Linear Relationships between Thermodynamic Parameters

(Part III) Application to Solvolysis Reaction

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Abstract

The general equation for the substituent effect test, which was derived in the previous paper, has been extended to correlate thermodynamic parameters of solvolysis reaction by modifying the potential energy term to represent the effect of changes in solvent composition. The linear fits of the new equation, \( \Delta H^\circ = a'Y + b'\Delta S^\circ \), were tested with 35 examples from literature and average correlation coefficient of 0.977 was obtained. Examination of results showed that the equation is generally applicable to solvolysis reaction and helps elucidate some of the difficulties experienced with the Grunwald-Winstein equation. It has been stressed that the linear enthalpy-entropy effect exists only between the external enthalpy and entropy of activation, and therefore strictly it is the linear external enthalpy-entropy effect.

要約

前報で説明した置換基効果一般関係式は、置換基効果を示す定数、\( Y \)と潜在エネルギー項を変数として、solvolysis反応に適用できることを示した。新しい関係式、\( \Delta H^\circ = a'Y + b'\Delta S^\circ \)の適用性は文献に示された35例の反応に対する直接関係を調査の結果を検討した。結果は平均相関係数0.977を示し、さらにこの方程式はsolvolysis反応に一般的に適用できることが示された。Grunwald-Winsteinの式が示す置換基の効果を説明することができるが、一般化されたenthalpy-entropy効果は外部enthalpyと外部entropyの限界であり、厳密に言えばenthalpy-entropy効果を説明することができる。

In the preceding two papers in this series, it was shown that the substituent effect can generally be tested with the equation (1).

\[ \Delta \overline{H}^\circ = a + b\Delta S^\circ \]  \( (a = -1.36p) \)

where \( \Delta \overline{H}^\circ \) and \( \Delta S^\circ \) are the constants dependent on the reaction system and the substrate, respectively. Thus \( a \) is a constant characteristic of temperature and solvent composition, and \( b \) a constant characteristic of substrate only.

It has been known that in general there is no linear relation between \( \Delta S^\circ \) and \( \Delta H^\circ \) in solvolysis, although several examples of solvolysis with linear relation have been reported by Leffler. Grunwald and Winston, however, correlated the rates of a solvolysis reaction by equation (3).

\[ \log \frac{k}{k_0} = mY \]  \( or \Delta \overline{H}^\circ = -1.36mY \)

where \( k \) and \( k_0 \) are the reaction constants in a given solvent and in 80% ethanol at 25°, \( m \) is a substrate.
constant, and Y is a solvent constant. The latter, Y, is a quantitative measure of solvent ionizing power in determining the rate constant of solvolysis reaction. The numerical values of Y for various solvents were determined by using arbitrarily chosen standard; t-butyl chloride at 25°C.

The two constants in eq. (3) are quite similar to those of the Hammett equation i.e., σ and ρ. In fact if the reference substrate used in the determination of σ and Y were the same it would lead to σ=m and ρ=Y.

Thus we are only to substitute m and Y in place of σ and ρ, to arrive at a new set of general equations for the solvolysis reaction,

\[\Delta H^\circ = a'Y + bL^2S^*\]
\[\Delta F^\circ = a'Y + (b-T) L^2S^*\]

where \(a' = -1.35m\)

In equation (4), a'Y represents the potential energy changes due to the changes in solvent composition.

Unlike in the test of the substituent effect, \(\Delta H^\circ\), \(\Delta S^*\) and \(\Delta F^\circ\) are not generally obtainable for the solvolysis reaction and therefore eq. (4) can not be applied generally except for the ethanol-water system since the standard quantities are chosen as those for 80% ethanol solution, i.e., \(\Delta H^\circ\), \(\Delta S^*\) and \(\Delta F^\circ\) are zero for 80% ethanol, and the constant b is dependent on the nature of solvent pair as will be shown below. The following alternative forms, (5), may be conveniently used for other solvent pairs for which eq. (4) is not applicable.

\[\Delta H^\circ = a'Y + bS^* + c\]
\[\Delta F^\circ = a'Y + (b-T) S^* + d\]

\(c\) and \(d\) are the intercepts; they are the values of \(\Delta H^\circ - a'Y\) and \(\Delta F^\circ - a'Y\) at \(S^* = 0\), or alternatively \(c = \Delta H^\circ - bS^*\) and \(d = \Delta F^\circ - (b-T)S^*\) at \(Y = 0\). Thus the plots of \(\Delta H^\circ - a'Y\) or \(\Delta F^\circ - a'Y\) vs. \(S^*\) should give a straight line of slope b or (b-T) respectively. If one of the eq. (5) holds, the other should also hold since the two are inter-dependent. In actual practice however the plot of \(\Delta H^\circ - a'Y\) vs. \(S^*\) is preferred in the linearity test as it was argued for eq. (1) that the plot of \(\Delta H^\circ - \sigma\) vs. \(\Delta S^\circ\) was preferable.

A linear correlation may be considered valid only when there are more than three points, and therefore three constants a', b and c are always determinable from the values of \(\Delta H^\circ\), Y and \(\Delta S^*\) for more than three solvent compositions. The relation a' = -1.35m also gives m, if required.

For the solvolysis of t-butylchloride at 25°C, \(\Delta H^\circ - bS^*\) for 80% ethanol was calculated to be 24.32 Kcal, which is in excellent agreement with the intercept 24.3 Kcal (at \(S^* = 0\)).

Table 1 shows the relevant constants for the fit of literature data to eq. (4) (or eq. (5)). Here again published data suitable for this purpose were limited since the rate constants at only one temperature were usually reported. Nearly all the data collected in Table 1 were taken from the works of Winston et al. The linearity was tested separately for each solvent pair whenever the solvolysis of a substrate was reported for more than one solvent pair, and the constants a' and b were determined. In addition, the linear correlation coefficient and the probable error of the fit were determined and included in the Table to show the linearity fits of the data. For 35 correlations (solvent pairs) studied with 11 compounds, the average correlation coefficient was 0.977 and the average of the probable error of the fit was 0.036. These compare well with the degree of my fits obtained by Fainberg and Winston.

The complex curves obtained by the plot of \(\Delta H^\circ\) vs. \(S^*\), and the ABC classification proposed by these authors to explain the curves are highly complicated indeed and the informations available from such analysis are ambiguous. These difficulties met by the mY correlation (eq. (3)) are due to the restricted nature of the relationship. With reference to the general equation (4) it can be readily seen that such complex curves are the results of neglecting the potential energy term, mY, in the enthalpy-entropy relationship, while the linear free energy relation (5) is not strictly applicable in general, without the entropy term.

The a'Y term

a', and therefore m of eq. (3), is defined as a constant characteristic of a substrate as σ is in eq. (1), and therefore it should not differ as the reaction medium is varied; a' should be constant irrespective of the solvent and temperature. Fainberg and Winston however observed in their mY correlation, a strong tendency for the data for each solvent pair to form a
Table 1 Correlation of the plot $\Delta H^* - a'Y$ vs. $\Delta S^*$ for solvolysis reaction

<table>
<thead>
<tr>
<th>Compound</th>
<th>$n^*$</th>
<th>Solvent range</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$r^*$</th>
<th>$\gamma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl chloride</td>
<td>69</td>
<td>0–100% EtOH-H$_2$O, 0–100% MeOH-H$_2$O, 0–100% AcOH-HCOOH</td>
<td>-1.36</td>
<td>300</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>t-Butyl bromide</td>
<td>8</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-1.50</td>
<td>349</td>
<td>0.999</td>
<td>0.017</td>
</tr>
<tr>
<td>o-Phenylethyl chloride</td>
<td>8</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-1.55</td>
<td>348</td>
<td>0.958</td>
<td>0.026</td>
</tr>
<tr>
<td>o-Phenylethyl bromide</td>
<td>9</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-1.20</td>
<td>315</td>
<td>0.993</td>
<td>0.088</td>
</tr>
<tr>
<td>Neophyl chloride</td>
<td>6</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-1.20</td>
<td>314</td>
<td>0.999</td>
<td>0.069</td>
</tr>
<tr>
<td>Neophyl bromide</td>
<td>7</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-1.20</td>
<td>314</td>
<td>0.999</td>
<td>0.076</td>
</tr>
<tr>
<td>Neopentyldimethyl-carbiny1 chloride</td>
<td>3</td>
<td>0–100% MeOH-H$_2$O</td>
<td>-1.20</td>
<td>314</td>
<td>0.999</td>
<td>0.076</td>
</tr>
<tr>
<td>Diisopropyl phosphorochloridate</td>
<td>5</td>
<td>0–100% EtOH-H$_2$O</td>
<td>-0.20</td>
<td>300</td>
<td>0.999</td>
<td>0.006</td>
</tr>
</tbody>
</table>

- Number of points involved.
- $a^* = 1.36m$.
- Slope, in °K.
- Correlation coefficient when $r = 1$, linearity is perfect.
- % Error of the fit.

Although the temperature variations of $m$ given in their reports are in the right direction ($m$ decreases as temperature increases, which is in accord with the negative temperature coefficient of $\Delta H^*$ found normally) and of the right order of magnitudes, another more plausible explanation is available, which recognizes the temperature dependent term missing from equation (3). Thus $b^*$ in eq. (4) is a constant characteristic of the reaction system. Thus $b^*$ is dependent on solvent pair and temperature as will be discussed in some detail in the next section. Therefore it is clear that
in eq. (4) "b" varies with the solvent composition and temperature, but $a'$ (therefore $m$) is independent from these, which are substantiated in Table 1.

For the solvolysis of diisopropyl phosphorochloridate and acid hydrolysis of ethyl dichloroacetate, $a'$ values were sufficiently small and the linearity of the plot, $\Delta H^\circ$ against $\Delta S^\circ$ were satisfactory. Such linearity is however limited to cases of negligible $a'Y$ only. This is an analogous situation as the limited applicability of the Leffler equation discussed in the previous paper. We could therefore conclude that the Leffler equation holds only for the type of reaction in which the internal enthalpy changes (therefore, the potential energy changes, since it was assumed that $\Delta S^\circ_{\text{int}} = 0$) are negligible as the substituent or the solvent composition is varied. In other words, the Leffler equation holds only when the total enthalpy changes represent only the external enthalpy changes. When however the internal enthalpy changes contribute significantly to the total enthalpy changes, the Leffler equation ceases to hold, while the general equations (1) and (4) hold regardless of the extent of the internal contribution. The linearity of the plots, $\Delta S^\circ$ vs. $\Delta H^\circ - a'Y$, or $\Delta H^\circ - a'Y$ vs. $\Delta S^\circ$, are in effect the linearity between the external enthalpies and the external entropies of activation, since $\Delta H^\circ = \Delta H^\circ_{\text{int}} + \Delta H^\circ_{\text{ext}}$, $a'Y = a'Y_{\text{int}} + a'Y_{\text{ext}}$, $\Delta H^\circ = a'Y = a'Y_{\text{int}} + a'Y_{\text{ext}}$, $\Delta H^\circ_{\text{int}} = a'Y_{\text{int}} + a'Y_{\text{ext}}$, $\Delta H^\circ_{\text{ext}}$, $\Delta S^\circ = \Delta S^\circ_{\text{int}} + \Delta S^\circ_{\text{ext}}$ by assumption $\Delta S^\circ_{\text{int}} = 0$, $\Delta S^\circ = \Delta S^\circ_{\text{ext}}$.

Thus in general it is the external quantities, $\Delta H^\circ_{\text{ext}}$ and $\Delta S^\circ_{\text{ext}}$, which are linearly related, not the total quantities. This linearity between the external quantities has been reported for many type of reactions and is known as the Compensation Law. The general applicabilities of equations (1) and (4), proven by the good lineairties obtained for the published data as reported in paper (2) and in the present paper, provide an excellent justification for the assumption made in their derivations that the linearity exists between external quantities.

The linear enthalpy-entropy effect, which has long been discussed by many authors, can therefore be concluded to exist only between the external enthalpy and entropy of activation.

The $b/a'Y$ term

$b$ is a constant characteristic of reaction system as it was demonstrated for eq. (1) in the previous paper. It has a dimension of absolute temperature $^\circ$K, and is obtainable as a slope of the plot, $\Delta H^\circ - a'Y$ against $\Delta S^\circ$. Thermodynamically it is a measure of the relative changes in enthalpy to those in entropy as solvent composition is varied successively in a solvent pair such as ethanol-water. Thus $b$ is characteristic of the solvent pair for a given substrate, as shown in Table 1. The solvent dependence of the slope, $m$, in $mY$ correlation found by Fainberg and Weinstein.
may therefore be attributable to the solvent dependence of $b$, but this was not apparent in mY fits since the term comprising $b$ was missing.

The $b$ value for t-butylchloride at 25° however was the same for all solvent pairs as shown by a single line of slope 300°K in Fig. 1. This must be also true for the mY fits of Fainberg and Winstein\(^\text{2}\) since it was a standard to determine $Y$ values. The excellent fit obtained with the plot $\Delta H^\text{a} - a'Y$ vs. $\Delta S^\text{a}$ however provides evidence that the equation (5), and hence (4), correlates thermodynamic quantities accurately.

The agreement shown by the equations (3) and (5) in obtaining a single line for all solvent pairs is limited to cases of $b-T=0$ or $\Delta S^\text{a}=0$. $b-T$ for the solvolysis of t-butylchloride at 25° was only 2°K, which gives negligible effect of the entropy term on $\Delta F^\text{a}$ compared with the experimental error in eq. (5). For example, $b-T$ $\Delta S^\text{a}$ is $0.04 \text{ Kcal at the largest, which}$ is well within the experimental error of $\Delta F^\text{a}$.\(^*\)

The situation is again exactly analogous with the relationship between the Hammett equation and eq. (1).\(^1\)

The calculated $b$ values varied approximately in the range 300±60°K, for most of the substrate in various solvent pairs. A notable exception to this general trend was the $b$ values for acetic acid-system. For few substrate, some of the solvent pairs containing acetic acid showed a considerable deviation in $b$ and less satisfactory linearity compared with others. When the point for pure water was included, the lines for separate solvent pairs converged generally at this point as shown in Fig. 2. This must be so because the pure water is common to all water containing solvent pairs. Here again however the anomaly was shown by acetic acid-system.

The precise cause of these divergences is obscure and may be a complex nature, but the considerations on dielectric constant of solvent and salt effect provide some insights into this problem.

The ionic association effect for the low dielectric constant solvents has been discussed in some length by R. P. Bell\(^\text{15}\). The low dielectric solvents such as acetic

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>78.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>58.5*</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6.2</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

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\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

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\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.

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\( \Delta H^\text{a} - a'Y \) vs. $\Delta S^\text{a}$ for solvolysis of $\alpha$-phenylethylbromide in various solvent system.
They pointed out that the salt effect, special or normal, was dependent on the substrate and on temperature. The normal salt effect, \( b_1 \) of their equation, 
\[
\Delta H = b_1 (1 + b_1 (\text{salt}))
\]
was a function of a substrate and temperature. Thus the salt effect for t-butyl chloride at 23°C (standard used in the determination of \( Y \) values) would not be in general the same as that of other compounds and at other temperatures.

The anomalous character of acetic acid was also mentioned by Winstein et al.\(^{10}\), who attributed it to the following factors: (1), the ionizing power of solvents, \( Y \), determined by the rates of solvolysis of chloride would not be quite suitable for correlating solvolysis rates of other leaving groups such as bromides, (2), the difference in the extent of ion pair return between substrates would be more serious in acetic acid, (3), the contribution of nucleophilic character of solvent would be dependent on the substrate.

All these are in fact the effects of the two factors considered above, i.e., low dielectric constant effect, and salt effect both of which were shown to be strongly dependent on substrate. Significant differences in the relative contributions of \( \Delta H^* \) and \( \Delta S^* \) to the solvolysis rates between those found for the carboxylic acid-containing solvents as opposed to the others noticed by Fainberg and Winstein in the comparison of the solvolysis of chlorides and bromides are quite consistent with the anomalous properties found for \( b_1 \) as shown in Table 1. The \( b \) is a measure of the relative contributions of \( \Delta H^* \) and \( \Delta S^* \) to rates of solvolysis, as it was mentioned at the beginning of this section.

Summary

Solvolysis reaction can be correlated in general with equation (4), which elucidates also the difficulties experienced with the Grunwald-Winstein equation, e.g., the complex curves of the plot of \( \Delta H^* \) vs. \( \Delta S^* \), the non-constancy of \( m \) and the anomalous characters found for certain types of solvents.

Equation (4) for the solvolysis is essentially identical as the equation (1) for the substituent effect. The internal enthalpy term was \( \sigma \) and \( a Y \) respectively and if the reference reaction used in the determination of \( \sigma \) and \( Y \) were the same, \( \sigma = m \), and \( p = Y \). A possible common standard may be the dissociation of dimethylanilinium ions for which evidence is available\(^{10}\) that \( \Delta S^* = 0 \) as substituents is varied, and \( \Delta H^* \) as solvent composition is varied. These two conditions are favorable for the determination of the respective constants, \( \sigma \) and \( Y \), since in the former the constant \( \sigma \) represents only the enthalpy changes and in the latter the constant \( Y \), represents only the entropy changes when these two conditions are satisfied.

This proposal is reasonable since in both processes, i.e., in the ionization of organic acids and in solvolysis reaction, the rates are determined by essentially the same step. Alternatively, we could choose the dissociation of benzoic acids or the solvolysis of benzyl chlorides, etc. In any case it is the matter of matching the numerical scales of \( \sigma \) and \( Y \) with a common standard, not of the nature of the two pairs of constants.

Thus we can generalize the two relationships as,
\[
\Delta H^* = a \sigma + b \Delta S^* \quad (7)
\]
where \( \pi \) is an independent variable for the potential energy changes and "a" and "b" are the dependent variables for a given substrate for the reaction in question; for substituent effect test, \( \pi = \sigma \) and \( a = -1.36 \pi \), and for solvent effect test \( \pi = Y \) and \( a = -1.36 \pi \).

The linear enthalpy-entropy effect exists only between the external quantities, and therefore strictly it is the linear external enthalpy-entropy effect. As a special case, in which changes in the internal enthalpy and entropy of activation are negligible, linearity may exist between the total experimental values of enthalpy and entropy of activation, as formulated by Leffler.

References

6) A.H. Fainberg and S. Winstein, ibid., 70, 1602 (1947).
   (c) A.H. Fainberg and S. Winsten, *ibid.*, 78, 2763, 2767 (1956).
   (e) A.H. Fainberg and S. Winsten, *ibid.*, 78, 2780 (1956).
   (f) S. Winsten and E. Clippinger, *ibid.*, 78, 2784 (1956).