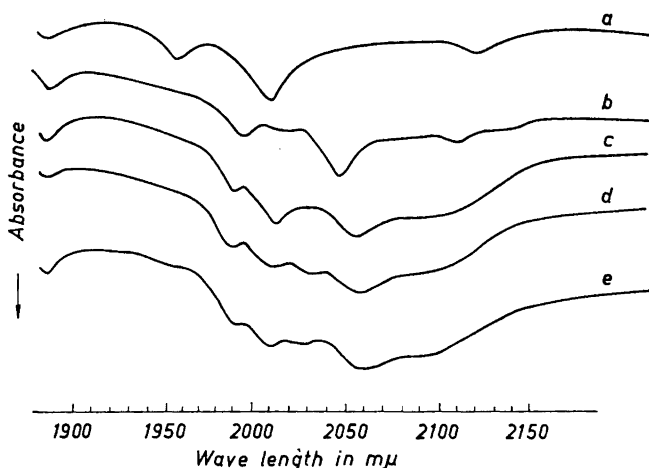| Compounds	Band maxima (cm^{-1})
Methyl alcohol	1 328
Ethyl alcohol	1 236
Propyl alcohol	1 210
Butyl alcohol	1 202
Amyl alcohol	1 200

Fig. 4. Combination bands of alcohols in CCl₄ (0.4 M). *a*) Methyl alcohol, *b*) ethyl alcohol, *c*) propyl alcohol, *d*) butyl alcohol, *e*) amyl alcohol.

From Table 3 we calculate that the average ratio between the absorbance of the two bending vibrations at the six different phenol concentrations is 2.9. The average ratio between the absorbances of the bands at $5\ 222\ cm^{-1}$ and $4\ 958\ cm^{-1}$ is 2.8, and the average ratio between the absorbances of the bands at $5\ 094\ cm^{-1}$ and $4\ 796\ cm^{-1}$ is 2.9. Why the combined vibration of bending and stretching vibrations should give rise to splitting of the combination bands is not known. It seems worthwhile to mention that similar splitting of the overtone bands of the C—H group is also observed [23].

THE BENDING AND COMBINATION BANDS OF ALCOHOLS]

The previous described technique of hydroxyl bands localisation has been used in an attempt to locate the bending and the combination bands of alcoholic hydroxyl groups. In this case we have been able to locate with certainty only one bending vibration band in the region $1\ 400-1\ 100\ cm^{-1}$. The frequencies of the bending vibrations of different alcohols are recorded in Table 4. The observed frequencies correspond with the frequencies of δ-OH vibrations put forward of Stuart and Sutherland [24]. The interesting observation which is also mentioned by Stuart and Sutherland [24] is that the frequency of the bending band of methyl alcohol is abnormally high. This anomaly of the methyl alcohol gives an argument that the combination vibration of the hydroxyl groups of alcohols observed in near infrared are composed of stretching and bending vibrations. The combination vibrations of the hydroxyl in methyl alcohol must in this case show the same strong displacement towards higher frequencies when it is compared with the other alcohols. This is exactly the case as shown in Fig. 4.

Another observation is that in methyl alcohol there are only two free hydroxyl bands in near infrared. In ethyl- and propyl alcohol we can recognize three and in the higher members of alcohols four free hydroxyl bands (Fig. 4.)

The intensities of the combination bands of alcohols are much lower than the intensities of the corresponding phenol bands. The same relation should therefore be expected to hold for the bending vibrations, and this may explain why the bending vibration bands of alcohols are more difficult to locate.

EXPERIMENTAL

The infrared spectra of the compounds studied were recorded on a Perkin-Elmer Spectrometer Model 21. The measurements were performed in carbon tetrachloride in sodium chloride cells of 1 mm thickness compensated against carbon tetrachloride. The temperature was maintained constant within a range of $\pm$ 1°C during the measurements.

The spectra in near infrared were recorded on a Beckman instrument, Model DK 2. The measurements were performed in carbon tetrachloride solution in quartz cells of 10 mm thickness compensated against carbon tetrachloride.

The compounds studied were synthesized according to descriptions in the literature [25,26].

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