Cross-interaction Constants as a Measure of the Transition-state Structure. Part 4.† Brønsted-type Cross-interaction Constants

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The Brønsted-type (β_{ij}) and the mixed Hammett–Brønsted type (λ_{ij}) cross-interaction constants are introduced, and inter-relationships between various parameters are deduced in order to provide some quantitative basis for the two parameters. The β_{ij} value represents a more direct measure of the transition-state structure and has the advantage of wider applicability over the Hammett-type constant (ρ_{ij}), which contains two constant factors corresponding to the interactions between substituents and reaction centres. The λ_{ij} values are found to be useful as a measure of the transition-state structure for a reaction series in which only one fragment involves a substituent change.

In previous reports[1] we examined the mechanistic significance of the Hammett-type cross-interaction constants, ρ_{ij} in equation (1), with a view to correlating the magnitude

$$\log(k_{ij}/k_{\mathrm{HH}}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

$|\rho_{ij}|$ with the transition-state (TS) structure, especially of S_N2 reactions (Scheme 1). In contrast to the simple Hammett coefficient ρ_i (or ρ_j), which is of limited use within a particular family of closely related reactions, we found that the magnitude of ρ_{ij} provides a quantitative measure of bond length r_{ij} between reaction centres R_i and R_j (i, j = X, Y, or Z in Scheme 1) when both substituents i and j interact with their respective reaction centres simultaneously in the TS.[2]

The cross-interaction constants ρ_{ij} defined by equation (1), however, cannot be applied for a reaction series with fragments in which no substituent changes are involved. For such series of reactions other types of linear free energy relationship, *e.g.*, Brønsted-type correlation,[3,4b] can be used to define corresponding cross-interaction parameters.

In this work, we introduce two such interaction parameters, which will allow us to extend the range of application to a wider scope of reaction types. We will also examine inter-relationships between the parameters in order to provide some quantitative basis for the parameters in the characterization of the TS structure.

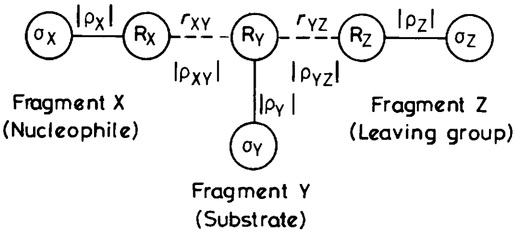
Inter-relationships between Parameters.—A Taylor expansion of $\log k_{ij}$ up to second order around $\Delta pK_i = \Delta pK_j = 0$, where $\Delta pK_i = pK_i - pK_{i=\mathrm{H}}$, defines a Brønsted-type cross-interaction constant, β_{ij}, by neglecting, as usual,[1a,2,4] the pure second-order terms of β_{ii} and β_{jj} in equation (2).

$$\begin{aligned}\log(k_{ij}/k_{\mathrm{HH}}) &= \beta_i\Delta pK_i + \beta_j\Delta pK_j + \beta_{ij}\Delta pK_i\Delta\rho K_j &(2a)\\ &= \beta'_i pK_i + \beta'_j pK_j + \beta'_{ij} pK_i pK_j + Re &(2b)\end{aligned}$$

where $\beta_i =$

$$\left(\frac{\partial \log k_{ij}}{\partial pK_i}\right), \beta_{ij} = \left(\frac{\partial^2 \log k_{ij}}{\partial\, pK_i \partial pK_j}\right) = \left(\frac{\partial\beta_i}{\partial pK_j}\right) = \left(\frac{\partial\beta_j}{\partial pK_i}\right)\cdots$$

Likewise, a mixed Hammett–Brønsted type cross-interaction constant, λ_{ij}, can be defined by expanding $\log k_{ij}$ around $\sigma_i = \sigma_j = 0$ and $\Delta pK_i = \Delta pK_j = 0$ in equation (3),



Scheme 1. Typical S_N2 TS.

$$\begin{aligned}\log(k_{ij}/K_{\mathrm{HH}}) &= \beta_i\Delta pK_i + \rho_j\sigma_j + \lambda_{ij}^{(i)}\Delta pK_i\sigma_j &(3a)\\ &= \rho_i\sigma_i + \beta_j\Delta pK_j + \lambda_{ij}^{(i)}\Delta pK_j\sigma_i &(3b)\end{aligned}$$

$$\text{where } \lambda_{ij}^{(i)} = \left(\frac{\partial^2 \log k_{ij}}{\partial pK_i \partial\sigma_j}\right) = \left(\frac{\partial\beta_i}{\partial\sigma_j}\right) = \left(\frac{\partial\rho_j}{\partial pK_i}\right)\cdots$$

It can be readily shown that:

$$\beta_{ij} = \beta'_{ij} \qquad (4a)$$

$$\left.\begin{aligned}\beta'_i &= \beta_i - \beta_{ij}pK_{j=\mathrm{H}}\\ \beta'_j &= \beta_j - \beta_{ij}pK_{i=\mathrm{H}}\end{aligned}\right\} \qquad (4b)$$

$$\begin{aligned}Re &= \beta_{ij}pK_{i=\mathrm{H}}pK_{j=\mathrm{H}} - \beta_i pK_{i=\mathrm{H}} - \beta_j pK_{j=\mathrm{H}}\\ &= -\log k_{\mathrm{HH}} \qquad (4c)\end{aligned}$$

Comparison of equations (1)–(3) leads to the following useful relations,

$$\left.\begin{aligned}\rho_i &= \beta_i\rho_e^i\\ \rho_j &= \beta_j\rho_e^j\end{aligned}\right\} \qquad (5)$$

$$\rho_{ij} = \beta_{ij}\rho_e^i\rho_e^j = \lambda_{ij}^{(i)}\rho_e^i = \lambda_{ij}^{(j)}\rho_e^j \qquad (6)$$

$$\left.\begin{aligned}\lambda_{ij}^{(i)} &= \beta_{ij}\rho_e^j = \rho_{ij}/\rho_e^i\\ \lambda_{ij}^{(j)} &= \beta_{ij}\rho_e^i = \rho_{ij}/\rho_e^j\end{aligned}\right\} \qquad (7)$$

$$\text{where} \quad \left.\begin{aligned}\Delta pK_i &= \rho_e^i\sigma_i\\ \Delta pK_j &= \rho_e^j\sigma_j\end{aligned}\right\} \qquad (8)$$

The parameters β_{ij} and λ_{ij} correspond to p_{xy} and p'_{xy}, respectively,[4b,5] which have been introduced by Jencks. The inter-relationships (4)–(8) allow us to deduce the mechanistic significance of these parameters based on our accumulated knowledge concerning the interpretation of the sign and magnitude of the Hammett-type cross-interaction constants ρ_{ij}.[1] Relations (6) and (7) show that $|\beta_{ij}|$ and $|\lambda_{ij}|$ are

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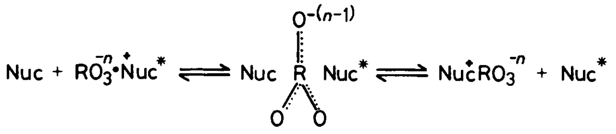
† Part 3 is ref. 1(*k*).



(R = P; n = 2 or R = S; n = 1)

Scheme 2.

proportional to $|\rho_{ij}|$, the proportionality constants being ρ_e^i and ρ_e^j. Thus the greater the magnitude of β_{ij} and λ_{ij}, the stronger is the interaction between reaction centres R_i and R_j and hence the shorter the distance r_{ij} (Scheme 1).[1] Obviously the Brønsted-type parameter, β_{ij}, will be useful as a measure of the TS structure for a reaction series in which structural variations in the nucleophile and the leaving group (LG) do not involve substituent changes. Equations (4a) and (4b) reveal that the use of pK_i rather than ΔpK_i in the Brønsted-type correlation, equation (2), leads to the same cross-interaction constant β_{ij}, but gives different β'_i ($\neq \beta_i$) and β'_j ($\neq \beta_j$) values in general. It is also true that the β_{ij} values obtained are dependent on the set of pK_a values used in the correlation equation (2); according to equations (6) and (8), for a value of ρ_{ij}, the β_{ij} value will differ depending on the value of ρ_e^i and/or ρ_e^j. For example, for the Z-substituted benzenesulphonates $^-OSO_2C_6H_4Z$, two types of pK values have been used; equation (9) defines a pK_a scale based on the conjugate acids of benzenesulphonates (as nucleophiles or LGs), *i.e.*, the proton acidity pK^{H^+},[6] whereas equation (10)

$$HOSO_2C_6H_4Z + H_2O \rightleftharpoons H_3O^+ + {}^-OSO_2C_6H_4Z \quad (9)$$

$$CH_3OSO_2C_6H_4Z + {}^-OSO_2C_6H_5 \rightleftharpoons CH_3OSO_2C_6H_5 + {}^-OSO_2C_6H_4Z \quad (10)$$

introduces an entirely different pK scale based on methyl transfer reactions (pK^{CH_3}),[7] for which ρ_e values are -0.67 and -2.99, respectively. Thus we need to adopt a standard procedure of using only the proton acidity pK_a values for the determination of β_{ij} (and λ_{ij}) in order that the magnitude of the β_{ij} (and λ_{ij}) values may serve as a quantitative measure of the TS structure.

The mixed parameter, λ_{ij}, has potentially useful applications, in a series of reactions in which only one fragment contains substituents (Scheme 1), *e.g.*, a series of reactions in which nucleophiles and substrates are varied but substituents are only varied in the latter.

Since normally the ρ_e values are negative, ρ_{ij}, and β_{ij} will have the same sign, while λ_{ij} may have a different sign. In general, but not necessarily always, the magnitude of ρ_{ij} will be the greatest and that of β_{ij} will be the smallest, $|\rho_{ij}|$ being greater by the product of two constants, $|\rho_e^i|$ and $|\rho_e^j|$, which represent the intensities of interaction between substituents (i and j) and respective reaction centres (R_i and R_j). Thus $|\beta_{ij}|$ represents a direct interaction between reaction centres R_i and R_j, whereas $|\rho_{ij}|$ reflects an indirect interaction between substituents i and j through reaction centres R_i and R_j. Whenever practicable, determination of both ρ_{ij} and β_{ij} will be useful as a cross-check of the quantitative measure of the distance r_{ij}.

Applications.—Some β_{XZ} values for S_N2 type reactions calculated by multiple linear regression using equation (2a) are presented in Table 1. As expected, the signs of β_{XZ} and ρ_{XZ} agree, and the magnitude of β_{XZ} is proportional to, but smaller than, that of ρ_{XZ}. For the phenacyl series (reactions D and F), however, $|\beta_{XZ}|$ is nearly constant, indicating that a similar bond distance r_{XZ} ($r_{XY} + r_{YZ}$ in Scheme 1) is involved in the TS. This is in contrast with the difference of $|\rho_{XZ}|$ by a factor of *ca.* two for the two phenacyl series due to a non-conjugating CH_2 group intervening between the benzene ring and the reaction centre, N, in the benzylamine nucleophiles, despite the fact that there is no significant change in the bond distance r_{XZ} in reality. This demonstrates that the Brønsted-type cross-interaction parameter is a more direct measure of the TS structure, while the Hammett-type parameters are mixed with constant factors (ρ_e^i and ρ_e^j) corresponding to the interactions between substituents and reaction centres, which, for most practical purposes, can be considered to remain intact during the activation process.[2]

The dissociative S_N2 reaction A has the smallest $|\beta_{XZ}|$ of 0.06, whereas the S_N reactions with twofold interaction pathways between the nucleophile and the LG in the TS (reactions B and E) give considerably greater $|\beta_{XZ}|$ values (0.32) as has been shown to be the case with $|\rho_{XZ}|$ values.[1c] For the associative S_N2 reactions (D and F), the magnitude of β_{XZ} (0.17–0.19) is more than three times greater than the value for the dissociative S_N2 reaction A, in addition, it is negative rather than positive.

There are some mixed series of aliphatic and aromatic amines in the literature for which ρ_{XZ} values cannot be determined but β_{XZ} values are obtainable. Two examples in which group transfers (PO_3^- and SO_3^-) are involved between aliphatic amines (Nuc) and pyridines (Nuc*) give $\beta_{XZ} = 0.023$ for PO_3^- transfer[8] and $\beta_{XZ} = 0.029$ for SO_3^- transfer[9] (Scheme 2). These values are very small indeed compared with those in Table 1. In both cases, the TS had little change in effective charge on the nucleophile (Nuc) and a large change in departing leaving group (Nuc*) relative to the reactant state, indicating weak bonding between R and entering atoms corresponding to an 'open' (or 'exploded') TS or a pre-association stepwise process.

Another example is the β_{XZ} value of 0.052 obtained for tosyl transfer between imidazoles and primary aliphatic amines[10] [equation (2)]; in this series five nucleophiles and three leaving groups contain no substituent that can be represented by the Hammett substituent constant σ. The magnitude of β_{XZ} (0.052) is greater by a factor of *ca.* two than that for the PO_3^- and SO_3^- transfers cited above, and hence suggests that the TSs are less 'exploded' than those proposed for the PO_3^- and SO_3^- transfers, as the authors[10] have concluded.

Some mixed Hammett–Brønsted type cross-interaction constants λ_{ij} calculated by multiple linear regression using equation (3a) are summarized in Tables 2 (λ_{XY}) and 3 (λ_{YZ}). These parameters contain only one constant factor (ρ_e^i) corresponding to the interaction between substituent (i) and reaction centre (R_i), so that the magnitudes are somewhat greater than the corresponding values of $|\beta_{ij}|$ but smaller than those of $|\rho_{ij}|$ with opposite sign, *e.g.*, $\lambda_{XY} > 0$, whereas $\rho_{XY} < 0$ and $\beta_{XY} < 0$. As expected, the magnitude of λ_{XY} (0.20–0.27), which is a measure of bond formation in the TS, does not show much variation for the typical S_N2 reactions with aniline nucleophiles (reactions G–K); this is an indication of a similar degree of bond formation, *i.e.*, $r_{XY} \simeq$ constant, for S_N2 reactions G–K with aniline nucleophiles, as concluded from the near constant values of $|\rho_{XY}|$ for the reactions. The size of λ_{XY} for reaction M is more than twice that for the other reaction (G–K) indicating a much greater degree of bond formation in the TS of the nucleophilic substitution reaction of a carbonyl compound with a worse LG, fluoride ion. Similarly, a comparison of reactions H ($\lambda_{XY} = 0.20$) and L ($\lambda_{XY} = 0.39$) also shows an increase in the degree of bond formation with fluoride LG. A striking increase in the degree of bond formation is noted in the S_N2 reactions with benzyamine nucleophiles (N–P); the increment of $|\lambda_{XY}|$ relative to the values for the reactions with anilines is seen to be inversely proportional to the nucleofugic power of the LG *i.e.*, the increase is in the order Br < Cl < F. This demonstrates an increase in bond formation in the TS with a stronger

Table 1. The Brønsted-type cross-interaction constants, β_{XZ}, for nucleophilic substitution reactions in methanol.

	Reaction[a]	β_X	β_Z	β_{XZ}	SD[c]	ρ_{XZ}	Correlation coefficient[b]	N[d]	Ref.
A	$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z \xrightarrow{35.0\text{ °C}}$	0.28	−2.24	−0.06	0.025	−0.10	0.996	20	11
B	$XC_6H_4NH_2 + YC_6H_4CH(CH_3)OSO_2C_6H_4Z \xrightarrow{25.0\text{ °C}}$	0.72	−1.60	−0.32	0.034	−0.56	0.998	16	12
C	$XC_6H_4N(CH_3)_2$[e] $+ YC_6H_4CH(CH_3)OSO_2C_6H_4Z \xrightarrow{35.0\text{ °C}}$	0.50	−2.00	−0.11	0.044	−0.24	0.989	15	1(*k*)
D	$XC_6H_4NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow{45.0\text{ °C}}$	0.73	−2.14	0.19	0.085	0.31	0.995	16	1(*h*)
E	$XC_6H_4NH_2 + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow{65.0\text{ °C}}$	0.44	−1.79	−0.28	0.054	−0.45	0.995	16	1(*h*)
F	$XC_6H_4CH_2NH_2$[f] $+ YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow{45.0\text{ °C}}$	0.73	−1.49	0.17	0.049	0.12	0.995	12	13

[a] pK_a Values for benzenesulphonic acids were taken from ref. 6. [b] 99% Confidence level. [c] Standard deviation. [d] Number of data points. [e] The pK_a values are taken from W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1937, 1622 and G. Thompson, *J. Chem. Soc.*, 1946, 1113. [f] The pK_a values are taken from L. F. Blackwell, A. Fischer, I. J. Miller, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 1964, 3588. *p*-Methoxybenzylamine had a peculiar pK_a value so that it was excluded from the correlation.

Table 2. Mixed Hammett–Brønsted type cross-interaction constants, λ_{XY}, for nucleophilic substitution reactions in methanol.

	Reactions	β_X	ρ_Y	λ_{XY}	SD	ρ_{XY}	Correlation coefficient	N	Ref.
G	$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_5 \xrightarrow{35.0\text{ °C}}$	0.30	−0.73	0.22	0.059	−0.62	0.998[a]	15	11
H	$XC_6H_4NH_2 + YC_6H_4SO_2Cl \xrightarrow{35.0\text{ °C}}$	0.72	0.91	0.20	0.052	−0.70	0.998	16	1(*i*)
I	$XC_6H_4NH_2 + YC_6H_4COCl \xrightarrow{35.0\text{ °C}}$	0.75	2.18	0.23	0.032	−0.68	0.998	12	1(*i*)
J	$XC_6H_4NH_2 + YC_6H_4CH_2Cl \xrightarrow{35.0\text{ °C}}$	0.58	−0.64	0.27	0.020	−0.75	0.999[a]	15	14
K	$XC_6H_4NH_2 + YC_6H_4CH_2Br \xrightarrow{35.0\text{ °C}}$	0.47	−0.51	0.25	0.092	−0.78	0.997[a]	20	1(*i*)
L	$XC_6H_4NH_2 + YC_6H_4SO_2F \xrightarrow{45.0\text{ °C}}$	0.48	1.15	0.39	0.020	−1.07	0.999	20	1(*i*)
M	$XC_6H_4NH_2 + YC_6H_4COF \xrightarrow{55.0\text{ °C}}$	1.14	1.73	0.61	0.083	−1.67	0.996	12	1(*i*)
N	$XC_6H_4CH_2NH_2 + YC_6H_4SO_2Cl \xrightarrow{35.0\text{ °C}}$	1.40	1.52	0.39	0.015	−0.39	0.999[b]	15	1(*i*)
O	$XC_6H_4CH_2NH_2 + YC_6H_6CH_2Br \xrightarrow{45.0\text{ °C}}$	1.15	−0.41	0.26	0.020	−0.38	0.998[b]	9	1(*i*)
P	$XC_6H_4CH_2NH_2 + YC_6H_4SO_2F \xrightarrow{45.0\text{ °C}}$	0.78	0.71	0.63	0.005	−0.67	0.999[b]	15	1(*i*)

[a] Benzyl system fits better with σ^+ rather than σ due to substantial positive charge development in the TS. [b] The sources of pK_a values are the same as shown in Table 1.

Table 3. The mixed Hammett–Brønsted type cross-interaction constants, λ_{YZ}, for nucleophilic substitution reactions in methanol.

	Reactions[a]	ρ_Y	β_Z	λ_{YZ}	SD	Correlation coefficient	N	Ref.
Q	$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z \xrightarrow{35.0\text{ °C}}$	−0.80	2.36	0.18	0.073	0.994	12	11
R	$XC_6H_4NH_2 + YC_6H_4CH(CH_3)OSO_2C_6H_4Z \xrightarrow{25.0\text{ °C}}$	−0.40	1.63	0.19	0.064	0.987	16	12
S	$XC_6H_4N(CH_3)_2 + YC_6H_4CH(CH_3)OSO_2C_6H_4Z \xrightarrow{35.0\text{ °C}}$	−0.45	2.01	0.26	0.091	0.983	16	1(*k*)
T	$CH_3OH + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow{65.0\text{ °C}}$	−0.43	1.81	−0.12	0.059	0.984	16	15
U	$XC_6H_4NH_2 + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow{60.0\text{ °C}}$	−0.16	1.73	0.11	0.050	0.994	20	1(*k*)
V	$XC_6H_4NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow{45.0\text{ °C}}$	0.65	2.12	−1.04	0.059	0.994	12	1(*g*)
W	$XC_6H_4CH_2NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow{45.0\text{ °C}}$	0.56	1.77	−0.82	0.040	0.996	12	13

[a] The sources of pK_a values are the same as shown in Table 1.

nucleophile, the increase being greater for the compounds with a worse LG. This sort of fine quantitative analysis is difficult with $|\rho_{XY}|$, since $|\rho_{XY}|$ is also dependent on the intervening group between substituent and reaction centre, which reduces $|\rho_{XY}|$ to an uncertain degree, albeit approximately; one such group is known to halve the magnitude of ρ_i or ρ_{ij} value in general.[11]

The λ_{YZ} values for reactions Q–S range from 0.18–0.26 with positive signs; the magnitude of λ_{YZ}, which is a measure of bond breaking, does not differ much from that of $|\lambda_{XY}|$, a measure of bond formation, for S_N2 reactions G–K, indicating that similar bond distances, r_{XY} and r_{YZ}, are involved in the TS for the S_N2 type of reaction. The magnitude of λ_{YZ} for reactions T and U are somewhat smaller but those for reactions V and W are much greater than the $|\lambda_{YZ}|$ values for reactions Q–S. This difference is mainly due to an intervening non-conjugating CH_2 group present between substituent Y and the reaction centre at the α carbon, and partially due to some aryl participation for reactions T and U, whereas for reactions V and W it is due to the minimal bond breaking involved in the TS. A small decrease in $|\lambda_{YZ}|$ for reaction of benzylamine (W) indicates that as the nucleophilicity increases from anilines (V) to benzylamines (W) the degree of bond breaking in the TS is increased.

We conclude that the use of the Brønsted-type cross-interaction constant β_{ij} has several advantages over the Hammett-type constant ρ_{ij}: (*a*) $|\beta_{ij}|$ represents a more direct measure of the TS structure with no involvement of constant factors corresponding to the interactions between substituents and reaction centres (ρ_e^i), and (*b*) $|\beta_{ij}|$ can be used for a reaction series in which structural variations of reactions do not necessarily involve substituent changes. There is also a drawback in the application of β_{ij} in that the pK_a values used in the correlation are in general those measured in water at 25.0 °C, while the actual rate data correlated are often those for other solvent systems and temperatures. This means that equations (5)–(7) do not exactly hold in practice.

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