Linear Relationships between Thermodynamic Parameters
(Part II) Applicability of New Equations

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熱力學函數間의 直線關係 (第2報) 適用性의 檢討

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Abstract

Linear relationships between thermodynamic parameters, $\Delta\Delta H^{\times} = a\sigma + b\Delta\Delta S^{\times}$, and $\Delta\Delta F^{\times} = a\sigma + (b-T)\Delta\Delta S^{\times}$, which were derived in the previous report have been tested with 57 reactions from literature. Linearities of plots $\Delta\Delta H^{\times} - a\sigma$ vs. $\Delta\Delta S^{\times}$ were generally good and the average correlation coefficient was 0.983 and the average of standard deviations from regression lines was 0.11. For 15 out of 57 reactions, Hammett plots were unsatisfactory and most of the reaction did not satisfy the Leffler equation. The general applicability of the new equations has been confirmed by the analysis of each reaction for which existing equations failed to correlate.

要　約

前報에서 誘導한 새로운 直線關係式, $\Delta\Delta H^{\times} = a\sigma + b\Delta\Delta S^{\times}$, 및 $\Delta\Delta F^{\times} = a\sigma + (b-T)\Delta\Delta S^{\times}$, 의 適用性을 57個反應으로 檢討하였다. 57個反應에 對한 $\Delta\Delta H^{\times} - a\sigma$, 對 $\Delta\Delta S^{\times}$의 直線關係 相關係數의 平均은 0.983이었고 直線으로부터의 標準偏差의 平均値는 0.11이었다. 57個反應中 15個反應에 對해서는 Hammett方程式이 成立되지 않았고, 또 大部分의 反應에 對해서 Leffler의 式이 成立하지 않았다. 이와같이 從來의 關係式이 成立하지 않는 反應도 새로운 關係式으로 說明되며, 그 理由를 檢討해 봄으로서 上記 2式이 더 一般的으로 適用되는 關係式임을 確認하였다.

In the previous report [1], we have derived a new set of equations(1), relating thermodynamic parameters for side chain or ring substitution reactions of meta and para substituted benzene derivatives.

$$\Delta\Delta H^{\times} = a\sigma + b\Delta\Delta S^{\times} \cdots\cdots (1\text{ a})$$
$$\Delta\Delta F^{\times} = a\sigma + (b-T)\Delta\Delta S^{\times} \cdots (1\text{ b})$$

Where a and b are constants characteristic of reaction system, σ the Hammett substituent constant and T the experimental mean temperature.

We have concluded that these equations were the more general forms of existing relationships, i. e., Hammett [2], Leffler [3] and Brown [4] equations, and should supersede them in the test of substituents eff-ect.

Since σ values are known and "a" values are also

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obtainable from the relation, $a = -1.36\rho$, or by calculation, plots of $\Delta\Delta S^{\times}$ against either $\Delta\Delta H^{\times} - a\sigma$, or $\Delta\Delta F^{\times} - a\sigma$ should give straight lines of slope b, or (b−T), respectively. Theoretical analyses showed that when there is a straight line relationship according to either (1a) or (1b), substituents exert their influence only on potential energy terms and thus the mechanism of reaction should not differ from one compound to another in a series [1].

In view of the general trend in reporting thermodynamic data (i. e., usually $\Delta H^{\times}$ and $\Delta S^{\times}$ are reported, although $\Delta F^{\times}$ may be derived from these or from rate constants) and the simplicity of expression, equation (1a) is preferable for linearity test. In our examination of published data, this principle has been adopted throughout.

The literature survey was by no means exhaustive,

but it was, in our opinion, sufficient to demonstrate the generality of equations(1).

A large number of kinetic data appeared in chemical journals were not suitable to our purpose since reaction constants were given at only one temperature, and therefore thermodynamic parameters were not obtain-able. Part of our survey was dependent on literatures quoted by Brown in his paper, [4] in which he postulated the linear enthalpy-entropy effect by classification into families.

Results of our analyses are summarized in Table 1.

Table 1

No.	Reaction	n^a	a^b	b^c	r^d	σ_H^e	Reference
1	Dissociation of benzoic acids in acetic acid	9	−1.36	298	0.998	0.02	(6)
2	Acid dissociation of phenols	5	−2.72	260	0.999	0.02	(5)
3	Solvolysis of t-cumyl chlorides containing m-directing substituents at 25°C	11	6.18	269	0.989	0.11	(7)
4	Solvolysis of p- and m-(trimethyl ammonium chloride)t-cumyl chlorides in 90% aq-acetone	3	6.20	767	1.000	0.00	(8)
5	Solvolysis of the nitro- and methoxy- phenyl dimethyl carbonyl chlorides, 25°C	5	0.50	750	0.999	0.05	(9)
6	Hydrolysis of ethyl-p-biphenyl carboxylates in 88.7% alcohol at 25°C	7	−0.85	317	0.997	0.01	(10)
7	Hydrolysis of benzoic anhydrides in 75% dioxane−25% water	9	−4.40	370	0.992	0.17	(11)
8	Hydrolysis of chloro methyl-aryl sulfides in 50% aq. -Dioxane	4	3.36	293	0.987	0.25	(12)
9	Hydrolysis of N, N-diaryl formamides in 20% dioxane-aq. 0.413N hydrogen chloride	7^f	−5.00	189	0.960	0.08	(13)
10	Alkaline hydrolysis of ethyl benzoates in 84% ethanol	5	−2.80	232	0.903	0.11	(14)
11	Alkaline hydrolysis of ethyl esters in 85% ethanol at 25°C	8	−3.50	276	0.983	0.03	(15)
12	Alkaline hydrolysis of ethyl p-alkyl benzoates	10	−3.42	303	0.992	0.04	(16)
13	Acid hydrolysis of ethyl benzoates in acetone-water solvent	8	−1.00	$\left(\begin{array}{l}\Delta\log PZ=0\pm0.12\\ \Delta\Delta H - a\sigma=0\pm0.19\end{array}\right.$			(17)
14	Acid hydrolysis of ethyl benzoates in ethanol-water solvent	8	−2.50	$\left(\begin{array}{l}\Delta\log PZ=0\pm0.45\\ \Delta\Delta H - a\sigma=0\pm0.37\end{array}\right.$			(17)
15	Alcoholysis of acid chlorides in 60:40 ether-alcohol	7^h	−2.63	319	0.996	0.13	(18)
16	Saponification of ethyl bezonates	9	−3.80	$\left(\begin{array}{l}\Delta\log PZ=0\pm0.16\\ \Delta\Delta H - a\sigma=0\pm0.15\end{array}\right.$			(19)
17	Saponification of some substituted ethyl benzoates in 80% ethanol	9	−3.09	291	0.993	0.05	(20)
18	Saponification of some substituted methyl benzoates in 80% methanol	9	−3.09	314	0.996	0.01	(20)
19	Saponification of ethyl-alkyl benzoates at 25° and 40° in 56% aq-acetone	5	−3.25	287	0.996	0.02	(21)
20	Saponification of some substituted ethyl benzoates, at 25°C	5	−3.00	1479	0.996	0.02	(22)
21	Saponification of some substituted n-propyl benzoates in 80% n-propyl alcohol	7	−3.30	290	0.998	0.01	(20)
22^f	Saponification of ethyl phenoxy acetates at 25°C in 87.3% aq-ethanol	5	−1.00	315	0.994	0.05	(23)
23^f	Hydrion catalyzed esterification of aromatic acids with methanol	9	0.50	275	0.976	0.09	(24)
24^f	〃　　　　　〃　　　　　〃	8	0.74	255	0.960	0.17	(25)
25^f	Hydrion catalyzed esterification of aromatic acids with cyclohexanol	7	0.50	361	0.970	0.26	(26)
26^f	Esterification of benzoic acids in methanol	5	−0.90	271	0.974	0.10	(27)

No.	Reaction	n^a	a^b	b^c	r^d	$\sigma_H{}^e$	Reference
27	Acid catalyzed esterification of substituted phenyl propiolic acids at 25—30°C	7	0.60	326	0.989	0.07	(28)
28^f	Rearrangement of allyl p-X-phenyl ethers	5	1.18	405	0.991	0.15	(29)
29	Rearrangement of cinnamyl p-methyl-phenyl ethers at 180°	10	1.00	452	1.000	0.00	(30)
30	Decomposition of peresters in chloro-benzene by Infrared	7	1.82	385	0.966	0.21	(31)
31^f	Thermal decomposition of substituted benzyl peroxides in acetophenone	11	0.10	555	0.970	0.16	(32)
32	Decomposition of bisulphite addition compounds in aq. solution at 20°, pH=3	8	0.30	310	1.000	0.00	(33)
33	Decomposition of bisulphite addition compounds in aq-solution at 20°, pH=5	5	0.50	288	0.997	0.03	(33)
34	Thermal dissociation of urethans in ethanolamine at 150°	9	—0.74	476	0.998	0.08	(34)
35	Pyrolysis of 1, 2 -diaryl ethyl acetates (1 -phenyl substituents)	5	—0.18	432	0.991	0.05	(35)
36^f	Pyrolysis of 1, 2 -diaryl ethyl acetates (2 -phenyl substitituents)	5	2.50	805	0.989	0.11	(35)
37^f	Ethoxide-catalyzed addition of aryl thiophenols to ethyl phenyl propiolate	5	2.00	335	0.973	0.10	(36)
38^f	Ethoxide-catalyzed addition of thiophenols to ethyl p-methoxy phenyl propiolate	6	1.25	249	0.975	0.17	(36)
39	Acid dissociation of aqueous phenols	4	—2.72	292	1.000	0.00	(37)
40	Dissociation of benzoic acids	5	—1.36	300	0.999	0.03	(38)
41	Schmidt reaction of benzhydryl azides	7	4.33	343	0.994	0.14	(39)
42	Formation of quarternary ammonium salts in nitrobenzene solution	5	4.00	$\begin{pmatrix}\Delta\log PZ=0\pm0.14 \\ \Delta\Delta H^x-a\sigma=0\pm0.13\end{pmatrix}$			(40)
43	Reaction of methyl iodide with dimethyl aniline in absolute methanol	8	4.00	$\begin{pmatrix}\Delta\Delta S^x=0\pm0.08 \\ \Delta\Delta H^x-a\sigma=0\pm0.09\end{pmatrix}$			(41)
44	Reaction of some substituted diaryl mercury compounds with hydrogen chlorides	6	3.80	318	0.997	0.19	(42)
45	Reaction of mercuric halides with dialkyl and diaryl mercury compounds	5	8.04	192	0.943	0.10	(43)
46	Reaction of substituted acetophenones with perbenzoic acid	6	3.50	254	0.958	0.27	(44)
47	Reaction of allyl bromide and N, N-dimethyl anilines in 25% aq-acetone	20	3.00	516	0.931	0.15	(45)
48	Kinetics of hydrogen exchange in dimethyl anilines at 65°C	9	5.49	310	0.941	1.08	(46)
49^f	Reaction of benzophenones with hydroxylamine in acidic 70% methanol at 50°C	11	—1.30	159	0.921	0.13	(47)
50^f	Reaction of aromatic aldehyde with n-butyl amine at 25°C	4	—4.50	766	1.000	0.00	(48)
51	Reaction of trimethyl amine with phenylacetates at 25°C	4	—3.00	254	0.997	0.03	(49)
52	Reaction of trimethyl amine with phenyl γ-(N, N-dimethyl amino)-butylates at 25°C	5	—3.40	2.68	0.998	0.26	(49)
53	Reaction of trimethyl amine with phenyl δ-(N, N-dimethyl amino)-valerates at 25°C	5	—3.40	215	0.990	0.16	(49)
54^f	Normal reaction of benzyl amine with styrene oxides in ethanol at 40°C	8	—1.30	328	0.997	0.04	(50)
55^f	Abnormal reaction of benzylamine with styrene oxides in ethanol at 40°C	8	2.00	330	0.996	0.06	(50)

No.	Reaction	n^a	a^b	b^c	r^d	σ_H^e	Reference
56	Adducts of iodine with various substituted amides	5	—1.00	223	0.994	0.02	(51)
57	Singlet-Triplet equilibrium of Ni (II) Aminotroponeimineates in $CDCI_3$	10^i	—3.00	862	0.983	0.24	(52)

a; The number of compounds involved in the calculation. b; $a = -1.37\rho$. See ref. (1) for the deviation. c; The slope of the regression line, °K. (53) d; The correlation coefficient. $r = 1$ represents a perfect line (53). e; The standard deviation of $\Delta\Delta H$-aσ from the regression line. (53) f; Reactions which give unsatisfactory Hammett's plot. g; m-CH_3, excepted since it was widely variant. h; Excluded p-F-benzoyl, which was far out of line. i; Excluded ϕ-p-CF_3, which was far out of line.

Typical examples of plots are also shown in Fig. 1, 2 and 3.
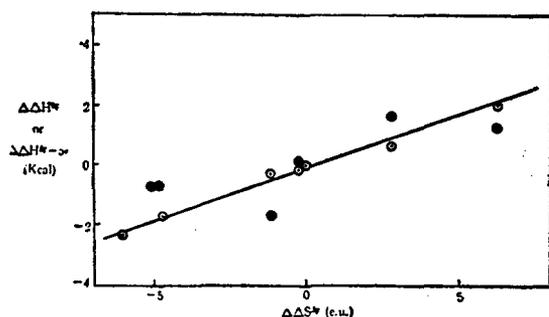
Fig. 1 Plots of equation (1a) (○) and Leffler equation (●) for reaction (41)
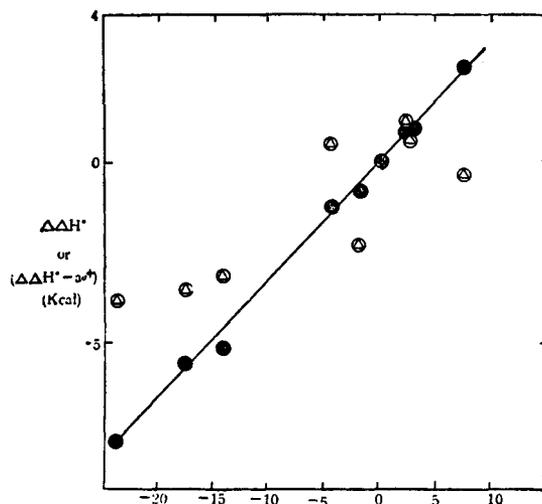
Fig. 3 Plots of equation (1a) (●) and Leffler equation (△) for reaction (48)
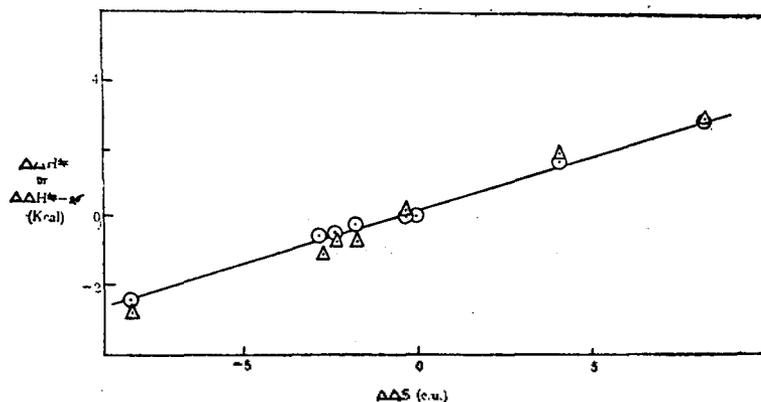
Fig. 2 Plots of equation (1a) (○) and Leffler equation (△) for reaction (54)

Since "a" value was usually obtainable either from the relationship a = —1.36ρ, or by calculation using least squares method, the slope of the linear plot ($\Delta\Delta H^* - a\sigma$) vs. $\Delta\Delta S^*$ can be determined and the linear fit tested. (53)

In general, linearities of plots, ($\Delta\Delta H^* - a\sigma$) vs. $\Delta\Delta S^*$, as required by equation (1a) were good. The average correlation coefficients for 52 reactions (5 reactions of class 1 below are excluded) was 0.983 and the average of standard deviations (σ_H) from regression lines was 0.11. For mere convenience of discussion we have classified reactions listed into the following general categories.

Class I.

For five reactions, (13), (14), (16), (42) and (43), entropy terms (or log PZ) were constant, i.e., $\Delta\Delta S^* = 0$, to within experimental errors. According to the equation (1a), it follows that $\Delta\Delta H^* - a\sigma$ should also be zero (within experimental error). We have therefore listed standard deviations of $\Delta\Delta S^*$ (or Δlog PZ), and

$\Delta\Delta H^*$-aσ, from zero for these reactions. It can be s eenfrom Table 1 that the standard deviation of $\Delta\Delta H^*$-a isσ comparable to that of $\Delta\Delta S^*$ for all five reactions, thus proving the applicabilitiy of equation (1a) for class of reaction.

It is interesting to note here that the reaction of methyliodide with substituted dimethylanilines and the acid hydrolysis of ethyl benzoates are characterized by the constant entropy changes. A natural corollary of this effect is that the Hammett equation is justly app‧ thisl icable, i.e.,

$$\Delta\Delta H^* = \Delta\Delta F^* = a\sigma \cdots\cdots (2)$$

$\Delta\Delta S^\circ$ for the dissociation of benzoic acids are not strictly zero but approximately so, as it was assumed in the derivation of equations(1). However the determination of Hammett substituent constant σ is justified only when $\Delta\Delta S^* = 0$, or $(b-T) = 0$, in equation (1b). This implies that reactions belonging to this class, (1), are better suited as standard reactions in the σ determination, while the use of benzoic acids dissociation for this purpose was not totally unjustified since (b-T) for the reaction turned out to be negligible $(=2°K)$. [40]

Class II

For 15 reactions (See, Table 1), fits of the Hamm‧ ett's plot were not satisfactory while equation (1a) gave good correlations as shown by r and σ_H. values. This divergence was predicted in the previous paper as a result of the restricted applicability of the Ham‧ mett equation, i.e., the Hammett relationship holds only in case of $\Delta\Delta F_{ext} = 0$. Close look at these data show the cause of the failure of the Hammett equa‧ tion, namely large influence of $\Delta\Delta F_{ext}$ term which is equal to (b-T) $\Delta\Delta S^*$. For reactions (31), (49) and (50), differences between the slope b and the mean experimental temperature T were 200, 160 and 470°K respectively. These amount to one Kcal for several entropy units of $\Delta\Delta S^*$. On the other hand, "a" values for these reactions were generally small (<1.00) giving negligible effect of "aσ" term compared with relatively large effect of (b-T) $\Delta\Delta S^*$term. Thus equation(2) does not hold and therefore the deviation from the Hammett relationship would result. Other reactions in this class had either small "a" values (therefore small "aσ" val‧ ues), or relatively large $\Delta\Delta S^*$ values, or combination of the two resulting the large influence of the second term in equation (1b). There are cases where reactions with large (b-T) still give good Hammett plots, e. g., reactions(4), (5) and (20). These reactions, however, were shown to have either large "a" values or small ranges in $\Delta\Delta S^*$ values giving satisfactory. Hammett relationships due to the combined effect of these. For most reactions, the range of $\Delta\Delta S^*$(in e.u.) was larger than that of $\Delta\Delta H^*$(in Kcal). We can conclude there‧ fore that the Hammett equation is a restricted form of the equation (1b) i.e., it applies only when a$\sigma \gg$ (b-T) $\Delta\Delta S^*$.

Class III

Plots of $\Delta\Delta H^*$vs. $\Delta\Delta S^*$ did not give straight lines in general, but only reactions with the numerical value of "a" less than approximately one showed satisfactory linearities. These are cases where the Leffler equation, (3), apparently holds.

$$\Delta H^* = \Delta H_o^* + \beta\Delta S^* \cdots\cdots (3)$$
$$\Delta H^* = (a\sigma + c) + b\Delta S^* \cdots (4)$$

Remembering that the equation(4) is just another expression of the equaton (1a). Thus, if "a" is small, "aσ" becomes negligible compared to a constant "c" and obviously $\Delta H_o^* = c$. Accordingly, the isokinetic temperature postulated by Leffler should also exist only in case of a$\sigma \ll$ c. This has been shown by Hepler and O'Hara [5] using reaction (2) of Table 1.

Equation (1a) gave excellent linear relationship for about a dozen reactions which Brown examined in his paper to show apparent linearitirs by separating into families with a common slope (β_o of his equation) of 300. A single line correlated all membess in a series and no classification was needed. Thus the classification into families in the plot of ΔH^* vs. ΔS^* is another specicl case of the general equation(1a). The existence of a universal constant, $\beta_o = 300°K$, postulated by Bro‧ wn is however doubtful. Only 16 out of 57 reactions had the b value of 300±20°K, and almost equal num‧ ber of reactions had either higher, or lower values of b. This means the slopes of regression lines, b or β_o are distributed randomly and do not show any definite trend. We therefore believe that the slope b is not a universal constant but is a constant dependent upon the nature of the reaction, just as the constant "a" is.

Concluding this paper we would like to mention fur‧

ther possibilities of extending equation (1) to other existing relationships, e.g., Grunwald-Winstein equation for solvolysis reaction. Studies on these aspects are in progress and will be reported subsequently.

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