Linear Relationships between Thermodynamic Parameters (Part III) Application to Solvolysis Reaction

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熱力學函數間의 直線關係(第3報) Solvolysis反應에의 應用

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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, $\Delta\Delta H^{*}=a'Y+b\Delta\Delta S^{*}$, 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에서 誘導한 置換基効果 一般關係式은 溶媒組成에 따르는 常數, Y 를 potential energy 項에 代置함으로서 solvolysis 反應에 適用할 수가 있다. 新方程式, $\Delta\Delta H^{*}=a'Y+b\Delta\Delta S^{*}$,의 適用性은 文獻에 報告된 35 個反應에 對한 直線關係를 調査해 봄으로서 檢討하였다. 結果로 平均 相關係數 0.977 을 얻었고, 따라서 이 方程式이 solvolysis反應에 一般的으로 適用됨을 밝혔고, 또 Grunwald-Winstein의 式이 지니는 몇몇 難點을 解決할 수가 있음을 알 수 있었다. enthalpy-entropy 直線効果는 外部 enthalpy와 外部 entropy에 限한 것이며, 嚴格히 말해서 外部 enthalpy-entropy 直線効果임을 强調하였다.

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

$$\Delta\Delta H^{*}=a\sigma+b\Delta\Delta S^{*}\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where $a=-1.36\rho$,

(or $\Delta\Delta F^{*}=a\sigma+(b-T)\Delta\Delta S^{*}$)

If one follows an entirely analogous line of reasoning, a similar equation of a general nature can be derived for the solvolysis reaction

In the derivation of eq. (1), the term $a\sigma$ represented the potential energy changes due to substituents, i.e.,

$$\Delta\Delta H^{*}_{int}=\Delta\Delta E^{*}_{p}=a\sigma$$

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where $a(a=-1.36\rho)$ and σ were the constants dependent on the reaction system and the substrate, respectively. Thus "a" is a constant characteristic of temperature and solvent composition, and "σ" a constant characteristic of substrate only.

It has been known that in general there is no linear relation between ΔS^{*} and ΔH^{*} in solvolysis [2], although several examples of solvolysis with linear relation have been reported by Leffler [3]. Grunwald and Winstein [4], however, correlated the rates of a solvolysis reaction by equation(3).

$$\left.\begin{array}{r}\log k/k_{o}=mY\\ \text{or }\Delta\Delta F^{*}=-1.36mY\end{array}\right\}\cdots\cdots\cdots\cdots(3)$$

where k and k_o 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 qnantitative measure of solvent ionizing power in determing the rate constant of solvolysis reaction. The numerical values of Y for various solvents were determind by using arbitrarily chosen standard; t-butyl chloride at 25°[4].

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 $\sigma=m$ and $\rho=Y$.

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.

$$\Delta\Delta H^{*}=a'Y+b\Delta\Delta S^{*}$$
$$\Delta\Delta F^{*}=a'Y+(b-T)\ \Delta\Delta S^{*}, \qquad \cdots\cdots\cdots\cdots(4)$$
where $a'=-1.36m$

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, $\Delta\Delta H^{*}$, $\Delta\Delta S^{*}$ and $\Delta\Delta F^{*}$ 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., $\Delta\Delta H^{*}$, $\Delta\Delta S^{*}$ and $\Delta\Delta F^{*}$ 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.

$$\Delta H^{*}=a'Y+b\Delta S^{*}+c$$
$$\Delta F^{*}=a'Y+(b-T)\Delta S^{*}+d \qquad \cdots\cdots\cdots\cdots(5)$$

c and d are the intercepts; they are the values of $\Delta H^{*}-a'Y$ and $\Delta F^{*}-a'Y$ at $\Delta S^{*}=0$, or alternatively $c=\Delta H^{*}-b\Delta S^{*}$ and $d=\Delta F^{*}-(b-T)\Delta S^{*}$ at $Y=0$. Thus the plots of $\Delta H^{*}-a'Y$ or $\Delta F^{*}-a'Y$ vs. ΔS^{*} 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 $\Delta H^{*}-a'Y$ vs. ΔS^{*} is preferred in the linearity test as it was argued for eq. (1) that the plot of $\Delta\Delta H^{*}-a\sigma$ vs. $\Delta\Delta S^{*}$ was preferrable [1].

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 ΔH^{*}, Y and ΔS^{*} for more than three solvent compositions. The relation $a'=-1.36m$ also gives m, if required.

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

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 Winstein 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) studieed 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 Winstein.

The complex curves obtained by the plot of ΔH^{*} vs. ΔS^{*}, and the ABC classification proposed by these authors[2] 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 (3) 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 Winstein 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. ΔS^{*} for solvolysis reaction

Compound	n[a]	Solvent range	a'[b]	b[c]	r[d]	p[e]
t-Butyl chloride[4]	69	0–100% EtOH-H_2O 0–100% MeOH-H_2O 0–100% AcOH-HCOOH 0–100% HCOOH-H_2O 0–100% AcOH-H_2O 0–90% Dioxane-H_2O 0–90% Me_2CO-H_2O 0–80% Dioxane-HCOOH	−1.36	300	1.000	0.000
t-Butyl bromide[5]	8	0–100% EtOH-H_2O	−1.50	349	0.990	0.017
	4	60–100% MeOH-H_2O	−1.50	450	0.928	0.108
	3	2.00M–8.00M H_2O-AcOH	−1.50	272	1.000	0.000
	5	40–90% Dioxane-H_2O	−1.50	354	0.999	0.018
α-Phenylethyl chloride[6]	9	0–100% EtOH-H_2O	−1.55	348	0.958	0.026
	5	0.5M–16.0M H_2O-AcOH	−1.55	338	0.997	0.004
	7	20–90% Dioxane-H_2O	−1.55	306	0.998	0.024
	5	60–100% MeOH-H_2O	−1.55	354	0.896	0.169
	4	24–100% AcOH-HCOOH	−1.55	287	0.991	0.061
α-Phenylethyl bromide[5]	9	0–100% EtOH-H_2O	−1.20	315	0.993	0.088
	5	50–100% MeOH-H_2O	−1.20	314	0.999	0.009
	7	30–90% Dioxane-H_2O	−1.20	244	0.995	0.076
	4	0.5M–8.00M H_2O-AcOH	−1.20	715	0.827	0.148
Neophyl chloride[7]	6	20–80% EtOH-H_2O	−1.20	360	0.987	0.065
	6	30–80% MeOH-H_2O	−1.20	349	0.984	0.076
	5	0–100% AcOH-HCOOH	−1.20	314	0.999	0.003
	4	4.00M–50% H_2O-AcOH	−1.20	458	0.980	0.053
Neophyl bromide[7]	7	20–90% EtOH-H_2O	−1.10	365	0.938	0.162
	7	30–90% MeOH-H_2O	−1.10	376	0.996	0.008
	5	0–100% AcOH-HCOOH	−1.20	243	0.969	0.022
	3	4.00M–16.00M H_2O-AcOH	−1.10	253	0.904	0.023
	4	20–50% Dioxane-H_2O	−1.10	204	0.985	0.033
Neopentyldimethyl-carbinyl chloride[8]	3	70–90.11% EtOH-H_2O	−0.90	238	0.999	0.004
Dineopentylmethyl-carbinyl chloride[8]	4	79.56–100% EtOH-H_2O	−0.95	251	0.957	0.021
Benzhydryl chloride[9]	3	70–90% Dioxane-H_2O	−1.36	293	1.000	0.000
Di-isopropyl phosphorochloridate[10]	5	0–100% EtOH-H_2O	−0.50	312	0.998	0.024
Ethyl dichloroacetate in acid[11]	4	50–80% Me_2CO-H_2O	−0.20	300	0.999	0.006

a. Number of points involved.
b. $a' = -1.36m$.
c. Slope, in °K.
d. Correlation coefficient[12]; when r=1.000 linearity is perfect.
e. Probable error of the fit[12].

separate line giving different m values.[5][6][7] They also found that the m was temperature dependent. All these are obviously contrary to the definition of m, and hence of a'. Such contradiction is not experienced with the general equation (4). Table 1 shows the constancy of a' for a given substrate throughout the solvent pairs, with only one minor exception.

Grunwald and Winstein[4] postulated the temperature dependence of m as in the following equation,

$$\frac{dm}{dT}=\frac{\Delta\Delta H^{*}}{2.303Y\cdot RT^{2}} \quad \cdots\cdots\cdots\cdots(6)$$

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 thel negative temperature coefficient of ΔH^{*} found normaly[13]) and of the right order of magnitudes, another more plausible explanation is available, which recognizes the temperature dependent term missing from equation (3). "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 [10] and acid hydrolysis of ethyl dichloroacetate[11], a' values were sufficiently small and the linearity of the plot, $\Delta H^{\neq}$ against $\Delta S^{\neq}$ 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[1]. 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 $\Delta\Delta S^{\neq}_{int}=0$) 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 linearities of the plots, $\Delta\Delta S^{\neq}$ vs. $\Delta\Delta H^{\neq}-a\sigma$, or $\Delta\Delta H^{\neq}-a'Y$, are in effect the linearities between the external enthalpies and the external entropies of activation,

since $\Delta\Delta H^{\neq}=\Delta\Delta H^{\neq}_{int}+\Delta\Delta H^{\neq}_{ext}$, $a\sigma=a'Y=\Delta\Delta H^{\neq}_{int}$

$\therefore \Delta\Delta H^{\neq}-a\sigma=\Delta\Delta H^{\neq}-a'Y=\Delta\Delta H^{\neq}_{ext}$,

and, $\Delta\Delta S^{\neq}=\Delta\Delta S^{\neq}_{int}+\Delta\Delta S^{\neq}_{ext}$, by assumption

$\Delta\Delta S^{\neq}_{int}=0$, $\therefore \Delta\Delta S^{\neq}=\Delta\Delta S^{\neq}_{ext}$.

Thus in general it is the external quantities, $\Delta H^{\neq}_{ext}$ and $\Delta S^{\neq}_{ext}$, 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.[14] The general applicabilities of equations (1) and (4), proven by the good linearities obtained for the published data as reported in paper(2) [1b] and in the present paper, provide an excellent justification for the assumption made in their derivations that the linearity exists between external quantities [1a].

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

The $b\Delta s^{\neq}$ term

b is a constant characteristic of reaction system as it was demonstrated for eq. (1) in the previous paper[1]. It has a dimension of absolute temperature °K, and is obtainable as a slope of the plot, $\Delta H^{\neq}-a'Y$ against $\Delta S^{\neq}$. 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 Winstein[5]

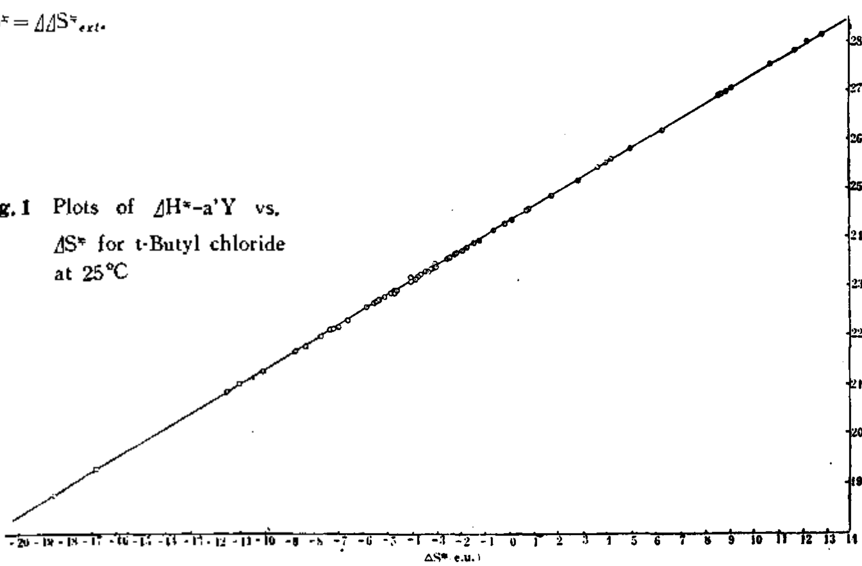

Fig. 1 Plots of $\Delta H^{\neq}$-a'Y vs. $\Delta S^{\neq}$ for t-Butyl chloride at 25°C

[7] 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[2] since it was a standard to determine Y values. The excellent fit obtained with the plot, $\Delta H^{*}-a'Y$ vs. ΔS^{*} 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 $\Delta\Delta S^{*}=0$. $b-T$ for the solvolysis of t-butylchloride at 25° was only 2°K, which gives negligible effect of the entropy term on ΔF^{*} compared with the experimental error in eq. (5). For example, $(b-T)\ \Delta S^{*}$ is 0.04 Kcal at the largest, which is well within the experimental error of ΔF^{*}.*

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 containning 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 containning solvent pairs. Here again however the anomally 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[15]. The low dielectric solvents such as acetic acid and dioxane (see Table 2) give rise to the association of the ionic species and in general such solvent system show a strong tendency for the degree of dissociation to be dependent on the substrate. Thus the extent of ion pair formation and the rate of its dissociation may considerably differ from one substrate to another in low dielectric media, giving anomalous properties for some substrate.

Table 2. Dielectric constants (ε) of various solvents at 25°C[16]

Solvent	ε
Water	78.5
Formic acid	58.5*
Methanol	32.6
Ethanol	24.3
Acetone	20.7
Acetic acid	6.2
Dioxane	2.2

* at 16°C.

Another to factor be taken into consideration is the salteffect. For thesolvolysis in carboxylic acid containning solvent, Winstein et al. added the corresponding lithium salts for the purpose of reducing the back reaction. They have studied the rate enhancing salt effects in acetolysis of various compounds[17] and concluded that such effects were mainly due to the increase of ionization rate and the reduction of ion pair return.**

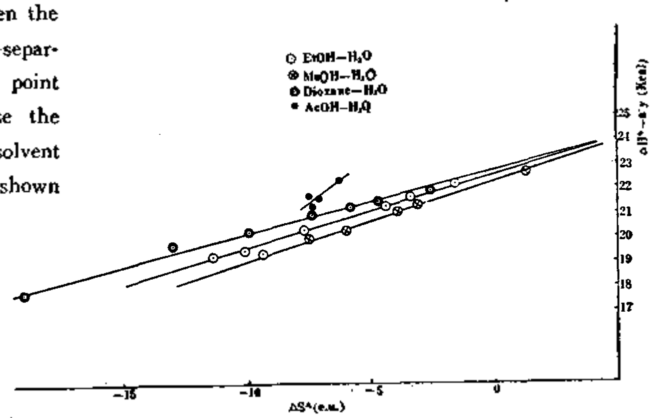

Fig. 2 Plot of $\Delta H^{*}-a'Y$ vs. ΔS^{*} for solvolysis of α-phenylethylbromide in vorious solvent system.

* The experimental error in ΔH^{*} was typically estimated to be 0.15Kcal and it is reasonable to assume that the error in ΔF^{*} be the same order of magnitude.

** Undissociated ion pair formed returning to the original neutral molecule. See ref. 17b) for the detail.

They pointed out that the salt effect, special or normal, was dependent on the substrate and on temperature. The normal salt effect, b_t of their equation, $k_t = k^\circ_t(1+b_t(\text{salt}))$, was a function of a substrate and temperature. Thus the salt effect for t-butyl chloride at 25° (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[5)18)], 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 ΔH^* and ΔS^* to the solvolysis rates between those found for the carboxylic acid-containning 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, as shown in Table 1. The b is a measure of the relative contributions of ΔH^* and ΔS^* to rates of solvolysis, as it was mentioned at the begining of this section.

Summary

Solvolysis reaction can be correlated in general with epuation (4), which elucidates also the difficulties experienced with the Grunwald-Winstein equation, e.g., the complex curves of the plot of ΔH^* vs. ΔS^*, 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 a σ and a'Y respectively and if the reference reaction used in the determination of σ and Y were the same, $\sigma = m$, and $\rho = Y$. A possible common standard may be the dissociation of dimethylanilinium ions for which evidence is available[19)] that $\Delta\Delta S^* = 0$ as substituents is varied, and $\Delta\Delta H^* = 0$ as solvent composition is varied. These two conditions are favorable for the determination of the respective constants, σ and Y, since in the former the constant σ reperesents only the enthalpy changes and in the latter the constant Y, represents only the entropy changes when these two conditións 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 σ and Y with a common standard, not of the nature of the two pairs of constants.

Thus we can generalize the two relationships as,

$$\Delta\Delta H^* = a\pi + b\Delta\Delta S^* \quad \cdots\cdots\cdots\cdots (7)$$

where π 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 $a = -1.36\rho$, and for solvent effect test $\pi = Y$ and $a = -1.36m$.

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

1) (a) Ikchoon Lee, *J. Korean Chem. Soc.*, **7**, 211 (1963)
   (b) Ikchoon Lee and Y. J. Park, *ibid.*, **7**, 238 (1963)
2) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 5937 (1957).
3) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).
4) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
5) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957).

6) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597 (1957).
7) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).
8) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).
9) S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957).
10) I. Dostrovsky and M. Halman, *J. Chem. Soc.*, 502 (1953).
11) P. M. Nair and E. S. Amis, *J. Am. Chem. Soc.*, **77**, 3452 (1955).
12) M. J. Moroney, "Facts from Figures", William Clowes and Sons, Ltd., London, 1951.
13) (a) B. Bensley and G. Kohnstam, *J. Chem. Soc.*, 287 (1956).
 (b) J. B. Hyne, R. Wills and R. E. Wonkka, *J. Am. Chem. Soc.*, **84**, 2914 (1962).
14) (a) R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962).
 (b) P. Ruetschi, *Z. physik, Chem.*, **14**, 277 (1958).
15) R. P. Bell, "The Proton in Chemistry", Methuen and Co., London, 1959. pp 54.
16) "Handbook of Chemistry and Physics", 41st. ed., Chem. Rubber Publishing Co.; Cleveland, Ohio, U. S. A., pp 2513.
17) (a) I. S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954).
 (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956).
 (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763, 2767 (1956).
 (d) A. H. Fainberg, G. C. Robinson and S. Winstein, *ibid.*, **78**, 2777 (1956).
 (e) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).
 (f) S. Winstein and E. Clippinger, *ibid*, **78**, 2784 (1956).
18) S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957).
19) Ikchoon Lee and Y. J. Park, unpublished data.