

Acknowledgement. The authors wish to thank the Inje Research and Scholarship Foundation for support of this work.

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Correlation Between Cross Interaction Constant and Bond Length in the S_N2 Transition State

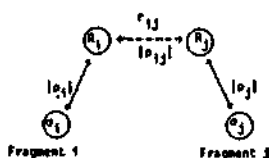
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A simple correlation between cross interaction constants ρ_{ij} and bond lengths in the transition state was obtained; it has been shown that ρ_{ij} corresponds to force constant of activation, which in turn is related to bond length by Badger's rule involving only universal constants. A satisfactory correlation between 4-31G ab initio calculated values of bond length and force constant for C-X stretching in the transition state of the methyl transfer reaction, $X^- + CH_3X = XCH_3 + X^-$, indicated that Badger's rule can be extended to bonds in the transition state. Independence of ρ_{ij} values from the variable charge transmission of reaction centers has been demonstrated with nearly constant, experimentally determined $|\rho_{XY}|$ values, and hence similar degree of bond formation, for various S_N2 reactions.

Introduction

Transition states (TS) can not be directly observed experimentally simply because reacting molecules do not remain near their TSs long enough to be accurately measured.¹ Selectivity parameters obtained by linear free energy relationships have, however, provided indirect measure of the TS structure within a series of reactions; Brønsted β values from rate-equilibrium relationships^{2,3} and Hammett ρ values from structure-reactivity relationships⁴ have been used as useful means of assessing relative bond tightness or looseness in the TS.



Scheme 1

The magnitude of a Hammett ρ_i reflects the intensity of interaction, relative to that for the benzoic acid dissociation

equilibria, between substituents (σ) and the reaction center (R) on fragment i ⁵ (e.g. in S_N2 reactions, a fragment refers to a nucleophile, substrate or leaving group)⁶ in the TS of a reaction; the stronger the interaction, the larger is the magnitude of $|\rho_i|$. Likewise $|\rho_j|$ reflects the intensity of interaction between substituents (σ) and the reaction center (R_j) on fragment j . However, the efficiency of charge transmission between reaction centers, R_i and R_j , in bond formation or bond cleavage may differ for different reaction series so that $|\rho_j|$ can at most serve as a relative measure of bond length r_{ij} within a series of reactions; $|\rho_j|$ values for different reaction series e.g. for different R_j such as R_k or R_b can not be compared to assess relative bond length (r_{ij}) between two reaction centers which corresponds to the bond being formed or broken in the TS.⁷

On the other hand, the magnitude of cross interaction constant, ρ_{ij} in eq (1), reflects the intensity of indirect interaction between two substituents on fragments i and j through the reaction centers, R_i and R_j , in the TS when both substituents interact with their respective reaction centers simultaneously in the TS of a reaction i.e., when R_i and R_j form a partners

which are involved in bond formation and/or bond breaking in the TS.⁶

$$\log(k_{ij}/k_{im}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (1)$$

There are of course other modes of interaction between substituents on i and j : a) direct or electrostatic interaction, b) manifold interaction in which additional interaction routes are provided by bridges formed by hydrogen bonding or the like.⁸ In the following discussions, we strictly confine ourselves to the systems where two substituents σ_i and σ_j interact indirectly through R_i and R_j as in scheme I.

Definition of the cross interaction constant ρ_{ij} , eq. (1), leads to,⁹

$$\rho_{ij} = \left(\frac{\partial^2 \log k_{ij}}{\partial \sigma_i \partial \sigma_j} \right) = \frac{\partial \rho_i}{\partial \sigma_j} = \frac{\partial \rho_j}{\partial \sigma_i} \quad (2)$$

Thus ρ_{ij} is the magnitude of the derivative of ρ_i (or ρ_j) with respect to σ_j (or σ_i); $|\rho_{ij}|$ reflects the effect of varying substituent σ_j of the fragment j , which will perturb R_j , on the effective reaction constant ρ_i of the other fragment i , which is felt at R_i in the TS (or vice versa). We will show that $|\rho_{ij}|$ does not suffer from the variable charge transmission of reaction centers, and relative magnitudes provide a direct measure of the TS structure.

Derivation of Correlations

One can define the potential energy of activation, V^* , as the energy difference between energy minima of reactants and saddle point.¹¹ A Taylor expansion of the potential energy of activation, V^* , around the point $\sigma_i = \sigma_j = 0$,^{12a} is then given by,

$$\begin{aligned} \delta V^* = V_{ij}^* - V_{00}^* &= \left(\frac{\partial V^*}{\partial \sigma_i} \right)_0 \sigma_i + \left(\frac{\partial V^*}{\partial \sigma_j} \right)_0 \sigma_j + \\ &+ \frac{1}{2} \left(\frac{\partial^2 V^*}{\partial \sigma_i^2} \right)_0 \sigma_i^2 + \frac{1}{2} \left(\frac{\partial^2 V^*}{\partial \sigma_j^2} \right)_0 \sigma_j^2 \\ &+ \left(\frac{\partial^2 V^*}{\partial \sigma_i \partial \sigma_j} \right)_0 \sigma_i \sigma_j + \text{higher derivative terms} \quad (3) \end{aligned}$$

If we assume that the small change with σ can be described by some kind of single coordinate analogous to a reaction coordinate denoted by r , then the change in r will be sufficiently small when σ is changed and the elements in the vector σ will vary linearly in relation to r ¹² so that $r_i = a \sigma_i$ and $r_j = b \sigma_j$, where a and b are constants.¹² Substitution of these into eq. 3, with neglect of higher terms, yields

$$\delta V^* = f_i^* r_i + f_j^* r_j + \frac{1}{2} f_{ii}^* r_i^2 + \frac{1}{2} f_{jj}^* r_j^2 + f_{ij}^* r_i r_j \quad (4a)$$

where $f_i^* = \left(\frac{\partial V^*}{\partial r_i} \right)_0$ = force of activation

and $f_{ij}^* = \left(\frac{\partial^2 V^*}{\partial r_i \partial r_j} \right)_0$ = force constant of activation

$$(-f_{ij}(TS) - f_{ij}(GS)) \quad (4b)$$

Let us now assume that the only important degree of freedom, and hence the reaction coordinate, in the TS (scheme I) is the bond length $r_{ij} = r_i + r_j$ so that changes in r_{ij} dominate the transition vector.¹³ Moreover, f_{ii}^* and f_{jj}^* represent the force constants of activation for stretching vibrations within the fragments i and j respectively; these will be normally

negligible since the distance between substituent σ and R can be taken as constant in the activation process (vide infra)¹⁴.

The second derivative terms in eq. (4) can be transformed into a normal coordinate of the form, (5)¹⁵ by solving secular de-

$$\frac{1}{2} \lambda Q^2 \quad (5)$$

terminant,¹²

$$\begin{vmatrix} f_{ii}^* - \lambda & f_{ij}^* \\ f_{ij}^* & f_{jj}^* - \lambda \end{vmatrix} = 0 \quad (6)$$

The eigenvalues of this 2×2 force constant matrix can be obtained readily, since $f_{ii}^* = f_{jj}^* = 0$ by assumption.¹⁴ Thus

$$\lambda = \pm f_{ij}^* \quad (7)$$

The negative eigenvalue represents a force constant of activation for the stretching a long reaction coordinate.^{13,15} Obviously, since $r_{00} = a \sigma_0 + b \sigma_0 = 0$,

$$Q = r_{ii} - r_{00} = r_{ij} = r_i + r_j \quad (8)$$

Thus r_{ij} is the displacement occurring in the activation process and f_{ij}^* is the force constant of activation for stretching of the bond R_i-R_j in Scheme 1. Eq. (4) then becomes,

$$\delta V^* = f_i^* r_i + f_j^* r_j + \frac{1}{2} f_{ij}^* r_{ij}^2 \quad (9)$$

and also from eq. (4) with neglect of f_{ii}^* and f_{jj}^*

$$\delta V^* = f_i^* r_i + f_j^* r_j + f_{ij}^* r_i r_j \quad (10)$$

$$\text{Thus, } f_{ij}^* = \left(\frac{\partial^2 V^*}{\partial r_i \partial r_j} \right)_0 = \left(\frac{\partial^2 V^*}{\partial \sigma_i \partial \sigma_j} \right)_0 \quad (11)$$

Since $r_i = a \sigma_i$ and $r_j = b \sigma_j$, eq. (10) can be transformed into

$$\delta V^* = F_i^* \sigma_i + F_j^* \sigma_j + F_{ij}^* \sigma_i \sigma_j \quad (12a)$$

with $F_i^* = \left(\frac{\partial V^*}{\partial \sigma_i} \right)_0$ and $F_{ij}^* = \left(\frac{\partial^2 V^*}{\partial \sigma_i \partial \sigma_j} \right)_0 = \text{const.} \times f_{ij}^*$

$$(12b)$$

On the other hand, transformation of eq. (1) leads to,

$$\begin{aligned} \delta \Delta G^* = \Delta G_{ij}^* - \Delta G_{00}^* &= -2.3RT \{ \rho_i \sigma_i + \\ &+ \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \} \quad (13a) \end{aligned}$$

$$\begin{aligned} \delta V^* = V_{ij}^* - V_{00}^* &= -2.3RT \{ \rho_i \sigma_i + \rho_j \sigma_j \\ &+ \rho_{ij} \sigma_i \sigma_j \} + \theta(T) \quad (13b) \end{aligned}$$

Where $\theta(T)$ is a term which includes corrections for zero-point energies and other temperature-dependent factors including entropy of activation.¹¹ Finally comparison of eqs (12) and (13b) leads to

$$\therefore f_{ij}^* \propto \rho_{ij} \quad (14)$$

Thus ρ_{ij} is directly proportional to the force constant of activation f_{ij}^* , which is in terms of displacement vector σ , at constant temperature.¹⁶ Thus neglect of ρ_{ii} and ρ_{jj} in eq. (1)⁹ naturally leads to $f_{ii}^* = 0$ and $f_{jj}^* = 0$ in eq. (6) according to this relation (14).

Badger's rule, eq. (15), correlates bond length r with force constant f with universal constants A and B , which are de-

Table 1. 4-31G Calculated Bond Length, r_{ij} , and force Constant, $f_{ij}(\text{TS})$, in the Transition State of Identity S_N2 Reactions, eq. (18)

X	$r_{ij}(\text{\AA})$	$f_{ij}(\text{TS}) \times 10^{-5}(\text{dyne cm}^{-1})$
F	1.827	3.674
OH	1.909	3.317
OCH ₃	1.924	3.232
NH ₂	2.008	2.795
NC	2.014	2.702
CN	2.112	2.417
CCH	2.124	1.913
CH ₃	2.161	1.998

pendent only on the rows of the periodic table for the two atoms being bonded, and is known to have wide range of applicability.¹⁶ It has been shown to apply between stretching-

$$r = A - B \log f \quad (15)$$

force constant and bond length for all types of bonds including those involved in excited states of molecules, ionic gaseous molecules such as NaCl, noble-gas clusters as well as covalent molecules such as N₂.¹⁶ It is not unreasonable, therefore, for us to expect that the rule can be extended to bonds in the TS. Thus, eq. (15) shows that r_{ij} and f_{ij}^* are related by

$$r_{ij} = A' - B' \log |f_{ij}^*| \quad (16)$$

Since log of a negative number is meaningless, only absolute values are significant; thus from eq. (14), $|f_{ij}^*| \propto |\rho_{ij}|$. And hence eq. (16) can be transformed into

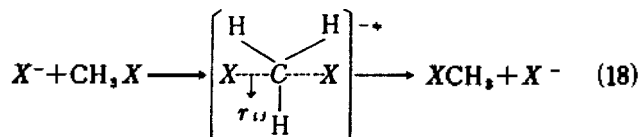
$$\begin{aligned} r_{ij} &= a - \beta \log |\rho_{ij}| \\ r_{ij} &= a + \beta \log \frac{1}{|\rho_{ij}|} \end{aligned} \quad (17)$$

where A' , B' , a and β should be *universal constants* at constant temperature. Eq. (17) demonstrates that the bond dist-

ance in the TS is linear with *logarithm of the inverse of* $|\rho_{ij}|$, and r_{ij} is *not directly proportional to the inverse of* $|\rho_{ij}|$.⁶ (The r_{ij} between atoms i and j in different rows can also be defined using a set of universal constants).¹⁶

Results and Discussion

In order to test applicability of eq. (16) for bonds and force constants in the TS, we have evaluated the C-X distances and stretching force constants in the trigonal bipyramidal five-coordinate TS for the identity S_N2 reactions, (18), by ab initio MO calculations with 4-31G basis set.¹⁷ We determined r_{ij} and $f_{ij}(\text{TS})$ values for eight nucleophiles of second row elements, X = CCH, CN, NC,



OH, F, NH₂, CH₃ and OCH₃, and these were subjected to linear regression analysis using eq. (16). The r_{ij} and $f_{ij}(\text{TS})$ values obtained are summarized in Table 1. A good linearity shown by a correlation coefficient of 0.996, with $A' = 8.026$ and $B' = 1.108$, supports strongly that the Badger's rule can be extended to apply for bonds in the TS.^{17b}

According to eq. (17), in the indirect interaction as well as in other modes of interactions, the major factor determining the intensity, or the magnitude of ρ_{ij} , is the distance r_{ij} between the two reaction centers, R_i and R_j , distance between substituents and reaction centers being practically constant during an activation process. Thus $|\rho_{ij}|$ constitutes a direct measure of bond length r_{ij} ; the distance r_{ij} is only dependent on $|\rho_{ij}|$, since a and β are the universal constants, and hence $|\rho_{ij}|$ is free from the variable charge transmission of the reaction centers.

For S_N2 reactions, relatively extensive $|\rho_{XY}|$ data are available (Table 2) so that our argument can be tested. Re-

Table 2. ρ_X and ρ_{XY} values for some S_N2 reactions

			ρ_X	ρ_{XY}	Corr. Coeff. ^a	Ref.
(A)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{SO}_2\text{Cl}$	$\xrightarrow[35.0^\circ\text{C}]{\text{MeOH}}$	-2.14	-0.70	0.998	18
(B)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{SO}_2\text{Cl}$	$\xrightarrow[25.0^\circ\text{C}]{\text{MeOH}}$	-2.15	-0.75	0.997	19
(C)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{CH}_2\text{Cl}$	$\xrightarrow[50.0^\circ\text{C}]{\text{EtOH}}$	-0.98	-0.77	0.974	20
(D)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{CH}_2\text{OSO}_2\text{Ph}$	$\xrightarrow[35.0^\circ\text{C}]{\text{MeOH}}$	-0.82	-0.62	0.998	7
(E)	$\text{XC}_6\text{H}_4\text{S}^- + \text{YC}_6\text{H}_4\text{CH}_2\text{Cl}$	$\xrightarrow[20.0^\circ\text{C}]{\text{MeOH}}$	-0.58	-0.62	0.982	21
(F)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{COCl}$	$\xrightarrow[35.0^\circ\text{C}]{\text{MeOH}}$	-2.24	-0.68	0.999	22
(G)	$\text{SC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Cl}$	$\xrightarrow[35.0^\circ\text{C}]{\text{MeOH}}$	-3.74	-0.69	0.997	23
(H)	$\text{XC}_6\text{H}_4\text{NH}_2 + \text{YC}_6\text{H}_4\text{CH}(\text{O}_2\text{S})\text{SO}_2\text{Ph}$	$\xrightarrow[25.0^\circ\text{C}]{\text{MeOH}}$	-2.20	-0.23	0.999	24

^a Correlation coefficient from multiple linear regression of $\log k_{xy}$ using eq. (1) with $i = X$ and $j = Y$.

ference to this Table reveals that for S_N2 reactions with relatively good leaving group (Cl or $-\text{OSO}_2\text{Ph}$), the range of variations in $|\rho_{XY}|$, the cross interaction constant between substituents X in the nucleophile and Y in the substrate, is much smaller than that in $|\rho_X|$; $\Delta|\rho_{XY}| = 0.15$ and $\Delta|\rho_X| = 3.16$. The spread in $|\rho_{XY}|$ values is an order of magnitude smaller than that for $|\rho_X|$. For example, reactions (A) and (E) differ in both nucleophile and substrate, but the difference in $|\rho_{XY}|$ is only 0.08, whereas $|\rho_X|$ differs by 1.56. Note that for reaction (E), $|\rho_{XY}|$ is actually greater than $|\rho_X|$. Other examples of large $|\rho_{ij}|$ have also been reported.^{6,8} Near constant values of $|\rho_{XY}|$ indicate that similar distances are involved between the two reaction centers in the nucleophile and substrate in the TS for the two reaction series; the degree of bond formation will therefore be similar in the two reaction series which belong to the same category of reaction, S_N2 .

For an S_N1 -like reaction of (H)²⁴, we obtained much smaller $|\rho_{XY}|$ value, i.e., much smaller degree of bond formation, $\sim 1/3$ of the value for the S_N2 reactions in Table 2, despite the large $|\rho_X|$ which is even greater than that for S_N2 reactions. The reaction (H) has been shown to proceed by an (S_N1 -like) intermolecular S_N1 mechanism.²⁴ Other types of applications, e.g. to $S_A N^6$, $E2^3$, and associative S_N2 mechanisms²⁵ have also been reported.

In conclusion, $|\rho_{ij}|$ values provide much better measure of the TS structure than $|\rho|$ values, and in fact better than any other experimental selectivity parameters for characterization of the TS structure. One obvious drawback in this approach is that relatively large number of rate constants k_{ij} are required, since both substituents in fragments i and j must be varied simultaneously within a reaction series in order to be able to obtain a $|\rho_{ij}|$ values by the multiple linear regression²⁶ using eq. (1).

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

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- Strictly, eq. (1) should be given, up to second order terms, as, $\log(k_{ij}/k_{HH}) = \rho_{iH}\sigma_i + \rho_{Hj}\sigma_j + \rho_{ii}\sigma_i^2 + \rho_{jj}\sigma_j^2 + \rho_{ij}\sigma_i\sigma_j$ where

$$\rho_{ii} = \frac{\partial \log k_{ii}}{\partial \sigma_i}, \quad \rho_{jj} = \frac{\partial \log k_{jj}}{\partial \sigma_j}$$

$$\rho_{ii} = \frac{\partial^2 \log k_{ii}}{\partial \sigma_i^2} = \frac{\partial \rho_{ii}}{\partial \sigma_i} (-\rho_{ii}) = 0$$

$$\rho_{ii} = \frac{\partial \rho_{ii}}{\partial \sigma_i} (-\rho_{ii}) = 0$$

- The last two relations, i.e., $\rho_{ii} = \rho_{jj} = 0$ are really the basis of the Hammett linear correlation.^{7,10} In general for $X \neq H$, $\rho_{iX} = (\partial \log k_{iX})/(\partial \sigma_i) \neq \rho_{iH}$ and ρ_{iX} is a function of σ_j . Likewise $\rho_{Hj} \neq \rho_{Xj}$ and ρ_{Xj} is a function of σ_i .
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 - Note that, we have pointed out in the previous communication,⁶ this assumption is a tenuous one when strong resonance effects are operative.
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Strictly speaking, in order for this relation (14) to hold, variations in entropies of activation, $\delta\Delta S^*$ should be either zero or proportional to those in enthalpies of activation, i.e., $\delta\Delta H^* = \beta \delta\Delta S^*$, as is usual, for a given series; O. Exner, in "Advances in Linear Free Energy Relationships", ed. N. B. Chapman: J. Shorter, Plenum, London, 1972, Chapter 1.
 - (a) Force constants at the TS geometries were calculated with 4-31G basis set. The C-X distances at the TS geometries agreed with those reported in: D. J. Mitchell, H. B. Schlegel, S. S. Shaik, S. Wolfe, *Can. J. Chem.*, **63**, 1642 (1985); (b) The f_{ij}^* values can be obtained by using eq. (4b). For the gas-phase S_N2 reactions, eq. (18), $f_{ij}(\text{GS})$ is the force constant in the reactant complex. We have found that eq. (15) holds for both $f_{ij}(\text{TS})$ and $f_{ij}(\text{GS})$, and hence for f_{ij}^* : I. Lee, C. H. Song, J. K. Cho, *J. Chem. Soc. Faraday 2*, Inpress.
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