

Aromatic Molecules as Hydrogen-Bonding Bases. An Investigation of the Interaction between an Aliphatic Alcohol and a Series of Alkylbenzenes

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The hydrogen-bonding interactions between *t*-butyl alcohol and a series of alkylbenzenes have been studied by infrared techniques in order to investigate the possible role of charge transfer in the interaction. The frequency shifts and intensities of the hydrogen-bonded OH stretching vibration and the equilibria have been studied. In agreement with a recently published theoretical treatment of the charge-transfer model of hydrogen bonding, a linear correlation between the ionization potential of the aromatic donor and the function $(\nu_F/\Delta\nu)^{1/2}$ was observed. While the 1:1 complex predominates over the range of concentrations studied, evidence for a 2:1 complex was also obtained. The formation constants, K_1 , for the 1:1 complexes were found to increase systematically with increasing methyl substitution, and a linear correlation between $\ln K_1$ and $\Delta\nu$ was observed. The intensities are interpreted in terms of a charge-transfer model which had been previously used to treat the vibrational intensities of acceptor molecules engaged in charge-transfer complexes. The model is found to give essentially the same quantitative relationship for the hydrogen-bonded complexes as was observed for the charge-transfer complexes, thus supporting the charge-transfer model of hydrogen bonding.

Introduction

In their recent book on hydrogen bonding Pimentel and McClellan¹ pose the question, "Do aromatics form hydrogen bonds?" Their conclusion, based on evidence in the literature, was affirmative; aromatics do participate in intermolecular hydrogen bonding with a number of proton donors. However, despite the vastness of the literature on hydrogen bonding, surprisingly few systematic studies have been made of interactions with aromatics. Infrared studies have been made of the interactions between aromatics and chloroform,² chloroform-*d*,³ methanol,³ methanol-*d*,² HCl,^{3,4} HBr,³ HI,³ phenol,³ pyrrole,³ thiophenol,³ *n*-butyl alcohol,³ *t*-butyl alcohol,⁵ and surface silanol groups (on silica).⁶⁻⁷ Schaefer and Schneider⁸ have studied the interaction between acetone and a number of aromatics by proton magnetic resonance. Finally, Tamres² has measured the heats of mixing of carbon tetrachloride and chloro-

form with a series of aromatics, and Cook, *et al.*,⁹ have determined freezing point diagrams of HCl in a series of methylbenzenes.

In spite of the great effort that has been devoted to the study of hydrogen-bonding phenomena in the past years, little progress has been made in the theoretical interpretation, primarily because of the complexity of the problem. Customarily, theoreticians utilize four distinct concepts in trying to formulate a theory of the hydrogen bond. These are electrostatic interaction, delocalization effects, repulsive forces, and dispersion forces.¹⁰ The great complexity of the problem is undoubtedly reflected in the observed variation in the relative importance of these concepts from system to system. Thus, a universal theoretical model of the hydrogen bond has been an elusive goal and will probably continue to be for some time.

It would seem to be of considerable value to study hydrogen-bonding systems in which one of the above concepts would be likely to predominate. For example, under the delocalization concept charge transfer has been alluded to a number of times as a dominant factor in hydrogen bonding.^{2,5,6,11,12} The similarity between the frequency shift and intensification of the OH stretching vibration due to hydrogen bonding and comparable changes in the frequency and intensity of halogen molecules engaged in charge-transfer complexing have been cited as evidence that hydrogen-bond formation and charge-transfer complex formation are closely related.¹³⁻¹⁵

On the basis of these considerations it was felt that an infrared study of the hydrogen-bonding interaction between an aliphatic alcohol and a series of alkylbenzenes would be worthwhile. In addition to measuring the frequency shifts and intensities of the hydrogen-bonded OH stretching vibration, the formation constants of the complex were estimated.

Experimental

Instrumentation. Spectra were recorded on a Perkin-Elmer Model 421 filter-grating spectrophotometer. The estimated spectral slit width was $\leq 2 \text{ cm}^{-1}$. The data manipulation was greatly facilitated by the utilization of a Perkin-Elmer Model 1 digital data recorder in

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

(2) M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

(3) M. Josien and G. Sourisseau, "Hydrogen Bonding," Pergamon Press Inc., New York, N. Y., 1959, p. 129.

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

(5) M. R. Basila, *ibid.*, **35**, 1151 (1961).

(6) G. A. Galkin; A. V. Kiselev, and V. I. Lygin, *Trans. Faraday Soc.*, **60**, 431 (1964).

(7) A. Terenin and V. Filimonov; ref. 3, p. 545.

(8) T. P. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

(9) D. Cook, Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **34**, 964 (1956).

(10) C. A. Coulson, ref. 3, p. 339.

(11) H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).

(12) P. G. Puranik and V. Kumar, *Proc. Indian Acad. Sci., Sect. A*, **58**, 29 (1963).

(13) W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958).

(14) W. B. Person, R. E. Humphrey, and A. I. Popov, *ibid.*, **81**, 273 (1959).

(15) W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, **82**, 29 (1960).

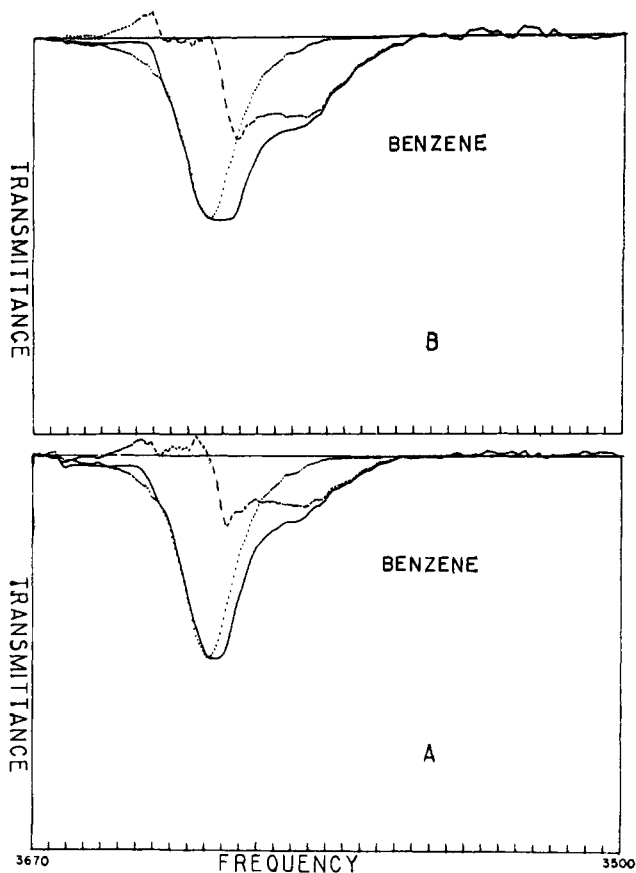


Figure 1. The OH stretching vibration in the hydrogen-bonded *t*-butyl alcohol-benzene complex: A, 10 vol. % benzene; B, 15 vol. % benzene; a, —; b,; c, - - - -.

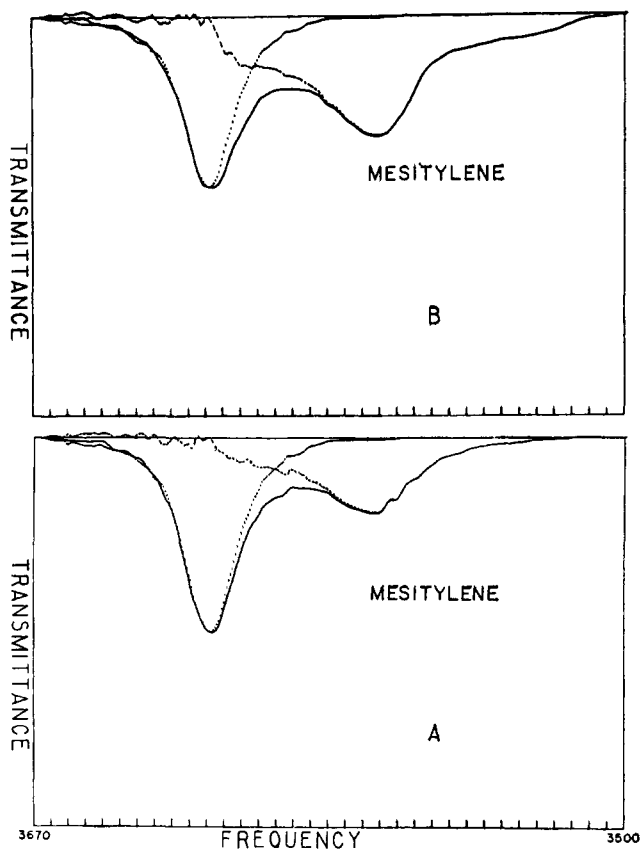


Figure 2. The OH stretching vibration in the hydrogen-bonded *t*-butyl alcohol-mesitylene complex: A, 15 vol. % mesitylene; B, 30 vol. % mesitylene; a, —; b,; c, - - - -.

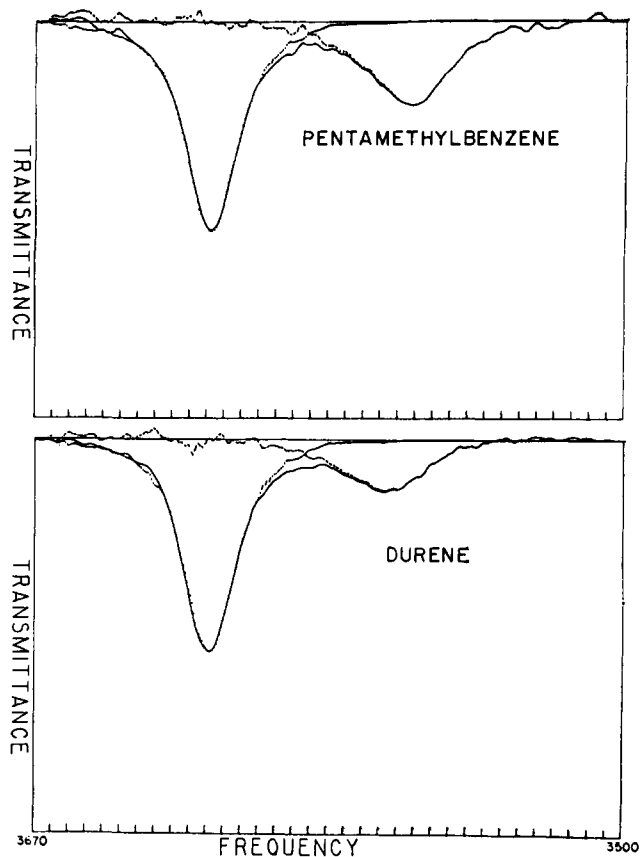


Figure 3. The OH stretching vibration in hydrogen-bonded complexes: a, —; b,; c, - - - -.

conjunction with an IBM 7090 digital computer and plotter. In addition to the spectrum produced by the Model 421, the frequency and transmittance values were recorded on paper tape every 0.5 cm^{-1} . Higher density data logging did not produce a significant change in the results and was, therefore, felt unnecessary.

Techniques. The spectra were recorded differentially because overlapping bands due to the aromatic component interfered with the measurement of the hydroxyl OH stretching vibration. A pair of matched cells having 15-mm. optical path lengths and equipped with sodium chloride windows was used. A CCl_4 solution containing the aromatic (5–20% by volume) was placed in the reference cell, and a similar one containing an identical concentration of the aromatic plus the alcohol ($4.3 \times 10^{-3} M$) was placed in the sample cell. Because of the aromatic absorption, transmission in the region of interest was limited to 40–60% in the most favorable (hexamethylbenzene) and 0–30% in the least favorable (benzene) cases. Obviously, these are rather severe operating conditions, and the signal-to-noise ratio was considerably lower than that observed under normal operating conditions, as is evident in the spectra of Figures 1–3. In the case of benzene, the instrument was essentially dead in the tail of the OH stretching band on the high frequency side as is evidenced by the large negative peak in the difference spectra in Figure 1. The spectrometer and sample compartment were continuously flushed with air from which the H_2O and CO_2 were removed.

Materials. The CCl_4 was Fisher certified reagent grade dried and stored over Ascarite. The *t*-butyl alcohol was Eastman White Label, which had been distilled, the center cut being retained for use. The aromatics were Baker reagent grade benzene, Phillips pure grade ethylbenzene and *o*- and *m*-xylene, Eastman White Label toluene, *p*-xylene, mesitylene, pentamethylbenzene, and hexamethylbenzene, and K & K durene and isodurene. All were used as received. Their purities were checked by mass spectroscopic or gas chromatographic methods and were considered adequate for the study.

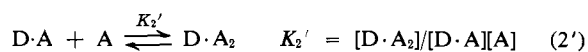
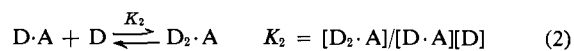
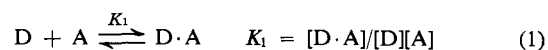
Treatment of Data. Essentially all of the data treatment was done on the IBM 7090 computer. The transmittance data were first converted to absorbance and then statistically smoothed using a modified least-squares procedure.¹⁶ The background was subtracted by assuming a linear base line between 3670 and 3500 cm^{-1} . The resulting spectrum (*a*) was integrated between the same limits. The spectrum of the nonhydrogen-bonded OH stretching vibration (*b*) between 3670 and 3500 cm^{-1} was subtracted from *a* after the peak absorbance of *b* at 3618 cm^{-1} was matched to the absorbance of *a* at the same frequency. The difference spectrum (*c*) and spectrum *b* were integrated. The integrated areas *b* and *c* and the initial alcohol and aromatic concentrations were then utilized in calculating the equilibrium constant *K* and the intensity of the hydrogen-bonded OH stretching vibration. The spectra *a*, *b*, and *c* were plotted by the computer plotter.

In order to minimize experimental error, each spectrum was run in duplicate. The areas *a*, *b*, and *c* were found to be quite reproducible; the observed variations were 1.6, 1.6, and 5.5%, respectively. These lead to possible variations in K_1 and A_B of 4–9 and 7%, respectively. Comparable errors were experienced in duplicate experiments so that the errors in K_1 and A_B are probably within 10%. It is felt that the $\Delta\nu$ -values can be estimated to within 1–2 cm^{-1} , which gives a possible error of 3–7%.

Results

In Figures 1 and 2 plots are given of the spectra *a*, *b*, and *c* of *t*-butyl alcohol hydrogen bonded to benzene and mesitylene at two aromatic concentrations. It is evident that there are three concentration-dependent, overlapping bands in the *t*-butyl alcohol–benzene spectrum in Figure 1. There is a band due to the free OH stretching vibration at 3618 cm^{-1} , a band due to the hydrogen-bonded OH stretching vibration at 3591 cm^{-1} , and an intermediate band around 3613 cm^{-1} . Similarly, two principal bands are observed in the *t*-butyl alcohol–mesitylene spectrum in Figure 2 at 3618 and 3569 cm^{-1} and a very weak band centered at approximately 3598 cm^{-1} . This latter band is somewhat smaller in relative intensity as compared to its counterpart in the *t*-butyl alcohol–benzene spectrum. In the *t*-butyl alcohol–pentamethylbenzene and *t*-butyl alcohol–durene spectra in Figure 3 only two bands are evident at 3618 and 3560 cm^{-1} and at 3618 and 3568 cm^{-1} , respectively. Inspection of the spectra of *t*-butyl alcohol bonded to the other aromatics reveals a smooth progression from benzene to hexa-

methylbenzene in which the prominence of the intermediate band near 3600 cm^{-1} diminishes and essentially disappears. Since the band exhibits a concentration dependence, it is likely that it corresponds to an additional complex species. The two most obvious possibilities are $\text{D}_2\cdot\text{A}$ or $\text{D}\cdot\text{A}_2$ where D is the aromatic and A the alcohol. The possible equilibria are



where K_1 , K_2 , and K_2' are the formation constants. The relative magnitudes of K_1 , K_2 , and K_2' have been measured for benzene, ethylbenzene, and mesitylene. The data were most complete for benzene, and it was found that the best fit was obtained for the equilibria described in (1) and (2). When (1) and (2') were used, a negative K_2' resulted. The values of K_1 and K_2 were 0.041 and 3.62 M^{-1} , respectively. The corresponding values for ethylbenzene were 0.23 and 0.29 M^{-1} , and for mesitylene 0.26 and 0.014 M^{-1} . The diminishing value of K_2 , as one goes from benzene to mesitylene, is to be expected since the steric effects of the substituents can be expected to inhibit complex formation. The K_2 value for toluene is essentially zero, which is contrary to what one would expect on the basis of the ethylbenzene results. We have not been able to explain this result; however, the data are less precise for ethylbenzene than for any other aromatic, and, since the numbers calculated are very sensitive to experimental error, the relative values of K_1 and K_2 given above may not be as close as indicated. For the present purposes, the data indicate that the importance of K_2 rapidly diminishes as one proceeds in the series from benzene to hexamethylbenzene. Therefore, we have made the approximation $K_2 = 0$ for all but benzene and ethylbenzene. The benzene and ethylbenzene data will not be utilized in the following discussion because of the large inherent error in evaluating K_1 and K_2 . The values of K_1 calculated for the other aromatics are given in Table I. Also given in Table I are the frequencies, ν_B , of the major hydrogen-bonded OH stretching band which are presumably due to the 1:1 complex and the relative frequency shifts, $\Delta\nu/\nu_F$, due to hydrogen bonding, where ν_F is the nonhydrogen-bonded OH stretching frequency, and $\Delta\nu = \nu_F - \nu_B$.

The integrated intensities, A_B , of the hydrogen-bonded OH stretching vibration in the 1:1 complex were estimated by assuming that the entire integrated area of *c* in the samples having the lowest aromatic concentrations was due to the 1:1 complex. These values are given in Table I along with the value, A_F , for the nonhydrogen-bonded vibration.

Discussion

Frequencies. A number of authors have reported correlations between the ionization potentials of aromatic bases and the hydrogen-bonded frequency shifts of an XH stretching vibration of the proton donor.^{3–6} These observations have been cited as evidence supporting the idea that charge transfer is important in this hydrogen-bonding system.⁵ Recently, Puranik and Kumar¹² have offered a theoretical treat-

(16) A. Savitzky and M. J. E. Golay, *Anal. Chem.*, **36**, 1627 (1964).

Table I. Spectroscopic Data and Formation Constants for the Hydrogen-Bonding Interactions between *t*-Butyl Alcohol and the Alkylbenzenes

Solvent no.	Solvent	K_1 at 26°, M^{-1}	ν_B , cm^{-1}	$\Delta\nu/\nu_F$, %	I_D^a		A_B , $M^{-1} cm^{-2} \times 10^{-4}$
					P.I.	E.I.	
	CCl_4	0	3618 ^b	0			0.27 ^b
1	Benzene- CCl_4	...	3591	0.75	9.25 ^c	9.56 ^d	...
2	Toluene- CCl_4	0.19	3583	0.97	8.82 ^c	9.18 ^d	0.53
3	Ethylbenzene- CCl_4	...	3585	0.90	8.76 ^c	9.12 ^e	...
4	<i>o</i> -Xylene- CCl_4	0.15	3580	1.05	8.56 ^c	9.04 ^d	0.87
5	<i>m</i> -Xylene- CCl_4	0.24	3578	1.11	8.56 ^c	9.05 ^d	0.49
6	<i>p</i> -Xylene- CCl_4	0.20	3579	1.08	8.45 ^c	8.99 ^d	0.57
7	Mesitylene- CCl_4	0.26	3569	1.34	8.40 ^c	8.74 ^d	0.60
8	Durene- CCl_4	0.26	3568	1.40	8.03 ^c	8.53 ^f	0.58
9	Isodurene- CCl_4	0.19	3566	1.44		8.53 ^f	0.97
10	Pentamethylbenzene- CCl_4	0.23	3560	1.60		8.34 ^f	0.80
11	Hexamethylbenzene- CCl_4	0.37	3549	1.91		8.15 ^f	0.77

^a P.I. = photoionization; E.I. = electron impact. ^b Values for ν_F and A_F . ^c Reference 17. ^d Reference 18. ^e Reference 19. ^f Reference 20. These values are theoretically calculated, based on the E.I. value for benzene.

ment of the charge-transfer model of hydrogen bonding. Utilizing the results of Mulliken's²¹ second-order perturbation theory calculation for loose 1:1 charge-transfer complexes, they derive the following relationship between $\Delta\nu/\nu_F$ and the ionization potential, I_D , of the donor (aromatic in this case) molecule

$$I_D = [^{5/2}\lambda(\nu_F/\Delta\nu)]^{1/2}cS + E + W \quad (3)$$

where c is a constant, S is the overlap integral between the donor orbital and the molecular orbital of the negative ion of the acceptor molecule, λ is a term related to the polarity of the acceptor orbital, E is the

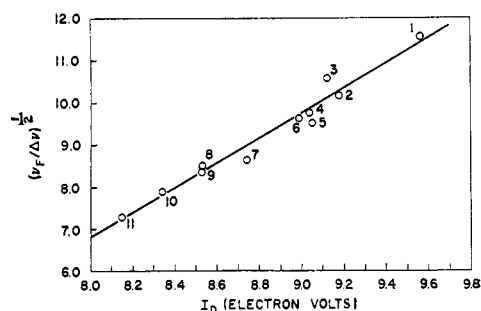


Figure 4. Correlation between $(\nu_F/\Delta\nu)^{1/2}$ and I_D (eq. 4). The numbers correspond to the aromatics listed in Table I.

electron affinity of the acceptor molecule, and W is the net energy of attraction between D^+ and A^- .¹² When the acceptor is the same in a series of complexes, as is *t*-butyl alcohol in the present case, c , λ , E , W , and S are constant (within limits). Therefore, (3) reduces to

$$I_D = C_1(\nu_F/\Delta\nu)^{1/2} + C_2 \quad (4)$$

where C_1 and C_2 are constants. Thus, a linear relationship should exist between I_D and $(\nu_F/\Delta\nu)^{1/2}$. The plot of (4) is given in Figure 4. Although both photoionization and electron impact I_D values are given in Table I, only the latter are plotted in Figure 4 because they are

(17) K. Watanabe, T. Nakayama, and J. Mottl, U. S. Department of Commerce, OTS Report No. 158317, 1959.
 (18) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).
 (19) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).
 (20) J. L. Franklin, *ibid.*, **22**, 1304 (1954).
 (21) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952).

more complete. A reasonably good linear correlation is observed. This correlation supports the argument that charge-transfer interactions are important in this hydrogen-bonding system.

Formation Constants. Examination of the K_1 values estimated in Table I reveals a systematic variation. With the exception of *o*-xylene, isodurene, and possibly pentamethylbenzene, there is a systematic increase in K_1 as the number of methyl substituents increases. Since a correlation is expected between $\Delta\nu$ and the heat of formation of the complex,²² ΔH_f , the increase in K_1 would be expected to reflect the increase in ΔH_f with increasing methyl substitution. This correlation between ΔH and $\Delta\nu$ has been demonstrated by Tamres² in the case where ΔH is the heat of mixing of chloroform or bromoform with a series of substituted benzenes. In the present case, a plot of $\ln K_1$ vs. $\Delta\nu/\nu_F$ is a reasonably good straight line as shown in Figure 5. Hence,

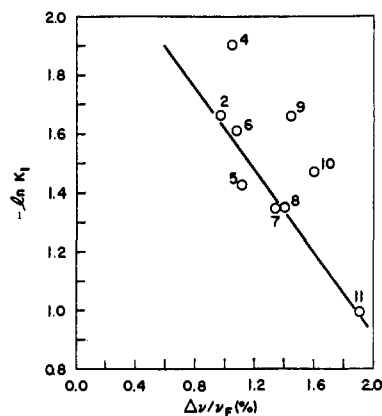


Figure 5. Correlation between $\ln K_1$ and $\Delta\nu/\nu_F$. The numbers correspond to the aromatics listed in Table I.

the increase in K_1 with increasing methyl substitution and presumably larger ΔH_f (as reflected by $\Delta\nu$) is reasonable. Of course, the expectation that K_1 and ΔH_f should be correlated is predicated on the assumption that the ΔS_f remains relatively constant or varies linearly. It has recently been pointed out²³ that such

(22) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).
 (23) C. R. Allen and P. G. Wright, *J. Chem. Educ.*, **41**, 251 (1964).

ΔH - K correlations for a series of related compounds often fail because an unexpected or nonlinear change occurs in the $T\Delta S$ term. Thus, any factor which leads to an unexpected change in ΔS_f will disrupt these correlations. This may be the case for *o*-xylene, isodurene, and pentamethylbenzene; however, the factors which could be responsible for such a change in ΔS_f are not evident at this time.

Intensities. The A_B values given in Table I exhibit characteristic hydrogen-bonding behavior; that is, there is an enhancement of the intensity of the hydrogen-bonded vibration which increases with increasing strength of the interaction. Again, *o*-xylene, isodurene, and pentamethylbenzene are exceptions to the general trend. The trend in intensities can be explained in terms of the model developed by Person and co-workers¹³⁻¹⁵ to treat the intensities of the I-X stretching vibration of molecules such as ICl and ICN engaged in charge-transfer complexes. According to this model, the hydrogen-bonded complexes can be considered in terms of two resonance structures



and a correlation should exist between the added effective charge, ϵ_D , and the relative change in force constant, $\Delta k/k$. The same correlation has been derived by Puranik and Kumar¹² in their theoretical treatment of the charge-transfer model for hydrogen bonding. The value of ϵ_D is estimated from the intensity of the hydrogen-bonded vibration. Tsubomura¹¹ has shown that the net bond moment derivative of a hydrogen-bonded complex can be approximated as

$$\frac{\partial \bar{\mu}_C}{\partial r} = \frac{\partial \bar{\mu}_F}{\partial r} + \frac{\partial \bar{\mu}_D}{\partial r} = \epsilon_0 + \epsilon_D \quad (5)$$

where the subscript F refers to the nonhydrogen-bonded vibration.²⁴ The assumption has been made that the hydroxyl group can be treated as a diatomic molecule in both the complexed and uncomplexed form. This approximation generally is quite good for weak complexes. The value of $\partial \bar{\mu}_C/\partial r$ is obtained from

$$\frac{\partial \bar{\mu}_C}{\partial r} = \left[\frac{3c^2}{\pi N\mu} \right]^{1/2} [A_B]^{1/2} \quad (6)$$

where μ is the reduced mass. The value of ϵ_0 is obtained from (6) by using A_F in place of A_B . The values of $\Delta k/k$ were calculated utilizing the diatomic molecule approximation. The calculated values of ϵ_D and $\Delta k/k$ are given in Table II, and a plot of the data is shown in Figure 6. A linear correlation is observed with the exception of *o*-xylene, isodurene, and pentamethylbenzene. The data (with the exception of the above three points) were fitted to a straight line by the least-squares method. The equation

$$\epsilon_D = 13.4(\Delta k/k) + 1.8 \times 10^{-2} \quad (7)$$

was derived. The intercept is virtually zero, as it

(24) It is well known that the sign of $\partial \bar{\mu}_C/\partial r$ cannot be determined from intensity measurements. It has arbitrarily been chosen to be positive, as have the other quantities in (5). This arbitrary choice of sign does not affect the results because in this approximation the signs of ϵ_0 and ϵ_D will always have to be the same, and, therefore, ϵ_D will have the same sign in all the molecules studied since the intensities are always greater (see Table I) in the hydrogen-bonded complexes.

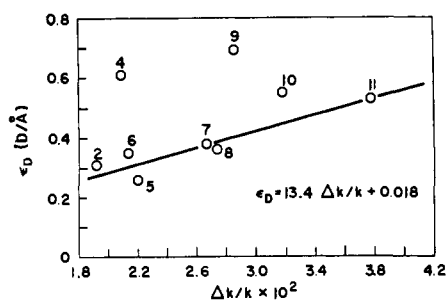


Figure 6. Correlation between ϵ_D and $\Delta k/k$. The numbers correspond to the aromatics listed in Table I.

should be. Person, *et al.*,¹⁵ derived the equation

$$\epsilon_D = 11.31(\Delta k/k) + 0.27 \quad (8)$$

for the stretching vibrations of ICl, ICN, Br_2 , and Cl_2 engaged in charge-transfer complexes and pyrrole and methanol in hydrogen-bonded complexes with benzene, ether, and trimethylamine. The intercept is zero within the average deviation of the data (± 0.33). The slopes of (7) and (8) are in very good agreement in view of the experimental difficulties encountered in both studies. In the light of this agreement, it appears that the quantitative behavior of the acceptor stretching vibration is the same in both hydrogen-bonded and charge-transfer complexes.

Table II. Calculated ϵ_D and $\Delta k/k$ for the *t*-Butyl Alcohol-Alkylbenzene Complexes

Solvent ^a	ϵ_D , D./Å.	$\Delta k/k \times 10^2$
2	0.31	1.93
4	0.61	2.09
5	0.26	2.20
6	0.35	2.14
7	0.38	2.69
8	0.36	2.74
9	0.69	2.86
10	0.55	3.18
11	0.53	3.78

^a See Table I for solvent identification.

It is not clear why the K_1 and A_B values of *o*-xylene, isodurene, and pentamethylbenzene deviate from the general behavior pattern. The directions of the deviations, *viz.*, K_1 smaller and A_B larger than normal, suggest that they are due to experimental error. However, if one assumes the K_1 values calculated from the line in Figure 5, the decrease in the ϵ_D -values of *o*-xylene and isodurene is not sufficient to cause them to fall near the line in Figure 6. On the other hand, the corrected ϵ_D -value for pentamethylbenzene does fall very near the line. It would seem, therefore, that experimental error would have to be ruled out as the cause of the deviations of *o*-xylene and isodurene since the magnitude of the change in K_1 required to bring the ϵ_D -values in line would be unrealistically large. The deviation of pentamethylbenzene may be in part due to experimental error. It should be noted, however, that the magnitude of the error in K_1 would have to be $\sim 30\%$, which is considerably beyond the estimated experimental error.