

Hexamethylphosphoramide as Proton Acceptor. Part 2. A Near-infrared Study of Its Heteroassociation with Substituted Phenols

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Values of the formation constants K_{11} , frequency shifts $\Delta\nu_{\text{OH}}$ and thermodynamic parameters ΔH , ΔG and ΔS have been determined by near-infrared spectrometry for the hydrogen-bonded acid-base complexes formed between eleven substituted phenols and hexamethylphosphoramide in carbon tetrachloride solution.

The aqueous pK_a values of the substituted phenols vary from 5.3 to 11.7. The values of the spectrometric quantities K_{11} , ΔH and $\Delta\nu_{\text{OH}}$ vary linearly with the acidity of the phenols except where pentahalophenols are the proton donors. In these phenols the OH group seems to be intramolecularly hydrogen bonded to a halogen atom. The + M effect is the obvious reason for the lower values of the spectrometric quantities for the *p*-fluorophenol-hexamethylphosphoramide complex than for the other *p*-halophenol-hexamethylphosphoramide complexes. K_{11} increases more rapidly with the acidity of the proton donor when substituted phenols are the proton donors than when alcohols are the proton donors. The Badger-Bauer relation holds, except for pentahalophenol-hexamethylphosphoramide complexes.

In most cases there are one or more additional hydrogen bonded OH absorption bands, obviously due to the interaction of ν_{OH} (bonded) vibrations with the overtones or combinations of lower frequency vibrations of the proton donor.

In the first part of this series the hydrogen bonding of hexamethylphosphoramide, $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ (HMPA), to ordinary and halogenated alcohols was studied.¹ HMPA was found to be a strong proton acceptor. This property is also evident from Taft's pK_{HB} value.² The base parameter, pK_{HB} , is a measure of the relative strength of the proton acceptor in a hydrogen-bonded complex, and of 117 bases studied, only a few phosphine oxides

have as great pK_{HB} values as HMPA has. Several submaxima were found in the absorption band of the alcohol-HMPA complex when the aqueous pK_a of the alcohol was less than 12.¹

For comparison and also to gain information about the substituent effect, the hydrogen bonding between HMPA and substituted phenols has been studied in the present work. Hexamethylphosphoramide- d_{18} (octadecadeuteriohexamethylphosphoramide, HMPA- d_{18} , $[(\text{CD}_3)_2\text{N}]_3\text{PO}$) has been used in studying the ν_{OH} bands of the complexes in the ν_{CH} region.

EXPERIMENTAL

Chemicals. Hexamethylphosphoramide, hexamethylphosphoramide- d_{18} and carbon tetrachloride were purified as described previously.¹ 2,6-Dimethylphenol (*zur Synthese*, E. Merck AG), 2,6-di-isopropylphenol and 2,6-di-*tert*-butylphenol (Aldrich Chemical Co.) were distilled under vacuum, b.p. 86°C/15 mmHg, 126°C/19 mmHg and 100–101°C/3 mmHg, respectively. *p*-Fluorophenol and pentafluorophenol (*purum*, Fluka AG) were sublimed at atmospheric pressure and dried in a desiccator over P_2O_5 . Pentabromophenol (EGA-Chemie KG) was recrystallized from ethanol and dried in a desiccator over P_2O_5 . *p*-Cresol, *p*-chlorophenol, *p*-bromophenol, pentachlorophenol (*puriss.*, Fluka AG) and phenol and α -naphthol (*pro analysi*, E. Merck AG) were used as received.

Measurements. The near-infrared spectra were recorded on a Beckman DK-2A spectrophotometer. All systems were recorded using the temperatures 0, 15, 25, 40 and 50°C. The concentrations used were about 0.03 M (2,6-di-*tert*-butylphenol) and from 0.0008 to 0.006 M (other phenols), the concentration of hexamethylphosphoramide varying from 0.0005 to 0.3 M depending on the system. The details

Table 1. Spectral data for 1:1 hydrogen-bonded complexes between phenols and HMPA in carbon tetrachloride at 25°C and the pK_a values ⁴⁻⁹ of phenols.

Phenol ^a	K_{11} M ⁻¹	$-\Delta H^\circ$ kJ mol ⁻¹	$-\Delta G^\circ$ kJ mol ⁻¹	$-\Delta S^\circ$ J K ⁻¹ mol ⁻¹	$\Delta\nu_{OH}$ cm ⁻¹	pK_a
1 Phenol	1820	29.9	18.6	37.7	> 464 ^b	9.95
2 <i>p</i> -Cresol	1440	29.9	18.0	40.0	> 460 ^b	10.26
3 α -Naphthol	3200	32.8	20.0	43.1	> 486 ^b	9.34
4 <i>p</i> -BrP	8220	32.9	22.3	35.5	> 496 ^b	9.34
5 <i>p</i> -ClP	8300	33.5	22.3	35.2	> 496 ^b	9.38
6 <i>p</i> -FP	4760	32.3	20.9	38.1	> 478 ^b	9.91
7 PBP	421	24.7	14.9	32.7	> 612 ^b	
8 PCP	1530	26.5	18.2	27.9	> 631 ^b	5.26
9 PFP	26800	35.0	25.2	32.6	> 737 ^b	5.52
10 DMP	126	20.1	12.0	27.2	430	10.63
11 DIPP	88.8	20.3	11.1	30.8	416	11.08
12 DTBP	5.50	12.8	4.23	28.8	444	11.70

^a *p*-BrP = *p*-bromophenol; *p*-ClP = *p*-chlorophenol; *p*-FP = *p*-fluorophenol; PBP = pentabromophenol; PCP = pentachlorophenol; PFP = pentafluorophenol; DMP = 2,6-dimethylphenol; DIPP = 2,6-di-isopropylphenol; DTBP = 2,6-di-*tert*-butylphenol, ^b complex band with several maxima, measured from the first maximum.

of the measuring procedure have been reported earlier.^{3,4}

The K_{11} values were calculated using eqn. (1).³

$$K_{11} = \frac{1 - A/A^\circ}{A/A^\circ [c_B^\circ - c_A^\circ (1 - A/A^\circ)]} \quad (1)$$

c_A° and c_B° are the initial concentrations of the acid and base, respectively, and A° and A are the absorbances at the frequency of the stretching vibration of the free hydroxyl group before and after the complex formation, respectively.

The ΔH values were obtained in the usual way from plots of $\log K_{11}$ against $1/T$ using the method of least squares. The quantities ΔG and ΔS were obtained from eqns. (2) and (3).

$$\Delta G = -RT \ln K_{11} \quad (2)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (3)$$

The IR spectra were recorded with Perkin Elmer 621 and Perkin Elmer 557 spectrometers under the same conditions as before.¹

The $\Delta\nu_{OH}$ values are estimated to be accurate within ± 5 cm⁻¹, ΔH and ΔG values within ± 2 kJ mol⁻¹, ΔS values within ± 2 J K⁻¹ mol⁻¹ and K_{11} values within 10%.

The non-SI units used were 1 M = 1 mol dm⁻³; 1 mmHg = 133.322 Pa.

RESULTS AND DISCUSSION

The experimental data obtained are presented in Table 1, which also contains the literature values of the aqueous pK_a 's of substituted

phenols. The symbols used for the phenols are explained in a footnote to Table 1.

Variation of the spectrometric quantities with the acidity of phenols. The dependence of $\log K_{11}$ on the acidity is linear except for the pentahalophenol-HMPA complexes, whose K_{11} values are much smaller than expected from their pK_a values (ca. 5) (Fig. 1). K_{11} increases more rapidly with the acidity of the proton donor in substituted phenol-HMPA complexes than in alcohol-HMPA complexes.¹

There are several submaxima in the hydrogen bonded ν_{OH} bands of phenols except 2,6-dialkylphenols. The frequency shifts $\Delta\nu_{OH}$ tabulated in Table 1 are measured from the maximum band nearest the free ν_{OH} band.

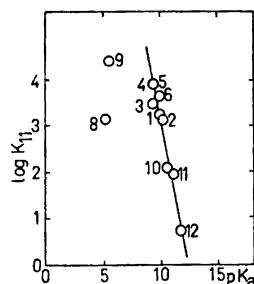


Fig. 1. The plot of $\log K_{11}$ against the pK_a of the phenol for the phenol-HMPA complexes at 25°C.

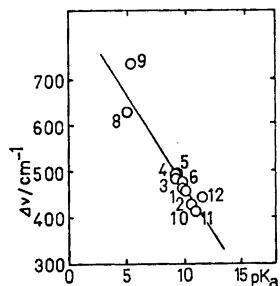


Fig. 2. The plot of $\Delta\nu\text{OH}$ against the pK_a of the phenol for the phenol-HMPA complexes. Temperature ambient. For the $\Delta\nu\text{OH}$ values of the points 8 and 9, see the text.

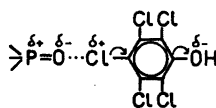
In the case of pentahalophenols the hydrogen bonded νOH bands are very broad, and the $\Delta\nu\text{OH}$ values are therefore only minimum values. In the cases of other phenols the sub-maxima do not seem to shift the top of the bonded νOH band, and $\Delta\nu\text{OH}$ can be regarded as "true" ones (cf. Fig. 4).

The variation of $\Delta\nu\text{OH}$ with the acidity of the proton donor is similar for substituted phenol-HMPA and the halogenated alcohol-HMPA complexes (Fig. 2). The $\Delta\nu\text{OH}$ values of the pentahalophenol-HMPA complexes are not "true" ones, because of the reasons mentioned above and of the intramolecular hydrogen bond between the OH group and the halogen of pentahalophenols. The intramolecular $\Delta\nu\text{OH}$ values of *o*-bromo-, *o*-chloro- and *o*-fluorophenols in CCl_4 are 78, 61 and 18 cm^{-1} , respectively.¹¹ The single νOH stretching vibration bands of pentahalophenols, at 3492 (PBP), 3521 (PCP) and 3577 cm^{-1} (PFP), are due to intramolecular hydrogen bonds. By comparison, the frequencies of νOH for *p*-halophenols are 3610 (*p*-BrP), 3614 (*p*-ClP) and 3618 cm^{-1} (*p*-FP).

In view of the intramolecular hydrogen bonds in pentahalophenols, the great decrease in the equilibrium constant and enthalpy is not surprising. Such a decrease is found also in the *o*-methoxyphenol-dimethyl sulfoxide complex compared with the phenol-dimethyl sulfoxide complex, $\Delta\nu\text{OH}$ being about the same in both cases.¹²

It has been maintained that the anomalies in the equilibrium constants of pentachlorophenol-phosphoryl compound complexes com-

pared with phenol-phosphoryl compound complexes are due to a dipole-dipole association:¹³ Scheme 1.



This kind of association may reduce the acidity of the proton donor or reduce the concentration of the proton acceptor. The solvation of a hydrogen-bonded complex by proton acceptor may also become more specific. On the basis of this study it is impossible to say whether this kind of association exists between HMPA, the P=O bond of which has 50 % ionic character.^{14,15} and pentahalophenols. There are no anomalies in K_{11} values when *p*-halophenols are the proton donors, although these phenols, too, could take part in such a dipole-dipole association.

The mesomeric effect (+*M*) in *p*-halophenols weakens the acidity by the same kind of mechanism as in dipole-dipole association. This acidity-weakening effect is reflected in both the K_{11} and $\Delta\nu\text{OH}$ values. The +*M* effect diminishes in the order $\text{F} > \text{Cl} > \text{Br}$, the effect of chlorine and bromine being almost the same.¹⁶ Thus the *p*-FP-HMPA complex has the smallest K_{11} and $\Delta\nu\text{OH}$ values of the three *p*-halophenol-HMPA complexes.

A steric effect has often been given as the reason for the small values of spectrometric

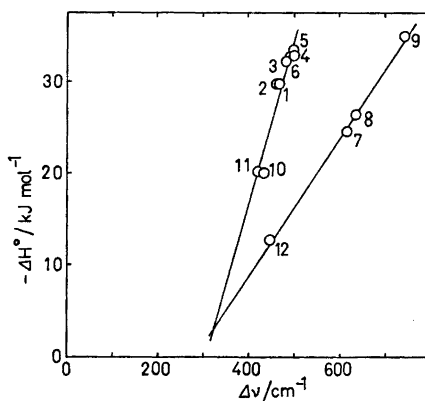


Fig. 3. The plot of $-\Delta H^\circ$ against $\Delta\nu\text{OH}$ for the phenol-HMPA complexes. For the $\Delta\nu\text{OH}$ values of the points 7, 8 and 9, see the text.

quantities obtained when 2,6-di-*tert*-butylphenol hydrogen bonds to proton acceptors.^{17,18} In this study no clear evidence of steric effect is seen. The $\Delta\nu\text{OH}$ value of the DTBP-HMPA complex is rather large compared with the pK_a or ΔH and K_{11} values (Figs. 1–3). But since $\Delta\nu\text{OH}$, on the one hand, and K_{11} or ΔH , on the other, measure different energetic changes in a hydrogen bonded system,¹⁹ it is not surprising that the variations in $\Delta\nu\text{OH}$ do not always correlate with the variations in K_{11} or ΔH .

The Badger-Bauer relation. The more the Badger-Bauer relation, *i.e.*, the linear dependence between ΔH and $\Delta\nu\text{OH}$, has been studied, the more convincing it has become that this relation holds only for a limited number of systems.^{20–23} In this study, where the same proton acceptor is used throughout, the Badger-Bauer relation holds for all but pentahalophenol-HMPA complexes (Fig. 3). The exceptional behaviour of pentahalophenol-HMPA complexes is not surprising in view of the small K_{11} and ΔH values mentioned earlier. It has been stated that in systems, where the proton acceptor is not varied, the Badger-Bauer relation will approximate the truth more closely than in systems where the proton donor is not varied.²³ In the latter case the line should even have a zero intercept.²⁰ When HMPA is the proton acceptor the intercepts are about -55 kJ mol^{-1} (with substituted phenols), 10 kJ mol^{-1} (with halogenated alcohols) and -19 kJ mol^{-1} (with ordinary alcohols), the slope being nearly the same for ordinary alcohol-HMPA and substituted phenol-HMPA complexes and less steep for halogenated alcohol-HMPA complexes.¹

Stymne and coauthors²² found it more satisfactory to plot ΔG than ΔH against $\Delta\nu\text{OH}$, owing to the higher accuracy. In this study, however, the plots are similar.

The double-scale enthalpy equation. The empirical double-scale enthalpy equation $-\Delta H = E_A E_B + C_A C_B$ is useful in predicting the enthalpies of hydrogen bond formation.^{24–27} The meanings of the products $E_A E_B$ and $C_A C_B$ have been explained previously.¹ At present, the parameters E_A and C_A are available only for a few of the phenols studied in this paper.

Table 2 shows the experimental enthalpy values and those calculated from the double-

Table 2. The literature values of the parameters E_A and C_A for phenols, and experimental and calculated (see text) enthalpy values of the phenol-HMPA complexes. The E_B and C_B values of HMPA are 1.52 and 3.55, respectively.

Phenol	E_A	C_A	$-\Delta H^{\circ}_{\text{calc}}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{\text{exp}}$ kJ mol ⁻¹
Phenol	4.33	0.442	34.1	29.9
<i>p</i> -Cresol	4.18	0.404	32.6	29.9
<i>p</i> -BrP	4.34	0.478	34.7	32.9
<i>p</i> -ClP	4.34	0.478	34.7	33.5
<i>p</i> -FP	4.17	0.446	33.1	32.3

scale enthalpy equation. The parameters E_A , E_B , C_A and C_B give the $-\Delta H$ values in the unit kcal mol⁻¹. The agreement between the calculated and experimental enthalpy values is satisfactory for all systems studied.

The form of the hydrogen-bonded complex absorption band. It was found earlier¹ that when HMPA hydrogen bonds to alcohols with pK_a smaller than 12, or to phenol, the νOH absorption band of the complex displays several submaxima. It has been proposed that these are due to Fermi resonance between $\nu\text{OH}(\text{bonded})$ and some combination vibrations of the proton donor.^{28,29} Except for 2,6-dialkylphenol-HMPA complexes, the complex absorption bands of systems studied in this work also display several submaxima. $\Delta\nu\text{OH}$ is therefore measured from the maximum $\nu\text{OH}(\text{bonded})$ band nearest the free νOH band.

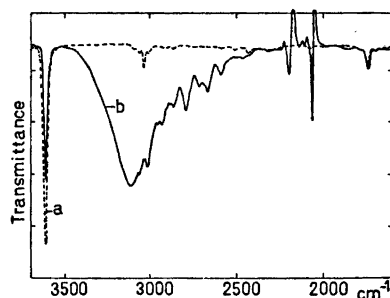


Fig. 4. Illustrative spectra: *a*, for *p*-ClP; and *b*, for the system *p*-ClP-HMPA- d_{18} . Solvent CCl_4 , temperature ambient, 10 mm cells with NaCl windows. Concentrations: *a*, 0.00344 M *p*-ClP (reference CCl_4); *b*, 0.00344 M *p*-ClP + 0.00226 M HMPA- d_{18} (reference 0.00226 M HMPA- d_{18}).

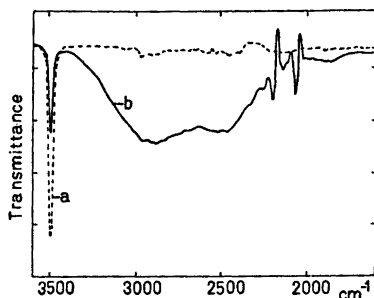


Fig. 5a. Illustrative spectra: *a*, for PBP; and *b*, for the system PBP–HMPA-*d*₁₈. Solvent CCl₄, temperature ambient, 5 mm cells with KBr windows. Concentrations: *a*, 0.00770 M PBP (reference CCl₄); *b*, 0.00770 M PBP + 0.0138 M HMPA-*d*₁₈ (reference 0.0138 M HMPA-*d*₁₈).

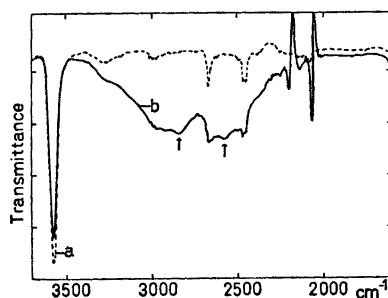


Fig. 5b. Illustrative spectra: *a*, for PFP; and *b*, for the system PFP–HMPA-*d*₁₈. Solvent CCl₄, temperature ambient, 5 mm cells with KBr windows. Concentrations: *a*, 0.00848 M PFP (reference CCl₄); *b*, 0.00848 M PFP + 0.00271 M HMPA-*d*₁₈ (reference 0.00271 M HMPA-*d*₁₈).

The contours of the absorption bands of the *p*-halophenol–HMPA complexes resemble those of the corresponding phenol complex²⁹ in the sense that there are six to nine rather sharp submaxima in both cases (Fig. 4). The negative absorptions in the ν CD vibration area are due to ν CD bands.⁵ On the other hand, the absorption bands of the pentahalophenol–HMPA complexes display only two maxima, the bands being very broad (see Figs. 5a and 5b). An examination of the contour of the complex band of the PFP–HMPA complex is complicated by the absorptions of PFP itself. It is obvious, however, that also in this case there are only two maxima due to hydrogen bonding, the minimum being much lower than

for other pentahalophenol–HMPA complexes. The band contours of pentahalophenol–HMPA complexes resemble those found for pentahalophenol–pyridine and pentahalophenol–triphenylphosphine oxide complexes.⁹ The minimum of the complex absorption band seems to be dependent only on the proton donor. As in the case of phenol,^{28,29} it is obvious that only the vibrations of the proton donor affect the band contour of the complex.

The absorption band of the α -naphthol–HMPA complex consists of many very small and sharp submaxima (Fig. 6). In the case of phenol, ν CC alone or ν CC with δ OH are found to participate in Fermi resonance with the complex absorption band. Thus the large number of C–C vibrations is probably one reason for the presence of many small submaxima in the α -naphthol–HMPA complex band. Although there exist detailed studies on the spectra of some of the substituted phenols studied here (*e.g.* Refs. 30–32), more work is needed to determine which vibrations are participating in Fermi resonance with the complex absorption bands, or to find other possible reasons for the submaxima of the absorption bands.

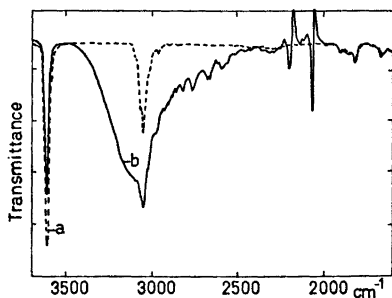


Fig. 6. Illustrative spectra: *a*, for α -naphthol; and *b*, for the system α -naphthol–HMPA-*d*₁₈. Solvent CCl₄, temperature ambient, 10 mm cells with NaCl windows. Concentrations: *a*, 0.00391 M α -naphthol (reference CCl₄); *b*, 0.00391 M α -naphthol + 0.00226 M HMPA-*d*₁₈ (reference 0.00226 M HMPA-*d*₁₈).

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