Evaluation of Novel Local Structural Parameters of Various Acids and Bases

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Novel local structural parameters representing the nature of functional group and residual moiety of acids and bases were evaluated successfully from the formation constants of the 1:1 hydrogen-bond complexation in CCl_4 reported in literatures.

Formation constants K_f (or log K_f) and enthalphies ΔH_f of the 1:1 Lewis acids-base and the 1:1 hydrogen-bond interactions in aprotic solvents have often been studied to elucidate the fundamental factors governing acid-base interactions. A generally accepted conclusion in the field is the difficulty in comparison of acids and bases on a single scale: as shown by Drago et al.,[1-3] Maria et al.,[4] and Abraham et al.,[5] at least four parameters are necessary to interpret ΔH_f and log K_f of acid-base interactions.

The family-independent and -dependent straight lines all of which converge on a single point are observed among log K_f of the 1:1 hydrogen-bond complexation in CCl_4.[6-10] From these characteristic linear relationships, the present authors[10] showed recently that log K_f can be expressed as a function of the nature of the functional group (expressed as η) and its residual moiety (expressed as ω) of acids and bases. As described in the previous paper,[10] 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 and withdrawing ability) of the residual moiety. The residual moiety is called the "supporting group," hereinafter. The η–ω equation is of importance as a new four parameter formalism of acid-base interactions. However, no η and ω value which is applicable quantitatively to the η–ω equation has been evaluated.

In the η-ω methodology, evaluation of the parameters η and ω of each acid and base is essential. Therefore, in the present study, evaluation of η and ω is attempted for various acids and bases. Prior to evaluation of the parameters, the following equation was introduced to separate temperature effects from η and ω, on the basis of the results in our preceding papers:[10,11]

$$\log K_{AB} = \frac{-(\eta_x^\circ + \eta_y^\circ)\,\omega_a^\circ\,\omega_b^\circ}{2.303RT} + \frac{\Delta S_f^\circ}{2.303R} \qquad (1)$$

where η_x° and ω_a° represent the acidic nature of the functional group and the supporting group of acid A, respectively, and are independent of temperature; η_y° and ω_b° represent the basic nature of the functional group and the supporting group of base B, respectively, and are independent of temperature; T and R stand for temperature (K) and the gas constant (8.314 $Jmol^{-1}K^{-1}$); and, as described in our preceding paper,[11] ΔS_f is apparently constant (-35.4 $Jmol^{-1}K^{-1}$).

The above equation was applied to the family-independent and -dependent linear relationships[11] among log K_f values of the 1:1 hydrogen-bond complexation of five OH- and NH-acids against fifteen phosphorus compounds in CCl_4. At the evaluation of η° and ω°, η_x°=5.00 and ω_a°=10.0 for phenol and η_y°=5.00 for carbonyls were introduced as numerical criteria. When these criteria are adopted, values of η and ω of various acids and bases become moderate in magnitude and are convenient for the comparison of acids and bases on the η and ω scales. Results are shown in Table 1. It was found that 180 log K values[12] measured at 288.15, 298,15, 308.15 and 318.15 K can be predicted from these η° and ω° values within ±0.12 in log K_f unit. Similar analysis was applied to the linear relationships[10] among log K_f values of 26 bases against p-fluorophenol, 5-fluoroindole, and phenol in CCl_4. Results are shown in Table 2. Values of log K_f predicted from η° and ω° values shown in Table 2 are in agreement with experimental values within ±0.10 in log K_f unit except for only two adducts. It is concluded from these results that values of η° and ω° which satisfy Eq. 1 can be determined successfully for various acids and bases. Since, at the present stage, values of η° and ω° of eleven acids and 29 bases have already been known, prediction is possible for log K_f values of 319 adducts at various temperatures.

Table 1. Values of parameters η° and ω° of OH and NH acids and phosphorus compounds

Acid and Base	η°	ω°
(Acid)		
Phenol	5.00	10.0
2-Naphthol	5.00	10.5
1-Naphthol	5.00	10.3
CF_3CH_2OH	5.00	9.92
CCl_3CH_2OH	5.00	8.91
CBr_3CH_2OH	5.00	8.61
Carbazole	7.57	6.47
Indole	7.57	6.15
Pyrrole	7.57	5.69
(Base)		
$(C_6H_5)_3P{=}O$	5.00	-266
$(CH_3O)_3P{=}O$	5.00	-231
$(C_6H_5O)_3P{=}O$	5.00	-198
$(C_6H_5)_3P{=}S$	0.665	-266
$(C_6H_5)_3P{=}Se$	0.546	-266

The strength of functional groups on the η° scale increases in the orders; OH (η_x°=5.00) < NH (7.57) for the acids, and =Se (η_y°=0.55) < =S (0.67) < =O (5.00) < -O- (14.6) < =N- (16.3) < >N- (77) for the bases. On the other hand, the strength of supporting groups on ω° scale increases in the orders: pyrrole (ω_a°=5.69) < indole (6.15) < carbazole (6.47) < 5-fluoroindole (6.63) < CX_3CH_2OH (8.61 - 9.92, X=F, Cl, or Br) < phenol (10.0) < naphthols (10.3∼10.5) for acids; and >N- bases (ω_b°= -29.6∼-15.2) < =N- bases (-127∼-66.2), -O- bases (-86.5∼-78.3) < = Se, =S and =O bases (-300∼-140). These orders

Table 2. Values of parameters η° and ω° of *p*-fluorophenol, 5-fluoroindole, and various bases

Acid and Base	η°	ω°
(Acid)		
p-Fluorophenol	5.00	10.5
5-Fluoroindole	7.57	6.63
(Base)		
Hexamethylphosphoramide	5.00	-293
Dimethyl sulfoxide	5.00	-238
N,N-Dimethylacetamide	5.00	-229
Tetramethylurea	5.00	-225
N,N-Dimethylformamide	5.00	-212
Diphenyl sulfoxide	5.00	-210
N,N-Dimethylchloroacetamide	5.00	-191
Cyclohexanone	5.00	-171
p-Methoxyacetophenone	5.00	-172
Benzaldehyde	5.00	-145
Tetrahydrofuran	14.6	-86.5
Diethyl ether	14.6	-78.3
sym-Tetramethylguanidine	16.3	-127
4-Dimethylaminopyridine	16.3	-119
Pyridine	16.3	-95.0
3-Bromopyridine	16.3	-79.2
3.5-Dichloropyridine	16.3	-66.2
Quinuclidine	77	-29.6
N,N-dimethylcyclohexylamine	77	-25.9
Diazabicyclo[2.2.2]octane	77	-26.8
Triethylamine	77	-24.9
Tri-n-butylamine	77	-22.6
N,N-dimethylaniline	77	-15.2
Triallylamine	77	-20.4

show that the nature of various functional groups and supporting groups can be compared quantitatively on a single scale, η° and ω°, respectively. For example, values of η°_y described above suggest that basic functional groups with π-electron and of larger atomic number are generally weak in strength. Such comparison is difficult when the four-parameter equations proposed by Drago et al.[1-3] (*E-C* equation) and Maria et al.[4] (*S-F* equation) are applied, because, in their methodologies, few attention was paid for the structure-strength relationships.

One important aspect of acid-base interactions is that the order of the strengths of acids (or bases) against a reference base (or acid) differs from that obtained by using a different reference acid (or base).[1,13] As shown in Table 3, a reversal in the order of strengths is observed for log K_f values 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_f predicted from η° and ω° values (see values in parentheses in Table 3), the η°-ω° methodology is reasonable with respect to reversals in the strengths of acids and bases. The order of η°_x and ω°_a for the acids are shown in Table 4. 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_f can be explained as follows: log K_f and ω°_a are in the same order when ω°_a is the dominant factor, on the other hand, log K_f and η°_x are in the same order when η°_x is the dominant factor. As described above, the η-ω equation can be applied to the reversal in log K_f values.

Table 3. Reversal in the order of log *K* between CCl_3CH_2OH and carbazole at 298 K

Reference base	log *K* of CCl_3CH_2OH[a]		log *K* of carbazole[a]
$(C_6H_5)_3P{=}O$	2.30 (2.30)	>	1.94 (1.94)
$(C_6H_5)_3P{=}S$	0.53 (0.50)	<	0.60 (0.63)

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

Table 4. The order of η° and ω° of CCl_3CH_2OH and carbazole

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

In conclusion, parameters η° and ω° evaluated here are applicable as novel quantitative scales of fundamental factors governing acid-base interactions and give a new view of acid-base chemistry.

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