

normal sulfates and their extremely weak electrolyte character accounts for the fact that Critchfield<sup>17</sup> observed a slight break at the second equivalence point in the potentiometric titration of 0.1 *M* sulfuric acid with morpholine ( $pK_{\text{BH}^+}^{\text{d}} = 16.6$ ).<sup>16</sup>

In a previous paper,<sup>2</sup> it was demonstrated that the bisulfate ion effectively becomes a much stronger acid in the presence of the hydrogen-bond donor *p*-bromophenol (HR) mainly as a result of formation of the stable conjugate  $\text{SO}_4^{2-} \cdot 4\text{HR}$ . For example, in the presence of 0.3 *M* HR the effective  $pK_{\text{HSO}_4^-}^{\text{d}}$  is 15.9 instead of 25.9 in its absence. Thus, it is expected that *p*-bromophenol will greatly affect the conductometric and potentiometric titration curves of bisulfate. Curve 3' in Figure 3 illustrates the conductometric titration curve of  $0.75 \times 10^{-3}$  *M* sulfuric acid with TMG in the presence of 0.3 *M* *p*-bromophenol. The large conductance at the first equivalence point (compare curves 3 and 3') is due to formation of the conjugate  $\text{HSO}_4^- \cdot (\text{HR})_x^-$ . The  $\text{BH}^+$  salt of this anion has a much greater  $K^{\text{d}}$  than  $\text{BHHSO}_4$ . A striking difference in conductance is observed between that at the first and second equivalence point in the presence and absence of *p*-bromophenol. In the presence of *p*-bromophenol

the conductance hardly changes between the first and second equivalence points. A quantitative interpretation of the results is not possible at this time. The hydrogen-bond donor HR enhances the dissociation of  $\{(\text{BH})_2\text{SO}_4\}_2$  into two molecules of monomer. The undissociated monomer undoubtedly will combine with HR. Moreover, HR will promote the dissociation  $\text{BHSO}_4^- \rightleftharpoons \text{BH}^+ + \text{SO}_4^{2-}$  because of its great affinity to  $\text{SO}_4^{2-}$ ,  $(\text{BH})_2\text{SO}_4 \cdot (\text{HR})_y$  being expected to be an intermediately strong electrolyte. Thus the main reactions may be  $\text{BH}^+ + \text{HSO}_4^- \cdot (\text{HR})_x \rightleftharpoons \text{B} + (4-x)\text{HR} \rightleftharpoons \text{BH}^+ + \text{BHSO}_4^- \cdot (\text{HR})_y \rightleftharpoons (\text{BH})_2\text{SO}_4 \cdot z\text{HR}$ . The claim of a relatively large dissociation constant of  $(\text{BH})_2\text{SO}_4 \cdot z\text{HR}$  is substantiated by the conductance of  $0.75 \times 10^{-3}$  *M* solution of the salt (curve 3', Figure 3).

The large increase in conductance after the second equivalence point is due to reaction of HR with B, with formation of the stable homoconjugate  $\text{HR}_2^-$ . Blank experiments with *p*-bromophenol and B have confirmed this postulate.

Because of the large increase of the effective  $K_{\text{HSO}_4^-}^{\text{d}}$ , the potentiometric titration of sulfuric acid with B in the presence of 0.3 *M* *p*-bromophenol yields two breaks (Figure 4), a pronounced one at formation of  $\text{HSO}_4^-$  and a less pronounced one at the second equivalence point.

(17) F. Critchfield and J. Johnson, *Anal. Chem.*, **26**, 1803 (1954).

## Enthalpies of Hydrogen Bonding and Changes in $\Delta\nu_{\text{OH}}$ for a Series of Adducts with Substituted Phenols

Russell S. Drago and T. David Epley<sup>1</sup>

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received July 22, 1968

**Abstract:** The enthalpies of adduct formation for a series of substituted phenols with various Lewis bases have been calorimetrically determined. The acids studied now include  $\text{C}_6\text{H}_5\text{OH}$ , *p*-*t*- $\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{OH}$ , *p*- $\text{ClC}_6\text{H}_4\text{OH}$ , and *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$ . The frequency shifts of the phenols upon complexation,  $\Delta\nu_{\text{OH}}$ , have been measured, and the values for all of the phenols studied are found to lie on the same plot of  $-\Delta H$  vs.  $\Delta\nu_{\text{O-H}}$ . The *E* and *C* parameters (*vide infra*) have been calculated for each of the phenols, and the measured enthalpies are nicely incorporated into this correlation. For a given donor, the enthalpy of adduct formation with this series of phenols correlates with the Hammett substituent constant of the phenol. A procedure is reported which makes it possible to predict enthalpies of adduct formation for any *meta*- or *para*-substituted phenol whose Hammett substituent constant is known with any donor that has been incorporated into the *E* and *C* correlation. The procedure is tested by application to *p*- $\text{FC}_6\text{H}_4\text{OH}$ . The enthalpies predicted this way can be checked with those measured from the O-H frequency shift correlation, eliminating the need for a tedious calorimetric determination of the enthalpy of adduct formation. The accuracy of the predicted enthalpy is as good as the accuracy of the experimental measurement,  $\pm 0.2$  kcal mole<sup>-1</sup>.

We have been involved in an extensive study of the hydrogen-bonding interaction as part of our program in the area of Lewis donor-acceptor interactions.<sup>2</sup> Recently,<sup>2b</sup> a linear relationship was demonstrated between the calorimetrically determined enthalpy of adduct formation and the change in the frequency of the O-H stretching vibration of phenol upon complexation. The relationship is linear over

the range of enthalpies from 4.8 to 9.0 kcal mole<sup>-1</sup>. The existence of a correlation between  $-\Delta H$  and  $\Delta\nu_{\text{OH}}$  has been often challenged,<sup>3-5</sup> but it now appears<sup>2</sup> that poor data or improperly designed experiments have invariably been the cause of claims that such a correlation does not exist. The correlation applies to a large range of donors, including various oxygen and nitrogen

(1) Abstracted in part from the Ph.D. thesis of T. D. Epley, University of Illinois, Urbana, Ill., 1968.

(2) (a) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962); (b) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).

(3) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer *ibid.*, **84**, 3221 (1962).

(4) D. A. K. Jones and J. G. Watkinson, *J. Chem. Soc.*, 2366 (1964).

(5) T. S. S. R. Murty, Doctoral Dissertation, University of Pittsburgh, 1967.

**Table I.** Calorimetric Data for *p*-Chlorophenol-Base Systems

Acid concn, <i>M</i>	Base concn, <i>M</i>	Total vol, ml (solvent)	Measd heat, cal	<i>K</i> , l. mole <sup>-1</sup>	- $\Delta H$ , kcal
[ <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub> ]	(CCl <sub>4</sub> )	H' <sup>a</sup>		
0.02142	0.05298	110.5	5.03	15.8 ± 1.4	5.0 ± 0.2
0.02156	0.10112	110.5	6.69		
0.02131	0.18394	110.5	8.67		
0.02152	0.47306	110.5	10.62		
[ <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> ]	(CCl <sub>4</sub> )	H'		
0.02120	0.03198	110.8	13.19 <sup>b</sup>	207 ± 25	7.3 ± 0.1
0.02154	0.10785	110.5	16.60 <sup>a</sup>		
0.02124	0.20392	110.5	16.81 <sup>a</sup>		
0.02158	0.38910	110.5	17.24 <sup>a</sup>		
[ <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH]	[C <sub>6</sub> H <sub>5</sub> N]	(CCl <sub>4</sub> )	H'		
0.02162	0.03004	110.8	10.73 <sup>c</sup>	116 ± 30	7.0 ± 0.2
0.02174	0.05766	111.0	14.37 <sup>c</sup>		
0.02124	0.11096	110.5	14.60 <sup>a</sup>		
0.02210	0.46217	110.5	16.84 <sup>a</sup>		
[ <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH]	[C <sub>6</sub> H <sub>5</sub> N]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>d</sup>		
0.01983	0.02132	110.1	11.50	211 ± 59	8.1 ± 0.1
0.01981	0.03284	110.2	13.95		
0.01978	0.06070	110.4	15.91		
0.01973	0.07683	110.7	16.17		
0.01960	0.15336	111.4	17.47		
<i>p</i> -[ClC <sub>6</sub> H <sub>4</sub> OH]	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> N]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>e</sup>		
0.01980	0.02014	110.3	13.28	226 ± 26	9.5 ± 0.1
0.01978	0.02687	110.4	15.20		
0.01976	0.03234	110.5	16.23		
0.01972	0.04832	110.8	17.91		
0.01967	0.06516	110.0	19.07		

<sup>a</sup> Corrected for the  $\Delta H_{\text{soln}}$  (3.11 kcal mole<sup>-1</sup>) of 0.5-ml aliquots of the stock solution (3.886 mole l.<sup>-1</sup>) of *p*-chlorophenol in CCl<sub>4</sub>. <sup>b</sup> Corrected for the measured  $\Delta H_{\text{soln}}$  (0.33 kcal mole<sup>-1</sup>) of DMA in CCl<sub>4</sub>. <sup>c</sup> Corrected for the measured  $\Delta H_{\text{soln}}$  (0.36 kcal mole<sup>-1</sup>) of pyridine in CCl<sub>4</sub>. <sup>d</sup> Corrected for the measured  $\Delta H_{\text{soln}}$  (1.90 kcal mole<sup>-1</sup>) of pyridine in C<sub>6</sub>H<sub>12</sub>. <sup>e</sup> Corrected for the measured  $\Delta H_{\text{soln}}$  (2.87 kcal mole<sup>-1</sup>) in C<sub>6</sub>H<sub>12</sub>.

donors. It permits evaluation of the enthalpy of adduct formation, without a tedious calorimetric experiment, by interpolation of the frequency shift. When a type of donor is studied which is completely different from those reported, the enthalpy should be calorimetrically evaluated on at least one system to incorporate said donor type into the correlation with confidence. The studies to date have involved phenol as the acceptor, and there is no reliable experimental information available to indicate whether other hydrogen-bonding acids will fall on the same plot, give a different straight-line plot, or lead to no correlation at all.

The existence of the frequency shift-enthalpy correlation was given substantial support by an analysis providing a theoretical basis for the relationship.<sup>6</sup> It was further predicted that other hydrogen-bonding acids should give linear correlations, and the slope of the line for a given acid should be a function of the inherent acidity of the hydroxyl compound. Thus, it is of interest to see if the presence of a substituent on the benzene ring will effect the acidity enough to require a different line for each substituted phenol or whether the change would be so slight that all phenolic compounds would fall, within experimental error, on the same frequency line that phenol does.

## Experimental Section

**Purification of Materials.** The solvents and donors used in this study were purified by procedures previously reported.<sup>2</sup>

Phenol and *p*-chlorophenol (Eastman White Label) were purified

according to a reported method<sup>7</sup> and the middle distillation fractions are stored under refrigeration in a light-free desiccator. These samples are then sublimed at 0.1 mm shortly before using.

*m*-Trifluoromethylphenol (Aldrich, Pierce) is dried over Linde 4A sieves and then distilled at reduced pressure three times until colorless and chromatographically pure.

*p*-Butylphenol (Eastman) is recrystallized twice from dry carbon tetrachloride and then sublimed with heating at 0.1 mm shortly before using.

**Procedure.** The calorimetric procedure employed is similar to that previously reported.<sup>2</sup> Two general procedures were employed depending upon the solubility of the phenols. Either the pure donor was added to a carbon tetrachloride solution of the phenol in the calorimeter or a very concentrated solution of the phenol (~4.5 *M*) was added to a carbon tetrachloride solution of the donor in the calorimeter. The latter procedure was employed for phenol and *p*-chlorophenol in CCl<sub>4</sub> and phenol in cyclohexane. Since *m*-trifluoromethylphenol is a liquid soluble in cyclohexane and CCl<sub>4</sub>, this same technique was employed with this acid. In all other systems reported, pure donor was added to the phenol solution in the calorimeter. Necessary corrections for the heat of solution were applied in all instances. The determination and calculation of the enthalpies and equilibrium constants were accomplished simultaneously from calorimetric data by a procedure similar to that reported previously.<sup>2</sup> A new program has been developed that uses a minimum seeking method<sup>8</sup> that has been incorporated into a general minimization routine, SIMPLEX.<sup>9</sup> In this program initial guesses are made for the enthalpy of reaction and the 1:1 equilibrium constant, and these two parameters are simultaneously varied until their best values are found with respect to a minimized CHSQ fit of the calculated and observed calorimetric heats. Some slight difference (generally ~0.1 kcal mole<sup>-1</sup>) in values calculated by this procedure and those previously reported<sup>2</sup> resulted.

(7) O. J. Draper and A. L. Pollard, *Science*, **109**, 448 (1949).

(8) J. A. Nelder and R. Mead, *Computer J.*, **8**, 308 (1965).

(9) The general minimization routine, SIMPLEX, has been copyrighted by J. P. Chandler of the University of Indiana Physics Department, 1965.

(6) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2874 (1967).

Table II. Calorimetric Data for *m*-Trifluoromethylphenol-Base Systems

Acid concn, <i>M</i>	Base concn, <i>M</i>	Total vol, ml (solvent)	Measd heat, cal	<i>K</i> , l. mole <sup>-1</sup>	- $\Delta H$ , kcal mole <sup>-1</sup>
[ <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub> ]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>a</sup>		
0.01540	0.03199	110.2	5.93	43 ± 7	6.8 ± 0.1
0.01563	0.07357	110.2	8.60		
0.01564	0.08882	110.2	8.97		
0.01549	0.22733	110.2	10.36		
0.01577	0.44467	110.2	11.40		
[ <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH]	[(CH <sub>2</sub> ) <sub>5</sub> C=O]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>a</sup>		
0.01923	0.09478	110.2	13.31	71 ± 15	7.4 ± 0.1
0.01919	0.18195	110.2	14.27		
0.01978	0.28719	110.2	15.17		
0.01958	0.43720	110.2	15.58		
[ <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> ]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>a</sup>		
0.01974	0.02890	110.2	19.39	Large	10.3 ± 0.4
0.01885	0.05286	110.2	19.55		
0.01919	0.10640	110.2	20.55		
0.01959	0.38403	110.2	22.93		
[ <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> ]	(CCl <sub>4</sub> )	H' <sup>b,c</sup>		
0.02158	0.02780	110.2	15.12	768 ± 166	7.3 ± 0.1
0.02065	0.04428	110.2	15.70		
0.02098	0.05618	110.2	16.35		
0.02048	0.06986	110.2	15.95		
0.02071	0.07344	110.2	16.13		
0.02070	0.08270	110.2	16.26		
0.02039	0.14354	110.2	16.25		
[ <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH]	[C <sub>6</sub> H <sub>5</sub> N]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>a</sup>		
0.01879	0.02468	110.2	13.98	400 ± 142	8.5 ± 0.1
0.01969	0.04500	110.2	16.59		
0.01942	0.09000	110.2	17.36		
0.01952	0.16638	110.2	18.03		

<sup>a</sup> Corrected for the  $\Delta H_{\text{soln}}$  (4.92 kcal mole<sup>-1</sup>) of *m*-trifluoromethylphenol in C<sub>6</sub>H<sub>12</sub>. <sup>b</sup> Measured by Dr. W. Partenheimer. <sup>c</sup> Corrected for  $\Delta H_{\text{soln}}$  (3.64 kcal mole<sup>-1</sup>) of *m*-trifluoromethylphenol in CCl<sub>4</sub>.

The precision of our experiment as manifested by the standard deviation in  $\Delta H$  is very high, often better than 0.05 kcal mole<sup>-1</sup>. The error limits reported for the enthalpies finally selected indicate the accuracy of our values. For several systems a slight trend (see Results) in the equilibrium constant and enthalpy values was noted with change in concentration of the donor, and our reported error was increased to take this into account. In general, we feel that many authors working on systems of this type employing spectrophotometric and this calorimetric technique have overestimated the accuracy of their results, and at best, most reported values for the enthalpy are within  $\pm 0.2$  kcal mole<sup>-1</sup> of the true standard thermodynamic values.

It is inherent in the nature of this calorimetric procedure that the size of the error in *K* increases with the magnitude of *K*. However, the error in the value for  $-\Delta H$ , our prime concern, becomes correspondingly less sensitive to the value of *K* when *K* is large, and an accurate enthalpy can still be obtained.

## Results

The concentrations, measured heats, and calculated thermodynamic parameters are presented in Tables I-III for various donors with *p*-chlorophenol, *m*-trifluoromethylphenol, and *p-t*-butylphenol, respectively. The values employed for the  $\Delta H_{\text{soln}}$  correction are average values from four to six determinations.

## Discussion

**Medium Effects.** As previously described,<sup>10</sup> the enthalpy change and equilibrium constant are determined by plotting the functional dependence of *K*<sup>-1</sup> and  $-\Delta H$  for a series of acid-base concentration pairs. The intersection of the lines for the different solutions indicates the value of *K*<sup>-1</sup> and  $-\Delta H$  that simultaneously fits

(10) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965).

all sets of data. Many of our systems show a triangular pattern arising from the spread of the interactions of lines arising from different concentration pairs. So instead of a single, sharp intersection point representing a unique solution of *K*<sup>-1</sup> and  $-\Delta H$  for all solutions studied, there is a monotonic increase in the calculated enthalpies with increasing base concentrations at a given value of *K*<sup>-1</sup>. This problem is most severe with weak donor, high-polarity molecules, e.g., CH<sub>3</sub>CN. By taking care to eliminate unnecessarily large base concentrations (an upper limit of 0.5 mole l.<sup>-1</sup> for most weak bases ranging downward to a maximum of 0.06 mole l.<sup>-1</sup> for strong bases having large *K*'s), it is possible to minimize these concentration effects.

An even more pronounced medium effect is seen when one compares, in Tables II and III, values obtained for identical acid-base pairs in the two "inert" solvents carbon tetrachloride and cyclohexane. Since cyclohexane shares with carbon tetrachloride such attributes as low dielectric constant, low dipole moment, lack of specific Lewis acid-base sites, and an even lower polarizability, it is commonly considered to be carbon tetrachloride's equal as a general-use "inert" solvent for studying acid-base interactions. However, in our work, the calculated  $\Delta H$  value in cyclohexane is found to be more negative than that measured in carbon tetrachloride. This cyclohexane enthalpy "enhancement" ranges from approximately 1.7 to 3.0 kcal mole<sup>-1</sup> (depending on the acid) for dimethylacetamide as base. The pyridine discrepancy is at most 0.5 kcal mole<sup>-1</sup> from our estimate of the correct value. The values in Table I show a discrepancy of 1.1 kcal mole<sup>-1</sup> in the

Table III. Calorimetric Data for *p*-Butylphenol-Base Systems

Acid concn, <i>M</i>	Base concn, <i>M</i>	Total vol, ml (solvent)	Measd heat, cal	<i>K</i> , l. mole <sup>-1</sup>	- $\Delta H$ , kcal mole <sup>-1</sup>
[ <i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> ]	(CCl <sub>4</sub> )	H' <sup>a</sup>		
0.01846	0.02754	110.3	7.18	79 ± 3	6.4 ± 0.1
0.01842	0.04633	110.5	9.51		
0.01840	0.05745	110.6	9.99		
0.01838	0.06714	110.7	10.54		
[ <i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> OH]	[CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> ]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>b</sup>		
0.01785	0.01713	110.2	10.10	274 ± 46	8.1 ± 0.2
0.01783	0.02569	110.3	11.89		
0.01783	0.02836	110.3	12.34		
0.01781	0.03929	110.4	13.92		
0.01780	0.04884	110.5	14.01		
0.01776	0.06710	110.7	14.99		
[ <i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> OH]	[C <sub>5</sub> H <sub>5</sub> N]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>c</sup>		
0.01784	0.02422	110.2	7.28	71.7 ± 0.3	7.2 ± 0.1
0.01781	0.04521	110.4	9.86		
0.01778	0.07014	110.6	11.26		
0.01776	0.07791	110.7	11.51		
[ <i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> OH]	[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N]	(C <sub>6</sub> H <sub>12</sub> )	H' <sup>d</sup>		
0.01783	0.01944	110.3	8.54	106 ± 5	8.3 ± 0.1
0.01780	0.02942	110.4	10.86		
0.01779	0.03352	110.5	11.21		
0.01778	0.03901	110.6	11.95		
0.01775	0.05066	110.8	13.15		

<sup>a</sup> Corrected for the  $\Delta H_{\text{soln}}$  (0.33 kcal mole<sup>-1</sup>) of DMA in CCl<sub>4</sub>. <sup>b</sup> Corrected for the  $\Delta H_{\text{soln}}$  (3.15 kcal mole<sup>-1</sup>) of DMA in C<sub>6</sub>H<sub>12</sub>. <sup>c</sup> Corrected for the  $\Delta H_{\text{soln}}$  (1.90 kcal mole<sup>-1</sup>) of pyridine in C<sub>6</sub>H<sub>12</sub>. <sup>d</sup> Corrected for the  $\Delta H_{\text{soln}}$  (0.284 kcal mole<sup>-1</sup>) of Et<sub>3</sub>N in C<sub>6</sub>H<sub>12</sub>.

CCl<sub>4</sub> and cyclohexane enthalpies, but the value in CCl<sub>4</sub> is expected to be at least 0.5 kcal mole<sup>-1</sup> low because of the interaction of CCl<sub>4</sub> with pyridine.

Although cyclohexane was routinely used as a solvent for pyridine and triethylamine to avoid the complicating interactions<sup>11-13</sup> with carbon tetrachloride, the large anomalies observed when it was used for studies on weaker, polar bases, especially dimethylacetamide, were quite unexpected.

The *m*-trifluoromethylphenol series is the one most extensively studied in cyclohexane. Numerous arguments can be presented which suggest that the  $\Delta H$  values of this acid with the bases ethyl acetate, cyclohexanone, and dimethylacetamide in cyclohexane were too large. These arguments are based upon the bulk of accumulated evidence for other acid-base systems and are summarized in Table IV. As can be seen, all of this evidence supports the suspicion that the cyclohexane data are incorrect. The most compelling evidence comes from the discrepancy in the measured enthalpy values in CCl<sub>4</sub> and cyclohexane for both *m*-trifluoromethylphenol and *p*-*t*-butylphenol interacting with CH<sub>3</sub>C(O)N(CH<sub>3</sub>)<sub>2</sub>.

The ideal solvent for acid-base reactions provides a medium containing "weakly" solvated, monomolecular acid and base species which can react to form a 1:1 adduct that will also be "weakly" solvated. Hopefully, all of the heats of solvation terms involved in the reaction will cancel out leaving a measured  $\Delta H$  which closely approximates a gas-phase value. In practice, only the phenols are known, *via* infrared evidence, to be monomolecular in both solvents; the bases are more highly associated. The molecular weight of approximately

Table IV. Predicted Enthalpies for *m*-Trifluoromethylphenol Compared to Those Measured in Cyclohexane

Base	- $\Delta H$ , kcal mole <sup>-1</sup> <sup>a</sup>	Predicted - $\Delta H$ , kcal mole <sup>-1</sup>
CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	6.8	5.0, <sup>b</sup> 5.2, <sup>c</sup> 5.1 <sup>d</sup>
(CH <sub>2</sub> ) <sub>2</sub> C=O	7.4	5.6 <sup>b</sup>
CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	10.3	7.1, <sup>b</sup> 7.4, <sup>c</sup> 7.3, <sup>d</sup> 7.3 <sup>e</sup>
C <sub>5</sub> H <sub>5</sub> N	8.5	8.7, <sup>b</sup> 8.7, <sup>c</sup> 8.7 <sup>d</sup>

<sup>a</sup> Measured in cyclohexane. Values taken from Table II. <sup>b</sup> Calculated from  $\Delta H$  vs.  $\Delta\nu_{\text{OH}}$  correlation; see next section. <sup>c</sup> Calculated from  $\Delta H$  vs.  $\sigma$  correlation; *vide infra*. <sup>d</sup> Calculated from *E* and *C* relationship; see Discussion. <sup>e</sup> Measured in CCl<sub>4</sub>.

0.01-0.2 *M* solutions of dimethylacetamide in carbon tetrachloride is 240 g mole<sup>-1</sup>, around three molecules per unit, while that of a nearly equal concentration of dimethylacetamide in cyclohexane is approximately 1000 g mole<sup>-1</sup>, almost 12 molecules per aggregate. The measurements were made in this study by vapor pressure osmometry. Obviously, the carbon tetrachloride solution more closely approximates the ideal base solution. Further, if the problem were only one of providing the additional energy needed to break up the base aggregates in order to form phenol adducts, one would expect a net loss in measured enthalpy instead of the enhancement found. Moreover, the system would not fit a 1:1 equilibrium constant expression. The conclusion, then, is that there exists some sort of extrasolvation effect (or effects) in cyclohexane which is related to a change in the nature of the reaction medium because of the large aggregates of dimethylacetamide present. We propose that the phenol adduct which possessed an enhanced dipole moment compared to those of the reactants<sup>14</sup> is solvated more extensively by the large aggregates in cyclohexane than by the smaller ones in CCl<sub>4</sub>. Indeed,

(11) P. Datta and G. M. Barrow, *J. Am. Chem. Soc.*, **87**, 3053 (1965).  
 (12) K. N. C. Doris and M. F. Former, *J. Chem. Soc., B*, 28 (1967).  
 (13) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **62**, 2063 (1966).

(14) E. Osawa and Z. Yoshida, *Spectrochim. Acta*, **23A**, 2029 (1967);  
 D. Hadzi, H. Ratajczak, and L. Sobczyk, *J. Chem. Soc., A*, 48 (1967).

Table V.  $\Delta\nu_{\text{OH}}$  Values for Phenol-Base Adducts

Acid, no. <sup>a</sup>	Base	$\Delta\nu_{\text{OH}}$ , cm <sup>-1</sup> <sup>b</sup>
Phenol		
1	CH <sub>3</sub> CN	150 <sup>18</sup>
2	CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	164
3	(CH <sub>3</sub> ) <sub>2</sub> CO	193
4	C <sub>4</sub> H <sub>8</sub> O	285
5	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	345
6	C <sub>5</sub> H <sub>5</sub> N	465 ± 10
7	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	556 ± 20 <sup>c</sup>
<i>p</i> -Chlorophenol		
8	CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	179
9	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	376 ± 8
10	C <sub>5</sub> H <sub>5</sub> N	491 ± 8
11	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	586 ± 20 <sup>c</sup>
<i>m</i> -Trifluoromethylphenol		
12	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	391 ± 8
13	C <sub>5</sub> H <sub>5</sub> N	544
<i>p</i> -Butylphenol		
14	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	320
15	C <sub>5</sub> H <sub>5</sub> N	441 ± 7
16	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	531 ± 15 <sup>c</sup>

<sup>a</sup> These numbers correspond to the labeled points for each phenol-base pair in Figure 1. <sup>b</sup> Estimated values at infinite dilution in CCl<sub>4</sub> as solvent. Unless otherwise stated the error limits are ± 5 cm<sup>-1</sup> or less. <sup>c</sup> There is controversy over this value. The O-H shift is so large that overlap of this vibration with C-H from the phenol and base interfere. Even if the correct  $\Delta\nu_{\text{OH}}$  is some 50 cm<sup>-1</sup> larger for all (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N donors, an equally good straight line with slightly different slope and intercept can be drawn through these data.

the enthalpy of adduct formation of DMA with phenol in cyclohexane is very close to the value measured in pure DMA. The enthalpies of formation of the phenol adduct with DMA measured in CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>, and DMA as solvents are 6.7,<sup>2</sup> 8.2,<sup>15</sup> and 7.9,<sup>5</sup> respectively. Better results are expected for donors that are not very polar in the solvent cyclohexane. For example, enthalpies of adduct formation for both pyridine and triethylamine in the solvent cyclohexane agree well with those predicted from  $\Delta\nu_{\text{OH}}$  and the *E* and *C* correlation. The value of 7.9 reported in DMA is that obtained by Murty<sup>5</sup> when his "anisole correction" is not utilized.

**Infrared Frequency Relationship.** As indicated in the introductory section, the existence of a linear relationship between the change in the infrared wave number of a phenolic (O-H) group upon coordination ( $\Delta\nu_{\text{OH}}$ ) and the measured enthalpy ( $\Delta H$ ) of that reaction is a controversial topic. Any successful empirical approach to this problem requires two things: (1) a respectable number of accurate enthalpy values and (2) correspondingly reliable  $\Delta\nu_{\text{OH}}$  values. Previous analyses of the situation suffered from the inaccuracies of spectrophotometrically determined enthalpies.

Allerhand and Schleyer<sup>16</sup> have demonstrated that the  $\Delta\nu_{\text{OH}}$  values of phenol adducts exhibit varying concentration dependencies which are a function of the base-solvent concentration. More care must be taken with  $\Delta\nu_{\text{OH}}$  measurements than has often been shown. The shift values reported in Table V were all checked for concentration effects and unless otherwise noted were measured in carbon tetrachloride. The error limits

(15) This value was determined by using *t*-butylphenol, but similar enthalpies are obtained for this acid and phenol. The enthalpy for phenol-DMA in pure DMA was stated incorrectly to be that for *t*-butylphenol in a previous communication: W. Partenheimer, T. D. Epley, and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 3886 (1968).

(16) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 371 (1963).

reflect the visually estimated degree of uncertainty in the measurements.

Purcell and Drago<sup>6</sup> have postulated that for a series of bases the slope of the  $\Delta\nu_{\text{OH}}$  vs.  $\Delta H$  line may vary for different phenolic acids according to the strength of the acid, each thereby requiring separate linear correlations. Thus, it was of interest to obtain the result of a systematic calorimetric study of a series of substituted phenols with a range of bases.

The substituted phenols used here were chosen to demonstrate a reasonably wide variation in the acidity of the (O-H) group without providing an alternative basic site to compete with the base, e.g., CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OH. *ortho*-Substituted phenols were omitted because of the possibility of intramolecular hydrogen bonding and the unpredictability of steric effects. All phenols were shown to be unassociated at the concentrations employed in our measurements.

Figure 1 is a least-squares plot of the values of  $\Delta\nu_{\text{OH}}$  vs. all of the available calorimetric data reported in this paper. The question of whether the data for all substituted phenols fit only the one line shown in this graph is best answered by first giving the equation found for the seven bases studied with phenol<sup>6</sup> itself.

$$-\Delta H \text{ (kcal mole}^{-1}\text{)} = 0.0105\Delta\nu_{\text{OH}} \text{ (cm}^{-1}\text{)} + 2.99 \quad (1)$$

with an estimated error in the slope of  $\pm 6.5 \times 10^{-4}$  and a standard deviation in the calculated  $\Delta H$  of  $\pm 0.22$  kcal mole<sup>-1</sup>. This can be compared with the over-all equation utilizing four phenolic acids for a total of 16 data points.

$$-\Delta H \text{ (kcal mole}^{-1}\text{)} = 0.0103\Delta\nu_{\text{OH}} \text{ (cm}^{-1}\text{)} + 3.08 \quad (2)$$

with an estimated error in the slope of  $\pm 4.6 \times 10^{-4}$  and a standard deviation in  $\Delta H$  of  $\pm 0.18$  kcal mole<sup>-1</sup>. These two equations can be taken as essentially identical within the over-all error limits set for our correlation of  $\pm 0.2$  kcal mole<sup>-1</sup>.

A further examination of the reported<sup>6</sup> theoretical justification of a linear relationship between  $\Delta\nu_{\text{OH}}$  and  $\Delta H$  is needed.  $\Delta H$  is divided into two terms:  $\delta E_{\text{OH}}$ , the change in the phenolic (O-H) bond energy, and  $E_{\text{HB}}$ , the bond energy of forming the new hydrogen bond to the base. Then by using an anharmonic diatomic oscillator and assuming the (O-H) anharmonicity constant,  $\chi_e$ , does not change on hydrogen bonding, the following relationship is derived

$$\delta E_{\text{OH}} = -\frac{hcN}{(4\chi_e)}\Delta\nu_{\text{OH}} \quad (3)$$

where *h* is Planck's constant in kcal sec molecule<sup>-1</sup>, *c* is the speed of light, *N* is Avogadro's number, and  $\Delta\nu_{\text{OH}}$  is an approximation of  $\delta\omega_e$ , the harmonic oscillator's vibrational energy in cm<sup>-1</sup>.

Unfortunately, it was necessary to assume that  $\chi_e$  was unchanged upon hydrogen-bond formation. In a series of papers by Sandorfy, *et al.*,<sup>17-20</sup> on the behavior of both free and hydrogen-bonded (O-H) anharmonicities in both gas and liquid carbon tetrachloride phases, it was concluded that "there is a well-pronounced increase in mechanical anharmonicity for the first over-

(17) G. Durocher and C. Sandorfy, *J. Mol. Spectrosc.*, **22**, 347 (1967).

(18) C. Berthomieu and C. Sandorfy, *ibid.*, **15**, 15 (1965).

(19) G. Durocher and C. Sandorfy *ibid.*, **15**, 22 (1965).

(20) A. F. Oldes and C. Sandorfy *ibid.*, **20**, 262 (1966).

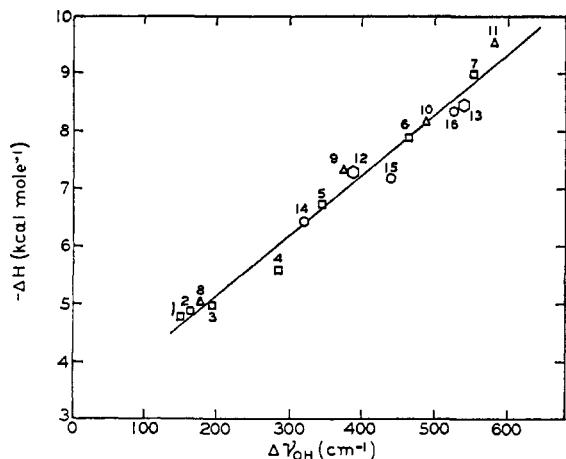


Figure 1. A plot of  $\Delta\nu_{\text{OH}}$  ( $\text{cm}^{-1}$ ) vs.  $\Delta H$  ( $\text{kcal mole}^{-1}$ ) for different phenol-base combinations:  $\circ$ , *p*-*t*-butylphenol as acid;  $\square$ , phenol as acid;  $\triangle$ , *p*-chlorophenol as acid;  $\circ$ , *m*-trifluoromethylphenol as acid. The number assigned to each point on the graph corresponds to the one listed for a specific acid base pair in Table V.

tone as a consequence of hydrogen bonding."<sup>19</sup> Further, they found<sup>20</sup> that there were significant changes in  $\chi_e$  depending on which set of overtone frequencies were used in its calculation, and that "the  $\chi_{12} = \chi_{23}$  approximation... breaks down completely when hydrogen bonds are formed." All of the measurements indicate a rather complex situation exists for hydrogen-bonded  $\chi_e$  values in which the contribution of higher anharmonic terms to the anharmonicity cannot be neglected. However, it is significant that all hydrogen-bonded examples studied by Sandorfy were either of the polymeric or intramolecularly bonded type. Thus one can question the generality of their conclusions and their pertinence to the phenol-base adduct model.

The relative importance of  $\chi_e$  also enters into the previous theoretical treatment<sup>6</sup> in another manner. Final recasting of the  $\Delta H$  vs.  $\Delta\nu_{\text{OH}}$  relationship in terms of eq 3 is

$$\Delta H = \left( \frac{1}{k'} - \frac{hcN}{4\chi_e} \right) \Delta\nu_{\text{OH}} + \text{constant} \quad (4)$$

where  $k'$  is the slope of a plot of  $\delta E_{\text{OH}}$  and  $E_{\text{HB}}$  and purportedly "is a measure of the susceptibility of the (O-H) bond to distortion by a Lewis base."

Since the work presented in this study has supposedly shown, within experimental error, that all phenolic acid-base reactions studied adhere to eq 2, we can, therefore, equate the following terms from eq 4.

$$\text{constant} = 3.08 \quad (5)$$

$$\left( \frac{1}{k'} - \frac{hcN}{4\chi_e} \right) = -0.0103 \quad (6)$$

Thus, for these phenols,  $k'$  is directly dependent on the relative values of  $\chi_e$ , all other terms being constants. Assume, as was done in the original paper, that  $\chi_e$  can be taken as the value measured for the nonhydrogen-bonded phenols. The question now becomes one of determining the relative changes in  $\chi_e$  for these phenols and assessing their effects on  $k'$ . For example, Purcell and Drago report carbon tetrachloride solution values of  $\chi_e$  (based on the average  $\chi_{13}$ ,  $\chi_{14}$ ,  $\chi_{34}$ ) for *p*-chlorophenol of  $2.29 \times 10^{-2}$  and for phenol of  $2.24 \times 10^{-2}$ .

Yet, by using more elaborate experimental methods, Sandorfy<sup>19</sup> reports phenol anharmonicities (based on the first and second overtones in carbon tetrachloride) of  $\chi_{12} = 2.20 \times 10^{-2}$ ,  $\chi_{23} = 2.15 \times 10^{-2}$ , and  $\chi_{13} = 2.20 \times 10^{-2}$ . Clearly, experimental error precludes any differentiation between the  $\chi_e$ 's, and therefore the  $k'$ 's, from the above data for the two phenols. It is interesting to note, keeping in mind our earlier reservations, that the anharmonicities of phenol,<sup>19</sup> upon polymerization, go to  $\chi_{12} = 3.44 \times 10^{-2}$ ,  $\chi_{23} = 2.69 \times 10^{-2}$ , and  $\chi_{13} = 3.07 \times 10^{-2}$ . If changes of such magnitude also occurred in the hydrogen-bonded adducts, there might be a significant difference between the  $\chi_e$  values of the two phenols, but these values, in turn, would probably be dependent upon the bases chosen and would leave us with no property solely that of the acid.

It seems fair to conclude from present data that the preliminary information upon which the  $k'$  values of phenol and *p*-chlorophenol were differentiated was insufficient and that no significant difference between these two phenols can be detected by this parameter. These results do not refute the theoretical model since it is likely that for substantially different acids both the slopes and the  $\chi_e$  values will differ. Studies on these systems are underway and will provide a better test of the correctness of the model.

**Hammett Substituent Constant Relationship.** Hammett's substituent constants,  $\sigma$ , were originally developed to predict the effect of ring substituents on the reactivity of the functional groups of many classes of aromatic compounds.<sup>21</sup> The Gibbs free energy,  $\Delta G$ , was originally correlated by these constants but there is ample evidence to support the existence of similar correlations with several other measurable parameters which are characteristic of the phenolic (O-H) groups. Linear correlations exist between Hammett substituent constants and both the change in the (O-H) frequencies of substituted phenols measured in carbon tetrachloride<sup>22-24</sup> and the logs of the (O-H) absorption intensities measured in the same solvent.<sup>22</sup> By use of a statistical thermodynamic approach, Ritchie and Sager<sup>21</sup> have shown, for linear harmonic oscillators, a theoretical expectation of a linear enthalpy and entropy relationship in systems such as substituted phenols and further suggested that this could lead to  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  all being linearly related to  $\sigma$ . Person<sup>25</sup> and Leffler<sup>26</sup> have also discussed linear  $\Delta H$  vs.  $\Delta S$  relationships, and such proportionality for several phenol-donor systems have been reported by Joesten and Drago.<sup>2a</sup> However, the possibility of obtaining a general set of  $\Delta H$  vs.  $\sigma$  correlations for a number of substituted phenols with a wide range of bases is practically unexplored.

A plot of  $\sigma$  for a series of *para*-substituted phenols vs.  $\Delta H$  appears in Figure 2. A reasonable linearity is seen for the four acids and bases shown. The line slopes,  $\rho'$ , can be seen to increase monotonically with increasing base strength. The  $\rho'$  values are 0.59 for ethyl acetate,

(21) See, for example, C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

(22) P. J. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 17 (1957).

(23) T. L. Brown, *J. Phys. Chem.*, **61**, 820 (1957).

(24) A. Cabana, J. L. Patenaude, C. Sandorfy, and P. M. G. Bavin, *ibid.*, **64**, 1941 (1960).

(25) W. B. Person, *J. Am. Chem. Soc.*, **84**, 536 (1962).

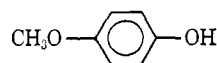
(26) J. E. Leffler, *J. Org. Chem.*, **31**, 533 (1966).

Table VI.  $E$  and  $C$  Numbers<sup>a</sup>

Molecule	$E_A$	$C_A$	Molecule	$E_B$	$C_B$
$C_6H_5OH$	4.22	0.591	$CH_3C(O)OC_2H_5$	0.836	1.96
$p\text{-ClC}_6H_4OH$	4.25	0.621	$CH_3C(O)N(CH_3)_2$	1.25	2.70
$m\text{-CF}_3C_6H_4OH$	4.43	0.658	$C_5H_5N$	0.943	6.62
$p\text{-}t\text{-C}_4H_9C_6H_4OH$	3.86	0.589	$(C_2H_5)_3N$	0.466	11.50

<sup>a</sup> The numbers reported here represent an improved set over those originally reported<sup>27</sup> by virtue of the increased amount of information now available.

1.58 for dimethylacetamide, 2.01 for pyridine, and 2.73 for triethylamine. The line slope for a given base invites a comparison to the  $\rho$  values found for different classes of reactants in  $\sigma$  vs.  $\Delta G$  relationships. Thus,  $\rho'$  is considered to be connected with the reactivity of the base. We are thus in a position to estimate the enthalpy of adduct formation for any *meta*- or *para*-substituted phenol with these four donors by interpolating  $-\Delta H$  for the Hammett substituent constant value from the plot in Figure 2. If the phenol is associated, *e.g.*



the value obtained will be that corresponding to the unassociated acid undergoing interaction. The magnitude of  $\Delta\nu_{OH}$  serves as an additional check on the interpolated enthalpy.

**$E$  and  $C$  Parameters.** The value of  $\rho'$  for other bases cannot be predicted and would have to be obtained by measuring enthalpies of adduct formation for each base with at least two substituted phenols. The  $E$  and  $C$  correlation<sup>27</sup> makes this unnecessary. In this treatment two empirical constants are determined for each acid ( $E_A$  and  $C_A$ ) and two for each base ( $E_B$  and  $C_B$ ) such that when substituted into eq 7, they reproduce the experimental enthalpies. If the Hammett substituent constant for the phenol substituent is known, four enthalpies of adduct formation of donors with this substituted phenol are available from Figure 2.  $E_A$  and  $C_A$  parameters for the substituted phenol can be obtained by solving the four simultaneous equations resulting from substituting the known  $\Delta H$ ,  $C_B$ , and  $E_B$  values into

$$-\Delta H = C_A C_B + E_A E_B \quad (7)$$

(Four enthalpies and reported  $C_B$  and  $E_B$  parameters for the four donors in Figure 2 lead to four equations.) With these  $E_A$  and  $C_A$  numbers the enthalpy of adduct formation can be calculated for this acid interacting with any donor that has been incorporated into the  $E$  and  $C$  correlation. This calculated heat can be compared with that interpolated from the  $\Delta\nu_{OH}$  plot.

Table VI lists  $E$  and  $C$  numbers for the molecules involved in this study. Within experimental error, all of the enthalpies of adduct formation are reproduced by substitution of these quantities into eq 7. Values of  $\rho'$  could now be calculated for any donor in the  $E$  and  $C$  correlation.

As a test of the proposals, we can estimate enthalpies of adduct formation for the hydrogen-bonding interaction of *p*-fluorophenol with various donors. By using the substituent constant value of +0.062, enthalpies of 4.9, 6.8, 7.8, and 9.1 are predicted for the ethyl

(27) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

acetate, *N,N*-dimethylacetamide, pyridine, and triethylamine adducts, respectively, from Figure 2. When the four simultaneous equations (eq 7) are solved,  $E_A$  and  $C_A$  values of 4.16 and 0.614, respectively, result. By

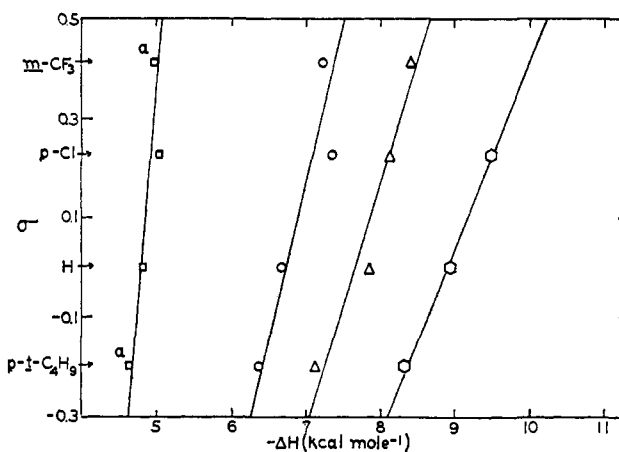


Figure 2. A plot of  $\sigma$  vs.  $-\Delta H$  (kcal mole<sup>-1</sup>) for four phenols reacting with four bases:  $\square$ , ethyl acetate as base;  $\circ$ , *N,N*-dimethylacetamide as base;  $\Delta$ , pyridine as base;  $\diamond$ , triethylamine as base; a,  $-\Delta H$  values calculated from eq 2.

using these  $E_A$  and  $C_A$  values along with those for various donors, we calculate the enthalpies listed in column 4, Table VII. These can be compared with the

Table VII. Various Predicted and Measured Enthalpies (kcal mole<sup>-1</sup>) of Hydrogen-Bond Formation to *p*-Fluorophenol

	$-\Delta H^a$	$\Delta\nu_{OH}$	$-\Delta H^b$	$-\Delta H$ (calcd $E$ and $C$ )	$-\Delta H^c$
THF	5.9	292	6.0	5.9	
DMF	7.2	297	6.1	6.5	
$Et_2O$	5.6	285	6.0	5.7	
$C_5H_5N$	7.4	489	8.1	7.9	7.8
DMSO		367	6.9	7.2	
$EtOAc$		176	4.9	4.8	4.9
$C_6H_5OCH_3$	3.1	164	4.8	...	
$(C_2H_5)_3N$	8.9	576	9.0	9.0	9.1
$CH_3CON(CH_3)_2$		357	6.8	6.9	6.8

<sup>a</sup> These enthalpies were determined by T. S. R. Murty and were kindly made available to us by Professor E. M. Arnett. We have selected values determined in  $CCl_4$  (except for pyridine). A few measured in the nonpolar donors as solvent were selected if solvent corrections were reported to be slight. The  $\Delta\nu_{OH}$  values were also reported by these authors. <sup>b</sup> Enthalpies predicted from  $\Delta\nu_{OH}$ . <sup>c</sup> Enthalpies interpolated from Figure 2 using the reported Hammett substituent constant for fluorine.

enthalpies calculated from reported values of  $\Delta\nu_{OH}$  for *p*-fluorophenol by using eq 2 (second column) and

those determined<sup>5</sup> calorimetrically which are listed in the first column.

The agreement between enthalpies from the Hammett substituent constant,  $E$  and  $C$  correlations, and  $\nu_{\text{OH}}$  are excellent. For the most part those calorimetrically determined are in good agreement. The donor DMF is less well behaved and may result from problems in purification. The frequency shift for the DMF adduct is unreasonable when compared to that of DMA. As previously reported,<sup>28</sup> there are two donor sites in anisole, and this also could be a complicating factor in this system giving rise to a poor  $\nu_{\text{OH}}-\Delta H$  correlation.

The many-sided procedures for estimating  $\Delta H$  on

(28) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **86**, 5240 (1964).

substituted phenol systems should enable one to readily estimate these enthalpies with considerable confidence. The medium effects demonstrated here must be seriously considered when pertinent to carrying out these measurements. If a measured piece of data is not consistent with the correlations presented here, the absence of medium or other complicating effects must be clearly demonstrated before one can conclude that these correlations are inapplicable. The consistency of these predictions with the Hammett substituent model should cause concern for those critics<sup>3-5</sup> of our correlations.

**Acknowledgment.** The authors acknowledge with thanks the generous support of the National Science Foundation through Grant No. 5498. T. D. E. is grateful to the Paint Research Institute for a fellowship.

## The Crystal Structure of $\pi$ -Cyclopentadienylbis(acetylacetonato)chlorozirconium(IV)

John J. Stezowski and Harry A. Eick

*Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. Received September 20, 1968*

**Abstract:** The crystal structure of  $\pi$ -cyclopentadienylbis(acetylacetonato)chlorozirconium(IV),  $\pi\text{-C}_5\text{H}_5(\text{C}_5\text{H}_7\text{O}_2)_2\text{-ZrCl}$ , which crystallizes with the symmetry of the monoclinic space group  $P2_1/c$ , has been determined by equiinclination Weissenberg single-crystal X-ray diffraction techniques. The theoretical density ( $1.553 \text{ g cm}^{-3}$ ) calculated for four molecules per unit cell with the observed lattice parameters ( $a = 8.42 \pm 0.01$ ,  $b = 15.66 \pm 0.01$ ,  $c = 15.17 \pm 0.02 \text{ \AA}$ ,  $\beta = 123^\circ 25' \pm 4'$ ) is in agreement with the measured value ( $1.556 \pm 0.005 \text{ g cm}^{-3}$ ). The final discrepancy factor,  $R = 0.092$ , results from a full-matrix least-squares refinement of visually estimated relative intensities for 1453 reflections ( $\sin \theta/\lambda \leq 0.54 \text{ \AA}^{-1}$ , Cu  $K\alpha$  radiation). The observed dodecahedral stereochemical configuration of the molecule is compatible with  $\pi$  bonding between the cyclopentadienyl ligand and the zirconium atom and also appears to allow  $d_{\pi}-p_{\pi}$  interaction between B oxygen and the zirconium atoms. Intermolecular forces within the lattice, which exhibits distinct layers, appear to be confined to van der Waal's interactions.

The compound  $\pi$ -cyclopentadienylbis(acetylacetonato)chlorozirconium(IV) presents an interesting opportunity to examine the properties of three classes of ligands: a monodentate chlorine, a bidentate acetylacetonato, and a  $\pi$ -bonded cyclopentadienyl ligand. The preparation of the neutral complex was reported by Brainina, *et al.*,<sup>1</sup> who postulated an octahedral molecular configuration, with the possibility of *cis* and *trans* isomerism. The infrared absorption spectrum was cited as support for a  $\pi$ -bonded cyclopentadienyl ligand and was not in conflict with octahedral stereochemistry.

An analogous compound,  $\pi\text{-C}_5\text{H}_5(\text{C}_5\text{H}_7\text{O}_2)\text{CrBr}$ , has been prepared by Thomas,<sup>2</sup> who postulated an apparently tetrahedral molecular configuration. In both of these complexes only one stereochemical site has been attributed to the cyclopentadienyl ligand, and the acetylacetonato ligand has been depicted in the keto rather than the enol form even though the latter would allow equivalent metal-oxygen bond formation.

Considerable attention has been devoted to theoretical treatment of bonding between a central

metal atom and a  $\pi$ -bonded cyclopentadienyl ligand. In a review of several of these calculations, Wilkinson and Cotton<sup>3</sup> indicate the probable formation of three bonding molecular orbitals between the metal and the ligand. This description of the  $\pi$ -bonding when applied to the above mixed ligand complexes might be expected to result in the stereochemistry of six- and eight-coordination for the chromium and zirconium complexes, respectively.

Several crystallographic investigations of acetylacetonato complexes have been compiled in a review by Lingafelter and Braun.<sup>4</sup> These authors establish the equivalence of the C-O and C-CH bond distances, an observation consistent with the enol configuration of the ligand.

A structure determination of the neutral complex,  $\pi\text{-C}_5\text{H}_5(\text{C}_5\text{H}_7\text{O}_2)_2\text{ZrCl}$ , represents an opportunity to examine the stereochemical effects of the three bonding molecular orbitals associated with the cyclopentadienyl ligand and the constraints imposed by the geometry of the acetylacetonato ligands. The four oxygen atoms from the acetylacetonato ligands and the chlorine atom

(1) E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **138**, 1369 (1961).

(2) J. C. Thomas, *Chem. Ind.* (London), 1388 (1956).

(3) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

(4) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).