

Intermolecular Hydrogen Bond Involving a π -Base as the Proton Acceptor. II.¹ Interaction between Phenol and Various π -Bases. Preliminary Infrared Study²

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The free-energy change and $\Delta\nu_{\text{OH}}$ of phenol in interaction with various π -bases were determined. The free-energy decrease of 1:1 complex formation involving alkylbenzenes and polynuclear aromatics as π -bases was anomalously large. This is interpreted in terms of insensitiveness of $-\Delta S$ to $-\Delta H$, which is to be expected from the large proton-accepting area covered by the π -orbital of the bases. Information was obtained which suggests the importance of charge-transfer mechanism in complex formation.

Introduction

It is now well recognized that π -bases such as aromatic hydrocarbons and olefins have proton-accepting ability as ethers or amines do in hydrogen bonding.³⁻⁸ In view of the rather large possibility of occurrence of this type of interaction in the chemical laboratory as well as in nature, a systematic study to clarify the characteristics of this type of hydrogen bond in comparison with the ordinary hydrogen bond seemed interesting. In this paper the proton-accepting power of a variety of simple π -bases including alkylbenzenes, polynuclear aromatics, and cyclohexene was evaluated by measuring the fundamental ν_{OH} absorption band of phenol in the presence of a large excess of π -bases in carbon tetrachloride in terms of $\Delta\nu_{\text{OH}}$ and the free energy change due to interaction. Free and bonded ν_{OH} absorption bands were separated by the method of Ōki and Iwamura.⁹ In this method a doublet band was assumed to be the sum of two curves which conform to the Lorentz equation¹⁰

$$\ln(I_0/I)_\nu = [a/(\nu - \nu_0)^2 + b^2] + [a'/(\nu - \nu_0')^2 + b'^2] \quad (1)$$

where I_0 and I are the incident and transmitted intensities of radiation of frequency ν (cm^{-1}); ν_0 and ν_0' are the frequencies of band centers; and a , a' , b , and b' are constants. From the integral intensities of divided component bands, equilibrium constant K for 1:1 OH $\cdots\pi$ -base complex formation

(1) Part I: Z. Yoshida, E. Ōsawa, and R. Oda, *J. Phys. Chem.*, **68**, 2895 (1964).

(2) Presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Sept. 1962.

(3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p. 202.

(4) R. West, *J. Am. Chem. Soc.*, **81**, 1614 (1959).

(5) N. Fuson, P. Pineau, and M. L. Josien, *J. chim. phys.*, **55**, 454, 464 (1958).

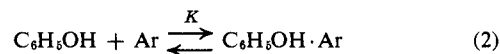
(6) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **35**, 1744 (1962), and the preceding papers of this series.

(7) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

(8) H. Dunken and H. Fritzsche, *Z. Chem.*, **2**, 345 (1962).

(9) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **31**, 769 (1958).

(10) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).



and $-\Delta F (= RT \ln K)$ were calculated

Results

In general, the agreement between the observed spectrum and the synthesized Lorentz curve is good except for minor deviations at the wings and valley between two peaks (Figure 1). The former deviation may be caused by the inherent sensitivity of the wing to the value taken for the half-intensity band width.¹⁰ Deviation at the valley may be caused by insufficient resolution power of the instrument used.¹¹ Nevertheless we believe that these deviations will have little effect on the conclusion obtained, since they are small and common in all spectra. Results of the $\Delta\nu$ determination and calculation of $-\Delta F$ values are summarized in Table I.

Discussion

Alkylbenzenes. Alkyl substituents on the benzene nucleus increase the relative basicity of alkylbenzenes toward (HF + BF₃)¹³ and HCl.¹⁴⁻¹⁶ We also confirmed this effect with methylbenzenes, as shown in Figure 2A; a linear relationship was observed between $\Delta\nu_{\text{OH}}$ and the number of methyl groups. Since $\Delta\nu$ is considered to be proportional to the energy of X-H \cdots Y interaction when X is fixed and Y substituents are changed within very closely related structures,^{8,17} it will be reasonable to interpret this effect in terms of the electron-repulsive effect of alkyl group. Surprisingly, however, $-\Delta F$ also increased with the increasing number of methyl substituent as indicated in Figure 2B. Although a similar tendency has been observed for the interaction of hydrogen chloride with π -bases,¹⁴ this is strange in the present case because, by the approach of a large molecule such as phenol near methylbenzene, a large entropy loss is expected to occur and to compensate for the enthalpy gain.

(11) This deviation was also observed by Ōki and Iwamura¹² in the ν_{OH} absorption bands of such compounds as 3-buten-1-ol and epichlorohydrin in which intramolecular interaction between the OH and π -electron exists. They found that there is another weak absorption in the valley between the free and bonded OH band which is assignable to the stretching mode of the internal rotation isomer. In our case, however, such an isomer cannot exist.

(12) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306, 567 (1959).

(13) D. A. McCoulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

(14) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(15) D. Cook, *J. Chem. Phys.*, **25**, 788 (1956).

(16) W. Strohmeier and A. Echte, *Z. Elektrochem.*, **61**, 549 (1957).

(17) (a) M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952); (b) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962); (c) F. Gramstad, *Spectrochim. Acta*, **19**, 829 (1963); (d) D. L. Powell and R. West, *ibid.*, **20**, 983 (1964); (e) R. West, D. L. Powell, M. K. T. Lee, and L. S. Whately, *J. Am. Chem. Soc.*, **86**, 3227 (1964).

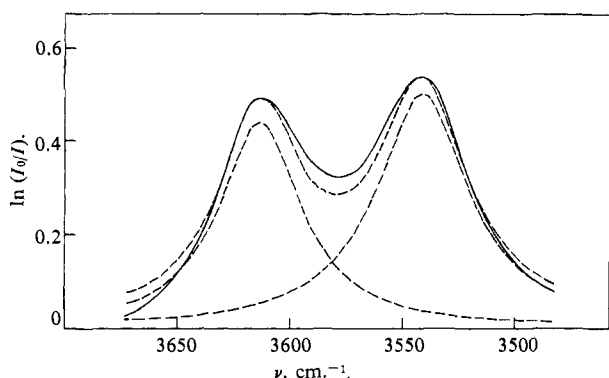


Figure 1. Spectrum of OH stretching absorption of 0.0217 mole/l. of phenol in the presence of 1.78 moles/l. of *p*-xylene (CCl₄, 20°).

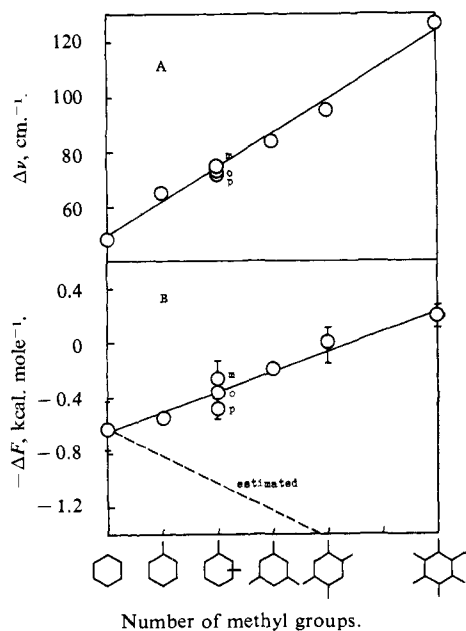


Figure 2. Dependence of $\Delta\nu$ and $-\Delta F$ of phenol-methylbenzene hydrogen-bonding formation on the number of methyl groups.

This type of compensation of enthalpy gain by entropy loss is known for the $\text{OH}\cdots\text{O}$ hydrogen bond.¹⁸ If a similar compensation occurred here it would be possible to evaluate the change in free energy of π -hydrogen bond formation with the change of the number of methyl groups on benzene by the use of (1) ΔH and ΔS values for phenol-benzene complex formation¹⁹ and (2) the relation between $\Delta\nu$ and the number of methyl groups (Figure 2A). The relation estimated is shown in Figure 2B as a dotted line. Observed $-\Delta F$ values are much higher than what has been estimated. This suggests that the $-\Delta S$ value of $\text{O-H}\cdots\pi$ -bonding is small compared to that of $\text{O-H}\cdots\text{O}$ bonding.²⁰ Since π -electrons are spread over the plane of benzene ring, it may be possible to assume that configuration of the complex is less restricted than that of the $\text{O-H}\cdots\text{O}$ complex in which proton-accepting electrons are localized in the 2p orbital of oxygen. This assumption seems to be supported by the observation that neither

(18) Reference 3, p. 220.

(19) Footnote *d* of Table I.

(20) When this paper was presented at the symposium³ in 1962, West²¹ reported at the same time the determination of ΔH° and ΔS° values of association of phenol to weak bases including aliphatic ethers and several π -bases and this estimation was partly ascertained.

(21) R. West, International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, D117; *cf. ref.* 17d,e.

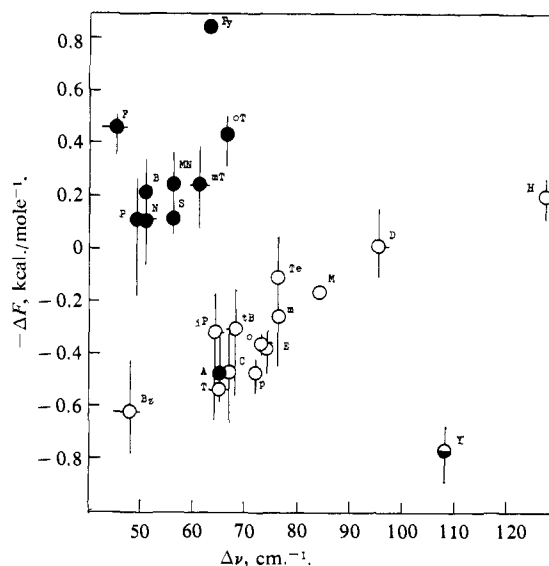


Figure 3. Plots of $-\Delta F$ vs. $\Delta\nu$: O, alkylbenzene; ●, polyphenylene and polyacene; ○, olefin (Py, pyrene; F, fluoranthene; oT, *o*-terphenyl; mT, *m*-terphenyl; MN, β -methyl-naphthalene; S, *trans*-stilbene; B, biphenyl; N, naphthalene; P, phenanthrene; H, hexamethylbenzene; D, durenene; M, mesitylene; Te, tetraline; m, *m*-xylene; o, *o*-xylene; p, *p*-xylene; E, ethylbenzene; tB, *t*-butylbenzene; iP, isopropylbenzene; C, cyclohexylbenzene; T, toluene; A, acenaphthene; Bz, benzene; Y, cyclohexene).

the *m*-xylene anomaly¹⁴ nor the hyperconjugation effect in the series of toluene-ethylbenzene-isopropylbenzene-*t*-butylbenzene¹⁴ (*cf.* Table I) exists. These results indicate that the $\text{O-H}\cdots\pi$ bond is not the σ -type but the more labile π -type,¹⁴ in which the phenol molecule in the complex might be possessed of some degree of freedom of movement over an isopotential plane within the framework of the diffused π -orbital.

Other Aromatic Hydrocarbons and Olefins. The nature of $\text{OH}\cdots\pi$ bonding seems to be more evident when comparison is made between mono- and polynuclear aromatics as the proton acceptor. As is seen in Figure 3, $-\Delta F$ values are increased in the following order: cyclohexene < alkylbenzenes < polynuclear aromatics. Although there is much uncertainty in the absolute values of $-\Delta F$, the order is significant. If, in a statistical sense, molecular symmetry of acceptor were the major contribution to the equilibrium constant, then the largest of all the compounds examined, benzene, with six equivalent bonds, should have the greatest $-\Delta F$ value.

A possible interpretation of this order may be that the area covered by the π -electron cloud increases in the same order. Entropy of complex will increase in this order. Since $\Delta\nu$ values are not greatly varied among aromatic bases (Figure 3), $-\Delta S$ will be the contributing factor in the comparison of $-\Delta F$ values.²²

Note on the Interaction Force. Further analysis of the data seems to suggest the importance of charge transfer in the $\text{OH}\cdots\pi$ interaction. First, $\Delta\nu$ values are roughly increased as the ionization potential of π -bases is decreased. This kind of relation has been noticed in the systems of HCl¹⁵- or phenol²³-alkylbenzenes.

(22) Indeed, according to West,²¹ $-\Delta S^\circ$ of association of phenol in CCl₄ with various bases decreases with the increase of proton-accepting area: aliphatic ether, 10-17; monoolefin, 6; alkylbenzene, 4-5; naphthalene, 2.8; phenanthrene 1.0 cal. deg.⁻¹ mole⁻¹.

Table I. Shifts of Phenolic ν_{OH} Fundamentals and Free-Energy Decreases on Intermolecular H-Bond Formation with Various π -Bases in CCl_4 Solution at 20°

π -Base	$\Delta\nu_{\text{OH}}$, cm. ⁻¹	Lit. value, cm. ⁻¹	$-\Delta F$, kcal./mole
Benzene	48 ± 3	47 ^a 56 ^b 53 ^c 58 ^a	-0.62 ± 0.20 ^d
Toluene	65 ± 2		-0.54 ± 0.03
<i>m</i> -Xylene	76 ± 1		-0.26 ± 0.20
<i>o</i> -Xylene	73 ± 2		-0.36 ± 0.04
<i>p</i> -Xylene	72 ± 1	66 ^a	-0.48 ± 0.08
Ethylbenzene	74 ± 1		-0.38 ± 0.10
Isopropylbenzene	64 ± 2		-0.32 ± 0.34
<i>t</i> -Butylbenzene	68 ± 2		-0.31 ± 0.26
Mesitylene	84 ± 1	73 ^a	-0.19 ± 0.03
Durene	95 ± 2		0.01 ± 0.16
Hexamethylbenzene	127 ± 0		0.20 ± 0.09
Cyclohexylbenzene	67 ± 0		-0.47 ± 0.21
Biphenyl	51 ± 1		0.21 ± 0.03
<i>o</i> -Terphenyl	66 ± 1		0.43 ± 0.12
<i>m</i> -Terphenyl	61 ± 2		0.24 ± 0.16
Tetraline	76 ± 1		-0.11 ± 0.27
Naphthalene	52 ± 2		0.11 ± 0.24
β -Methylnaphthalene	56 ± 1		0.24 ± 0.13
Acenaphthene	65 ± 2		-0.48 ± 0.16
Fluoranthene	45 ± 3		0.46 ± 0.11
Phenanthrene	48 ± 0		0.11 ± 0.30
Pyrene	(63) ^e		(0.8) ^e
<i>t</i> -Stilbene	56 ± 0		0.11 ± 0.05
Cyclohexene	108 ± 1	95 ^a	-0.77 ± 0.12

^a Reference 4. ^b C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956). ^c T. Shimanouchi and Y. Ikeda, the 8th Discussion on Infrared and Raman Spectroscopy, Tokyo, Oct. 1961. ^d Recently Shimanouchi and Ikeda^c reported $-\Delta H = 1.7 \pm 0.2$ kcal./mole, $-\Delta S = 8.3 \pm 0.3$ cal./deg. mole, and $-\Delta F = 0.66 \pm 0.2$ kcal./mole (20°). ^e Uncertain because of the small intensity of interacted OH absorption caused by poor solubility of pyrene in CCl_4 .

Intensity of the ν_{OH} band provides important information on the nature of the bonding. Results of the plots of intensity of bonded OH against $\Delta\nu_{\text{OH}}$ ^{24,25} as well as the plots of ϵ_a , the added effective charge due to complex formation, against $\Delta k/k$, the relative change in force constant due to complex formation,²⁶ seem to indicate that the contribution of charge transfer is considerable. But, since the accuracy of the intensity measurement was not satisfactory because of instrumental limitation, we shall reserve judgment until it is repeated on the grating spectrophotometer.

Experimental

All materials were of highest purity reagents available in the market. They were purified further immediately before use by ordinary methods.

Measurement of Infrared Spectra. Spectra were taken using a Shimadzu AR-275 II S double pass infrared spectrophotometer with NaCl optics. The mechanical slit width was kept constant at 18 μ . The spectral slit width was calculated according to Ramsay¹⁰ using the refractive index data of Conn and Avery²⁷

(23) M. L. Josien and G. Sourisseau in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p. 129.

(24) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

(25) E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

(26) W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958); W. B. Person, R. E. Humphrey, and A. I. Popov, *ibid.*, **81**, 273 (1959); W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, **82**, 29 (1960).

(27) G. K. T. Conn and D. G. Avery, "Infrared Methods," Academic Press, New York, N. Y., 1960, p. 58.

to be 10 cm.⁻¹ at 3500 cm.⁻¹. The region from 2.5 to 3.1 μ was scanned at the speed of 0.25 μ /min. Resolution power at this speed is 1.5 cm.⁻¹. Sealed liquid cells of 0.141-cm. thickness were used throughout at 20° .

Two spectrograms were taken separately for one combination of donor and acceptor at a given concentration: (1) about 0.02 mole/l.²⁸ with phenol and 0.1–3 moles/l. with proton acceptor in CCl_4 in the sample cell and CCl_4 in the reference cell; (2) only proton acceptor at the same concentration in CCl_4 in the sample cell and CCl_4 in the reference cell. The transmission (%) ratio of the spectrum of (1) to (2) was calculated at every frequency and converted to the $\ln(I_0/I)$ scale. Thus, the absorption spectrum of phenol in CCl_4 solution in the presence of a large excess of proton acceptor was obtained.

Special cautions were taken in the dehydration of materials. After having been dried by known methods, they were kept over phosphorus pentoxide. Direct addition of this drying agent to the sample solution²⁹ caused considerable decrease of the ν_{OH} band intensity, presumably because of adsorption of phenol onto the drying agent.

Analysis of the Absorption Spectra. Shifts of the OH stretching absorption bands due to complex formation being small, ν_{OH} absorption band was usually a doublet. Calculation of the equilibrium constant in eq. 2 consists of (i) separating the doublet into the component bands, and (ii) estimating the concentration of free phenol from the integral intensity of the ν_{OH} (free) band.

(i) **Separation.** Six unknown parameters (ν_0 , ν_0' , a , a' , b , and b') in eq. 1 were determined by "trial and error" repeating until the sum of the calculated component curves agreed with the observed as closely as possible. Every trial calculation involved the correction of the apparent intensity $\ln(T_0/T)$ and apparent half-width $\Delta\nu^{a_{1/2}}$ to true figures, $\ln(I_0/I)$ and $\Delta\nu^{t_{1/2}}$, by the use of Ramsay's table.¹⁰ The half-width of the thus separated ν_{OH} (free) band was 41.5 ± 1.1 cm.⁻¹, which agreed rather well with that of phenol in the absence of bases, 43.3 ± 1.3 cm.⁻¹.

(ii) **Estimation of the Concentration of the Complex.** From the calibration curve of phenol concentration against $\ln(I_0/I)_{\nu_{\text{max}}}\Delta\nu^{t_{1/2}}$ ³⁰ which had been drawn in advance, the equilibrium constant K in eq. 2 and the free-energy change were calculated by eq. 3 and 4.

$$K = \frac{[\text{phenol}]_{\text{bound}}}{[\text{phenol}]_{\text{free}}[\text{acceptor}]_{\text{free}}} = \frac{([P]_0 - [P]_f)/[P]_f([A]_0 - [P]_0 + [P]_f)}{\quad} \quad (3)$$

$$-\Delta F = RT \ln K \quad (4)$$

where the zero subscript designates the initial state, R is the gas constant, and T is 293°K. This procedure was repeated at three or four different concentrations.

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(28) At this concentration self-association of phenol is negligibly small.

(29) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958).

(30) Proportional to integral intensity.¹⁰