

Linear Relationships between Thermodynamic Parameters (Part V)

Critical Evaluation and Mechanistic Significances of the Relationship.

by

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熱力學函數間의 直線關係 (第 5 報)

關係式의 評價와 反應機構上의 意義

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要 約

一般式中の potential energy 變數로서 σ 와 Y 를 使用할 수 있음을 밝혔고 또 關係式의 反應機構上의 意義를 論하였다. Benzyl chlorides 의 solvolysis 反應 data 를 適用함으로써 物質常數 a' 는 2個의 뚜렷한 系列을 形成하며 置換基常數 σ 와는 各系列마다 別途로 直線關係를 가지며 이로서 S_N1 으로부터 S_N2 로의 反應機構의 變化를 알 수가 있었다.

Abstract

Justifications for the use of σ and Y as independent potential energy variables in the general equation have been reviewed and some mechanistic significances of the relationship discussed. Analysis of the activation parameters for the solvolysis of benzyl chlorides in ethanol-water mixture showed that there are two distinct series of substrate constants a' , which can be correlated linearly within a series with the substituent constants σ conforming to the generally accepted concept of change in mechanism from S_N1 to S_N2 .

In the previous reports in this series¹⁾, we have shown that the following set of equations correlated the substituent effect and the medium effect of solvolysis reaction.

$$\left. \begin{aligned} \delta \Delta H^\ddagger &= a\pi + b \cdot \delta \Delta S^\ddagger \\ \delta \Delta F^\ddagger &= a\pi + (b-T) \cdot \delta \Delta S^\ddagger \end{aligned} \right\} \dots\dots\dots (1)^*$$

* Following Leffler and Grunwald²⁾, new symbol $\delta(\delta_M$ for medium and δ_R for substituent effects) has been adopted. Thus Δ represents changes associated only with chemical reactions and δ effects of medium and substituent.

where π is the independent potential energy variable for substituent or solvent composition, and a and b are the dependent variables for the reaction system. It has been demonstrated that the potential energy factor π can be conveniently replaced with σ for substituent effect and Y for medium effect.

The use of empirical constants σ and Y as the potential energy variables is obviously justified only if the reference standards used in the determination of the constants i. e., dissociation constants of benzoic

acids²⁾ and the rate constants of solvolysis of *t*-butyl chloride at 25°C³⁾, represented potential energy variations or the quantities proportional to them. In our examination of published data with these practical expressions, however, we have tacitly assumed that they did.

In this paper we will examine this aspect to show that the substitution of σ and Y for the potential energy variable π is quite reasonable and justifiable. In addition we will discuss mechanistic significances of the fit of equation (1).

Substituent Effect

The choice of substituent constant σ as the potential energy variable is in accord with Hammett's original idea²⁾. He has stressed that the linear relationship between free energies is essentially the relation between the potential energy terms of the rate and equilibrium equations and can be expressed as

$$\Delta E_{p1} = \rho \Delta E_{p2} + \text{constant} \dots \dots \dots (2)$$

Thus he chose the dissociation of benzoic acids in aqueous medium at 25°C as a standard reference for the potential energy variation and denoted the standard quantity as σ .

The only difference between his treatment and ours is that we have separated activation parameters into two parts; internal and external part. In this manner we were able to show that the total entropy or the kinetic energy term is not necessarily be constant within a series of reaction in order to be able to test substituent effect with σ . Numerous examples have been reported which showed the linear relationship between external enthalpy and entropy of activation⁵⁾, and for these processes the external terms are compensated. Thus we are justified in separating this compensating external quantities from the total observed values, and giving an independent potential energy variable, the internal enthalpy. This treatment therefore assumes the constancy of internal entropy of activation only and consequently internal rotations, etc., are not considered to be affected by the substituents.

Campbell and Gilow⁶⁾ showed that the Hammett correlation is applicable to substituent effects on ultraviolet absorption bands of 2-aroil-cyclohexanones. Their relationship, (3), derived from the Hammett equation is quite similar to eq. (1).

It is known that electronic transitions contribute negligibly to the entropy changes.

$$\delta_{R\nu} \left[\frac{hc}{2.3RT} \right] = -\sigma\rho - \frac{\delta_R \Delta S}{2.3R} \dots \dots \dots (3)$$

$\delta_R \Delta S$ can therefore reasonably be assumed to be zero in eq. (3), and the spectra shifts due to substituents, $\delta_{R\nu}$, become a measure of potential energy changes. The linearity between $\delta_{R\nu}$ and σ is thus an indicative of the σ being potential energy variable. The idea of separating thermodynamic parameters into internal and external parts lead Hepler* to the essentially same conclusion that σ represented ΔH_{int} i. e., potential energy variation⁷⁾. Thus he arrived at eq. (4) below.

$$\rho\sigma = -\frac{\Delta H_{int}}{2.303RT} = \left[\frac{C}{2.303RT} \right] \left[\frac{-\Delta H_{int}}{C} \right] \dots \dots \dots (4)$$

He identified $\frac{C}{2.303RT}$ with ρ and $-\frac{\Delta H_{int}}{C}$ with σ , but did not specify the nature of the constant C . According to our analysis however, ΔH_{int} in eq. (4) is a potential energy factor for the reaction concerned, and C should be $(\partial_R \Delta H_{int})_{benzoic}$ i. e., a potential energy factor determined by a standard reaction, giving $\sigma = -\frac{1}{2.303RT} (\partial_R \Delta H_{int})_{benzoic}$ and $\rho = \frac{\partial_R \Delta H_{int}}{(\partial_R \Delta H_{int})_{benzoic}}$ instead¹⁰⁾. This is again in support of the substitution of σ for the potential energy variable.

The fit of any kinetic data for a series of meta and para substituted compounds to eq. (1) implies simply that the substituents exert their influences on the rate of reaction solely through potential energy term and the kinetic energy terms are compensated each other i. e., $\delta \Delta H_{ext} = b \cdot \delta \Delta S^\ddagger$. Thus there is a linear correlation between external enthalpy and external entropy of activation. For the reaction that the internal kinetic energy is also affected by the substituent as in the ortho compounds, eq. (1) fails to correlate the thermodynamic data.

Since a and b are the constants characteristic of the reaction, the fit of eq. (1) would also show the constancy in reaction mechanism throughout the series. What are the significances of the new relationship (1) as compared to the Hammett equation? To consider this point, we will compare the applicabilities of the

* This paper has come to the attention of the author only after publication of Part I and II of this series.

two relationships to various data from literature. Four cases may arise from such comparison.

(1). Both relationships equally hold. Most of the reactions which satisfied the Hammett relation also gave satisfactory correlation with eq. (1). This simply shows that for many reactions $\partial_R \Delta F^{\ddagger}_{ext} = (b-T) \partial_R \Delta S^{\ddagger} \approx 0$, and we can understand why the Hammett equation has been so successful in relating the reaction rates of various series of reactions in spite of the restricted nature of the relationship.

(2). The Hammett relation holds while eq. (1) does not. Reactions belonging to this category has not been found as far as the author is aware of.

(3). The Hammett relation does not apply while eq. (1) does. Some examples of this category has already been reported¹⁰⁾. Since this class provides the real significance of eq. (1), few examples will be considered. A notable example is the esterification of substituted benzoic acids in methanol catalyzed with hydrogen chloride.⁸⁾ This reaction does not follow the Hammett relationship; neither does it give a good linearity with the Leffler equation. The fit to eq. (1) was however satisfactory. The esterification of benzoic acids involves side chain reactions as in the ionization of benzoic acids and saponification of its esters. These latter reactions are well correlated with the Hammett equation as well as with eq. (1). Thus it is reasonable to expect the esterification reaction to follow the same normal behaviour in thermodynamic properties. The scatter of the Hammett plots is most probably attributable to relatively large value of $\partial_R \Delta S^{\ddagger}$ and $(b-T)$ terms, since this will affect the total free energy which includes the external free energy term, i.e., $\partial_R \Delta S^{\ddagger}(b-T)$. Another example in this category is the reaction of substituted benzophenones with hydroxylamine in 70% methanol containing acetic acid-sodium acetate buffer⁹⁾. This reaction gives a curve that is concave down for the Hammett plot, but shows a reasonable degree of correlation ($r=0.92$) with eq. (1). This reaction series apparently does not involve the change in mechanism, which is in accord with the expectation.

It is also to be noted that in many cases the linearities are better with eq. (1) than the corresponding plots of the Hammett equation. Good examples are the normal and abnormal reactions of benzylamine

with styrene oxides in ethanol at 40°C.¹⁰⁾ This reactions give badly scattered plots of the Hammett relationship, while linearities are excellent with eq. (1) ($r=0.997$ and 0.996).

(4). Lastly there is a class of reactions which can not be correlated with either of the equations. In order the test by eq. (1) to be sufficient, the absence of correlation with eq. (1) should also give no linearity with the Hammett plot. A classical example of this type can be found in the reactions of benzyl halides.¹¹⁾ It has been established that the solvolysis of benzyl chlorides with electron withdrawing groups favour S_N2 mechanism, while those with electron-releasing groups proceed with S_N1 mechanism.¹²⁾

Thus there is a change in mechanism within a series and no correlation is expected with eq. (1), nor with the Hammett equation. The plot of eq. (1) actually gave a scatter of points even after allowing for the temperature dependent nature of the thermodynamic parameters due to the relatively large value of ΔC_p for this reaction.¹³⁾ We have discussed two different mechanistic series for benzyl chlorides solvolysis fully in the next paragraph.

The four categories discussed are summarized in Table 1.

Table 1

Category	Hammett eq.	eq. (1)	Examples
1	A	A	Numerous
2	A	N	None
3	N	A	Some
4	N	N	Some*

A: Applicable

N: Not applicable

*: This category includes only those reactions with meta and para substituted compounds, and theoretically all the reaction series with the change in mechanism should belong to this category.¹¹⁾

General conclusions to be drawn from the above discussion are;

- (1) The Hammett substituent constants, σ , can justly be used as potential energy variable.
- (2) The test provided by eq. (1) is a sufficient nature and in this respect it is more general compared with the Hammett equation.

On the other hand however the Hammett relation

has an advantage over eq. (1), i. e., the rate constant at only one temperature can be used for the test while eq. (1) requires those at several temperatures (at least two) since it involves enthalpies and entropies of activation. The usefulness of the Hammett equation is attributable to another important empirical fact, which is not clearly understood theoretically. That is the compensating effect of the external terms in rates and equilibria equation. It was shown previously that the changes in external enthalpy of activation due to substituents are proportional to the changes in entropy of activation¹¹. In many reaction series b is sufficiently near to the experimental temperature T and $(b-T)$ becomes negligible. There are also other causes of this cancellation effect and this was considered in the previous work¹¹.

Medium Effect

Medium effect may also be conveniently treated by separation of enthalpies of activation into potential and kinetic energy contributions. In our previous report,¹⁰ we have substituted Y for the potential energy term in solvolysis reactions. Thus eq. (1) gave,

$$\left. \begin{aligned} \partial_M \Delta H^\ddagger &= a'Y + b \cdot \partial_M \Delta S^\ddagger \\ \partial_M \Delta F^\ddagger &= a'Y + (b-T) \cdot \partial_M \Delta S^\ddagger \end{aligned} \right\} \dots\dots\dots (5)$$

In analogy with the substituent effect, our assumptions were $a'Y = \partial_M \Delta H_{int}^\ddagger$, where a' being the susceptibility of the solvolysis reaction to changes in solvent polarity. Thus $a' = \frac{\partial_M \Delta H_{int}^\ddagger}{(\partial_M \Delta H_{int}^\ddagger)_S}$, where subscript S denotes the standard reaction, i. e., solvolysis of *t*-butyl chloride at 25°C. The first term on the right hand side in eq. (5) represents the potential energy changes and the second kinetic energy changes as the solvent composition is varied. Grunwald and co-workers¹⁴ have shown that the solvent and structural parameters, mY and $\rho\sigma$, are interchangeable as can be related by

$$\left. \begin{aligned} m - m_0 &= C(\sigma - \sigma_0) \\ \rho_Y - \rho_{Y_0} &= C(Y - Y_0) \end{aligned} \right\} \dots\dots\dots (6)$$

where C is a constant, subscript 0 signifies the standard, and other symbols have their usual meanings. This interchangeability was the basis of derivation of eq. (5) from the general eq. (1). Admittedly, however, the choice of Y for the potential energy variable was rather unfortunate since Y originally

represented the free energy changes due to variations in solvent composition and no justification was given at that time. On the other hand the choice was not altogether unreasonable as it will be shown below that Y at least is proportional to the internal enthalpy changes or the potential energy changes in a substrate due to the solvent composition for S_N1 solvolysis.

Empirically Kosower¹⁵ has shown that the effect of solvent on spectra which he measured with a quantity Z , was proportional to Y . He found that the position of the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide measured the extent of interaction of a dipole with a cybotactic region of a solvent and the transition energies corresponding to the charge-transfer bands were linear in Y , a kinetic measure of solvent polarity. He attributes the change in Z -values to the effect of the net dipole moment of the cybotactic region in the ground state of the complex. Thus he visualizes the process as the transformation of the solute dipole vector upon excitation by light absorption while the dipole moment of the cybotactic region cannot change during light absorption (the Franck-Condon principle) and no electrostatic solvent-solute interaction should exist in the excited state at the instant of formation.

Recently the importance of the ground state solvation effect, i. e., the effect of the net dipole moment of the cybotactic region in the ground state, has been reported by Arnett et al.¹⁶ They have studied the heats of solution of *t*-butyl chloride in ethanol-water mixtures and concluded that virtually all of the activation energy minimum in the solvolysis can be associated with changes in solvation of the ground state, leaving transition state changes in solvation negligible. It is interesting to note in this connection that the study of ionization potentials of substituted benzyl compounds lead to the conclusion that the free energy of solvation is a linear function of the energy of ion pair formation¹⁷ which in turn would certainly be a measure of activation energy in S_N1 solvolysis, since in this type of reaction bond-breaking is almost complete in the transition state. Thus the solvent effect in S_N1 solvolysis would entirely be the effect of ground state solvation, and the solvation free energy is a measure of activation energy. If we remember that

the contribution of electronic transition to the entropy term is negligible, Z -value can be considered to represent potential energy effect of solvent medium, and the above discussion shows that the activation process in S_N1 solvolysis also involves essentially the same effect; in the solvolysis by S_N1 mechanism the activation involves formation of partially ionized transition state and the solvent effect involved in this process would be similar to that of electron transition by light absorption. It is a natural corollary from this argument that we should obtain a parallelism between Y and Z . Thus we are lead to conclude that Y measures changes in microscopic dipole field produced by the cybotactic region of the solvent in the ground state as is believed to be for Z . a' then measures the susceptibility of the reaction to changes in this microscopic dipole field.

Y is thus a parameter which is linear in Z and in potential energy changes. How then can it be accounted for that Y on the one hand being free energy of activation can also be a potential energy changes on the other hand?

The following treatment should give a satisfactory answer to this question. For the *t*-butyl chloride solvolysis at 25°C,

$$Y = \partial_M \Delta F_S^\ddagger = (\partial_M \Delta H_{int.}^\ddagger)_S + (\partial_M \Delta H_{ext.}^\ddagger)_S - T \partial_M \Delta S_S^\ddagger$$

If we substitute, $\partial_M \Delta H_{ext.}^\ddagger = b \partial_M \Delta S^\ddagger$, i. e., if we assume compensating effect of the kinetic energy terms,

$$Y = \partial_M \Delta F_S^\ddagger = (\partial_M \Delta H_{int.}^\ddagger)_S + (b - T) \partial_M \Delta S_S^\ddagger \quad (7)$$

For solvation in polar solvents the values of b near 268°K are not uncommon and this was attributed to the formation of solvated complexes, since the molecular complex formation is often found to proceed with negligible free energy changes even when the change in enthalpy amounts to several kilocalories⁹. Obviously these are the cases in which the external enthalpy and entropy terms cancel out approximately. In solvolysis reactions in general however internal enthalpy effect may also be involved and the total free energy change may not be negligible. Even in such cases we often find that the compensating effect of the external terms do result in the negligible external free energy changes to give $(b - T) \partial_M \Delta S_S^\ddagger = 0$.¹⁰

* We have shown in the previous paper that for the standard reaction $b = 300^\circ\text{K}$ and $T = 398^\circ\text{K}$, and the condition is satisfied. This condition was discussed in some detail in Part III.

Thus equation (7) now simplifies to

$$Y = \partial_M \Delta F_S^\ddagger = (\partial_M \Delta H_{int.}^\ddagger)_S = \text{potential energy changes} \dots \dots (8)$$

This probably means that in the solvolysis of *t*-butyl chloride the effect of microscopic dipole field of cybotactic region of the ground state is the dominant fact or influencing the overall free energy changes since the kinetic terms are compensated each other.

The compensating effect is however limited to the external terms because we know that the total terms give so-called Thurber-shaped curves when enthalpies and entropies are plotted⁹.

Another interesting aspect of eq. (1) is that we can certainly substitute Z values of Kosower in place of π , giving

$$\partial_M \Delta H^\ddagger = a'' Z + b \partial_M \Delta S^\ddagger \dots \dots \dots (9)$$

For electronic transitions, $\partial_M \Delta S^\ddagger \approx 0$, and therefore

$$\partial_M \Delta H^\ddagger = a'' Z$$

$$\text{or } \Delta H^\ddagger = a'' Z + \text{constant} \dots \dots \dots (10)$$

This is the form actually proposed by Kosower¹⁵ and was successfully applied in the analysis of various electronic transitions e. g., $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Kosower applied eq. (10) to $\pi \rightarrow \pi^*$ transitions and found a'' to be a negative quantity while $n \rightarrow \pi^*$ transitions gave positive values.

Mechanistically, we would expect any solvolysis reaction in which the medium effect can be represented by the potential energy changes to follow or satisfy eq. (1). It has been confirmed that S_N1 type reactions generally conformed to eq. (1).¹⁰

This is quite consistent since in S_N1 type solvolysis solvent ionizing power, Y , seem to represent the potential energy variation due to the medium changes as has been discussed above.

Application of eq. (1) to other type of solvolysis, i. e., S_N2 , is also satisfactory at least in few cases that have been tested by the author. For example, application to the data of Hyne and co-workers for the solvolysis of benzyl chlorides¹³ in water-rich ethanol-water mixtures gave excellent correlation as shown in Table 2. These data are accurate enough to warrant close scrutiny.

Table 2 shows that the linear fits of the solvolysis data are perfect for all compounds tested, and only for the two, *p*-nitro and *o*-nitro, the linearity seems to deteriorate slightly. In view of the generally acce-

Table 2

Benzyl chloride	$T^{\circ}\text{C}$	$a'^{1)}$	$b^{1)}$	$r^{2)}$	$S^{3)}$	$\sigma^{4)}$
-H	31.75	-0.877	302.9	1.000	0.011	0
-H	69.40	-0.877	291.8	1.000	0.016	0
<i>m</i> -CH ₃	31.75	-0.974	303.5	1.000	0.019	-0.066
<i>p</i> -CH ₃	31.75	-1.209	292.8	1.000	0.000	-0.311
<i>o</i> -CH ₃	31.75	-1.062	287.0	1.000	0.028	-0.17
<i>p</i> -Cl	51.63	-0.762	270.4	1.000	0.017	0.114
<i>m</i> -NO ₂	69.4	-0.658	304.4	1.000	0.015	0.674
<i>p</i> -NO ₂	69.4	-0.665	309.7	0.997	0.054	0.790
<i>o</i> -NO ₂	69.4	-0.738	291.8	0.995	0.045	0.80

- 1) a' and b are calculated by the least squares method.
- 2) r is the linear correlation coefficient.
- 3) s is the standard deviation of the constant C , which is given by, $C = (\Delta H^{\ddagger} - a'Y) - b\Delta S^{\ddagger}$. See Ref. (1c) for the detail.
- 4) For meta and para compounds, σ values are electrophilic substituent constants¹⁹⁾, σ^+ , and for ortho compounds Taft's ortho substituent¹⁹⁾ constants are given.

pted S_N2 mechanisms for nitro compounds, however, the excellent linearities obtained for them constitute evidence in support of the general nature of eq. (1), although admittedly the data analyzed are too scarce. The linearities for nitro compounds also imply that even though bond-forming may have progressed further compared to bond-breaking in the transition state, the degree of partial charge developed on carbon and halogen atoms can still be correlated with the solvent ionizing power Y .

This may in turn mean that $a'Y$ term is the representative of a gradual variation in the degree of ionic character in the bonds that are breaking, and factors involved in the bond-forming process are included in the external activation parameters. Thus we can measure the S_N1 -like character of a solvolyzing substrate with the constant a' . This is substantiated in Table 2 where it can be seen that compounds solvolyzing with more S_N1 -like character have larger absolute values of a' compared with those of nitro compounds and the magnitude increases continuously as the electron-releasing ability of the substituent increases.

The same trend is also shown by the alkyl series as can be seen in Table 3, where we have tabulated m values (note that $a' = -1.36m$) and other relevant data. m -values for the solvolysis of methyl, ethyl and

Table 3

Alkyl series	m^a	r^b	$I(\text{e. v.})^c$	ΔH^{\ddagger} (kcal) ^d	$\Delta\Delta E^{\ddagger}$ (kcal) ^e	σ^{*f}
CH ₃	0.26	0.113	9.95	220	0.4 ^g	1.47
C ₂ H ₅	0.34	0.053	8.78	192	0.7 ^g	0.98
<i>n</i> -C ₃ H ₇	—	—	8.69	177	1.5 ^g	0.88
<i>i</i> -C ₃ H ₇	0.54	0.030	7.90	168	2.1	0.49
<i>n</i> -C ₄ H ₉	0.33	—	8.64	—	—	0.86
<i>t</i> -C ₄ H ₉	0.94	0.021	7.42	149	3.1	0.00

- a) m -values of Grunwald and Winstein correlation $\log k/k_0 = mY$, for bromides.²⁰⁾ $-1.36m = a'$.
- b) Probable error of the fit to mY equation.²⁰⁾
- c) Ionization potentials of alkyl radicals in electron volts.²¹⁾
- d) ΔH^{\ddagger} for gas phase $\text{RCl} \rightarrow \text{R}^{\cdot} + \text{Cl}^{\cdot}$.²²⁾
- e) Depth of activation energy minima relative to $\Delta E^{\ddagger}_{\text{H}_2\text{O}}$ for halides solvolysis in *n*-ethanol-water, or acetone-water mixtures.²³⁾
- f) Taft's polar substituent constants, based on *t*-butyl as the standard.²⁴⁾
- g) Values of benzenesulfonates.²⁵⁾

n-butyl halides are low and the linearities poor. These compounds are also characterized by having high gas phase heat of ionization, ΔH^{\ddagger} , and high ionization potentials of the corresponding radicals, I . Small degree of susceptibility for ionization (small m) and high energy required for ionization are quite consistent to the generally accepted mechanism, S_N2 , for these compounds in the solvolysis.

The depth of activation energy minimum in the solvolysis $\Delta\Delta E^{\ddagger}$ is considered to be a measure of susceptibility of a substrate to changes in microscopic dipole field of the surrounding medium²³⁾. Approximate proportionality between m and $\Delta\Delta E^{\ddagger}$ is then in support of the above argument.

Since a' or m is a constant characteristic of substrate, for a series of substituted benzene (or alkyl) compounds this constant is expected to be linear with the substituent constant σ (or Taft's polar substituent constant σ^*).

The solvolysis of benzyl chlorides involve the development of electron deficient center in the transition state and the use of electrophilic substituent constant, σ^+ , is justified¹⁸⁾.

Fig. 1 shows the plot of a' against σ for benzyl chlorides, and Fig. 2 the plot of m against Taft's polar substituent for alkyl series.

Anomalous behavior of *o*-nitro compound may be of steric origin. Similarities shown by the two curves are

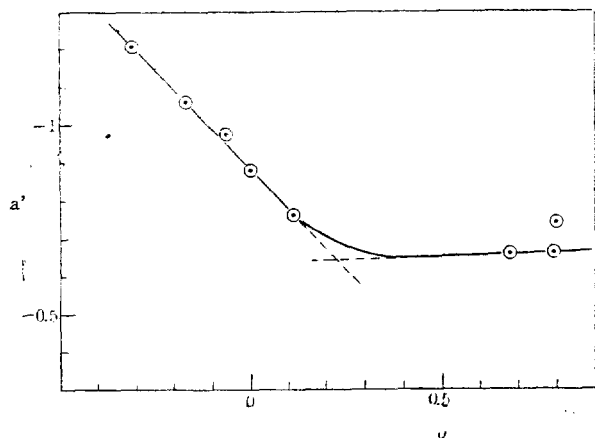


Fig. 1 Plot of a' against σ for the S_N2 solvolysis of benzyl chlorides.

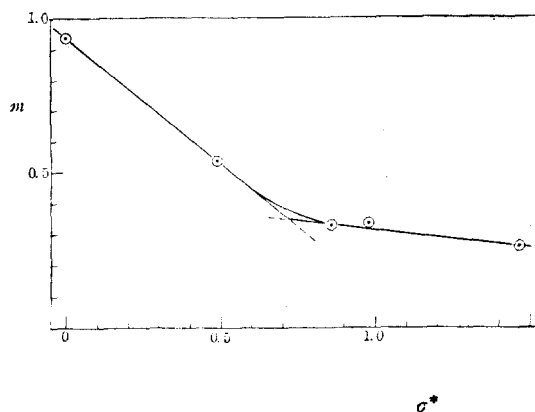


Fig. 2 Plot of m against σ^* for the solvolysis of alkyl halides.

however quite striking. In these Figures, two straight line portions representing two mechanisms, S_N1 and S_N2 , are easily identifiable and the change-over in mechanism is shown to be smooth. For the solvolysis of benzyl chlorides, compounds with the substituent constant of less than approximately 0.25 fall on S_N1 series and those with σ^* in the range 0.2~0.4 constitute a true borderline cases. Unfortunately no points are available in this adjoining part. It may prove rewarding to obtain experimental data for meta-halogen substituted compounds in this respect.

Ionization potentials for alkyl radicals of progressive α -methyl substitution i. e., methyl, ethyl, isopropyl and *t*-butyl, also show a smooth curve with σ^* , which could be analyzed into two component lines²¹⁾.

The slopes of the two composite lines in Fig. 1 and 2 are in fact the constant C of eq. (6) above. For the S_N1 series of benzyl chlorides, C was determined to be 1.03. C value for S_N2 series is shown to be near zero, although the determination of its precise value is not warranted at present. This can be taken as a strong indication that the susceptibility of the S_N2 solvolysis reaction to changes in solvent polarity is quite negligible.

For S_N1 series,

$$a' - a'_0 = 1.03 (\sigma - \sigma_0),$$

Therefore, $a' = 1.03\sigma - 0.877$,(11)

This in turn gives,

$$\delta_R \delta_M \Delta H^\ddagger = (1.03\sigma - 0.877)Y + b\delta_R \delta_M \Delta S^\ddagger \dots (12)$$

where the reference standard is the solvolysis of unsubstituted benzyl chloride (σ_0) in 80% ethanol-water mixture (Y_0), and $\delta_R \delta_M \Delta H^\ddagger = \Delta H^\ddagger_{\sigma} - \Delta H^\ddagger_{\sigma_0}$, etc.

The activation parameters for the S_N1 solvolysis of benzyl chlorides by Hyne et al¹³⁾, conform well to these equations.* The same treatment may also be applied to the S_N2 series, but we must await for more data for this series. The fact that we have two different values of C giving two relationships is in support of two mechanisms operating in the benzyl chlorides solvolysis.

Other points to be noted in Table 2 are;

1. The temperature effect on the substrate constant a' is negligible for the parent benzyl chloride, as expected¹⁰⁾.
2. b values for most compounds in S_N1 series are not very different from the mean experimental temperature T , and makes the external free energy term fairly small so that eq. (1) may be approximated into the Grunwald-Winstein equation. On the other hand, for the reaction of strong S_N2 character we would expect the greater probability for the activation parameters to conform to the Leffler equation since the effect of $a'Y$ term may be sufficiently small due to small a' values.

In conclusion we have given some evidence in support of the potential energy character of the term $a'Y$ in eq. (5), and the generality of eq. (1) (or the modified form (5)) in correlating activation parameters

* Eq. (12) has been tested in the form $\delta_R \delta_M \Delta H^\ddagger = (1.03\sigma - 0.877)Y + b \cdot \delta_R \cdot \Delta S^\ddagger + C$, where C was 27.21. Eq. (12) can be used if activation parameters for 80% ethanol-water were available.

of solvolysis reaction in varying medium.

In addition we have shown the use of eq. (1) in identifying two mechanisms manifested within a series of solvolysis reaction for substituted benzyl chlorides and alkyl halides.

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