Linear Relationships between Thermodynamic Parameters

(Part II) Applicability of New Equations

By Ikchoon Lee and Yong Ja Park
Atomic Energy Research Institute, Korea

熱力學常數間的直線關係（第2報）適用性的検討
李 益春*・朴 錦子**

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Abstract

Linear relationships between thermodynamic parameters, \( \Delta H^s = a + b \Delta S^s \), and \( \Delta F^s = a + (b - T) \Delta S^s \), which were derived in the previous report have been tested with 57 reactions from literature. Linearities of plots \( \Delta H^s - a \) vs. \( \Delta S^s \) 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.

契約

前報にて誘導した新式の直線関係式，\( \Delta H^s = a + b \Delta S^s \)及 \( \Delta F^s = a + (b - T) \Delta S^s \)の適用性を57項反応

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

para substituted benzene derivatives.

\[ \Delta H^s = a + b \Delta S^s \ldots \ldots (1a) \]

\[ \Delta F^s = a + (b - T) \Delta S^s \ldots (1b) \]

Where \( a \) and \( b \) are constants characteristic of reaction system, \( a \) 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 effect.

Since \( a \) values are known and "\( a \)" values are also

obtainable from the relation, \( a = -1.36a \), or by calculation, plots of \( \Delta S^s \) against either \( \Delta H^s - a \), or \( \Delta F^s - a \) 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 \( \Delta H^s \) and \( \Delta S^s \) are reported, although \( \Delta F^s \) 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 obtainable. Part of our survey was dependent on literatures quoted by Brown in his p. p. p, in which he postulated the linear enthalpy-entropy effect by classification into families.

Results of our analyses are summarized in Table 1.

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<td>Hydrolysis of N, N-diallyl amomium salts in 20% dioxane-aq. 0.413N hydrogen chloride</td>
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<td>Alkaline hydrolysis of ethyl benzoates in 85% ethanol</td>
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<td>25</td>
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Table 1
<table>
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<tr>
<th>No.</th>
<th>Reaction</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
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<td>27</td>
<td>Acid catalyzed esterification of substituted phenyl propionic acids at 25–30°C</td>
<td>0.60</td>
<td>326</td>
<td>0.989</td>
<td>0.07</td>
<td>(26)</td>
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<tr>
<td>28</td>
<td>Rearrangement of allyl p-X-phenyl ethers</td>
<td>1.18</td>
<td>405</td>
<td>0.961</td>
<td>0.15</td>
<td>(29)</td>
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<tr>
<td>29</td>
<td>Rearrangement of cinnamyl p-methyl-phenyl ethers at 180°C</td>
<td>1.00</td>
<td>452</td>
<td>1.000</td>
<td>0.00</td>
<td>(30)</td>
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<tr>
<td>30</td>
<td>Decomposition of peresters in chloro-benzene by Infrared</td>
<td>1.82</td>
<td>385</td>
<td>0.966</td>
<td>0.21</td>
<td>(31)</td>
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<tr>
<td>31</td>
<td>Thermal decomposition of substituted benzyl peroxides in acetophenone</td>
<td>0.10</td>
<td>555</td>
<td>0.970</td>
<td>0.16</td>
<td>(32)</td>
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<td>32</td>
<td>Decomposition of bisulphite addition compounds in aq. solution at 20°C, pH=3</td>
<td>0.30</td>
<td>310</td>
<td>1.000</td>
<td>0.00</td>
<td>(33)</td>
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<td>33</td>
<td>Decomposition of bisulphite addition compounds in aq-solution at 20°C, pH=5</td>
<td>0.50</td>
<td>288</td>
<td>0.997</td>
<td>0.03</td>
<td>(33)</td>
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<td>34</td>
<td>Thermal dissociation of urethans in ethanolamine at 150°C</td>
<td>-0.74</td>
<td>476</td>
<td>0.988</td>
<td>0.08</td>
<td>(34)</td>
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<tr>
<td>35</td>
<td>Pyrolysis of 1, 2-diaryl ethyl acetates (1-phenyl substituents)</td>
<td>0.18</td>
<td>432</td>
<td>0.991</td>
<td>0.05</td>
<td>(35)</td>
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<tr>
<td>36</td>
<td>Pyrolysis of 1, 2-diaryl ethyl acetates (2-phenyl substituents)</td>
<td>2.50</td>
<td>805</td>
<td>0.980</td>
<td>0.11</td>
<td>(35)</td>
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<td>37</td>
<td>Ethoxide-catalyzed addition of aryli thiophenols to ethyl phenyl propionate</td>
<td>2.00</td>
<td>335</td>
<td>0.973</td>
<td>0.10</td>
<td>(36)</td>
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<tr>
<td>38</td>
<td>Ethoxide-catalyzed addition of thiophenols to ethyl p-methoxy phenyl propionate</td>
<td>1.25</td>
<td>249</td>
<td>0.975</td>
<td>0.17</td>
<td>(36)</td>
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<tr>
<td>39</td>
<td>Acid dissociation of aqueous phenols</td>
<td>-2.72</td>
<td>292</td>
<td>1.000</td>
<td>0.00</td>
<td>(37)</td>
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<td>40</td>
<td>Dissociation of benzoic acids</td>
<td>-1.36</td>
<td>300</td>
<td>0.999</td>
<td>0.03</td>
<td>(38)</td>
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<td>41</td>
<td>Schmidt reaction of benzaldehyd azides</td>
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<td>343</td>
<td>0.994</td>
<td>0.14</td>
<td>(39)</td>
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<td>42</td>
<td>Formation of quaternary ammonium salts in nitrobenzene solution</td>
<td>4.00</td>
<td>1.40</td>
<td>(log $PZ=0±0.14$)</td>
<td>$\Delta H^<em>+\Delta S^</em>=0±0.08$</td>
<td>(40)</td>
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<td>43</td>
<td>Reaction of methyl iodide with dimethyl aniline in absolute methanol</td>
<td>3.60</td>
<td>318</td>
<td>0.997</td>
<td>0.19</td>
<td>(41)</td>
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<td>44</td>
<td>Reaction of some substituted diaryl mercury compounds with hydrogen chlorides</td>
<td>8.04</td>
<td>192</td>
<td>0.943</td>
<td>0.10</td>
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<td>45</td>
<td>Reaction of mercuric halides with dialkyl and diaryl mercury compounds</td>
<td>3.50</td>
<td>254</td>
<td>0.958</td>
<td>0.27</td>
<td>(43)</td>
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<td>46</td>
<td>Reaction of substituted acetophenones with perbenzoic acid</td>
<td>3.00</td>
<td>516</td>
<td>0.931</td>
<td>0.15</td>
<td>(45)</td>
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<tr>
<td>47</td>
<td>Reaction of allyl bromide and N, N-dimethyl anilines in 25% aq-acetone</td>
<td>5.49</td>
<td>310</td>
<td>0.941</td>
<td>1.08</td>
<td>(46)</td>
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<td>48</td>
<td>Kinetics of hydrogen exchange in dimethyl anilines at 65°C</td>
<td>1.30</td>
<td>159</td>
<td>0.921</td>
<td>0.13</td>
<td>(47)</td>
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<td>49</td>
<td>Reaction of benzophenones with hydroxylamine in acidic 70% methanol at 50°C</td>
<td>4.50</td>
<td>766</td>
<td>1.000</td>
<td>0.00</td>
<td>(48)</td>
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<td>50</td>
<td>Reaction of aromatic aldehyde with n-butyl amine at 25°C</td>
<td>3.00</td>
<td>254</td>
<td>0.997</td>
<td>0.03</td>
<td>(49)</td>
</tr>
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<td>3.40</td>
<td>268</td>
<td>0.988</td>
<td>0.26</td>
<td>(49)</td>
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<td>52</td>
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<td>3.40</td>
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<td>0.990</td>
<td>0.16</td>
<td>(49)</td>
</tr>
<tr>
<td>53</td>
<td>Reaction of trimethyl amine with phenyl $\beta$-(N,N-dimethyl amino)-valerates at 25°C</td>
<td>3.40</td>
<td>215</td>
<td>0.990</td>
<td>0.16</td>
<td>(49)</td>
</tr>
<tr>
<td>54</td>
<td>Normal reaction of benzyl amine with styrene oxides in ethanol at 40°C</td>
<td>-1.30</td>
<td>328</td>
<td>0.997</td>
<td>0.04</td>
<td>(50)</td>
</tr>
<tr>
<td>55</td>
<td>Abnormal reaction of benzylamine with styrene oxides in ethanol at 40°C</td>
<td>2.00</td>
<td>330</td>
<td>0.985</td>
<td>0.06</td>
<td>(50)</td>
</tr>
</tbody>
</table>
No. | Reaction | \( n^a \) | \( a^b \) | \( b^c \) | \( r^d \) | \( \sigma_H^e \) | 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) Aminotroponeimines in CDCl3 | 10^f | -3.00 | 862 | 0.983 | 0.24 | (52) |

\( a \): The number of compounds involved in the calculation, \( b \): \( a = -1.37p \). See ref. (1) for the deviation, \( c \): The slope of the regression line, \( °K \). \( d \): The correlation coefficient, \( r = 1 \) represents a perfect line. \( e \): The standard deviation of \( \Delta H - a \) from the regression line. \( f \): Reactions which give unsatisfactory Hammett's plot, \( g \): m-CHg, excepted since it was widely variant, \( h \): Excluded p-F-benzyl, which was far out of line, \( i \): Excluded \( -p-CF \), 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. 2 Plots of equation (1a) (○) and Leffler equation (△) for reaction (54)

Fig. 3 Plots of equation (1a) (○) and Leffler equation (△) for reaction (48)

In general, linearities of plots, \( \langle \Delta H^a - a \rangle \) vs. \( \Delta S^a \), 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 \( (\sigma_H) \) from regression lines was 0.11. For more 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 \( FZ \)) were constant, i.e., \( \Delta S^a = 0 \), to within experimental errors. According to the equation (1a), it follows that \( \Delta H^a - a \) should also be zero (within experimental error). We have therefore listed standard deviations of \( \Delta S^a \) (or \( \log FZ \)), and
$\Delta H^* - \lambda \sigma$, from zero for these reactions. It can be seen from Table 1 that the standard deviation of $\Delta H^*$-a is comparable to that of $\Delta S^*$ for all five reactions, thus proving the applicability of equation (1a) for class of reaction.

It is interesting to note here that the reaction of methyl iodide with substituted dimethyl anilines and the acid hydrolysis of ethyl benzoates are characterised by the constant entropy changes. A natural corollary of this effect is that the Hammett equation is justly applicable, i.e.,

$$\Delta H^* = \Delta H^* \rho^{=} = \sigma \Delta S^*$$

(2)

$\Delta S^*$ 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 $\sigma$ is justified only when $\Delta S^*=0$, or $(b-T)=0$, in equation (1b). This implies that reactions belonging to this class, (1), are better suited as standard reactions in the $\sigma$ 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 ($=2^\circ K$).

Class II

For 15 reactions (See, Table 1), fits of the Hammett's plot were not satisfactory while equation (1a) gave good correlations as shown by $r$ and $\sigma$, values. This divergence was predicted in the previous paper as a result of the restricted applicability of the Hammett equation, i.e., the Hammett relationship holds only in case of $\Delta S^*=0$. Close look at these data show the cause of the failure of the Hammett equation, namely large influence of $\Delta S_{res}$ term which is equal to $(b-T) \Delta S^*$. For reactions (31), (48) and (50), differences between the slope $b$ and the mean experimental temperature $T$ were 209, 160 and 470$^\circ$K respectively. These amount to one Kcal for several entropy units of $\Delta S^*$. On the other hand, $\sigma$ values for these reactions were generally small ($<1.00$) giving negligible effect of $\sigma$ term compared with relatively large effect of $(b-T) \Delta S^*$ 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 $\sigma$ values (therefore small $\sigma$ values), or relatively large $\Delta S^*$ 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 $\sigma$ values or small ranges in $\Delta S^*$ values giving satisfactory, Hammett relationships due to the combined effect of these. For most reactions, the range of $\Delta S^*$ (in e, u) was larger than that of $\Delta H^*$ (in Kcal). We can conclude therefore that the Hammett equation is a restricted form of the equation (1b), i.e., it applies only when $a \rho^{=} (b-T) \Delta S^*$.

Class III

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

$$\Delta H^* = \Delta H_0^* + \beta S^*$$

(3)

$$\Delta H^* = (\sigma + c) + \beta S^*$$

(4)

Remembering that the equation (4) is just another expression of the equation (1a). Thus, if "a" is small, "ao" becomes negligible compared to a constant "c" and obviously $\Delta H_0^* = c$. Accordingly, the isokinetic temperature postulated by Leffler should also exist only in case of $ao \equiv c$. This has been shown by Hepler and O'Hara 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 linearity by separating into families with a common slope ($\beta$, of his equation) of 300. A single line correlated all members in a series and no classification was needed. Thus the classification into families in the plot of $\Delta H^*$ vs. $\Delta S^*$ is another special case of the general equation (1a). The existence of a universal constant, $\beta = 300^\circ$K, postulated by Brown is however doubtful. Only 16 out of 57 reactions had the b value of $300 \pm 20^\circ$K, and almost equal number of reactions had either higher, or lower values of b. This means the slopes of regression lines, b or $\beta$, 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., Gruenwald-Winstein equation for solvolysis reaction. Studies on these aspects are in progress and will be reported subsequently.

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