25°. Preliminary studies[18] in the polar solvent $ClCH_2CH_2Cl$ at 25° with bases 10, 11, 16, 20, 48, and 57 (Tables V and VII) indicate that $\Delta$ values are 10 to 20% less than corresponding values in $CCl_4$, except for triethylamine which is 10% larger. Thus, with the possible exception of the latter, there is no F nmr evidence of an appreciable enhancement in any hydrogen-bonded ion pairs. If the latter were present to a measurable extent in $CCl_4$, this form should be further increased in the polar $ClCH_2CH_2Cl$ solvent.

We therefore conclude that in $CCl_4$ $p$-$FC_6H_4OH$ forms only the hydrogen-bonded complex with all of the bases of Table V. Our results are consistent with these hydrogen-bonded complexes having a rather well-defined and a relatively low extent (up to ~30%) of apparent proton transfer.[3]

In accord with the conclusion that there is a small extent of proton transfer in these hydrogen-bonded complexes is the fact that there is *no* simple correspondence between base strength as measured by the standard free energy of hydrogen-bonded complex formation of $p$-$FC_6H_4OH$ in $CCl_4$ and corresponding aqueous $pK_A$ values of base. Figure 2 shows the complete scatter pattern which results from a plot of $pK_A$[19] *vs.* log $K_f^{25°}$ values for bases having a variety of common functional groups. This subject is considered in detail in paper V of this series.[5]

**Acknowledgment.** We are pleased to acknowledge the valuable assistance provided for this work by the preliminary studies made with 0.1 $M$ $p$-$FC_6H_4OH$ by Dr. M. G. Schwartz.[20] We are also pleased to acknowledge the preliminary studies of Mr. Joseph Mitzky in $ClCH_2CH_2Cl$ solutions.

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(18) Unpublished results of Mr. Joseph Mitzky.

(19) The $pK_A$ values shown in Figure 2 for hexamethylphosphoramide (−1.4) and dimethyl sulfoxide (−2.6) are unpublished results of Dr. J. R. Rakshys, obtained by the method of Haake (P. Haake, R. D. Cook, and G. H. Hurst, *J. Am. Chem. Soc.*, **89**, 2650 (1967)).

(20) M. G. Schwartz, Ph.D. Thesis, The Pennsylvania State University, Dec 1965.

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# Studies of Hydrogen-Bonded Complex Formation with $p$-Fluorophenol. V. Linear Free Energy Relationships with OH Reference Acids[1]

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*Received March 7, 1969*

**Abstract:** Linear free energy relationships have been established in the formation of hydrogen-bonded complexes of various OH reference acids with a wide variety of proton acceptors. The effects of temperature, solvent, and substituents have been examined. A unique base parameter, $pK_{HB}$, has been defined which measures the relative strength of the acceptor in hydrogen-bonded complex formation with any suitable OH reference acid. $pK_{HB}$ values do not correlate with aqueous $pK_A$ values, except within series having a common functional center and variable electronic effects of substituents. $pK_{HB}$ values also are not applicable to reference acids involving internal hydrogen bonding and are presumably not applicable to systems in which there is substantial formation of the hydrogen-bonded ion pair (in mobile equilibrium with the hydrogen-bonded complex). Evidence is presented that the $pK_{HB}$ scale is applicable (at least qualitatively) to other relatively weak interactions between bases and a "shielded" center of positive charge. The highly dispersed family relationships between $pK_{HB}$ and corresponding $pK_A$ values are indicated to be useful in distinguishing the atomic center of complexing in polyfunctional bases.

The effect of molecular structure on the strength of the hydrogen bond is a subject of diverse interests.[2,3a] These include, for example, the structure and reactivity of proteins and many other natural products, solvation effects in many chemical reactions and in spectroscopic measurements, and transition-state characteristics in proton-transfer processes.

There have been in recent years several extensive studies[4] of the effects of structure on base strengths toward a common reference acid, as measured by the formation constant, $K_f$, for the 1:1 hydrogen-bonded

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(1) This work was supported in part by the Public Health Service, Projects GM14078 (Irvine), AI-07766 (Princeton).

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

(3) (a) D. Hadzi, "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1957; (b) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

(4) (a) G. Aksnes, and T. Gramstad, *Acta Chem. Scand.*, **14**, 1475 (1960); (b) T. Gramstad, *ibid.*, **15**, 1337 (1961); 16, 807 (1962); (c) T. Gramstad and S. I. Snaprud, *ibid.*, 16, 999 (1962); (d) T. Gramstad and W. J. Fuglevik, *ibid.*, 16, 1369, 2368 (1962); (e) T. Gramstad, *Spectrochim. Acta*, **19**, 497, 829 (1963); (f) T. Gramstad and W. J. Fuglevik, *ibid.*, **21**, 343 (1965); (g) U. Blindheim and T. Gramstad, *ibid.*, **21**, 1073 (1965); (h) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2696, 3817 (1962); (i) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967); (j) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *ibid.*, **84**, 3221 (1962); (k) D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964); (l) R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *J. Am. Chem. Soc.*, **86**, 3227 (1964); (m) H. Dunken and H. Fritzsche, *Z. Chem.*, **1**, 127 (249 (1961); **2**, 345 (1962); (n) Z. Yoshida and E. E. Osawa, *J. Am. Chem. Soc.*, **88**, 4019 (1966); (o) C. J. Creswell and A. L. Allred, *ibid.*, **85**, 1723 (1963); (p) E. M. Arnett, T. S. S. R. Murty, P. von R. Schleyer, and L. Joris, *ibid.*, **89**, 5955 (1967); (q) D. Gurka, R. W. Taft, L. Joris, and P. von R. Schleyer, *ibid.*, **89**, 5957 (1967); (r) D. Gurka and R. W. Taft, *ibid.*, **91**,

**Table I.** Summary of Linear Free Energy Eq 1 Results

| Reference acid | Temp, °C | *m* | *c* | SD | RMS | Bases |
|---|---|---|---|---|---|---|
| Ethanol | 25 | 0.51 | −0.53 | 0.03 | 0.44 | 27,31,37,41,59,94 |
| Methanol | 20 | 0.55 | −0.30 | 0.06 | 1.14 | 16,18,44,73,78,82,85,88,94,104 |
| Methanol | 25 | 0.51 | −0.39 | 0.07 | 0.43 | 27,37,41,44,59,94 |
| Methanol | 50 | 0.39 | −0.18 | 0.06 | 0.90 | 16,18,73,78,82,84,85,88,94,104 |
| α-Naphthol | 20 | 0.92 | +0.18 | 0.06 | 2.71 | 16,18,73,78,82,84,85,88,94,104 |
| α-Naphthol | 50 | 0.86 | −0.11 | 0.03 | 2.25 | 16,18,73,78,82,84,85,88,94,104 |
| 2,2,2-Trifluoroethanol | 0 | 0.98 | 0.05 | 0.05 | 1.84 | 24,30,31,46,47,49,59,111 |
| 2,2,2-Trifluoroethanol | 25 | 0.92 | −0.17 | 0.04 | 1.76 | 24,30,31,47,59,111 |
| 2,2,2-Trifluoroethanol | 50 | 0.85 | −0.34 | 0.06 | 1.25 | 24,30,31,46,47,49,59,111 |
| Phenol | 20 | 0.94 | −0.02 | 0.07 | 1.87 | 5,16,18,27,37,44,47,54,58,60,64,78,84,86,92,93,94,100,108,111 |
| Phenol | 25 | 0.97 | −0.13 | 0.09 | 1.55 | 18,27,30,37,42,43,44,47,54,58,64,68,94,111 |
| Phenol | 50 | 0.89 | −0.31 | 0.08 | 1.41 | 1,5,7,16,18,27,29,37,44,47,54,58,60,71,78,84,93,94,100,108,111 |
| Hexafluoropropanol | 0 | 1.23 | +0.63 | 0.12 | 2.86 | 24,30,31,46,47,49,59,111 |
| Hexafluoropropanol | 25 | 1.16 | +0.32 | 0.09 | 2.78 | 24,30,31,47,59,111 |
| Hexafluoropropanol | 50 | 1.07 | +0.08 | 0.07 | 2.04 | 24,30,31,46,49,59,111 |

complex. It has frequently been suggested that there may be analogy between the hydrogen-bonded complex and the transition state for a rate-determining proton transfer reaction. The generality of the Brønsted catalysis law (log $k = m \log K_a + c$) for the latter reactions suggests further the possibility of a generalized linear free energy relationship between corresponding log $K_f$ and p$K_A$ values for a series of bases. Gordon[5] in an excellent review of this field in 1961 indicated that the rather meager data then available did *not* appear to support this possibility. In collaborative studies recently reported in which *p*-fluorophenol was used as the reference acid, it was established conclusively that the aqueous p$K_A$ and log $K_f$ (in $CCl_4$) scales of base strengths for a variety of common organic functional groups are unrelated.[4r]

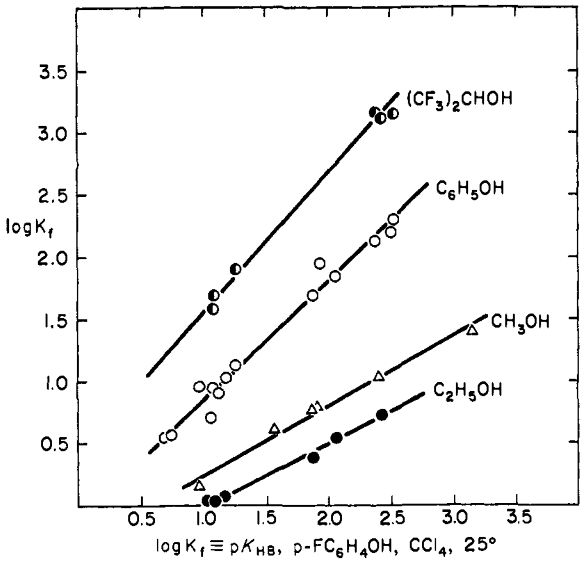

Figure 1. Linear free energy relationships in the formation of hydrogen-bonded complexes of OH reference acids, $CCl_4$.

In this paper the generality of the effects of base structure on log $K_f$ values obtained for the hydrogen-bonded complexes of *p*-fluorophenol in $CCl_4$ at 25° is examined in light of existing literature data[4,6] for other OH reference acids. Generalized linear free energy relationships (LFER) of satisfactory precision for hydrogen-bonded complex formation in $CCl_4$ are found for such acids as $CH_3OH$, $CF_3CH_2OH$, $(CF_3)_2CHOH$, phenol, and α-naphthol. These LFER's make it useful to assign a parameter, the p$K_{HB}$ value, to a base representing its relative base strength in hydrogen-bonded complex formation with (presumably) any suitable OH reference acid. p$K_{HB}$ values have been examined in terms of the dual substituent parameter equation for electronic effects of various substituents. Finally, family LFER's between corresponding aqueous p$K_A$ and p$K_{HB}$ values have been established and their significance has been considered.

## LFER's for Hydrogen-Bonded Complex Formation in $CCl_4$ Solution

Figure 1 illustrates typical linear free energy relationships between log $K_f$ values for several indicated reference acids plotted *vs.* corresponding values for *p*-fluorophenol. The solvent in each case is $CCl_4$ and the temperature is 25° (or 20° for phenol). The LFER equation is

$$\log K_f = m(\log K_f)_0 + c \qquad (1)$$

where $(\log K_f)_0$ is the logarithm of the formation constant of the hydrogen-bonded complex of *p*-$FC_6H_4OH$ in $CCl_4$ at 25° and *m* and *c* are constants characteristic of the reference acid, the solvent, and the temperature. Table I summarizes the LFER's based upon the literature data in $CCl_4$. Table I lists values of *m* and *c*, the standard deviation (SD), and root mean square of log $K_f$ values (RMS), and indicates the bases upon which the relationship is based. The numbers under the latter heading refer to the bases as designated in Table II.

The quality of the fit is excellent with SD/RMS = 1–6%. In view of the well-known difficulty in obtaining precise values of $K_f$, most of the deviations from the LFER appear to be random and of the same order as the estimated experimental errors. The success of eq 1 makes it useful to define base parameter, p$K_{HB}$, which measures the relative base strength in hydrogen-bonded complex formation with (presumably) any

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4794 (1969); (s) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, P. von R. Schleyer, submitted for publication; (t) A. Kivinen, J. Murto, and L. Kilpi, *Suomen Kemistilehti*, 40B, 301 (1967); (u) A. W. Baker, H. O. Kerlinger, and A. T. Shulgin, *Spectrochim. Acta*, 20, 1467 (1964); (v) L. Joris and P. von R. Schleyer, *Tetrahedron*, 24, 5991 (1968).

(5) J. E. Gordon, *J. Org. Chem.*, 26, 738 (1961).

(6) A recent tabulation of literature data is provided by A. S. N. Murthy and C. N. R. Rao, *Appl. Spectry. Rev.*, 2(1), 69 (1968).

suitable OH reference acid. Because of extensive and generally critically confirmed data,[4r,s] the standard reaction selected to define the $pK_{HB}$ value is the formation of the hydrogen-bonded complex of $p$-$FC_6H_4OH$, $CCl_4$, 25°, *i.e.*

$$pK_{HB} \equiv \log (K_f)_0 \tag{2}$$

From eq 1 and 2

$$pK_{HB} = [\log (K_f) - c]/m \tag{3}$$

In the absence of data for a given base to obtain the $pK_{HB}$ value from eq 2, a secondary value may be obtained from eq 3 using literature data for one of the reactions of Table I. In this manner an extensive set of $pK_{HB}$ values has been derived and is given in Table II. No attempt has been made to make Table II complete. Instead, $pK_{HB}$ values are given for 117 bases representing 16 different functional groups, in which the single atomic center of complex formation is presumably known. Included with most functional types are representative cases showing structural (substituent) effects within that category. Secondary values of $pK_{HB}$ from eq 3 are based largely upon the results of Gramstad[4a-g] with $C_6H_5OH$, $CCl_4$, 20°.

**Effect of Temperature.** The $m$ and $c$ values of Table I from the work of Kivinen and Murto[4t] with trifluoroethanol and hexafluoropropanol at 0, 25, and 50° are directly proportional to $1/T$ (both decrease with increasing temperature). These relationships are illustrated in Figure 2. Similar results hold within the probable significance of $m$ and $c$ values for phenol and $\alpha$-naphthol based upon the results of Gramstad[4a-g] at 20 and 50°. The $m$ and $c$ values for methanol at 50° are not in accord, but this probably reflects the lower precision of these data.

The linear shielding free energy (SEE) relationship obtained by use of the $p$-fluoro F nmr probe in $p$-$FC_6H_4OH$ has been interpreted[4r] to mean that values of $\log (K_f)_0 \equiv pK_{HB}$ are approximately proportional to the potential (electronic) energy change, $\Delta E_p{}^0$, on hydrogen-bonded complex formation. In light of this interpretation, eq 1 is suggested to be based upon a linear relationship between corresponding potential energy changes for the different OH reference acids. In accord with this suggestion, the relationships[7] between $\log K_f$, $\Delta G_{(T)}{}^\circ$, and $\Delta E_p{}^\circ$ lead to the conclusion that the constants, $m$ and $c$, as observed, are both proportional to $1/T$. That is

$$\log K_f = \frac{-\Delta G_{(T)}{}^\circ}{2.303RT} = \frac{-\Delta E_p{}^\circ + RT \ln (\pi Q)}{2.303RT} = \frac{-\Delta E_p{}^\circ}{2.303RT} + \log (\pi Q)$$

From the assumed special kinetic energy term condition:[7] $\log (\pi Q) \cong (k/T)(\Delta E_p{}^\circ)$, where $k$ is a constant at a given temperature and for a given reference acid. Then

$$\log (K_f)_0 \equiv pK_{HB} = b(\Delta E_p{}^\circ)_0 \ (T = 298)$$

and

$$\log K_f = \Delta E_p{}^\circ (d/T)$$

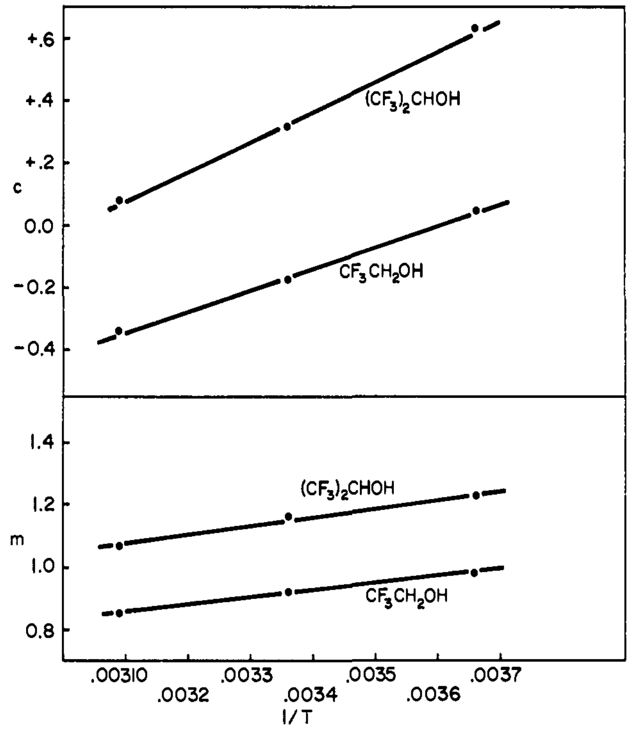

Figure 2. The $1/T$ dependence of $c$ and $m$ parameters.

where $b$ and $d$ are constants. Therefore, if

$$\Delta E_p{}^\circ = n(\Delta E_p{}^\circ)_0 + c'$$

it follows that

$$\log K_f = \left(\frac{nd}{bT}\right) pK_{HB} + \frac{c'd}{T}$$

or

$$\log K_f = m(pK_{HB}) + c$$

where $m \propto (1/T)$ and $c \propto (1/T)$.

**Effect of Structure of Reference Acid.** For the reference acids of Table I there is no general relationship between either the $m$ or $c$ parameters and the acidity as measured by either aqueous $pK_A$ values or by ir shifts, $\Delta\nu$. For the aliphatic series of acids there is, however, a qualitative correlation suggested by the limited available data given in Table III. Both $m$ and $c$ tend to increase with increasing $pK_A$. For the aromatic acids, phenol, $p$-$FC_6H_4OH$, and $\alpha$-naphthol, both $m$ and $c$ are distinctly less than their $pK_A$ value and the above trend for aliphatic acids would indicate. This result is reminiscent of Brønsted relationships for which different structural types of OH acids tend to display different slopes.[8]

Further work is needed to establish general relationships between the acidities of reference acids and the $m$ and $c$ constants of eq 1. It is of particular interest to determine whether eq 1 is applicable to reference acids other than OH type, *e.g.*, -NH, SH, and C-H, and, if so, the relationship of $m$ and $c$ values to acidity.

**Effect of Solvent.** Data in solvents other than $CCl_4$ are meager. However, Gramstad[4d,e] has reported

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(7) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 569.

(8) R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.* (London), A197, 141 (1949).

**Table II.** p$K_{\mathrm{HB}}$ Values

| | Base | H |
|---|---|---|
| | A. Aldehyde | |
| 1 | *p*-Nitrobenzaldehyde | 0.36 |
| 2 | Propionaldehyde | 0.71 |
| 3 | *n*-Butyraldehyde | 0.78 |
| 4 | *p*-Chlorobenzaldehyde | 0.79 |
| 5 | Benzaldehyde | 0.83 |
| 6 | *p*-Methoxybenzaldehyde | 1.10 |
| 7 | *p*-N,N-Dimethylaminobenzaldehyde | 1.55 |
| | B. Alkyl Halide | |
| 8 | Cyclohexyl fluoride | −0.05 |
| | C. Amine, Primary | |
| 9 | β,β,β-Trifluoroethylamine | 0.59 |
| 10 | Propargylamine | 1.48 |
| 11 | Cyclopropylamine | 1.64 |
| 12 | Benzylamine | 1.75 |
| 13 | *n*-Butylamine | 2.11 |
| | Tertiary | |
| 14 | Triallylamine | 1.23 |
| 15 | Tri-*n*-propylamine | 1.45 |
| 16 | Tri-*n*-butylamine | 1.57 |
| 17 | N,N-Dimethylbenzylamine | 1.58 |
| 18 | Triethylamine | 1.91 |
| 19 | N,N-Dimethyl-*n*-propylamine | 1.98 |
| 20 | N,N-Dimethylcyclohexylamine | 2.07 |
| | D. Carboxylic Acid Fluoride | |
| 21 | Benzoyl fluoride | −0.30 |
| 22 | *n*-Butyl fluoride | −0.16 |
| 23 | *n*-Propionyl fluoride | −0.13 |
| | E. Carboxylic Amide | |
| 24 | N,N-Dimethyltrifluoroacetamide | 1.18 |
| 25 | N,N-Dimethyl-*p*-nitrobenzamide | 1.62 |
| 26 | N,N-Dimethylchloroacetamide | 1.68 |
| 27 | N,N-Dimethylformamide | 2.06 |
| 28 | N,N-Dimethylbenzamide | 2.22 |
| 29 | N-Methyl-2-pyrrolidone | 2.37 |
| 30 | N,N-Dimethylacetamide | 2.38 |
| 31 | Tetramethylurea | 2.42 |
| | F. Carboxylic Ester | |
| 32 | Ethyl chloroacetate | 0.69 |
| 33 | β-Propiolactone | 0.78 |
| 34 | Ethyl benzoate | 0.88 |
| 35 | Methyl acetate | 1.00 |
| 36 | Ethyl propionate | 1.02 |
| 37 | Ethyl acetate | 1.08 |
| 38 | γ-Valerolactone | 1.30 |
| 39 | γ-Butyrolactone | 1.33 |
| | G. Ether | |
| 40 | Anisole | 0.02 |
| 41 | Dioxane | 0.71[a] |
| 42 | Di-*t*-butyl ether | 0.71 |
| 43 | Di-benzyl ether | 0.72 |
| 44 | Diethyl ether | 0.98 |
| 45 | Di-*n*-butyl ether | 1.02 |
| 46 | Diisopropyl ether | 1.05 |
| 47 | Tetrahydrofuran | 1.26 |
| 48 | Tetrahydropyran | 1.23 |
| | H. Ketone | |
| 49 | 1,1,1-Trifluoroacetone | −0.19 |
| 50 | Biacetyl | 0.33 |
| 51 | Acetylacetone | 0.48 |
| 52 | *sym*-Dichloroacetone | 0.48 |
| 53 | Benzophenone | 0.97 |
| 54 | Acetophenone | 1.13 |
| 55 | Methyl *t*-butyl ketone | 1.04 |
| 56 | Di-*t*-butyl ketone | 1.04 |
| 57 | Methyl isopropyl ketone | 1.04 |
| 58 | Methyl ethyl ketone | 1.18 |
| 59 | Acetone | 1.18 |
| 60 | Cyclohexanone | 1.30 |
| 60a | Xanthone | 1.37 |
| 61 | *p*-Methoxyacetophenone | 1.40 |
| 62 | Acetylferrocene | 1.64 |
| 63 | Flavone | 1.99 |
| 64 | 2,6-Dimethyl-γ-pyrone | 2.50 |
| | I. Nitrile | |
| 65 | Benzonitrile | 0.79 |
| 66 | *p*-Methoxybenzonitrile | 0.99 |
| 67 | β-Ethoxypropionitrile | 1.05 |
| 68 | Acetonitrile | 1.05 |
| 69 | *p*-N,N-Dimethylaminobenzonitrile | 1.38 |
| | J. Nitro Compound | |
| 70 | Nitrobenzene | 0.73 |
| | K. N-Oxides | |
| 71 | Pyridine N-oxide | 2.76 |
| | L. Phosphine Oxide | |
| 72 | Triphenyl phosphate | 1.73 |
| 73 | Diethoxytrichloromethylphosphine oxide | 2.00 |
| 74 | Dimethoxyphosphine oxide | 2.25 |
| 75 | Diethylfluorophosphine oxide | 2.27 |
| 76 | Diethoxydichloromethylphosphine oxide | 2.27 |
| 77 | Diethoxyphosphine oxide | 2.37 |
| 78 | Trimethyl phosphate | 2.40 |
| 79 | Dimethoxyethylphosphine oxide | 2.44 |
| 80 | Diethoxychloromethylphosphine oxide | 2.55 |
| 81 | Triethyl phosphate | 2.73 |
| 82 | Diethoxymethylphosphine oxide | 2.77 |
| 83 | Diethoxy-N,N-diethylaminophosphine oxide | 2.90 |
| 84 | Triphenylphosphine oxide | 3.16 |
| 85 | Trimethylphosphine oxide | 3.49 |
| 86 | Hexamethylphosphoramide | 3.56 |
| 87 | Tri-*n*-propylphosphine oxide | 3.60 |
| 88 | Triethylphosphine oxide | 3.64 |
| | M. Pyridine | |
| 89 | 3,5-Dichloropyridine | 0.75 |
| 90 | 2-Bromopyridine | 0.94 |
| 91 | Pyrimidine | 1.05[a] |
| 92 | 3-Bromopyridine | 1.26 |
| 93 | Quinoline | 1.85 |
| 94 | Pyridine | 1.88 |
| 95 | 2-*n*-Butylpyridine | 1.88 |
| 96 | Isoquinoline | 1.93 |
| 97 | Acridine | 1.97 |
| 98 | 3-Methylpyridine | 1.97 |
| 99 | 2-Methylpyridine | 2.01 |
| 100 | 4-Methylpyridine | 2.03 |
| 101 | 2,6-Dimethylpyridine | 2.13 |
| 102 | 2,4-Dimethylpyridine | 2.17 |
| 103 | 4-Methoxypyridine | 2.14 |
| 104 | 2,4,6-Trimethylpyridine | 2.30 |
| 105 | 4-N,N-Dimethylaminopyridine | 2.81 |
| | N. Sulfoxide | |
| 106 | Diethyl sulfite | 0.98 |
| 107 | Methyl *p*-nitrophenyl sulfoxide | 1.58 |
| 108 | Diphenyl sulfoxide | 2.03 |
| 109 | Methyl phenyl sulfoxide | 2.15 |
| 110 | Dibenzyl sulfoxide | 2.28 |
| 111 | Dimethyl sulfoxide | 2.53 |
| 112 | Di-*n*-butyl sulfoxide | 2.60 |
| | O. Sulfide | |
| 113 | Diethyl sulfide | 0.11 |
| 114 | Di-*n*-butyl sulfide | 0.26 |
| 115 | Di-*t*-butyl sulfide | 0.21 |
| | P. Unsaturated Hydrocarbons | |
| 116 | Azulene | 0.02 |
| 117 | 4,6,8-Trimethylazulene | 0.33 |

[a] Statistical factor of 2 has been applied.

Table III

| Acid | p$K_A$[9] | $m$[a] | $c$[a] |
|---|---|---|---|
| $C_2H_5OH$ | −15.9 | 0.51 | −0.53 |
| $CH_3OH$ | −15.5 | 0.51 | −0.39 |
| $CF_3CH_2OH$ | −12.4 | 0.92 | −0.17 |
| $(CF_3)_2CHOH$ | −9.3 | 1.16 | +0.32 |

[a] At 25°.

Table IV. Solvent Effects, $C_6H_5OH$, 20°

| Solvent | $m$ | $c$ | SD | RMS | Bases |
|---|---|---|---|---|---|
| $CS_2$ | 1.00 | −0.03 | 0.019 | 2.58 | 16,27,84,94 |
| $CCl_4$ | 0.97 | −0.08 | 0.049 | 2.28 | 7,16,27,48,73,74,81,84,88,94 |
| $CCl_4$–cyclohexane (80:20) | 0.95 | −0.03 | 0.106 | 2.09 | 7,16,27,48,73,74,81,84,88,94 |
| $CCl_4$–$CBr_4$ (80:20) | 0.85 | 0.00 | 0.090 | 2.29 | 7,16,27,48,73,74,81,84,88,94 |

Table V. Summary of $\rho$ Values

| Base | p$K_{HB}$ | $\rho$ | SD | RMS | Substituents |
|---|---|---|---|---|---|
| Benzonitrile | 0.79 | −0.35 | 0.041 | 1.32 | H, $p$-$OCH_3$,[a] $p$-$N(CH_3)_2$[a] |
| Benzaldehyde | 0.83 | −0.45 | 0.082 | 1.12 | $p$-$NO_2$, $p$-$Cl^-$,[a] H, $p$-$OCH_3$,[a] $p$-$N(CH_3)_2$[a] |
| Phenyl methyl sulfoxide | 2.15 | −0.72 | | | $p$-$NO_2$, H |
| N,N-Dimethylbenzamide | 2.22 | −0.77 | | | $p$-$NO_2$, H |
| Pyridine | 1.88 | −1.31 | 0.060 | 2.11 | 3,5-Cl, 3-Br, H, 4-$CH_3$, 4-$OCH_3$, and 4-$N(CH_3)_2$ |

[a] $\sigma^+$ value used, since the protonated functional groups are presumably of the electron-deficient type.

results with phenol in $CS_2$, in $CCl_4$–$C_6H_{12}$ (80:20, w/w), and in $CCl_4$–$CBr_4$ (80:20, w/w). The results of the application of eq 1 to these data are given in Table IV.

The results for the $c$ parameters for the four solvents of Table IV indicate very little if any solvent effect. On the other hand, the decrease in $m$ value between $CS_2$ and $CCl_4$–CBr (80:20) is apparently real and may reflect some effect of solvent on the extent of proton transfer in the hydrogen-bonded complex. However, the precision of fit is somewhat poorer in the mixed than in the pure solvents, suggesting some relatively small effects of specific solvation of the bases.[4e] In any case, as found, only small solvent effects are anticipated by the striking observation of Arnett, *et al.*,[4s] that the enthalpy of complex formation is nearly the same at high dilution in $CCl_4$ as in pure base (including very polar bases).

**Substituent Effects on p$K_{HB}$ Values.** The electronic effects of substituents on p$K_{HB}$ parameters may be examined with the aid of structure–reactivity relationships in both the aromatic and aliphatic series. Present data are meager but several preliminary indications seem significant.

The second atom of the functional group is presumably the atomic site of complex formation for the four bases: benzonitrile, benzaldehyde, phenylmethyl sulfoxide, and N,N-dimethylbenzamide. Thus the mean distance between *meta* or *para* substituents in the phenyl groups and the reaction center for hydrogen bonding is similar. In aqueous ionization equilibria, *e.g.*, benzoic acids or benzylammonium ions, there is evidence that this condition leads to nearly identical Hammett $\rho$ values.[10] However, the available p$K_{HB}$ values for these bases with *meta* and *para* substituents appear to indicate that the $\rho$ values for the hydrogen-bonded complex formation equilibria are distinctly not equal, but instead tend to increase with increasing value of p$K_{HB}$ for the unsubstituted base. The results of fitting to the Hammett relationship[11] (or with Brown[12] $\sigma^+$ values where appropriate) are given in Table V, *i.e.*, p$K_{HB}$ = $\sigma\rho$ (or $\sigma^+\rho$).

Although definite confirmation must await the results of further substituent studies with these bases, the provisional conclusion to be drawn from the results of Table V is that in the hydrogen-bonded complex formation equilibria, $-\rho$ increases both with increasing p$K_{HB}$ value of the functional group and decreasing distance between substituent and the atomic reaction center. The latter condition clearly prevails in the much larger $-\rho$ value for pyridine than that for the other bases of Table V.

Substituents in two series, $XC(=O)CH_3$ and $XC(=O)N(CH_3)_2$, have been examined by use of the dual substituent parameter equation[13]

$$\mathrm{p}K_{HB} = \sigma_I\rho_I + \sigma_R{}^+\rho_R$$

Although the precision of fit of the relationship is not as good as that considered to be really satisfactory (*i.e.*, SD/RMS $\leqslant$ 10%), the data are reasonably well accommodated. The poorer precision is undoubtedly to be associated with the fact that the $\sigma_R{}^+$ scale is based upon substituent effects acting across the benzene ring while in the present application the substituent is directly bonded to the carbonyl carbon. For example, the $C_6H_5$ substituent as expected is poorly behaved in particular, and has not been included in the correlations. The results of the fittings are given in Table VI which lists values of $\rho_I$, $\rho_R$, $\lambda \equiv \rho_R/\rho_I$, SD, and RMS, and indicates the substituents used.

In addition to the $\sigma_R{}^+$ scale of $\pi$ delocalization effects, fitting has also been carried out using the $\sigma_R$ scale.[13] In series 1, there is no difference in precision of fit with these two scales, but, in series 2, the former scale is fitted

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(9) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960); the value for hexafluoropropanol is estimated on an additive substituent effect basis.

(10) R. W. Taft and I. C. Lewis, *ibid.*, **80**, 2436 (1958).

(11) L. P. Hammett, *Chem. Rev.*, **17**, 125 (1935).

(12) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(13) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968); $\sigma_R$ and $\sigma_R{}^+$ values are from an unpublished tabulation of S. Ehrenson and R. W. Taft.

Table VI. Application of the Dual Substituent Parameter Equation to Substituent Effects on Hydrogen-Bonded Complex Formation by Carbonyl Compounds

| Resonance parameters | $\rho_I$ | $\rho_R$ | $\lambda$ | SD | RMS | Substituent X |
|---|---|---|---|---|---|---|
| | | | 1. $(CH_3)_2NC(=O)X$ | | | |
| $\sigma_R{}^+$ | −2.25 | −0.19 | 0.084 | 0.10 | 0.56 | $CF_3$, $CH_2Cl$, H, $CH_3$, $N(CH_3)_2$ |
| $\sigma_R$ | −2.18 | −0.60 | 0.275 | 0.11 | 0.56 | $CF_3$, $CH_2Cl$, H, $CH_3$, $N(CH_3)_2$ |
| | | | 2. $CH_3C(=O)X$ | | | |
| $\sigma_R{}^+$ | −2.01 | −0.70 | 0.348 | 0.18 | 0.90 | $CH_3CO$, $CF_3$, H, F, $CH_3$, $OCH_3$, $N(CH_3)_2$ |
| $\sigma_R$ | −2.25 | −1.71 | 0.76 | 0.35 | 0.90 | $CH_3CO$, $CF_3$, H, F, $CH_3$, $OCH_3$, $N(CH_3)_2$ |

with significantly improved precision, just as $\sigma^+$ values give the best results for the compounds of Table V. It is to be noted that the values of $\rho_I$ are essentially independent of whether $\sigma_R{}^+$ or $\sigma_R$ is used and are approximately equal for both series. On the other hand, the values of $\rho_R$ (or $\lambda$) are markedly influenced by the common substituent group at the carbonyl carbon. When the latter is $CH_3$, the value of $\lambda$ is of the same order of magnitude[13] as that for Hammett $\sigma_{(m)}$, but when the latter is the powerful $\pi$ donor substituent, $N(CH_3)_2$, $\rho_R$ and $\lambda$ are reduced to very low levels.

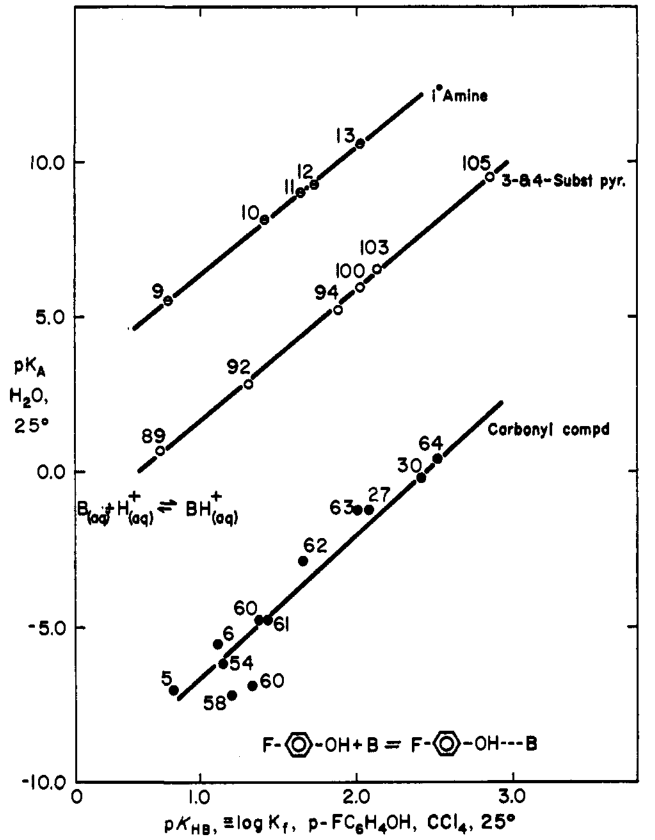

Figure 3. Family linear free energy relationships in the comparison of base strengths of $H^+(aq)$ *vs.* *p*-$FC_6H_4OH$.

These applications of structure–reactivity relationships, together with earlier reports of $\sigma^*\rho^*$ relationships,[14] indicate promise that general relationships for describing effects of base structure on $pK_{HB}$ values may be achieved.

**Comparison of the $pK_{HB}$ and $pK_A$ Scales of Base Strength.** It was established in companion work[4r] that these scales for different functional groups have little or nothing in common. However, there have been several reports of parallel family substituent effects on these two scales.[4b,v,15] Substituent effects covering very substantial ranges in $pK_A$[16] have been obtained[4r] for three different functional groups: polar-substituted primary amines, 3- and 4-substituted pyridines, and polar-substituted carbonyl compounds. In Figure 3 is shown a plot of $pK_A$ *vs.* $pK_{HB}$ for these three reaction series. Three essentially parallel (family) lines satisfactorily describe the relationship between $pK_A$ and $pK_{HB}$ for these compounds. The carbonyl family exhibits some scatter (notably aliphatic ketones are below aromatic ketones) at the low $pK_A$ range which may be largely associated with the difficulty in obtaining thermodynamic aqueous $pK_A$ values by indicator methods in concentrated mineral acid solutions.[16d,17]

The intercept differences between the three family LFER's of Figure 3 are dramatic in their magnitudes. Thus, *for equal values of* $pK_{HB}$ (or formation constant, $K_f$, of *p*-$FC_6H_4OH$, $CCl_4$, 25°), a member of the pyridine family has a $pK_A$ which is 5 powers of ten less than that of the corresponding member of the amine family. For the member of the carbonyl family compared to the corresponding member of the amine family, the figure is a $pK_A$ of 13 powers of ten less!

In the absence of additional data one can invoke the assumption that the effects of polar substituents on other kinds of functional groups would be to generate additional family LFER's of parallel slopes to those of Figure 3. With such an assumption, one can compare the $pK_{HB}$ value of each functional group family at $pK_A = 0$ (*i.e.*, the $pK_{HB}$ intercepts in Figure 3). These intercepts for a number of different functional groups are as shown in Table VII. This comparison of $pK_{HB}$ values at equal $pK_A$ of the base reveals a correlation with the electronegativity of the acceptor atom. As the electronegativity of the hydrogen acceptor increases there is an increase in the formation constant of the hydrogen-bonded complex at equal base $pK_A$ ($pK_{HB}$ at $pK_A = 0$). For example, the increased s character of the unshared pair orbital increases the electronegativity of nitrogen[18] in the sequence amine < pyri-

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[14] (a) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963); (b) T. Gramstad, *Spectrochim. Acta*, **20**, 729 (1964); (c) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **86**, 5240 (1964).

[15] J. Rubin and G. S. Panson, *J. Phys. Chem.*, **69**, 3089 (1965).

[16] References for $pK_A$ values: (a) P. Love, R. B. Cohen, and R. W. Taft, *J. Am. Chem. Soc.*, **90**, 2455 (1968); (b) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth & Co. (Publishers), Ltd., London, 1965; (c) A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964); (d) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[17] C. C. Greig and C. D. Johnson, *J. Am. Chem. Soc.*, **90**, 6433 (1968).

[18] C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952, p 207.

**Table VII**

| Functional group | $pK_{HB}$[a] |
|---|---|
| Primary amine | −0.6 |
| Pyridine | +0.5 |
| Sulfide | +1.4 |
| Ether | +1.7 |
| Carbonyl | +2.4 |
| Sulfoxide | +3.0 |
| Nitrile | +3.4 |
| Phosphine oxide | +3.9 |

[a] Where $pK_A = 0$.

dine < nitrile. The intercept, $pK_{HB}$ at $pK_A = 0$, also sharply increases in this sequence. Similarly, the electronegativity and intercept for carbonyl oxygen are greater than that of ether oxygen, which in turn are greater than that of sulfide sulfur. These results provide a basis of comparison which accords qualitatively with the Pauling rule[19] that the strength of the hydrogen bond increases the greater the electronegativity of the two atoms forming the bond.

For monovalent oxygen bases the increasing values of $pK_{HB}$ at $pK_A = 0$ for sulfoxides and phosphine oxides over carbonyl compounds probably do not result from any substantial increase in electronegativity of oxygen in this sequence. Instead, a much more important variable is probably the inductive and conjugative effects of the atom bonded to oxygen. These effects are reasonably expected to increase the base strength of oxygen in the order: $>\mathrm{C}{=}\mathrm{O} < >\mathrm{S}^{+}{\doteq}\mathrm{O}^{-} < \geqslant\mathrm{P}^{+}{\doteq}\mathrm{O}^{-} < \geqslant\mathrm{N}^{+}{-}\mathrm{O}^{-}$. Further, since $pK_A$ values are influenced by the hydration of both the acid and base forms, differential hydration effects are expected to play an important role in the intercept relations of Figure 3. The relatively large $pK_{HB}$ values for sulfoxides and phosphines do indeed suggest that $pK_A$ hydration effects are particularly important for these functional groups.[20] It would be extremely interesting to plot for families of bases as in Figure 3 $pK_{HB}$ values *vs.* gaseous proton affinities (*i.e.*, to obtain comparison of $pK_{HB}$ at equal proton affinity). Such a plot in comparison with Figure 3 perhaps offers the most promising means of evaluating the role of $pK_A$ hydration effects. Unfortunately, the required gaseous proton affinities are presently unavailable.

The slopes of the family LFER's of Figure 3 are each 4.8. Thus, these results provide no evidence of increasing slopes with increasing $pK_{HB}$ value at $pK_A = 0$. In view of the wide range of $pK_A$ values covered within each of the three families, this result is of particular interest. In the previous section, evidence was presented that the Hammett $-\rho$ value for the hydrogen-bonded complex formation equilibrium for certain families increases with increasing $pK_{HB}$ value of the parent member. These two results imply, therefore, that the Hammett $\rho$ value for the corresponding aqueous ionization equilibrium also increases with increasing $pK_{HB}$ value of the parent member. Although previous interpretation[10] suggested that this result would be unexpected (*cf.* previous discussion relative to Table V), the recent results of Andersen, *et al.*,[21] are indeed consistent. These authors determined the $\rho$ value for the ionization of the conjugate acids of *meta-* and *para-*substituted phenyl methyl sulfoxides in acetic anhydride–$HClO_4$. Their result together with the $\rho$ value for the ionization of conjugate acids of *meta-* and *para-*substituted benzaldehydes obtained by Yates and Stewart[22] in $H_2SO_4$–$H_2O$ and the $\rho$ value for the ionization of 3- and 4-substituted pyridinium ions[16] in $H_2O$ do appear to indicate that the $\rho$ values for ionization are about four to five times larger than for the corresponding hydrogen-bonded complex formation equilibria with *p*-$FC_6H_4OH$ in $CCl_4$. These $\rho$ values are summarized in Table VIII.[23]

**Table VIII**

| Base | $\rho$[a] | $\rho$[b] |
|---|---|---|
| Benzaldehyde | −1.7 | −0.45 |
| Phenyl methyl sulfoxide | −3.7 | −0.72 |
| Pyridine | −6.2 | −1.31 |

[a] For protonation, $H_2O$, 25°. [b] For H-bonded complexing, *p*-$FC_6H_4OH$, $CCl_4$, 25°.

It is of interest to note in Figure 3 that the amides, N,N-dimethylformamide and acetamide, are members of the carbonyl family. Since Figure 3 is highly discriminating between amines and carbonyl compounds, the presence of the amides in the latter family offers further compelling evidence (albeit indirect) of O protonation in both the aqueous ionization[24] and the hydrogen-bonded complex formation equilibria.

The above-mentioned discrimination also has important consequences with respect to other bases having more than a single atomic center of complexing. The bases, *p*-dimethylaminobenzonitrile and *p*-dimethylaminobenzaldehyde, are specific examples. For N-protonation of the latter, the $pK_A$ can be estimated reliably using the $\sigma$ value for the *p*-CHO substituent[25] and the Hammett $\rho$ value for aqueous ionization of N,N-dimethylanilines,[26] giving +3.2. For O-protonation the $pK_A$ value is estimated using the Brown $\sigma^+$ value for the *p*-$N(CH_3)_2$ substituent[12] and the Hammett $\rho$ value for ionization of benzaldehydes,[22] giving −4.2. It is clear from these figures that N-protonation of aqueous base is distinctly more spontaneous than O-protonation. On the other hand, the point for the $pK_{HB}$ value (1.55) and the N-protonation $pK_A$ value for this base does not fall on, or even near, the amine family line of Figure 3. Instead, the $pK_{HB}$ and O-protonation $pK_A$ values give a point which satisfactorily fits the carbonyl family line. Consequently, in hydrogen-bonded complex formation with *p*-dimethylaminobenzaldehyde, complexing is indicated to occur on

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[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, Chapter 9.

[20] A plot of ir $-\Delta\nu_{MeOH}$ values *vs.* corresponding values of the F nmr $\Delta$ (both in $CCl_4$) gives family relationships qualitatively very similar to Figure 3, with the notable feature that the points for all monovalent oxygen bases, $>\mathrm{C}{=}\mathrm{O}$, $>\mathrm{S}^{+}{\doteq}\mathrm{O}^{-}$, $\geqslant\mathrm{P}^{+}{\doteq}\mathrm{O}^{-}$, tend to define a single "family" line. This result, which will be discussed fully in a subsequent publication, appears to support the notion that special hydration effects enter in Figure 3.

[21] K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

[22] K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).

[23] In view of the much smaller $\rho$ values for hydrogen-bonded complex formation than for corresponding aqueous $pK_A$, it is probably significant that the $\sigma_R{}^+$ scale of resonance effects appears to apply equally well to both equilibria.

[24] G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

[25] R. T. C. Brownlee and R. W. Taft, *ibid.*, **90**, 6537 (1968).

[26] R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

oxygen. This conclusion is, of course, consistent with the much greater $pK_{HB}$ value at $pK_A = 0$ for the carbonyl than the primary amine family.

**Limitations.** Gramstad has reported formation constants for pentachlorophenol complexes with a variety of bases in $CCl_4$ solutions. He noted that larger formation constants are obtained for this acid than for phenol if the acceptor is a nitrogen base. However, for oxygen bases, Gramstad found smaller formation constants for pentachlorophenol than phenol. In view of the well-known internal hydrogen bonding between *o*-Cl and OH functions,[4u] it appears highly probable that the competition between intramolecular and intermolecular hydrogen bonding is responsible for this behavior. In particular, $pK_{HB}$ values probably do not apply to any reference acid which involves internal hydrogen bonding.

The wide dispersion in the family LFE relationships between $pK_A$ and corresponding $pK_{HB}$ values (Figure 3) suggests that $pK_{HB}$ values will not be applicable to reference acids (and solvent conditions) for which there is appreciable formation of hydrogen-bonded ion pairs (in mobile equilibrium with hydrogen-bonded complexes). Unpublished results of Mr. J. Mitsky with *p*-fluorophthalimide are consistent with this conclusion.

**Other Applications of the $pK_{HB}$ Scale.** In previous work it has been shown that the extent of proton transfer in the hydrogen-bonded complexes of *p*-$FC_6H_4OH$ is relatively small.[4q,7] As a consequence, there is for different functional groups a complete lack of correspondence between the $pK_{HB}$ and aqueous $pK_A$ scales of base strength.[4r] It seems reasonable to suppose that other relatively weak interactions between bases and a shielded center of positive charge may give rise to a stability order which either follows or is more similar to the $pK_{HB}$ scale. The applicability of the $pK_{HB}$ scale to reference acids of the N–H, S–H, C–H type is of interest in this connection.

Rakshys and Taft have recently carried out extensive studies of the effects of pure solvents on the fluorine nuclear magnetic resonance shieldings of *m*- and *p*-$FC_6H_4$ alkyl- and aryl-substituted "onium" ions (ammonium, carbonium, phosphonium, and sulfonium).[27] The measurements were made at 25° at salt concentrations of 0.001 *M* or less using *m*-fluorophenyltriphenylphosphonium ion as the internal reference. The solvent effects were found to be well correlated by the product of a solvent–cation complexation parameter, $L_s$, and a cation sensitivity parameter, $m_R{}^+$. These and other results suggest that $L_s$ is an approximate measure of the stability of a generalized class of weak organic cation–molecule complexes (which specifically do not involve hydrogen-bonding interactions). A remarkable parallelism is found between values of $L_s$ and $pK_{HB}$ as shown in Table IX for a variety of bases. Also included in Table IX are values of the solubility parameter, $pK_{S(solv)} - pK_{S(MeOH)}$, for $(C_6H_5)_4As^{+-}B(C_6H_5)_4$ obtained recently by Alexander and Parker,[28] which also show qualitatively parallel behavior.

**Table IX**

| Base | $L_s$ | $pK_{HB}$ | $pK_{S(solv)} - pK_{S(MeOH)}$ |
|---|---|---|---|
| Acetonitrile | 2.85 | 1.05 | −3.3 |
| Pyridine | 3.75 | 1.88 | |
| N,N-Dimethylformamide | 4.23 | 2.06 | −4.8 |
| Trimethyl phosphate | 4.28 | 2.40 | |
| N,N-Dimethylacetamide | 4.40 | 2.38 | −5.1 |
| Tetramethylurea | 4.40 | 2.42 | |
| N-Methyl-2-pyrrolidone | 4.41 | 2.37 | |
| Dimethyl sulfoxide | 4.55 | 2.53 | −5.2 |
| Hexamethylphosphoramide | 5.22 | 3.56 | −5.4 |

Zaugg, Horrom, and Borgwardt[29] have presented evidence that the acceleration of the rate of alkylation of sodiomalonic esters in benzene solution which is brought about by the addition of small amounts of base additives results from the specific solvation of the sodium cation. The rate enhancement factor produced by 0.3 *M* additive in the alkylation of diethyl sodio-*n*-butylmalonate with *n*-butyl bromide in benzene at 25° was taken as a measure of the strength of solvation of the sodium ion. It was noted in particular that the solvation strengths so obtained did not parallel the base strength toward aqueous proton (*i.e.*, the order of $pK_A$ values).

Table V indicates the general qualitative parallelism which exists between the rate enhancement factors obtained by Zaugg and corresponding $pK_{HB}$ values.

Parker[30] has noted that the order of increasing cation solvation (*e.g.*, the increasing values in Table X) apparently applies at least qualitatively to other alkali metal ions, *e.g.*, $Li^+$ and $K^+$, and to solvates of transition metal compounds, *e.g.*, $CuCl_2$, $FeCl_3$, $CrCl_3$, etc.

**Table X**

| Base | Zaugg rate factor | $pK_{HB}$ |
|---|---|---|
| Benzophenone | 1.2 | 0.97 |
| Pyridine | 1.4 | 1.88 |
| N,N-Dimethyltrifluoroacetamide | 1.7 | 1.18 |
| N,N-Dimethylformamide | 7.0 | 2.06 |
| N,N-Dimethylacetamide | 8.7 | 2.38 |
| N-Methyl-2-pyrrolidone | 11.0 | 2.37 |
| Dimethyl sulfoxide | 15 | 2.53 |
| Hexamethylphosphoramide | 54 | 3.56 |

These results support the hypothesis that there are distinctly different orders of base strength applicable for relatively weak interactions of bases with a shielded center of positive charge compared to those for the relatively strong interactions such as occur with a proton.

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(27) J. W. Rakshys, Jr., and R. W. Taft, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Sept 1967, V-39; J. W. Rakshys, Jr., Ph.D. Thesis University of California, Irvine, June 1967.

(28) R. Alexander and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 5549 (1967).

(29) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *ibid.*, **82**, 2895 (1960).

(30) A. J. Parker, *Quart. Rev.* (London), 163 (1962).