

fluctuations is divergent, since we have considered the nonlinear terms up to the third order in  $\epsilon$ . 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:  $\rho_{ii} = \rho^+ + \rho^-$ ,  $\rho^+ - \rho^- = 1$ ,  $\beta_{ii} = \beta_N + \beta_L$  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  $\rho/\rho_e$  for the determination of corresponding  $\beta$  values instead of plotting  $\log k$  vs  $\rho K_{H_i}$ , once  $\rho_e$  values for standardizing equilibria are obtained.

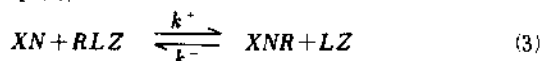
Cross interaction between two substituents has become a useful concept in the study of reaction mechanisms.<sup>1</sup> Multiple linear regression analysis<sup>2</sup> involving experimental rate constants  $k_{XZ}$  together with  $\sigma_X$  and  $\sigma_Z$  values provides us with the cross interaction constant  $\rho_{XZ}$  for the interaction between two substituents X and Z in accordance with eq. (1)<sup>3</sup>.

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

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

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

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  $\rho_X$  and  $\rho_Z$  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,

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

where  $\rho^+ = \rho_{iH}$  and  $\rho^- = \rho_{Hi}$ . Obviously  $\rho^+ \neq \rho^-$  in general.

Hereafter, we adopt a convention that  $\rho^+$  (for  $k^+$ ) =  $\rho^+$  and  $\rho^-$  (for  $k^-$ ) =  $\rho^-$ . It has been shown that the neglect of second order term in the Marcus equation leads to<sup>4)</sup>

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

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

To be consistent with the approximations adopted in the derivation of eq. (1)<sup>3</sup>, we neglect the term in  $\sigma_i^2$ , which simplifies eq. (6) to

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

Since  $K_{H_i} = k_{H_i}/k_{iH} = k^+/k^-$ , ( $K_{H_i} = K_{iH}^{-1}$ ) (8)

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

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

Definition of Brønsted's coefficient  $\beta$  leads us to more useful correlations for the identity reactions.<sup>6</sup>

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

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  $\beta$  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)  $\beta_N$  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  $\beta_{ii}$  (eq. 11a). Thus if R gains more from N than it loses to L, i.e.,  $\beta_N > |\beta_L|$ ,  $\beta_{ii}$  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) that<sup>7</sup>

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

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

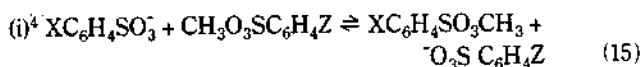
Reference to eqs (5), (9) and (11) reveals that we need only two Hammett's coefficients or only one Brønsted's coefficient in order to be able to determine other Hammett's as well as all Brønsted's coefficients. For example, if we have  $\rho^L$  and  $\rho_e$ , use of eqs (5) and (9) leads to  $\rho^N$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

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

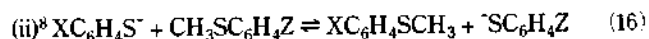
$$\beta_R + \beta_N = \beta_{ii}, \quad \beta_N - \beta_R = 1 \quad (13)$$

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

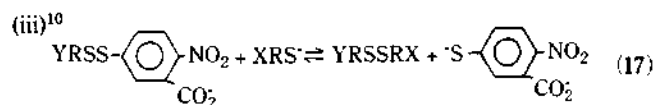
We will now present some examples of application. Best examples are provided by the works of Lewis et al.<sup>4,8</sup>



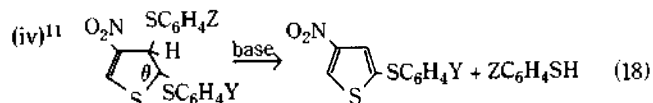
For X = Z,  $\rho_{ii}$  determined directly was 0.60<sup>9</sup>, and  $\rho_e$  was found to be 2.94<sup>5</sup>. This gives us  $\rho^N = -1.17$ ,  $\rho^L = 1.77^9$ ,  $\beta_{ii} = -0.20$ ,  $\beta_N = 0.40$  and  $\beta_L = -0.60$ . Since  $\beta_{ii}$  is negative, the methyl carbon will be positively 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  $\beta$  values for other reactions involving benzenesulfonates can be conveniently determined by dividing  $\rho^N$  and/or  $\rho^L$  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  $\beta_{ii}$  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  $\rho_{ii}$  value obtained was -0.93 ( $r = 0.928$ ) and since in this reaction  $\text{RX} = \text{RY} =$  thiophenoxides,  $\beta$  values were obtained by division of  $\rho$  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)<sub>ip</sub> mechanism, in which leaving group loss is rate limiting. The  $\rho_{ii}$  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<sup>(14)</sup> where various normalized  $\beta$  values are required.

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- J. Shorter, *Correlation Analysis of Organic Reactivity*; Research Studies Press: Chichester, 1982; p20.
- In the derivation of this equation, terms in  $\sigma_X^2$ , i.e.,  $\sigma_X^2$  or  $\sigma_Y^2$  are neglected.<sup>(11c,d)</sup>
- 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

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

6. A. Williams, *Acc. Chem. Res.* **17**, 425 (1984).
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  $\rho$  values given in ref. (4). Their values are really for  $\rho_{Xi}$  and  $\rho_{iX}$ , where  $X = 3,5\text{-Cl}_2$ , which are in general different from  $\rho_{Hi}$  and  $\rho_{iH}$ , 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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## Photo-enhanced Reduction of Conjugated Enones with $\text{NaBH}_4$

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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 ( $n, \pi^*$ ) 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.<sup>1,2,3</sup> Wittkop and his coworkers reported enhanced reduction of steroidal ketones by sodium borohydride on irradiation with UV light.<sup>4</sup> It was also recently reported that cyclohexanones were nearly quantitatively reduced to cyclohexanols by sodium borohydride in diglyme on irradiation.<sup>5</sup> 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<sup>a</sup> of Various Enones with Sodium Borohydride

| Entry No. | Compound   | Conversion <sup>b</sup> Yield (%)<br>h | $\Delta$ |
|-----------|--|--|----------|
| 1         |  | 42                                     | 43       |
| 2         |  | 8                                      | 7        |
| 3         |  | 33                                     | 35       |
| 4         |  | 82                                     | 12       |
| 5         |  | 99                                     | 68       |
| 6         |  | 100                                    | 41       |
| 7         |  | 68                                     | 68       |

<sup>a</sup>Irradiation of enones for 2h at room temperature except **1** and **4** which were irradiated for 1 h. <sup>b</sup>Yield 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.