

fluctuations is divergent, since we have considered the nonlinear terms up to the third order in ϵ . The higher order terms should be included, if necessary.

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13. Comparison of the present result with other models will be given in detail in a forthcoming paper.

Cross Interaction Between Identical Groups

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Various useful relations involving Hammett's and Brønsted's coefficients are derived for cross interactions between identical groups: $\rho_{ii} = \rho^N + \rho^L$, $\rho^L - \rho^N = 1$, $\beta_{ii} = \beta_N + \beta_L$ and $\beta_N - \beta_L = 1$. The use of these relations enable us to correctly interpret the transition state structure. Another advantage of the use of these relations is to use ρ/ρ_e for the determination of corresponding β values instead of plotting $\log k$ vs ρK_{lg} , once ρ_e values for standardizing equilibria are obtained.

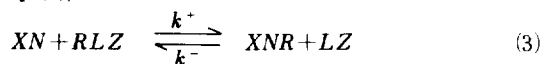
Cross interaction between two substituents has become a useful concept in the study of reaction mechanisms.¹ Multiple linear regression analysis² involving experimental rate constants k_{XZ} together with σ_X and σ_Z values provides us with the cross interaction constant ρ_{XZ} for the interaction between two substituents X and Z in accordance with eq. (1)³.

$$\log(k_{XZ}/k_{HH}) = \rho_X \sigma_X + \rho_Z \sigma_Z + \rho_{XZ} \sigma_X \sigma_Z \quad (1)$$

Replacing one of the substituents by H, e.g. Z = H, in eq. (1) reverts to the simple Hammett equation(2); the ρ_X and ρ_Z values in eq. (1) should therefore be more rigorously represented as ρ_{XH} and ρ_{HZ} .

$$\log(k_X/k_H) = \rho_X \sigma_X \quad (2)$$

Let us consider a reversible nucleophilic substitution (S_N) reaction, eq. (3),



where XN and LZ represent a nucleophile with a substituent X and a leaving group with a substituent Z, respectively.

The ρ_X and ρ_Z in eq. (1) now becomes the reaction constants for substituent variations in the nucleophile and leaving group. For an identity S_N reaction, i.e., XN = LZ,

$$\log(k_{ii}/k_{HH}) = (\rho^N + \rho^L) \sigma_i + \rho_{ii} \sigma_i^2 \quad (4)$$

where $\rho^N = \rho_{iH}$ and $\rho^L = \rho_{Hi}$; Obviously $\rho^N \neq \rho^L$ in general.

Hereafter, we adopt a convention that ρ^+ (for k^+) = ρ^L and ρ^- (for k^-) = ρ^N . It has been shown that the neglect of second order term in the Marcus equation leads to⁽⁴⁾

$$\rho^+ + \rho^- = \rho_{ii} \quad \text{i. e.,} \quad \rho^L + \rho^N = \rho_{ii} \quad (5)$$

$$\text{Thus,} \quad \log(k_{ii}/k_{HH}) = \rho_{ii} (\sigma_i + \sigma_i^2) \quad (6)$$

To be consistent with the approximations adopted in the derivation of eq. (1)³, we neglect the term in σ_i^2 , which simplifies eq. (6) to

$$\log(k_{ii}/k_{HH}) = \rho_{ii} \sigma_i \quad (7)$$

$$\text{Since} \quad K_{ii} = k_{ii}/k_{iH} = k^+/k^-, \quad (K_{ii} = K_{iH}^{-1}) \quad (8)$$

$$\rho_e = \rho^+ - \rho^-, \quad \text{i. e.,} \quad \rho_e = \rho^L - \rho^N \quad (9)$$

where ρ_e is the Hammett's coefficient for the equilibrium constant K_{Hi} ⁵, and $\rho^+ = \rho^L = \rho_{Hi}$ and $\rho^- = \rho^N = \rho_{iH}$. Eqs. (5) and (9) constitute a set of fundamental relations for the identity exchange reactions.

Definition of Brønsted's coefficient β leads us to more useful correlations for the identity reactions.⁶

$$\beta_L = \frac{d \log k}{d \rho K} = \frac{d \log k^+}{d \sigma} / \frac{d \rho K}{d \sigma} = \frac{\rho^+}{\rho_e} = - \frac{\rho^L}{\rho_e} \quad (10a)$$

Likewise,

$$\beta_N = -\frac{\rho^N}{\rho_e} \quad (10b)$$

From eqs(5) and (9), finally we obtain

$$\beta_N + \beta_L = \beta_{ii} \quad (11a)$$

$$\beta_N - \beta_L = 1 \quad (11b)$$

The relations (10) and (11) indicate that β values are the magnitude of normalized charge transfer; $\beta_N (>0)$ is the charge transferred from N to the reaction center R, while $\beta_L (<0)$ is the charge transferred from R to L. In other words, the reaction center R gains (positive) β_N electronic unit from N and loses (negative) $|\beta_L|$ electronic unit to L. Overall, one electron shift (normalization) is involved (eq. 11b), whereas in the transition state (TS) charge balance at R equals to β_{ii} (eq. 11a). Thus if R gains more from N than it loses to L, i.e., $\beta_N > |\beta_L|$, β_{ii} will be positive and hence the reaction center will be negatively charged by $|\beta_{ii}|$, whereas if R loses more, then $\beta_N < |\beta_L|$ and R will be charged positive by $|\beta_{ii}|$. In the latter (former) case, the TS will be loose (tight) and bond breaking (formation) has been achieved more than bond formation (breaking) although the TS will be symmetrical.

It can be shown readily from eq. (11) that⁷

$$\left. \begin{aligned} \beta_L &= \frac{1}{2} (\beta_{ii} - 1), \quad \beta_{ii} = 2\beta_L + 1 \\ \beta_N &= \frac{1}{2} (\beta_{ii} + 1), \quad \beta_{ii} = 2\beta_N - 1 \end{aligned} \right\} \quad (12)$$

These expressions show that the β_N and β_L values differ from $+1/2$ and $-1/2$ by $\pm 1/2|\beta_{ii}|$.

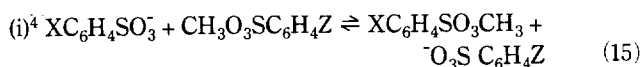
Reference to eqs (5), (9) and (11) reveals that we need only two Hammett's coefficients or only one Brønsted's coefficient in order to be able to determine other Hammett's as well as all Brønsted's coefficients. For example, if we have ρ^L and ρ_e , use of eqs (5) and (9) leads to ρ^N and ρ_{ii} , and all β values can be obtained by eqs (10) and (11). On the other hand, if we have β_L , then use of eqs (10)-(12) will give us β_N and β_{ii} values. The process of β_L or β_N determination by plotting $\log k$ vs pK is tantamount to division of ρ^N or ρ^L by ρ_e .

The argument presented above can be extended to other identity processes such as between XN and RY or between RY and LZ, where Y is a substituent on the substrate R. The relations corresponding to those for the N,L pair can be similarly obtained. For example

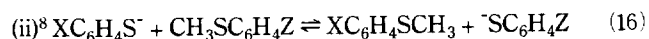
$$\beta_R + \beta_N = \beta_{ii}, \quad \beta_N - \beta_R = 1 \quad (13)$$

$$\beta_R + \beta_L = \beta_{ii}, \quad \beta_R - \beta_L = 1 \quad (14)$$

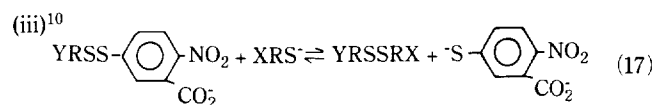
We will now present some examples of application. Best examples are provided by the works of Lewis et al.^{4,8}



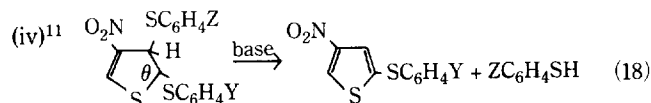
For $X=Z$, ρ_{ii} determined directly was 0.60⁹, and ρ_e was found to be 2.94⁵. This gives us $\rho^N = -1.17$, $\rho^L = 1.77$ ⁹, $\beta_{ii} = -0.20$, $\beta_N = 0.40$ and $\beta_L = -0.60$. Since β_{ii} is negative, the methyl carbon will be positively charged by 0.2 unit indicating bond cleavage is ahead of bond formation; the TS will have a rather loose symmetrical structure. The equilibrium (15) may serve as a standardizing equilibrium, and β values for other reactions involving benzenesulfonates can be conveniently determined by dividing ρ^N and/or ρ^L values for the reactions by $\rho_e = 2.94$.



For this identity exchange (for $X=Z$), $\rho^L = 1.75$ and $\rho_e = 3.73$ were obtained directly from experimental data; derived values gave $\rho^N = -1.98$, $\rho_{ii} = -0.23$, $\beta_{ii} = 0.08$, $\beta_N = 0.54$ and $\beta_L = -0.46$. Contrary to example(i), $\beta_N > |\beta_L|$ and β_{ii} is positive, implying that the methyl carbon is in this case negatively charged by 0.08 unit. The TS is relatively tight and bond making is ahead of bond breaking at the TS. The equilibrium (16) may serve as a standardizing equilibrium for the reactions involving thiophenoxide with $\rho_e = 3.73$.



This is a rare example where $X=Y$ provides an identity exchange between the substrate and the nucleophile. The ρ_{ii} value obtained was -0.93 ($r = 0.928$) and since in this reaction $\text{RX} = \text{RY} =$ thiophenoxides, β values were obtained by division of ρ values by $\rho_e = 3.73$ ¹²; use of eq. (13) gives us $\beta_N = 0.38$, $\beta_R = -0.62$ and $\beta_{ii} = -0.24$. Thus the reaction center S bears a net positive charge of 0.24. The YRS fragment loses more (by 0.24 unit) to the leaving group than it gains from the nucleophile, i.e., the TS is a rather loose one.



This reaction is known to proceed by the (E1cB)_{ip} mechanism, in which leaving group loss is rate limiting. The ρ_{ii} for $Y=Z$ was obtained to be 3.17 ($r = 0.994$). By adopting $\rho_e = 3.73$ ⁽¹²⁾, and using eq. (14) we get $\beta_L = -0.92$, $\beta_R = 0.08$ and $\beta_{ii} = -0.85$. This indicates that at the TS the reaction center carbons lose to the leaving group nearly a whole unit charge which was present originally; bond breaking is thus nearly complete at the TS in this reaction.

We conclude that the relations derived in the present work can be useful in the elucidation of reaction mechanism, especially in the TS mapping⁽¹⁴⁾ where various normalized β values are required.

Acknowledgements. We thank the Korea Science and Engineering Foundation and the Ministry of Education for support of this work.

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- In the derivation of this equation, terms in σ_X^2 , i.e., σ_X^2 or σ_X^2 are neglected.^(1c,d)
- E. S. Lewis, and D. D. Hu, *J. Am. Chem. Soc.* **106**, 3292 (1984).
- In general, $K_{ji} = \frac{k_{ji}}{k_{ij}} = \frac{k^+}{k^-}$ for any fixed substituent j.

However application of eq. (1) leads to

$$\begin{aligned} \rho_e &= d \log K_{ji} / d \sigma_i = d \log \frac{k_{ji}}{k_{ij}} / d \sigma_i = \rho_{Hi} + \rho_{ij} \sigma_j - \rho_{iH} \rho_{ij} \sigma_j \\ &= \rho_{Hi} \rho_{iH} = d \log K_{Hi} / d \sigma_i \end{aligned}$$

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7. These relations, (12), correspond to eq. (11) of ref.(3).
8. E. S. Lewis, and S. Kukes, *J. Am. Chem. Soc.* **101**, 417 (1979).
9. For this reaction, $\rho_{ii} = 0.60$ and $\rho_e = 2.94^5$ give the correct values of $\rho^+ = \rho^L = \rho_{Hi} = 1.77$ and $\rho^- = \rho^N = \rho_{iH} = -1.17$, which differ from ρ values given in ref. (4). Their values are really for ρ_{Xi} and ρ_{iX} , where $X = 3,5\text{-Cl}_2$, which are in general different from ρ_{Hi} and ρ_{iH} , since eq. (1) leads to $d \log k_{Xi}/d \sigma_i = \rho_{Hi} + \rho_{Xi} \sigma_X$ whereas $d \log k_{Hi}/d \sigma_i = \rho_{Hi}$. Thus the discrepancy between $\rho_{ii} = \rho^+ + \rho^- = +0.73$ and $\rho_{ii} = +0.6$ by direct determination is not really due to an uncertainty but originates from misconception.
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11. G. Petrillo, M. Novi, G. Garbarino, and C. Deil 'Erba, *J. Chem. Soc., Perkin 4*, 1741 (1985).
12. The methylation equilibrium⁴ in example (ii) above is much better than the protonating equilibrium normally used^{13,14} as a standardizing equilibrium⁶ in this case, although the reaction center is not a methyl carbon.
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Photo-enhanced Reduction of Conjugated Enones with NaBH_4

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The reduction of some cyclic conjugated enones with electron-donating substituent on C-3 by sodium borohydride was accelerated on irradiation. The photo-enhanced reduction seems to undergo through zwitterionic species formed from the (n, π^*) triplet state of conjugated enones, followed by hydride attack to yield unsaturated or saturated alcohols.

Introduction








There have been some attempts to change the reactivities of metal hydrides by photo-excitation.^{1,2,3} Witkop and his coworkers reported enhanced reduction of steroidal ketones by sodium borohydride on irradiation with UV light.⁴ It was also recently reported that cyclohexanones were nearly quantitatively reduced to cyclohexanols by sodium borohydride in diglyme on irradiation.⁵ The compounds are inert or very slowly reduced under the same condition without irradiation.

Stimulated by these results, we examined the photo-enhanced borohydride reduction of conjugated enones by sodium borohydride.

Results and Discussion

The effect of UV light on the reduction of various conjugated enones by sodium borohydride was studied and the results are shown in Table 1. Irradiation had no influence on the reduction of acyclic and cyclic conjugated enones studied except 3-methyl cyclic enones. The conversion yields of reduction of **4**, **5**, and **6** to saturated or unsaturated alcohols without irradiation were 12, 68, 41% in 2 h, but increased up to 82, 99, and 100% on irradiation under the same conditions. Different from the other enones, the enones which have

Table 1. Light Effect on the Reduction^a of Various Enones with Sodium Borohydride

Entry No.	Compound	Conversion ^b Yield (%) h	Δ
1		42	43
2		8	7
3		33	35
4		82	12
5		99	68
6		100	41
7		68	68

^aIrradiation of enones for 2h at room temperature except **1** and **4** which were irradiated for 1 h. ^bYield of reduced alcohol (sum of saturated and unsaturated alcohol produced).

photocatalyzed effect are cyclic and have a methyl group on C-3. Since the difference of **5** from **3** is only the 3-methyl

*Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.