An Interpretation of Convergent Linear Energy Relationships Observed for 1 : 1 Hydrogen-Bond Complexation of OH– and NH–Acids with Phosphorus Compounds in Carbon Tetrachloride

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A thermodynamic interpretation is presented of the convergent linear relationships observed among the $\log K$ (K; equilibrium constant) values of 1 : 1 hydrogen-bond complexation of nine OH– and NH–acids against five phosphorus compounds in CCl_4. Straight lines converging on a single point are plotted from the $\log K$ values at different temperatures. The slopes of the lines correspond to the temperature ratio and the convergence point reflects the apparent constant value of ΔS° ($-35.4\ \mathrm{J\,mol^{-1}\,K^{-1}}$). Sets of family-independent or family-dependent straight lines all of which converge on the same point can be plotted from the $\log K$ values of the acids (or bases) against two reference bases (or acids). The convergence point also reflects the constancy of the apparent ΔS° value and the slopes of the lines correspond to the ΔH° ratio. The thermodynamic features can be correlated with local structures of the acids and bases. The interpretation presented here can be applied to other systems and is of importance as a new view of 1 : 1 hydrogen-bond systems.

Vast amounts of thermodynamic data such as $\log K$ (or ΔG°), ΔH°, ΔS°, and the frequency shift in spectroscopic quantities have already been accumulated[1)] for 1 : 1 hydrogen-bond complexation in various aprotic solvents. These thermodynamic and spectral data are important for elucidating essential properties of acid-base interactions and constructing acidity and basicity scales as reported by, for example, Drago et al.,[2—4)] Taft et al.,[5—8)] Sherry and Purcell,[9,10)] Terent'ev,[11)] and Kamlet et al.[12—14)]

In recent years, Abraham et al.[15—21)] found by applying a statistical analysis to 1 : 1 hydrogen-bond complexation in CCl_4 that a straight line which passes through a specific point (-1.1, -1.1) is frequently observed among $\log K$ 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 lines are independent of the families of acids (e.g., phenols and imides) or bases (e.g., carbonyls, ethers, and pyridines). The convergence point is called the "magic point".[15—21)] Family-independent LFERs are used to construct acidity and basicity scales: Abraham et al. proposed a new hydrogen-bond acidity scale α_2^{H}[15—17,20,21)] and a basicity scale β_2^{H}[16,19—21)] on the basis of convergent linear relationships. Values of $\log K$ are correlated with these scales by the following equation:

$$\log K = m\alpha_2^{\mathrm{H}}\beta_2^{\mathrm{H}} + c, \tag{1}$$

where m and c are constant terms determined by the temperature and the solvent.

On the other hand, a set of family-dependent LFERs,[22,23)] rather than family-independent LFERs, is observed for some base-reference acid systems. Family-dependent LFERs are also an important feature of 1 : 1 hydrogen-bond complexation in aprotic solvents. Abraham et al.[23)] showed that family-independent and -dependent LFERs can be explained in terms of the angle θ proposed by Maria et al.,[24)] a quantitative expression of the electrostatic:covalent ratio contributing to adduct formation. The present authors[25)] found recently that the family-dependent lines, as well as the family-independent lines, converge on the magic point and that the convergent linear relationships can be explained by regarding the acid and base molecules as being composed of both a functional group and a residual moiety, as expressed by the following equation:

$$\log K = (\eta_{\mathrm{x}} + \eta_{\mathrm{y}})\omega_{\mathrm{a}}\omega_{\mathrm{b}} + \log K_0, \tag{2}$$

where η_{x} and η_{y} depend on the functional group of the acid and the base, respectively, ω_{a} and ω_{b} depend on the residual moiety of the acid and the base, respectively, and $\log K_0$ is a constant term.

The convergent family-independent and -dependent LFERs are important general features observed in 1 : 1

hydrogen-bond complexation in CCl_4. However, explanation of the convergent straight lines has scarcely been attempted. In the present study, the 1 : 1 complexation of OH– and NH–acids with phosphorus compounds in CCl_4 has been analyzed thermodynamically to interpret the convergent LFERs.

Data for Analysis

Ruostesuo et al.[26] reported formation constants, K ($dm^3\,mol^{-1}$), of the 1 : 1 hydrogen-bond complexation of nine OH– or NH–acids against five phosphorus compounds at 288.15—318.15 K in CCl_4 determined by means of IR-spectroscopy. All $\log K$ values subjected to the present study were calculated from these formation constants and are listed in Table 1 together with the ΔH° ($kJ\,mol^{-1}$) values reported by Ruostesuo et al.[26] It is important that two acid families (OH and NH families) and three base families (=O, =S, and =Se families) are included in the systems.

Results and Discussion

Temperature Dependency of log *K* Values. The equilibrium of 1 : 1 hydrogen-bond complexation between acid A and base B in an inert solvent can be expressed generally as follows:

$$A + B \overset{K_{AB}}{\rightleftharpoons} AB. \tag{3}$$

In the above equilibrium, $\log K_{AB}$ is correlated with the change of enthalpy (ΔH°_{AB}) and of entropy (ΔS°_{AB}) by the following equation:[27,28]

$$\log K_{AB} = \frac{-\Delta H^\circ_{AB}}{2.303RT} + \frac{\Delta S^\circ_{AB}}{2.303R}, \tag{4}$$

where R is the gas constant ($8.314\ J\,mol^{-1}\,K^{-1}$) and T stands for the temperature (K).

When the above equation is applied to the complexation of acids A_i (i=1,2,3,...) with bases B_j (j=1,2,3,...) at T_1 and T_2 K, the following equations are obtained:

$$\log K^{T_1}_{A_iB_j} = \frac{-\Delta H^\circ_{A_iB_j}}{2.303RT_1} + \frac{\Delta S^\circ_{A_iB_j}}{2.303R}, \tag{5}$$

$$\log K^{T_2}_{A_iB_j} = \frac{-\Delta H^\circ_{A_iB_j}}{2.303RT_2} + \frac{\Delta S^\circ_{A_iB_j}}{2.303R}. \tag{6}$$

From the above equations, the relation between $\log K_{A_iB_j}$ at T_1 and T_2 K is expressed as follows:

$$\log K^{T_2}_{A_iB_j} = \frac{T_1}{T_2}\log K^{T_1}_{A_iB_j} + (1 - \frac{T_1}{T_2})\frac{\Delta S^\circ_f}{2.303R}, \tag{7}$$

where ΔS°_f represents $\Delta S^\circ_{A_iB_j}$.

If the variable ΔS°_f is virtually constant for a set of adducts A_iB_j, Eq. 7 suggests that straight lines of slope T_1/T_2 would results from the plots of $\log K^{T_2}_{A_iB_j}$ vs. $\log K^{T_1}_{A_iB_j}$ and that all such lines would pass through a point ($\Delta S^\circ_f/2.303R$, $\Delta S^\circ_f/2.303R$) independent of temperature.

Figure 1 shows the relations between $\log K$ values at various temperatures (288.15, 308.15 or 318.15 K) and those at 298.15 K obtained from the data shown in Table 1. The straight lines shown in the figure were determined based on Eq. 7 by applying the least squares method to the plots under the condition that the slope of the line is equal to T_1/T_2 and that ΔS°_f is constant. A set of straight lines converging on a single point (−1.85, −1.85) results. From this, it can be concluded based on Eq. 7 that $\Delta S^\circ_f/2.303R$ is virtually constant (=−1.85) for all of the adducts and that the slope of the lines is equal to the temperature ratio, T_1/T_2.

It is probable that a set of straight lines similar to that shown in Fig. 1 can be obtained when values other than −1.85 are applied as $\Delta S^\circ_f/2.303R$. However, Eq. 7 suggests that the slope r of these lines is equal to T_1/T_2 only when the optimal $\Delta S^\circ_f/2.303R$ is applied. The difference between the slope r and the ratio T_1/T_2 obtained from the data shown in Table 1 by applying various $\Delta S^\circ_f/2.303R$ values is shown in Fig. 2. Since the condition $r - T_1/T_2 = 0$ (thus, r is equal to T_1/T_2) is satisfied only when $\Delta S^\circ_f/2.303R = -1.85 \pm 0.05$ for all of the lines, it is concluded based on Eq. 7 that the optimal convergence point is at −1.85, −1.85 in accordance with the results shown in Fig. 1. The position of the convergence point shows that the optimal value of ΔS°_f is $-35.4\ J\,mol^{-1}\,K^{-1}$ for all of the adduct formation reactions.

For the three sets of data used for the plots shown

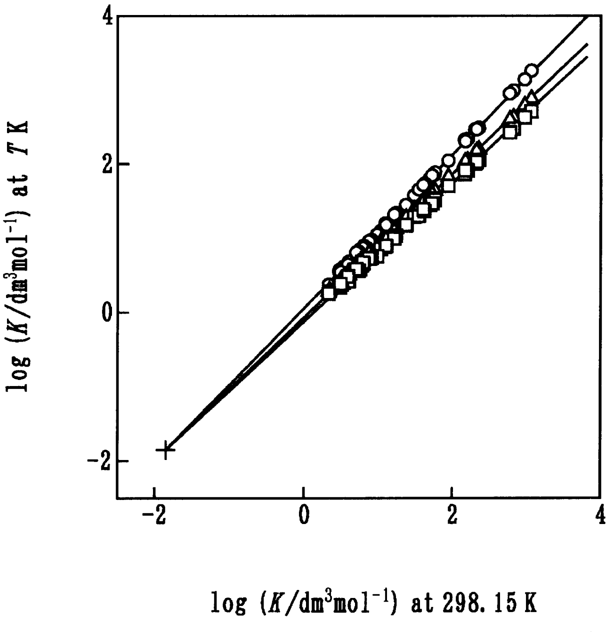

Fig. 1. Effects of temperature on $\log K$ values of OH– and NH–acids against phosphorus compounds in CCl_4. Values of $\log K$ of the vertical axis are obtained at: ○, 288.15 K; △, 308.15 K; and □, 318.15 K. Slope of the lines is equal to the ratio of temperature. The convergence point given as "+" locates at (−1.85, −1.85).

Table 1. Thermodynamic Data of the 1 : 1 Hydrogen-Bond Complexation of OH– and NH–Acids with Phosphorus Compounds in CCl_4

Base	Acid	$\log(K/\mathrm{dm^3\,mol^{-1}})$				ΔH_f°
		288.15 K	298.15 K	308.15 K	318.15 K	$\mathrm{kJ\,mol^{-1}}$
$(C_6H_5)_3P{=}O$	2-Naphthol	3.26	3.06	2.88	2.71	−32.2
	1-Naphthol	3.14	2.97	2.79	2.63	−30.0
	Phenol	2.99	2.82	2.63	2.48	−30.4
	CF_3CH_2OH	2.95	2.77	2.60	2.43	−30.7
	CCl_3CH_2OH	2.47	2.30	2.15	2.01	−27.0
	CBr_3CH_2OH	2.33	2.16	2.01	1.87	−26.8
	Carbazole	2.05	1.94	1.83	1.71	−20.0
	Indole	1.86	1.75	1.64	1.54	−19.7
	Pyrrole	1.58	1.48	1.39	1.29	−19.7
$(CH_3O)_3P{=}O$	2-Naphthol	2.49	2.35	2.20	2.06	−25.2
	1-Naphthol	2.47	2.32	2.18	2.03	−25.8
	Phenol	2.34	2.20	2.05	1.92	−24.9
	CF_3CH_2OH	2.31	2.17	2.04	1.92	−22.8
	CCl_3CH_2OH	1.81	1.69	1.56	1.45	−21.2
	CBr_3CH_2OH	1.66	1.54	1.42	1.30	−21.0
	Carbazole	1.45	1.37	1.28	1.18	−16.1
	Indole	1.34	1.23	1.13	1.04	−15.4
	Pyrrole	1.10	1.03	0.96	0.86	−12.2
$(C_6H_5O)_3P{=}O$	2-Naphthol	1.89	1.76	1.64	1.52	−22.4
	1-Naphthol	1.85	1.72	1.60	1.47	−22.1
	Phenol	1.74	1.62	1.50	1.37	−21.3
	CF_3CH_2OH	1.72	1.60	1.49	1.39	−19.4
	CCl_3CH_2OH	1.32	1.21	1.10	1.00	−18.7
	CBr_3CH_2OH	1.20	1.09	0.98	0.89	−18.9
	Carbazole	1.18	1.10	0.99	0.90	−16.0
	Indole	1.05	0.98	0.87	0.76	−16.6
	Pyrrole	0.85	0.78	0.74	0.69	−9.38
$(C_6H_5)_3P{=}S$	2-Naphthol	0.98	0.90	0.82	0.74	−14.1
	1-Naphthol	0.96	0.87	0.80	0.73	−13.5
	Phenol	0.86	0.78	0.70	0.64	−13.1
	CF_3CH_2OH	0.85	0.75	0.65	0.59	−13.1
	CCl_3CH_2OH	0.62	0.53	0.47	0.41	−12.7
	CBr_3CH_2OH	0.58	0.48	0.41	0.34	−14.1
	Carbazole	0.69	0.60	0.51	0.43	−11.8
	Indole	0.56	0.50	0.45	0.39	−9.65
	Pyrrole	0.37	0.34	0.31	0.29	−4.85
$(C_6H_5)_3P{=}Se$	2-Naphthol	0.90	0.80	0.74	0.66	−13.1
	1-Naphthol	0.87	0.79	0.74	0.68	−13.4
	Phenol	0.82	0.73	0.67	0.57	−13.1
	CF_3CH_2OH	0.81	0.70	0.62	0.59	−13.3
	CCl_3CH_2OH	0.59	0.51	0.44	0.38	−12.2
	CBr_3CH_2OH	0.56	0.47	0.40	0.35	−13.4
	Carbazole	0.65	0.59	0.54	0.49	−10.1
	Indole	0.55	0.49	0.44	0.39	−8.00
	Pyrrole	0.38	0.33	0.29	0.26	−7.00

in Fig. 1, the value of $\Delta S_f^\circ/2.303R$ which gives straight lines of the minimum standard deviation is in the range from −1.2 to −0.7. Since such lines are different from those satisfying $r=T_1/T_2$, the simple least squares method without consideration of the relation between the slope and the temperature ratio is unsuitable for determining the convergence point.

Linear relationships between ΔH° and ΔS°, which are generally called compensation effects, have often been observed[29)] for various 1 : 1 hydrogen-bond complexation systems. The compensation effects suggest that the value of ΔS°, as well as ΔH°, varies from one adduct to another. Actually, ΔS° values determined by Ruostesuo et al.[26)] for the systems shown in Table 1 vary from −49.2 to $-9.77\ \mathrm{J\,mol^{-1}\,K^{-1}}$ and a very rough linear relationship is observed between the values of ΔH°

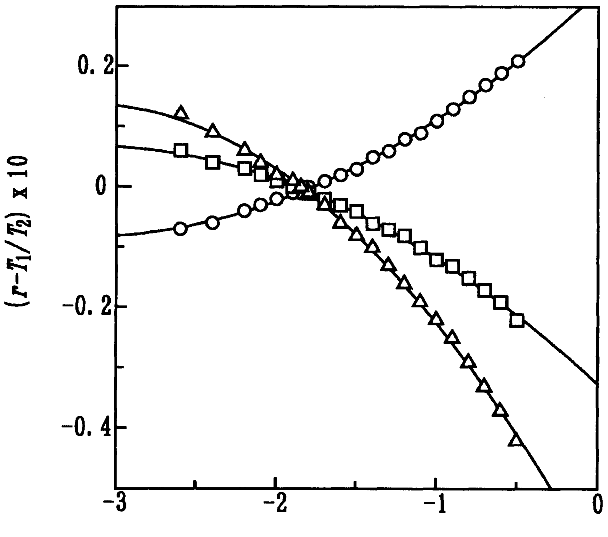

Fig. 2. Difference of slope r and T_1/T_2 as a function of the value of $\Delta S^\circ/2.303R$. T_1 is 298.15 K. T_2 is ○, 288.15 K; □, 308.15 K; △, 318.15 K.

and ΔS°. Thus, at first glance, the constancy of ΔS°_f obtained here seems to contradict the compensation effects.

To understand the influence of the change of ΔS°_f on the $\log K^{T_2}_{A_iB_j}$ vs. $\log K^{T_1}_{A_iB_j}$ plots, the effect of ΔS°_f on the entropy relating term, $\{1-(T_1/T_2)\}\ \Delta S^\circ_f/2.303R$, in Eq. 7 was estimated. These results are summarized in Table 2. Although ΔS°_f values from −49.2 to −9.77 J mol^{-1} K^{-1} have been applied, the variation of the entropy relating term is, at most, ±0.065 in $\log K$ units which is comparable to the experimental error of the $\log K$ values (<±0.21) estimated from the data of Ruostesuo et al.[26] Therefore, the constancy of ΔS° observed here is reasonable within experimental error as to the $\log K^{T_2}_{A_iB_j}$ vs. $\log K^{T_1}_{A_iB_j}$ plots. Since ΔS°_f varies from one adduct to another, the constant value of ΔS°_f (−35.4 J mol^{-1}K^{-1}) obtained here can be regarded as an apparent value representing a kind of average of all the ΔS°_f values.

It is concluded from the results described above that the slope of the $\log K^{T_2}_{A_iB_j}$ vs. $\log K^{T_1}_{A_iB_j}$ plots is equal to the temperature ratio and the appearance of the convergence point is due to the apparent ΔS° value being a constant that is independent of the adducts.

Table 2. Effect of Variation of ΔS° on the Term $\{1-(T_1/T_2)\}\ \Delta S^\circ/2.303R$

T_1 / K	T_2 / K	ΔS° / J mol^{-1} K^{-1}	$(1-\frac{T_1}{T_2})\frac{\Delta S^\circ}{2.303R}$
298.15	288.15	−49.2 — −9.77	−0.053±0.036
298.15	308.15	−49.2 — −9.77	0.050±0.033
298.15	318.15	−49.2 — −9.77	0.097±0.065

Effects of Reference Bases on log *K* Values. When the term ΔS° is virtually constant for the reaction of a set of acids A_i (i=1,2,3,...) against reference bases B_1 and B_2 at T K, the following equations can be derived from Eq. 4 by expressing ΔS°_{AB} as ΔS°_f:

$$\log K_{A_iB_1} = \frac{-\Delta H^\circ_{A_iB_1}}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}, \tag{8}$$

$$\log K_{A_iB_2} = \frac{-\Delta H^\circ_{A_iB_2}}{2.303RT} + \frac{\Delta S^\circ_f}{2.303R}. \tag{9}$$

From the above equations, the following equation is derived:

$$\log K_{A_iB_2} = \frac{\Delta H^\circ_{A_iB_2}}{\Delta H^\circ_{A_iB_1}}\log K_{A_iB_1} + (1-\frac{\Delta H^\circ_{A_iB_2}}{\Delta H^\circ_{A_iB_1}})\frac{\Delta S^\circ_f}{2.303R}. \tag{10}$$

If not only the term ΔS°_f but also $\Delta H^\circ_{A_iB_2}/\Delta H^\circ_{A_iB_1}$ is constant for all of the acids, the above equation suggests that the plots of $\log K$ values of a set of acids against a reference base vs. those against another base would give a straight line of slope $\Delta H^\circ_{A_iB_2}/\Delta H^\circ_{A_iB_1}$ and all such lines would converge on a point ($\Delta S^\circ_f/2.303R$, $\Delta S^\circ_f/2.303R$). The convergence point would exists at (−1.85, −1.85) in the present systems because ΔS°_f is −1.85, as described above.

Figure 3 shows plots of $\log K$ values at 298.15 K of the nine acids against $(CH_3O)_3P{=}O$ or $(C_6H_5)_3P{=}S$ vs. those against $(C_6H_5)_3P{=}O$. The point shown by "+" in the figure stands for the convergence point (−1.85, −1.85) expected from the results shown in Fig. 1. When

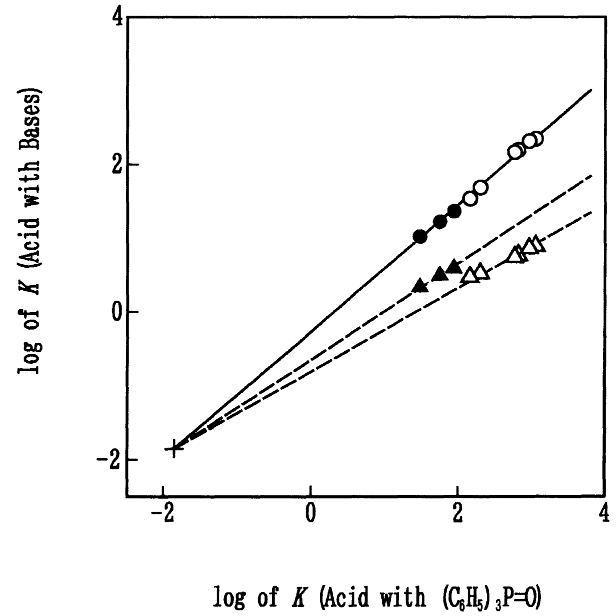

Fig. 3. Relation between $\log K$ values of acids against $(C_6H_5)_3P{=}O$ and those against $(CH_3O)_3P{=}O$ and $(C_6H_5)_3P{=}S$ obtained at 298.15 K in CCl_4. ○ and △, OH–acids; ● and ▲, NH–acids. Reference bases for the vertical axis are: ○ and ●, $(CH_3O)_3P{=}O$; △ and ▲, $(C_6H_5)_3P{=}S$. The convergence point shown by "+" locates at (−1.85, −1.85).

$(C_6H_5)_3P{=}O$ and $(CH_3O)_3P{=}O$ are used as the reference base, a family-independent straight line that extrapolates to (−1.85, −1.85) can be plotted as shown by the solid line. Equation 10 suggests that the linear relationship is due to the constancy of the ratio $\Delta H^{\circ}_{A_iB_2}/\Delta H^{\circ}_{A_iB_1}$, which is equal to the slope of the line, independent of the acids. When $(C_6H_5)_3P{=}S$ and $(C_6H_5)_3P{=}O$ are used as the reference base, two family-dependent straight lines both of which can be extrapolated to the point (−1.85, −1.85) are plotted as shown by the broken lines. Thus, Eq. 10 suggests that the ratio of ΔH° is virtually constant only within each family of acids. It is important that all lines shown in Fig. 3 are considered to be converging on the point (−1.85, −1.85), because, as determined from Eq. 10, the appearance of the convergence point at (−1.85, −1.85) suggests that the apparent ΔS°_{f} value is constant (=−35.4 $\mathrm{J\,mol^{-1}\,K^{-1}}$) independent of the acids and bases.

As summarized in Table 3, family-independent or -dependent LFERs all of which converge on the point (−1.85, −1.85) can be plotted for all of the acids-reference base systems. When Eq. 10 is applied to the results, it is concluded for all of the acids-reference base systems that the appearance of the convergence point can be ascribed to the apparent ΔS°_{f} value being constant and that the linear relationships are due to the constancy of the ratio $\Delta H^{\circ}_{A_iB_2}/\Delta H^{\circ}_{A_iB_1}$, which is equal to the slope of the lines, at least within each family of acids.

Effects of Reference Acids on log *K* Values. For 1 : 1 hydrogen-bond complexation of a set of bases B_j (j=1,2,3,...) against reference acids A_1 and A_2, the following equation is derived from Eq. 4 by procedures similar to those used for Eq. 10:

$$\log K_{A_2B_j} = \frac{\Delta H^{\circ}_{A_2B_j}}{\Delta H^{\circ}_{A_1B_j}}\log K_{A_1B_j} + \left(1 - \frac{\Delta H^{\circ}_{A_2B_j}}{\Delta H^{\circ}_{A_1B_j}}\right)\frac{\Delta S^{\circ}_{f}}{2.303R}. \tag{11}$$

The above equation suggests that if the terms $\Delta H^{\circ}_{A_2B_j}/\Delta H^{\circ}_{A_1B_j}$ and ΔS°_{f} are constant, the plots of log *K* of a set of bases against reference acids A_1 and A_2 would give straight lines which pass through a point ($\Delta S^{\circ}_{f}/2.303R$, $\Delta S^{\circ}_{f}/2.303R$) corresponding to (−1.85, −1.85) in the present systems. The slope of the line would be equal to $\Delta H^{\circ}_{A_2B_j}/\Delta H^{\circ}_{A_1B_j}$.

The plots of log *K* values at 298.15 K of the five bases against 2-naphthol or carbazole vs. those against phenol are shown in Fig. 4. In the figure, the point "+" is located at −1.85, −1.85 which matches the convergence points shown in Figs. 1 and 3. A family-independent straight line which can be extrapolated to −1.85, −1.85 can be plotted in the phenol/2-naphthol systems as shown by the solid line. In the phenol/carbazole systems, as shown by the broken line, P=O bases give a straight line, but sulfide and selenide bases deviate from

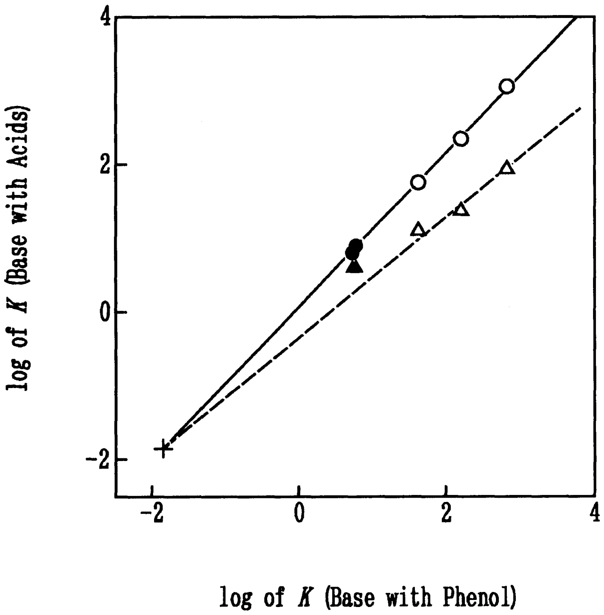

Fig. 4. Relation between log *K* values of bases against phenol and those against 2-naphthol and carbazole. Reference acids for the vertical axis are: ○ and ●, 2-naphthol; △ and ▲, carbazole. ○ and △, P=O base; ● and ▲, $(C_6H_5)_3P{=}S$ or $(C_6H_5)_3P{=}Se$. The convergence point shown by "+" locates at (−1.85, −1.85).

Table 3. Linear Relationships Converging on a Point (−1.85, −1.85) Observed among log *K* Values of OH– and NH–Acids against Phoshorus Compounds in CCl_4 at 298.15 K

Reference base 1	Reference base 2	Functional group	Slope of line	Standard deviation	Number of data	Family dependency[a]
$(C_6H_5)_3P{=}O$	$(CH_3O)_3P{=}O$	OH, NH	0.86	0.035	9	×
	$(C_6H_5O)_3P{=}O$	OH, NH	0.75	0.083	9	×
	$(C_6H_5)_3P{=}S$	OH	0.57	0.031	6	○
		NH	0.65	0.016	3	○
	$(C_6H_5)_3P{=}Se$	OH	0.55	0.057	6	○
		NH	0.65	0.016	3	○
$(C_6H_5)_3P{=}S$	$(C_6H_5)_3P{=}Se$	OH, NH	0.98	0.030	9	×

a) ○: Family-dependent Line; ×: Family-independent Line.

the line. Since the functional group of the sulfide and the selenide differs from that of the P=O bases, their deviation from the broken line may be ascribed to family-dependent behaviors: each of these bases is thought to be on a different straight line.

Family-independent or -dependent LFERs, all of which converge on the point −1.85, −1.85 can be plotted for all the bases-reference acid systems. Features of these lines are summarized in Table 4. When Eq. 11 is applied to the results, it is concluded for all of the bases-reference acid systems that the appearance of the convergence point can be ascribed to the apparent ΔS_f° value being constant and that the linear relationships are due to the constancy of the ratio $\Delta H^\circ_{A_2B_j}/\Delta H^\circ_{A_1B_j}$, which is equal to the slope of the lines, at least within each family of bases.

The Cause of the Magic Point. As mentioned in the introduction, family-independent and -dependent LFERs, both of which converge on the magic point, are regarded as general features observed in 1 : 1 hydrogen-bond complexation systems. Since the behaviors are in accord qualitatively with those observed here, it is suggested based on Eqs. 10 and 11 that the cause of the LFERs converging on the magic point can also be ascribed to two thermodynamic features: the constancy of the ratios of ΔH° ($\Delta H^\circ_{A_iB_2}/\Delta H^\circ_{A_iB_1}$ in Eq. 10 and $\Delta H^\circ_{A_2B_j}/\Delta H^\circ_{A_1B_j}$ in Eq. 11) and the constancy of the apparent ΔS_f° value as an average of the ΔS_f° values ranging from −49.2 to −9.77 J mol^{-1} K^{-1}. On the other hand, ΔS_f° calculated from the magic point is −21.1 J mol^{-1} K^{-1} which is in the range of variation of the apparent ΔS_f° value obtained here. Thus, the magic point (−1.1, −1.1) is in accord with the convergent point obtained here within experimental error.

It is concluded that the appearance of the magic point is due to the constancy of the apparent ΔS_f° value independent of the acids and bases. The results suggests that the constant term $\log K_0$ in Eq. 2 is virtually equal to $\Delta S^\circ_{AB}/2.303R$ in Eq. 4.

Interpretation of Family-Independent and -Dependent Behaviors. As reported on the basis of Eq. 2 in our preceding paper,[25] if two reference acids have the same functional group, a family-independent LFER of bases-reference acid systems would be expected. On the other hand, if two reference acids have different functional group, a set of family-dependent LFERs would be expected. Similar features would be expected from Eq. 2 for acids-reference base systems: For example, family-dependent LFERs would result only when two reference bases have different functional group.

When the equality of the constant term $\log K_0$ in Eq. 2 and $\Delta S^\circ_{AB}/2.303R$ in Eq. 4 is taken into consideration, the following equation is derived from Eqs. 2 and 4:

$$-\Delta H^\circ_{AB} = 2.303RT(\eta_x + \eta_y)\omega_a\omega_b. \qquad (12)$$

For the reactions of a series of acids A_i ($a_i{-}x_i$; $i = 1,2,3,\ldots$) with reference bases B_1 ($b_1{-}y_1$) and B_2 ($b_2{-}y_2$), the following equation is obtained from the above equation:

$$\frac{\Delta H^\circ_{A_iB_2}}{\Delta H^\circ_{A_iB_1}} = \frac{(\eta_{x_i} + \eta_{y_2})\omega_{b_2}}{(\eta_{x_i} + \eta_{y_1})\omega_{b_1}}. \qquad (13)$$

If the two reference bases have the same functional group ($\eta_{y_2} = \eta_{y_1}$), the term $\Delta H^\circ_{A_iB_2}/\Delta H^\circ_{A_iB_1}$ in the above equation would be a constant ($=\omega_{b_2}/\omega_{b_1}$) which depends only on the residual moieties of the reference bases. In such a case, as determined from Eq. 10, the plots of $\log K_{A_iB_2}$ vs. $\log K_{A_iB_1}$ give a family-independent line of slope $\omega_{b_2}/\omega_{b_1}$. On the other hand, if the two reference bases have different functional groups

Table 4. Linear Relationships Converging on a Point (−1.85, −1.85) Observed among log *K* Values of Phoshorus Compounds against OH– and NH–Acids in CCl$_4$ at 298.15 K

Reference acid 1	Reference acid 2	Functional group	Slope of line	Standard deviation	Number of data	Family dependency[a]
Phenol	2-Naphthol	=O, =S, =Se	1.04	0.028	5	×
	1-Naphthol	=O, =S, =Se	1.03	0.011	5	×
	CF_3CH_2OH	=O, =S, =Se	0.99	0.008	5	×
	CCl_3CH_2OH	=O, =S, =Se	0.89	0.046	5	×
	CBr_3CH_2OH	=O, =S, =Se	0.86	0.071	5	×
	Carbazole	=O	0.82	0.085	3	○
		=S, =Se	0.94	0.015	2	○
	Indole	=O	0.78	0.088	3	○
		=S, =Se	0.90	0.014	2	○
	Pyrrole	=O	0.72	0.080	3	○
		=S, =Se	0.84	0.013	2	○
Carbazole	Indole	=O, =S, =Se	0.96	0.012	5	×
	Pyrrole	=O, =S, =Se	0.89	0.021	5	×

a) ○: Family-dependent line; ×: Family-independent line.

($\eta_{y_2} \neq \eta_{y_1}$), the term $\Delta H^\circ_{A_iB_2}/\Delta H^\circ_{A_iB_1}$ in Eq. 13 would become constant only for acids with the same functional group ($\eta_x =$ constant). In such a case, as seen from Eq. 10, the plots of $\log K_{A_iB_2}$ vs. $\log K_{A_iB_1}$ would give a set of family-dependent straight lines whose slopes differ from one family to another depending on the functional group of the acids.

For the reactions of a series of bases $B_j(b_j-y_j;\ j=1,2,3,\ldots)$ with reference acids $A_1(a_1-x_1)$ and $A_2(a_2-x_2)$, the following equation is obtained from Eq. 12:

$$\frac{\Delta H^\circ_{A_2B_j}}{\Delta H^\circ_{A_1B_j}} = \frac{(\eta_{x_2}+\eta_{y_j})\omega_{a_2}}{(\eta_{x_1}+\eta_{y_j})\omega_{a_1}}. \qquad (14)$$

From the similarity of Eq. 14 to Eq. 13, it is easy to see that a family-independent straight line of slope $\omega_{a_2}/\omega_{a_1}$ is expected when the two reference acids have the same functional group ($\eta_{x_2}=\eta_{x_1}$) and a set of family-dependent lines is expected when the two reference acids have different functional groups ($\eta_{x_2} \neq \eta_{x_1}$).

As shown in Tables 3 and 4, family-independent LFERs exist when two reference bases or acids have the same functional group, as in =O/=O, OH/OH, and NH/NH systems. These results agree with the theoretical expectation described above. On the other hand, all the family-dependent LFERs shown in Tables 3 and 4 exist only when reference bases or acids have different functional groups, as in =O/=S, =O/=Se, and OH/NH systems. These results also agree with the theoretical expectations described above.

A special behavior is observed in the plots obtained by using $(C_6H_5)_3P{=}S$ and $(C_6H_5)_3P{=}Se$ as a reference base: although these bases have different functional group (=S and =Se), a family-independent LFER with a slope close to unity (0.98) is plotted. An important point is that these bases have the same residual moiety, $(C_6H_5)_3$, with the same ω_b value. When Eq. 13 is applied to the result, the family-independent behavior can be ascribed to the equality of the η_y value ($\eta_{=Se} \approx \eta_{=S}$) of these bases and the slope close to unity is due to the equality of the ω_b value.

As described above, all of the family-independent and -dependent LFERs shown in Tables 3 and 4 can be interpreted thermodynamically by applying Eqs. 10, 11, 12, 13, and 14.

Conclusion

It has been revealed that the convergent linear relationships among $\log K$ values of the 1:1 hydrogen-bond complexation of OH– and NH–acids against phosphorus compounds can be ascribed to two thermodynamic features: the constancy of the ΔH° ratio and the constancy of the apparent ΔS° value of both the acids-reference base and the bases-reference acid systems. The interpretation presented here can be applied to the convergent LFERs observed in other 1:1 hydrogen-bond complexation systems.

The family-independent and -dependent LFERs so far have been ascribed to the difference of the electrostatic : covalent ratio contributing to the adduct formation expressed in terms of the angle θ. On the other hand, the results obtained here suggest that the convergent LFERs can be explained thermodynamically based on the constancy of the apparent ΔS° value and the constancy of the ΔH° ratio. The interpretation presented here is of importance as a new view of 1:1 hydrogen-bond complexation in inert solvents.

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