© 2000 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 73, 1485—1490 (2000)

Evaluation of Novel Local Structural Parameters of Acids and Bases for 1 : 1 Hydrogen-Bond Complexation I. OH-, NH-Acids and Phosphorus Bases in Carbon Tetrachloride

Shozi Mishima,* Tsuyoshi Nakajima, and Tsuneo Fujii†

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University,
Wakasato 4-17-1, Nagano 380-8533

†Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University,
Wakasato 4-17-1, Nagano 380-8533

(Received September 14, 1999)

Novel local structural parameters, η° and ω°, representing the nature of the functional group and the residual moiety (supporting group) of acid and base molecules, respectively, have been evaluated for the first time for the 1 : 1 hydrogen-bond complexation of nine OH- or NH-acids and five phosphorus bases in CCl_4. An evaluation of η° and ω° was carried out by making use of convergent linear relationships among the $\log K$ values and by introducing three numerical criteria. For acid-base complexation, all of the 180 $\log K$ values at 288.15—318.15 K and 45 ΔH_f° values were reproduced from the η and ω values within the experimental error. The reversals in the order of $\log K$ and ΔH_f° observed in the system could be reasonably explained by applying the η° and ω° scales.

To compare and predict the strength of acids and bases has been one of the major subjects of many chemists. Especially, in the field of 1 : 1 Lewis acid-base and 1 : 1 hydrogen-bond complexation in aprotic solvents, vast amounts of formation constants K_f (or $\log K_f$), enthalphies ΔH_f and other thermodynamic quantities have already been accumulated and applied to elucidate the fundamental characteristics governing acid-base interactions. A generally accepted conclusion in the field is the difficulty to compare acids and bases on a single strength scale. As shown by Pearson,[1—3] Drago et al.,[4—6] Maria et al.,[7] and Abraham et al.,[8] at least four parameters are necessary to interpret the difference in $\log K_f$ and ΔH_f of acid-base reactions.

For 1 : 1 hydrogen-bond complexation in CCl_4, an interesting feature was found by Abraham et al.[9—15] In this system, straight lines which pass through a specific point, called the magic point, are often observed among the $\log K_f$ values of various acids (or bases) against two different reference bases (or acids). These convergent linear relationships are called family-independent LFERs (linear free-energy relationships), because the LFERs are independent of the families of acids (e.g., phenols and imides) or bases (e.g., carbonyls, ether, and pyridines). On the other hand, it is also known that a set of family-dependent LFERs,[8,16] rather than family-independent LFERs, are observed for some base-reference acid systems.

The present authors[17] have reported that the family-independent and -dependent LFERs closely correlate with the local-structures of the acids and bases. Acid and base molecules can be regarded as comprising two local-structural units, a functional group and a residual moiety (called supporting group, hereinafter). Further, the value of $\log K$ of an acid A and base B can be correlated with the nature of the local structures by the following equation:

$$\log K_{AB} = (\eta_x + \eta_y)\omega_a\omega_b + \log K_0, \tag{1}$$

where η_x and η_y represent the nature of the functional group of the acid and the base, respectively, ω_a and ω_b represent the nature of the supporting group of the acid and the base, respectively, and $\log K_0$ is a constant term responsible for the magic point. As described in a previous paper,[17] η may be related to the size or related factors of the functional group and ω may be related to the electronic factors (electron-donating or -withdrawing ability) of the supporting group.

In the preceding paper,[18] the present authors analyzed the thermodynamic properties of the 1 : 1 hydrogen-bond complexation of OH- and NH-acids with phosphorus compounds in CCl_4 and showed that the following equation can be applied quantitatively to the 1 : 1 hydrogen-bond complexation of acid A and base B:

$$\log K_{AB} = \frac{-\Delta H^\circ_{AB}}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}, \tag{2}$$

where ΔH°_{AB} and ΔS°_f represent the change in the enthalpy and the entropy, respectively, and R and T stand for the gas constant and temperature, respectively. It was shown based on Eq. 2 that the magic point appears at (−1.85, −1.85) for the plots of $\log K_{AB}$ values of various acids (or bases) against two different reference bases (or acids) and that the appearance of the magic point can be ascribed to the constancy of the apparent ΔS°_f value (-35.4 J mol^{-1} K^{-1}). It was also shown based on the similarity between Eqs. 1 and 2 that ΔH°_{AB} can be correlated with the local structural parameters, η and ω, by the following equation:

$$-\Delta H^\circ_{AB} = 2.303RT(\eta_x + \eta_y)\omega_a\omega_b. \tag{3}$$

Although, Eqs. 1 and 3 are important as a novel formulation to correlate $\log K$ or ΔH°_{AB} with the local structures of acid and base molecules, an evaluation of η and ω has been difficult, because of too many variables being included in these equations. Only formal ω_b values[17] were evaluated by regarding all bases as having a common functional group.

In the present study, a method was developed for the simultaneous evaluation of η and ω for OH- and NH-acids and phosphorus bases by making use of the family-independent LFERs observed for the acid-base system.

Data for Analysis

The values of $\log K$ subjected to the present study were obtained from the data reported by Ruostesuo et al.,[19] and are listed in Table 1. Two acid families (OH and NH family) and three base families (=O, =S, and =Se family) are included in the system. As reported in the preceding paper,[18] family-independent and -dependent LFERs, both of which converge to the magic point (-1.85, -1.85), are observed among the $\log K$ values in these systems. The values of ΔH° shown in Table 1 were calculated from the $\log K$ values reported by Ruostesuo et al.[19] by a similar method to that of Ruostesuo et al., except for ΔS°_f being regarded as a constant (-35.4 J mol^{-1} K^{-1}). The slopes of the family-dependent LFERs given in Table 2 were obtained in the preceding paper[18] from the data given in Table 1, and were utilized to evaluate η and ω of acids and bases in the present study.

Results and Discussion

Separation of Temperature Effects on η and ω. Prior to an evaluation of the local structural parameters, the following equation is introduced based on Eq. 3 to separate the temperature effects on the local structural parameters:

$$-\Delta H^\circ_{AB} = (\eta^\circ_x + \eta^\circ_y)\omega^\circ_a\omega^\circ_b, \tag{4}$$

where η°_x, η°_y, ω°_a, and ω°_b are the local-structural parameters obtained at 298.15 K. The following equation can be obtained by applying Eq. 4 to Eq. 2:

$$\log K_{AB} = -\frac{(\eta^\circ_x + \eta^\circ_y)\omega^\circ_a\omega^\circ_b}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}, \tag{5}$$

where, ΔS°_f can be regarded as being virtually constant (-35.4 kJ mol^{-1} K^{-1}). The above equation is of importance as a general equation to correlate $\log K$ at various temperatures with the nature of the local structures of acids and bases for 1 : 1 hydrogen-bond complexation.

For the reaction of a set of acids A_i ($i = 1, 2, 3, \cdots$) with two reference base, B_1 and B_2, the following equations are obtained from Eq. 5:

$$\log K_{A_iB_1} = \frac{-(\eta^\circ_{x_i} + \eta^\circ_{y_1})\omega^\circ_{a_i}\omega^\circ_{b_1}}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}, \tag{6}$$

$$\log K_{A_iB_2} = \frac{-(\eta^\circ_{x_i} + \eta^\circ_{y_2})\omega^\circ_{a_i}\omega^\circ_{b_2}}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}, \tag{7}$$

where subscripts x_i, y_1, and y_2 stand for the functional group of A_i, B_1, and B_2, respectively, and subscripts a_i, b_1, and b_2 stand for the supporting group of A_i, B_1, and B_2, respectively. From the above equations, the following equations are derived:

$$\log K_{A_iB_2} = R_x \log K_{A_iB_1} + (1 - R_x)\frac{\Delta S^\circ_f}{2.303R}, \tag{8}$$

$$R_x = \frac{(\eta^\circ_{x_i} + \eta^\circ_{y_2})\omega^\circ_{b_2}}{(\eta^\circ_{x_i} + \eta^\circ_{y_1})\omega^\circ_{b_1}}. \tag{9}$$

Equation 8 suggests that the plots of $\log K_{A_iB_2}$ vs. $\log K_{A_iB_1}$ give a straight line of slope R_x, defined by Eq. 9, and that all of these straight lines converge to a specific point ($\Delta S^\circ_f/2.303R$, $\Delta S^\circ_f/2.303R$), which agrees with the magic point.

Evaluation of η° and ω° of Phosphorus Compounds. As a first step to evaluate η° and ω° of acids and bases, three numerical criteria are introduced: $\eta^\circ_x = 5.00$ and $\omega^\circ_a = 10.0$ for the functional group (OH) and the surpportig group (C_6H_5) of phenol, respectively, and $\eta^\circ = 5.00$ for the functional group (=O) of carbonyl bases. It was preliminary confirmed that these criteria are convenient in magnitude for the comparison of various acids and bases on the η° and ω° scale.

When Eqs. 8 and 9 are applied to the linear relationships observed among $\log K$ of OH-acids against reference bases $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ (or $(C_6H_5)_3P{=}Se$), the following equation is derived from Eq. 9, because these phosphorus bases have the same supporting group:

$$\eta^\circ_{y_2} = R_x(\eta^\circ_{OH} + \eta^\circ_{=O}) - \eta^\circ_{OH}, \tag{10}$$

where subscript y_2 represents the functional group =S or =Se. In the above equation, R_x is equal to the slope of the family-dependent straight line of OH-acids against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ (or $(C_6H_5)_3P{=}Se$) shown in Table 2. Thus, $\eta^\circ_{=S}$ and $\eta^\circ_{=Se}$ can be evaluated from the slopes shown in Table 2 by applying the following numerical criteria: $\eta^\circ_{OH} = 5.00$ and $\eta^\circ_{=O} = 5.00$. The results are given in Table 3.

When Eq. 5 is applied to the reaction of phosphorus compounds against phenol ($\eta^\circ_x = 5.00$, $\omega^\circ_a = 10.0$), the term $\Delta S^\circ_f/2.303R$ can be regarded as being constant ($= -1.85$), and the values of $\log K$ are already known, as listed in Table 1. Thus, for each of the phosphorus compounds, an evaluation of ω°_b from η°_y values given in Table 3 becomes possible by applying Eq. 5. The results of calculations are also given in Table 3.

The values of $\log K$ for the bases against phenol are also given in Table 3. By comparing the values of η°_y and ω°_b with the $\log K$ values, it can be seen that a stronger base which gives a larger $\log K$ value has a larger η°_y and a smaller ω°_b value. Therefore, the strength of the functional group expressed in the η°_y scale increases in the order: =Se (η°_y =

Table 1. Thermodynamic Data for the 1 : 1 Hydrogen-Bond Complexation of OH- and NH-Acids against Phosphorus Compounds in CCl_4 at 298.15 K

Base	Acid	$\log (K/\mathrm{dm^3\ mol^{-1}})^{a)}$	$\Delta H^\circ/\mathrm{kJ\ mol^{-1}}^{b)}$
$(C_6H_5)_3P{=}O$	2-Naphthol	3.06 (3.06)	−28.0 (−28.0)
	1-Naphthol	2.97 (2.97)	−27.5 (−27.5)
	Phenol	2.82 (2.81)	−26.7 (−26.7)
	CF_3CH_2OH	2.77 (2.77)	−26.4 (−26.4)
	CCl_3CH_2OH	2.30 (2.30)	−23.7 (−23.7)
	CBr_3CH_2OH	2.16 (2.16)	−22.9 (−22.9)
	Carbazole	1.94 (1.94)	−21.6 (−21.6)
	Indole	1.75 (1.75)	−20.5 (−20.6)
	Pyrrole	1.48 (1.48)	−19.0 (−19.0)
$(CH_3O)_3P{=}O$	2-Naphthol	2.35 (2.41)	−24.0 (−24.4)
	1-Naphthol	2.32 (2.33)	−23.8 (−23.9)
	Phenol	2.20 (2.20)	−23.1 (−23.1)
	CF_3CH_2OH	2.17 (2.16)	−23.0 (−22.9)
	CCl_3CH_2OH	1.69 (1.76)	−20.2 (−20.6)
	CBr_3CH_2OH	1.54 (1.63)	−19.3 (−19.9)
	Carbazole	1.37 (1.44)	−18.4 (−18.8)
	Indole	1.23 (1.28)	−17.6 (−17.9)
	Pyrrole	1.03 (1.04)	−16.4 (−16.5)
$(C_6H_5O)_3P{=}O$	2-Naphthol	1.76 (1.81)	−20.6 (−20.9)
	1-Naphthol	1.72 (1.74)	−20.4 (−20.5)
	Phenol	1.62 (1.62)	−19.8 (−19.8)
	CF_3CH_2OH	1.60 (1.59)	−19.7 (−19.6)
	CCl_3CH_2OH	1.21 (1.24)	−17.5 (−17.6)
	CBr_3CH_2OH	1.09 (1.14)	−16.8 (−17.1)
	Carbazole	1.10 (0.97)	−16.9 (−16.1)
	Indole	0.98 (0.83)	−16.2 (−15.3)
	Pyrrole	0.78 (0.63)	−15.0 (−14.2)
$(C_6H_5)_3P{=}S$	2-Naphthol	0.90 (0.93)	−15.7 (−15.9)
	1-Naphthol	0.87 (0.88)	−15.5 (−15.6)
	Phenol	0.78 (0.79)	−15.0 (−15.1)
	CF_3CH_2OH	0.75 (0.77)	−14.8 (−15.0)
	CCl_3CH_2OH	0.53 (0.50)	−13.6 (−13.4)
	CBr_3CH_2OH	0.48 (0.42)	−13.3 (−13.0)
	Carbazole	0.60 (0.63)	−14.0 (−14.2)
	Indole	0.50 (0.51)	−13.4 (−13.5)
	Pyrrole	0.34 (0.33)	−12.5 (−12.5)
$(C_6H_5)_3P{=}Se$	2-Naphthol	0.80 (0.87)	−15.1 (−15.6)
	1-Naphthol	0.79 (0.82)	−15.1 (−15.3)
	Phenol	0.73 (0.73)	−14.7 (−14.8)
	CF_3CH_2OH	0.70 (0.71)	−14.6 (−14.6)
	CCl_3CH_2OH	0.51 (0.45)	−13.5 (−13.1)
	CBr_3CH_2OH	0.47 (0.37)	−13.2 (−12.7)
	Carbazole	0.59 (0.60)	−13.9 (−14.0)
	Indole	0.49 (0.48)	−13.3 (−13.3)
	Pyrrole	0.33 (0.30)	−12.5 (−12.3)

a) Values in the parentheses are those calculated from η° and ω°. b) Values estimated from temperature dependency of $\log K$ by regarding $\Delta S^\circ_f = -35.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Values in the parentheses are those calculated from η° and ω°.

0.546) < =S (0.655) < =O (5.00). As described in a previous paper,[17] the order of the η°_y values may be related to the size or related factors of the functional group. Actually, the strength of the phosphorus bases expressed in the η°_y scale increases with a decrease in the atomic number of the functional group. On the other hand, the strength order of the supporting group in the ω°_b scale increases in the order: $(C_6H_5O)_3P$ ($\omega^\circ_b = -198$) < $(CH_3O)_3P$ (-231) < $(C_6H_5)_3P$ (-266). Since ω°_b may be related to the electronic factor of the supporting group,[17] the order of ω°_b obtained here may be in agreement with the order of the electron-donating ability of the supporting groups.

Table 2. Family-Dependent LFERs Conversing on the Magic Point (−1.85, −1.85,) Observed among log *K* Values of OH- and NH-Acids against Phosphorus Compounds in CCl_4 at 298.15 K

Reference base 1	Reference base 2	Functional group	Slope of line
$(C_6H_5)_3P{=}O$	$(C_6H_5O)_3P{=}S$	OH	0.567
		NH	0.652
	$(C_6H_5O)_3P{=}Se$	OH	0.555
		NH	0.649

Table 3. Values of Local Structural Parameters η_y°, ω_b° and log *K* against Phenol of Phosphorus Compounds

Base	η_y°	ω_b°	$\log(K/\mathrm{dm^3\,mol^{-1}})$
$(C_6H_5)_3P{=}O$	5.00[a)]	−266±1[b)]	2.82
$(CH_3O)_3P{=}O$	5.00	−231	2.20
$(C_6H_5O)_3P{=}O$	5.00	−198	1.62
$(C_6H_5)_3P{=}S$	0.665	−266±1[b)]	0.78
$(C_6H_5)_3P{=}Se$	0.546	−266±1[b)]	0.73

a) Numerical criterion of η_y°. b) The mean of values for the three bases.

Table 4. Values of Local Structural Parameters η_x° ω_a°, and log *K* against $(C_6H_5)_3P{=}O$ of OH- and NH-Acids

Acid	η_x°	ω_a°	$\log(K/\mathrm{dm^3\,mol^{-1}})$
2-Naphthol	5.00	10.5	3.06
1-Naphthol	5.00	10.3	2.97
Phenol	5.00[a)]	10.0[b)]	2.82
CF_3CH_2OH	5.00	9.92	2.77
CCl_3CH_2OH	5.00	8.91	2.30
CBr_3CH_2OH	5.00	8.61	2.16
Carbazol	7.57±0.12[c)]	6.47	1.94
Indole	7.57±0.12[c)]	6.15	1.75
Pyrrole	7.57±0.12[c)]	5.69	1.48

a) Numerical criterion of η_x°. b) Numerical criterion of ω°. c) The mean of two values obtained from family-dependent LFERs of the acids against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ or $(C_6H_5)_3P{=}Se$.

Evaluation of η° and ω° of NH- and OH-Acids. When Eq. 9 is applied to linear relationships observed for two families of acids with functional groups x_1 and x_2 against reference bases, B_1 (composed of y_1 and b_1) and B_2 (composed of y_2 and b_2), the following equations are obtained:

$$R_{x_1}=\frac{(\eta_{x_1}^\circ+\eta_{y_2}^\circ)\omega_{b_2}^\circ}{(\eta_{x_1}^\circ+\eta_{y_1}^\circ)\omega_{b_1}^\circ}, \tag{11}$$

$$R_{x_2}=\frac{(\eta_{x_2}^\circ+\eta_{y_2}^\circ)\omega_{b_2}^\circ}{(\eta_{x_2}^\circ+\eta_{y_1}^\circ)\omega_{b_1}^\circ}, \tag{12}$$

and

$$\frac{R_{x_2}}{R_{x_1}}=\frac{(\eta_{x_2}^\circ+\eta_{y_2}^\circ)(\eta_{x_1}^\circ+\eta_{y_1}^\circ)}{(\eta_{x_2}^\circ+\eta_{y_1}^\circ)(\eta_{x_1}^\circ+\eta_{y_2}^\circ)}. \tag{13}$$

Equation 13 suggests that a family-dependent LFER is observed when the condition $R_{x_1}\neq R_{x_2}$ is satisfied. It can be seen from the right-hand terms of the equation that the condition may be realized only when $\eta_{x_1}^\circ\neq\eta_{x_2}^\circ$ and $\eta_{y_1}^\circ\neq\eta_{y_2}^\circ$ are satisfied, simultaneously.

When the above equation is applied to the family-dependent LFERs observed for OH- and NH-acids against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ (or $(C_6H_5)_3P{=}Se$), η_{NH}° can be expressed as:

$$\eta_{NH}^\circ=\frac{R_{OH}\,\eta_{y_2}^\circ(\eta_{OH}^\circ+\eta_{=O}^\circ)-R_{NH}\,\eta_{=O}^\circ(\eta_{OH}^\circ+\eta_{y_2}^\circ)}{R_{NH}(\eta_{OH}^\circ+\eta_{y_2}^\circ)-R_{OH}(\eta_{OH}^\circ+\eta_{=O}^\circ)}, \tag{14}$$

where y_2 stands for the functional group =S or =Se. Thus, by substituting the η° values given in Table 3 and the slopes given in Table 2 to Eq. 14, η_{NH}° can be evaluated. The results are listed in Table 4.

When Eq. 5 is applied to the reaction of OH- and NH-acids against $(C_6H_5)_3P{=}O$ ($\eta_y^\circ=5.00$, $\omega_b^\circ=-266$), the values of log *K* given in Table 1 can be applied, and the term $\Delta S_f^\circ/2.303R$ is regarded as being a constant ($=-1.85$). Thus, for each of the acids, evaluating of ω_a° becomes possible by substituting the η_x° value of each functional group. The results are given in Table 4.

The values of log *K* of the OH- and NH-acids against $(C_6H_5)_3P{=}O$ are also given in Table 4. By comparing the values of ω_a° with the log *K* values, it can be seen that an acid with a larger ω_a° value is strong. The strength of the acids in the ω_a° scale is in the order: Pyrrole ($\omega_a^\circ=5.69$) < Indole (6.15) < Carbazole (6.47) < CBr_3CH_2OH (8.61) < CCl_3CH_2OH (8.91) < CF_3CH_2OH (9.92) < Phenol (10.0) < 1-Naphthol (10.3) < 2-Naphthol (10.5). Since ω_a° may be related to the electronic factor of the supporting group,[17] the order of ω_a° obtained here may be in agreement with the order of the electron-withdrawing ability of the supporting groups. On the other hand, it can be seen from Eq. 5 that an acid with a larger η_x° value is strong. Thus, the strength of the acids in the η_x° scale is in the order: OH ($\eta_x^\circ=5.00$) < NH (7.57). As described in the previous paper,[17] the difference in η_x° may be related to the size or a related factor of the functional groups.

Calculation of log *K* and ΔH° from η° and ω°. When the values of η° and ω° given in Tables 3 and 4 are applied to Eqs. 4 and 5, the values of log *K* at various temperatures and ΔH° can be calculated. In Table 1, the values given in parenthesis are the values of log *K* and ΔH° obtained from η° and ω°. The 45 log *K* values obtained from η° and ω° are in accord with those obtained experimentally within ±0.15 in the log *K* unit. The deviation is small enough compared with the experimental error of the log *K* values (< ±0.21). Similarly, the 45 ΔH° values obtained from η° and ω° are in accord with those obtained experimentally within ±0.89 in the ΔH° unit. From these results, it is concluded that all η° and ω° values have been successfully evaluated.

As shown in the preceding paper,[17] the values of log *K* at 288.15, 298.15, 308.15, and 318.15 K are already known for complexation between the acids and bases given in Table 1. The values of log *K* at various temperatures can also be calculated by substituting the η° and ω° values given in Tables 3 and 4 and the value of the temperature to Eq. 5. The plots in Fig. 1 show the relation between the log *K* values calculated from η° and ω° and those obtained experimen-

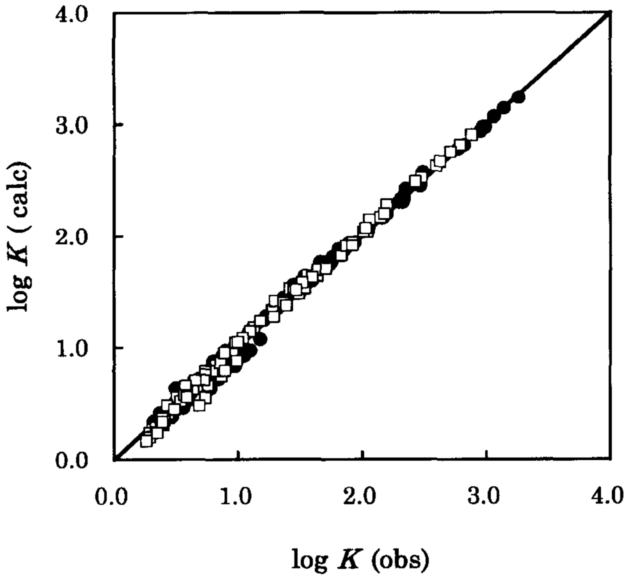

Fig. 1. Relation between 180 log (K/dm^3 mol^{-1}) values observed experimentally, log K(obs), and calculated from η° and ω°, log K(calc), for the complexation of nine OH- or NH-acids against five phosphorus bases at 288.15, 298.15, 308.15, and 318.15 K in CCl_4. ●: 288.15 and 298.15 K, □: 308.15 and 318.15 K.

tally. A good straight line with a unit slope is established for all 180 plots (the standard deviation = 0.056). From the results, it is concluded that the local structural parameters, η° and ω°, evaluated here can be applied to predicting log K at various temperatures.

Interpretation of Reversal in the Order of log K. One important aspect of acid-base interaction is that the order of the strength of acids (or bases) against a reference base (or acid) differs from that obtained by using a different reference acid (or base).[2,4] It can be seen from a careful survey of the values given in Table 1 that several reversals in the order of log K and ΔH° are observed: for example, as shown in Table 5, there are reversals in the order of log K and ΔH° of CCl_3CH_2OH and carbazole against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$. Since the same reversal is observed for the log K and ΔH° estimated from the η° and ω° values given in the parentheses, the η°–ω° methodology is reasonable with respect to reversals in the strengths of the acids and bases. The values of ω°_a and η°_x of the acids are given in Table 6. The order of ω°_a shows that CCl_3CH_2OH is stronger than carbazole. On the contrary, the reverse order is expected from the η°_x values. Thus, the reversal in log K and ΔH° can be explained as follows: log K (and ΔH°) and ω°_a are in the same order when ω°_a is the dominant factor; on the other hand, log K (and ΔH°) and η°_x are in the same order when η°_x is the dominant factor. It has been confirmed that all reversals observed in Table 1 can be explained similarly.

Table 6. The Order of η°_x and ω°_a for CCl_3CH_2OH and Carbazole

Parameter	CCl_3CH_2OH		Carbazole
ω°_a	8.91	>	6.47
η°_x	5.00	<	7.57

Plots of log K of CCl_3CH_2OH and carbazole against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ are shown in Fig. 2. The solid and broken lines show the family-dependent LFERs given by OH- and NH-acids, respectively. It can be seen that the order of log K of the acids is CCl_3CH_2OH > carbazole against $(C_6H_5)_3P{=}O$; on the other hand, CCl_3CH_2OH < carbazole against $(C_6H_5)_3P{=}S$. It can also be seen from the results that NH-acids including carbazole in the range from A to B on the broken line show a reversal of log K compared with that of CCl_3CH_2OH. The results suggest that the reversal in the order of log K appears only when family-dependent behaviors are observed. When Eq. 13 is applied to the results, it is concluded that the reversal in the order of log K appears only for the reaction of different family of acids ($\eta^\circ_{x_1} \neq \eta^\circ_{x_2}$) and two

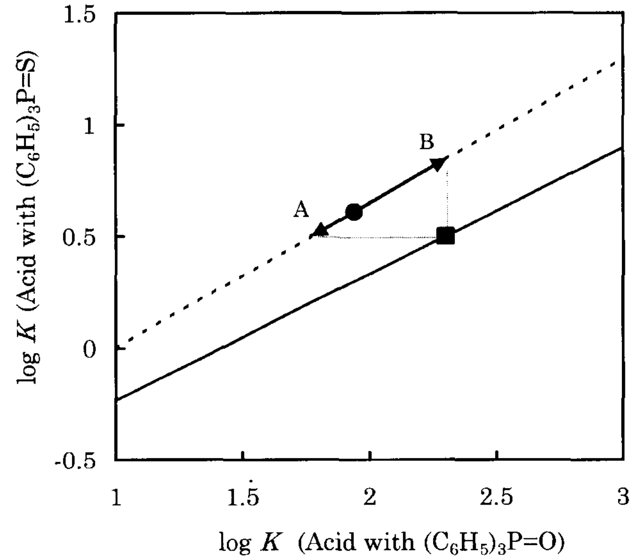

Fig. 2. Relation between log (K/dm^3 mol^{-1}) values of CCl_3CH_2OH and carbazole against $(C_6H_5)_3P{=}O$ and $(C_6H_5)_3P{=}S$ at 298.15 K in CCl_4. ■: CCl_3CH_2OH, ●: carbazole. The solid and broken lines show the family-dependent LFERs given by OH- and NH-acids, respectively.

Table 5. Reversal in the Order of log K and ΔH°_f between CCl_3CH_2OH and Carbazole at 298.15 K

Reference	log (K/dm^3 mol^{-1})			ΔH°_f/kJ mol^{-1}		
base	CCl_3CH_2OH[a]		Carbazole[a]	CCl_3CH_2OH[a]		Carbazole[a]
$(C_6H_5)_3P{=}O$	2.30 (2.30)	>	1.94 (1.94)	−23.7 (−23.7)	<	−21.6 (−21.6)
$(C_6H_5)_3P{=}S$	0.53 (0.50)	<	0.60 (0.63)	−13.6 (−13.4)	>	−14.0 (−14.2)

a) Values in parentheses are those calculated from η° and ω°.

reference bases with different functional groups ($\eta^\circ_{y_1} \neq \eta^\circ_{y_2}$).

Conclusion

Novel local structural parameters of acids and bases, η° and ω°, have been evaluated for the first time in 1 : 1 hydrogen-bond complexation in CCl_4. It has also been shown that the values of η° and ω° can be utilized to estimate the $\log K$ values at various temperatures and ΔH° values, and that the reversals in the order of $\log K$ and ΔH° can be correlated with the nature of local structures expressed by the η° and ω° scale. These results suggest that η° and ω° can be used as quantitative strength scales for the functional group and the supporting group, respectively, for 1 : 1 hydrogen-bond complexation.

In the conventional four-parameter equations proposed by Drago et al.[4—6] and Maria et al.,[7] little attention is paid to the structure-strength relationships observed for acid–base interactions. Therefore, the η°–ω° methodology developed here is of importance as a new quantitative approach to elucidate the fundamental characteristics governing acid–base interactions.

The reversals in the order of $\log K$ and ΔH° can be explained quantitatively by applying the η°–ω° methodology developed here. In general, the reversals in the order of ΔH° have been explained in terms of the difference in the hardness (or softness) factor based on the HSAB concept,[1—3] or the difference in the electrostatic:covalent ratio contributing to the interaction based on the *E*–*C* equation.[4—6] Since the approach developed here based on the difference in the nature of local structures differs clearly from that of the HSAB concept and of the *E*–*C* equation, it gives us an inportant new view for the reversals in the order of $\log K$ and ΔH°.

References

1 R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

2 R. G. Pearson, *J. Chem. Educ.*, **45**, 581 (1968).

3 R. G. Pearson, *J. Chem. Educ.*, **45**, 643 (1968).

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

5 R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).

6 R. S. Drago, *J. Chem. Educ.*, **51**, 300 (1974).

7 P-C. Maria, J-F. Gal, J. Franceschi, and E. Fargin, *J. Am. Chem. Soc.*, **109**, 483 (1987).

8 M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, P. J. Taylor, P-C. Maria, and J-F. Gal, *J. Phys. Org. Chem.*, **2**, 243 (1989).

9 M. H. Abraham, P. P. Duce, P. L. Grellier, D. V. Prior, J. J. Morris, and P. J. Taylor, *Tetrahedron Lett.*, **29**, 1587 (1988).

10 M. H. Abraham, P. L. Grellier, D. V. Prior, R. W. Taft, J. J. Morris, P. J. Taylor, C. Laurence, M. Berthelot, R. M. Doherty, M. J. Kamlet, J-L. M. Abboud, K. Sraidi, and G. Guihéneuf, *J. Am. Chem. Soc.*, **110**, 8534 (1988).

11 M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris, and P. J. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, **1989**, 699.

12 M. H. Abraham, P. P. Duce, D. V. Prior, D. G. Barratt, J. J. Morris, and P. J. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, **1989**, 1355.

13 M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, and P. J. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, **1990**, 521.

14 M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, P. J. Taylor, and R. M. Doherty, *J. Org. Chem.*, **55**, 2227 (1990).

15 M. H. Abraham, *Chem. Soc. Rev.*, **22**, 73 (1993).

16 J. Mitsky, L. Joris, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 3442 (1972).

17 S. Mishima, I. Matsuzaki, and T. Nakajima, *J. Chem. Soc.*, *Faraday Trans.*, **89**, 4279 (1993).

18 S. Mishima and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **68**, 3403 (1995).

19 P. Ruostesuo, U. Salminen, and R. Liias, *Spectrochim. Acta*, *Part A*, **43A**, 1135 (1987).