A Simple Harmonic Oscillator Model of the Intrinsic Barrier to Group Transfer

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The intrinsic barrier in group-transfer reactions has been shown to correspond to the coupling energy of two identical harmonic oscillators. It has also been shown that the barrier, $\Delta G_{XX}^{\ddagger}$, can be represented as $\Delta G_{XX}^{\ddagger} = \frac{1}{2} f(r_X - r_0)^2 + \Delta G_{00}^{\ddagger}$ where r_X is the distance to the crossing point of the two oscillators and r_0 is the distance to the energy minimum. In considering a series of related reactions, the force constant, *f*, can be regarded as constant within a particular series and the intrinsic barriers of the series are shown to correlate with either approximate linearity of positive gradient in the E region and negative gradient in the C region; or as a parabolic curve in the B region centred on the minimum.

Examples of reactions belonging to each region are given and the following two relations are shown to hold in all cases of the intrinsic, controlled reaction series:

$$r_X = \lambda\sigma + r_0 \quad \lambda < 0$$
$$\Delta \log|\rho_{XY}| = k\sigma_Z \quad k > 0$$

where ρ_{XY} is the cross-interaction constant between substituents in the nucleophile (X) and substrate (Y), σ_Z is the substituent constant for the leaving group, and λ and *k* are constants. Thus these two relations constitute important criteria for intrinsic-barrier controlled reaction series. For thermodynamically controlled reaction series, the sign of the two constants is reversed, *i.e.* $\lambda > 0$ and $k < 0$.

The Marcus equation (1)[1] expresses the kinetic barrier, $\Delta G^{\ddagger}$, as

$$\Delta G^{\ddagger} = \Delta G^{\ddagger} + \Delta G_0{}^0/2 + (\Delta G^0)^2/(16\,\Delta G_0{}^{\ddagger}) \qquad (1)$$

the sum of an intrinsic, $\Delta G_0{}^{\ddagger}$, and the thermodynamic, ΔG^0, barriers,* together with a second-order term.† Although the Marcus equation was originally derived for electron-transfer reactions in solution,[1a] it has been shown to apply to hydrogen-atom transfers,[1b] proton transfers,[1d] and group transfers, especially methyl-transfer reactions (2).[1e–i]

$$X^- + CH_3Y \rightleftharpoons XCH_3 + Y^- \qquad (2)$$

With the advent of ion cyclotron resonance (i.c.r.) spectroscopy, studies of gas-phase S_N2 reactions have provided a direct means of determining experimentally the intrinsic barriers involved in the gas-phase methyl-transfer reactions.[1e,f,2] Alternatively, several elegant studies involving solution-phase methyl-transfer reactions by Lewis *et al.*[2,3] have provided kinetic data from which the intrinsic barriers can also be determined for solution-phase reactions.

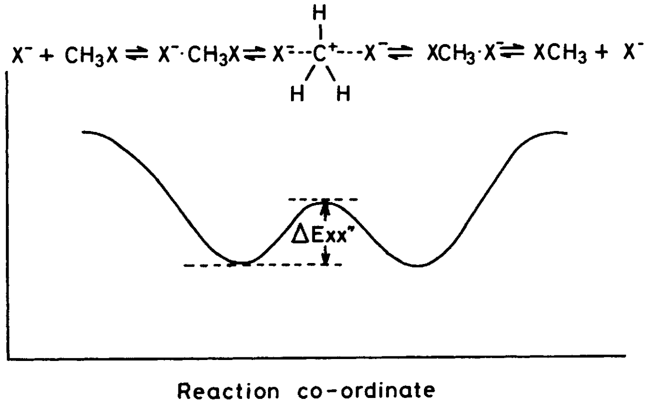

Figure 1. Double-well potential-energy surface for the gas-phase identity S_N2 reaction, $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$.

Theoretically the intrinsic barriers can be obtained by MO calculation[4] as the energy difference between the transition state (TS) and the ion–molecule cluster, *i.e.*, the height of the central barrier in Figure 1. For an identity-exchange reaction, X = Y in equation (2), $\Delta E^0 = 0$ so that the activation barrier becomes equal to the intrinsic barrier,* $\Delta E^{\ddagger} = \Delta E_0{}^{\ddagger}$.

Comparison of experimental[1f] and theoretical intrinsic barriers[4] for some of the identity-exchange reactions is given in Table 1 and agreement between the two is only moderate. However this is understandable considering the difficulties in determining experimental values ‡ and the adequacy of the use of the 4-31G basis set for this type of calculation.[5]

Various interpretations of the significance of the intrinsic barrier are offered. (*i*) Brauman *et al.*[1f] correlated the gas-phase identity-exchange barriers, $\Delta E_{XX}{}^{\ddagger}$, with the methyl-cation affinity E_{mc} of the nucleophile defined as the heterolytic-bond-dissociation energy of the CH_3–X bond.

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* The free-energy form of equation (1) is usually used for solution-phase reactions, but the application of the potential-energy form:

$$\Delta E^{\ddagger} = \Delta E_0{}^{\ddagger} + \Delta E^0/2 + (\Delta E^0)^2/16\,\Delta E_0{}^{\ddagger} \qquad (1')$$

is more intuitive and appropriate for gas-phase and theoretical studies.[1f]

† For solution-phase reactions, the work terms, which are largely made up of solvent–solute interactions, should be included in equation (1). However they are independent of structure throughout a series of related reactions and hence if the solvent is constant, the work terms can be dropped from the Marcus equation[1g] as in equation (1).

‡ Errors in $\Delta E_{XX}{}^{\ddagger}$ are reported to be within a few kcal mol^{-1}.[1f]

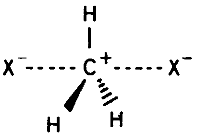
Table 1. Comparison of experimental (gas-phase) and theoretical (4-31G level) values of $\Delta E_{XX}^{\ddagger}$ (kcal mol^{-1}) for $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$.

	$\Delta E_{XX}^{\ddagger}$	
X	Expt.[1f]	Theoret.[4]
HCC	41.3	50.4
CN	35.0	43.8
CH_3O	26.6	23.5
CH_3S	24.2	15.6
F	26.2	11.7
Cl	10.2	5.5
NC	—	28.5
OH	—	21.2
OF	—	18.8
OOH	—	18.5

$$CH_3X \longrightarrow CH_3^+ + X^-$$

$$\Delta H^0 = E_{mc}(X^-) = D_0(CH_3\text{–}X) - E_{ea}(X) + E_i(CH_3)$$

where D^0 is the bond dissociation energy, $E_{ea}(X)$ is the electron affinity of the X radical and $E_i(CH_3)$ is the methyl-radical ionization potential. They interpreted the correlation as a consequence of charge separation in the trigonal-bipyramidal penta-co-ordinate (TBP–5C) TS, (**1**) of the exchange reaction.



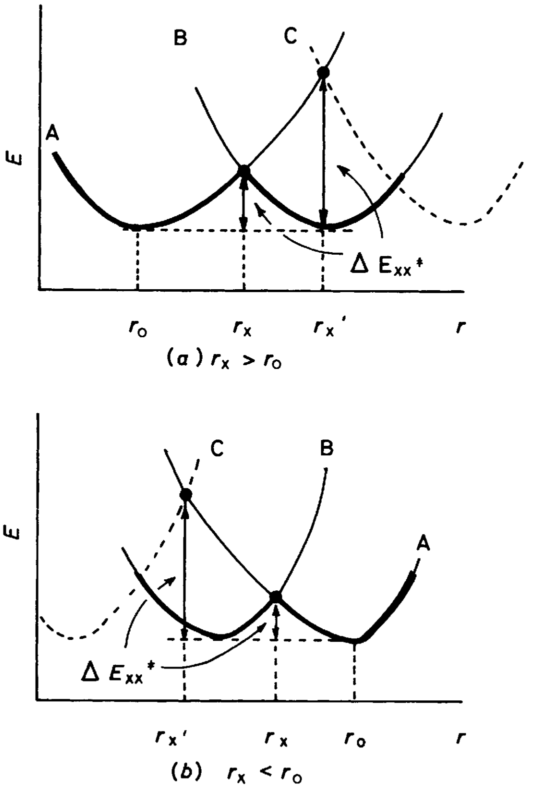
(**1**)

(*ii*) Wolfe *et al.*[4c] correlated their $\Delta E_{XX}^{\ddagger}$ values calculated using the 4-31G basis set with the deformation energies, ΔE_{def}, of CH_3X in the TBP–5C TS formation, especially with the C–X stretching energies, ΔE_R.

Although these rationalizations seem reasonable, they are unsatisfactory in two respects. (*i*) These correlations deal with deformation energies of CH_3X only, whereas the $\Delta E_{XX}^{\ddagger}$ values should reflect energy changes in both CH_3X and the nucleophile X^- which is shown by the existence of a TS structure, (**1**). (*ii*) All Xs are included arbitrarily in a single correlation. The present work seeks to show that any such correlation should be made for distinct groups according to the period of the bonding atoms as, H^-; OH^-, F^-, CN^-, *etc.*; Cl^-, SH^-, *etc.*, since the central carbon in CH_3X is fixed.[6] *

Discussion

Simple Harmonic Oscillator Model.—The TBP-5C TS, (**1**), of an identity S_N2 reaction can be represented as two identical harmonic oscillators, C–X, with force constant f which are symmetrically coupled as in Figure 2(*a*).[7] The crossing point of the two oscillators at r_X provides a common energy for the coupled system and the height of the barrier at r_X, which is the intrinsic barrier $\Delta E_{XX}^{\ddagger}$ defined in Figure 1, is given by



(*a*) $r_X > r_0$

(*b*) $r_X < r_0$

Figure 2. Coupling of the two harmonic oscillators. Oscillators, B and C, cross oscillator A at r_X and r_X' giving barriers, $\Delta E_{XX}^{\ddagger}$, between them.

$$\Delta E_{XX}^{\ddagger} = \tfrac{1}{2}f(r_X - r_0)^2 + \Delta E_{00}^{\ddagger} \qquad (3)$$

where $\Delta E_{00}^{\ddagger}$ is a median barrier for the series at $r_X = r_0$.[6] Similarities in the potential-energy profiles in Figure 1 and 2 are obvious. As the two oscillators separate, the crossing point, r_X appears at a greater distance and the barrier height rises accordingly. This corresponds to a larger stretching vibration in the TBP–5C TS, (**1**).

When r_X is shorter than r_0 as in Figure 2(*b*), equation (3) still applies; the shorter r_X, the higher the barrier, and hence $\Delta E_{XX}^{\ddagger}$ will be greater.

This model may be more accurate as $r_X \simeq r_0$, since the harmonic-oscillator model of the potential-energy function is especially applicable near the bottom of the well.

According to equation (3), the intrinsic barrier to the identity S_N2 reaction (2) with a particular X(= Y) can be given by a point on a parabolic curve for a harmonic oscillator, A, in Figure 2. If the stretching, r_X, in the TBP–5C TS, (**1**), is greater than that of a hypothetical minimum at r_0,† the barrier will be represented as a point on the right-hand branch of the curve; the intrinsic barrier originates in the stretching or expanding beyond r_0 (E region). Alternatively if $r_X < r_0$, then the barrier will be represented by a point on the left-hand branch of the curve; the intrinsic energy corresponds to the compression energy (C region). Therefore, any intrinsic barrier should belong to either the C or the E region. However, near the bottom of the well, *i.e.*, $r_X \simeq r_0$, a different relation will apply (see below) between $\Delta E_{XX}^{\ddagger}$ and r_X so that a borderline (B) region is formed, as shown in Figure 3.

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* Badger's rule was shown to hold also for the TBP–5C TS, (**1**), and the parameter a_{ij} obtained indicated that the carbon centre in the TS had a covalent bond radius of a fourth-row element, *i.e.*, the median bond length of the series is far longer in the TS than that expected for the normal bonds of the first-row element. This dramatic stretching of the covalent radii in the TBP–5C TS provided a median intrinsic barrier, $\Delta E_{00}^{\ddagger}$, which is common to the series at $r_X = r_0$.

† This minimum point may not always be observed in practice, since the range covered by a series is usually small; it is only when the reaction series covers the B region, in Figure 3, that the minimum point is encountered.

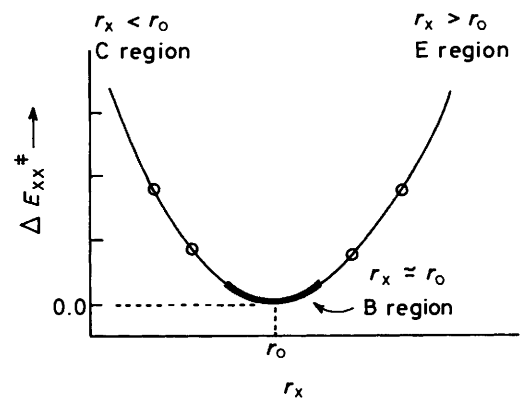

Figure 3. A parabolic curve representing three regions. Two points on each region of the curve correspond to the two crossing points given in Figures 2(*a*) and 2(*b*), respectively.

Application.—Let us now consider a series of *n* related identity (X = Y) S_N2 reactions, (2), with X = $X_1, X_2, \ldots\ldots X_n$. The intrinsic barrier can be calculated approximately using equation (3) for each member of the series as:

$$\begin{array}{l} \Delta E_{11}^{\ddagger} = \tfrac{1}{2} f_1 (r_1 - r_O)^2 + \Delta E_{OO}^{\ddagger} \\ \Delta E_{22}^{\ddagger} = \tfrac{1}{2} f_2 (r_2 - r_O)^2 + \Delta E_{OO}^{\ddagger} \\ \vdots \\ \Delta E_{nn}^{\ddagger} = \tfrac{1}{2} f_n (r_n - r_O)^2 + \Delta E_{OO}^{\ddagger} \end{array} \qquad (4)$$

Making the further assumption that in this series the force constant is almost invariant so that $f_1 \simeq f_2 \simeq \ldots\ldots \simeq f_n$, the *n* equations, (4), can be combined to give equation (3).

$$\Delta E_{XX}^{\ddagger} = \tfrac{1}{2} f (r_X - r_O)^2 + \Delta E_{OO}^{\ddagger} \qquad (3)$$

If for this series, r_X values were greater than r_O, the intrinsic barriers, $\Delta E_{XX}^{\ddagger}$, will be given by points in the E region of a curve similar to that in Figure 3 and will form an approximately straight line provided the range covered by $\delta\Delta E_{XX}^{\ddagger}$ or $r_X - r_O$ is sufficiently small, *i.e.*, equation (5) will apply and have a positive slope, α.

$$\delta\Delta E_{XX}^{\ddagger} = \alpha(r_X - r_O) \qquad (5)$$

Similarly, if for the series $r_X < r_O$, the $\Delta E_{XX}^{\ddagger}$ values will be linearly related to $(r_X - r_O)$ with a negative slope α in the C region. When, however, r_X values are not much different from r_O, $r_X \simeq r_O$ *i.e.*, in the B region, no such linearity will be expected but parabolic behaviour will be observed in accordance with equation (3). We emphasize that for any series of identity-exchange reactions the intrinsic barriers should belong to one of the regions, E, C, or B, provided the range covered by the series is sufficiently small.

Table 2. The distance, r_X/Å, force constants, f_X/mdyn Å^{-1}, of the C–X bond in the TS, (**1**), and the intrinsic barrier, $\Delta E_{XX}^{\ddagger}$/kcal mol^{-1}, calculated using the 4-31G basis set for reaction: $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$ (mdyn Å^{-1} = 10^2 N m^{-1}; 1 kcal = 4.184 kJ).

X^-	r_X[6]	f_X[6]	$\Delta E_{XX}^{\ddagger}$[4]
CH_3	2.161	1.998	—
CCH	2.124	1.913	50.4
CN	2.112	2.417	43.8
NC	2.014	2.702	28.5
NH_2	2.008	2.795	—
OF	1.932	3.194	18.8
OCH_3	1.924	3.232	23.5
OOH	1.920	3.281	18.5
OH	1.909	2.317	21.2
F	1.827	2.674	11.7

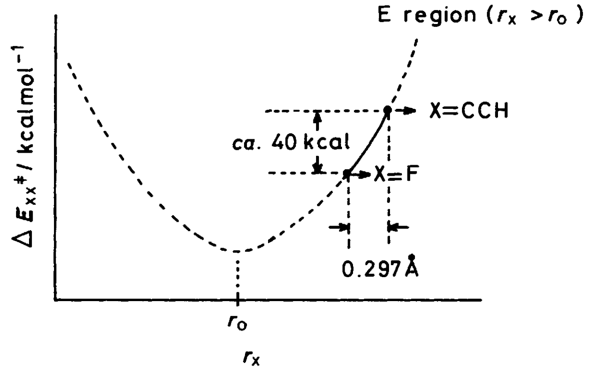

Figure 4. Approximate straight line in the E region for the identity S_N2 reactions, $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$, (4-31G results).

Example 1.—The identity S_N2 *reactions* (2) (X = Y) *with anionic nucleophiles or nucleofuges of the first-row elements*, X^- = F, OH *etc.*[4,6] The *ab initio* MO theoretical results with 4-31G basis set on r_X, f_X, and $\Delta E_{XX}^{\ddagger}$ are summarized in Table 2. Plots of $\Delta E_{XX}^{\ddagger}$ *vs.* r_X yielded a straight line with a positive slope, α (124.85) and correlation coefficient of 0.973* *i.e.*, equation (5) holds with α > 0. Thus the series belongs to the E region, Figure 4. The range of the intrinsic barrier covered in this series was relatively wide, $\delta\Delta E_{XX}^{\ddagger}$ *ca.* 40 kcal mol^{-1}.

How can we rationalize this linearity? There are two aspects to consider. (*i*) Why is the slope, α, positive? *i.e.*, why is the $\Delta E_{XX}^{\ddagger}$ higher when r_X is greater? (*ii*) Why does the force constant behave as an apparent invariant despite the substantial variation in f_X values in Table 2? We will elaborate on these questions in detail.

(*a*) In general the total energy change, ΔE_T, involved in the two interacting systems can be represented as a sum of deformation, ΔE_{def}, and interaction, ΔE_{In}, energies.[8] The former is positive, $\Delta E_{def} > 0$, and is greater than the negative value of the latter, $\Delta E_{In} < 0$.

$$\Delta E_T = \Delta E_{def} + \Delta E_{In} > 0$$
$$\text{since} \qquad |\Delta E_{def}| > |\Delta E_{In}|. \qquad (6)$$

Of the four major component energies comprising ΔE_{In},[9] *i.e.*, electrostatic ΔE_{es}, exchange repulsion ΔE_{ex}, polarization ΔE_{pl} and charge transfer ΔE_{ct}, energies, the charge-transfer interaction is the most important stabilizing component especially for a relatively short-range interaction as in the TS. This interaction is operationally important[10] since this is the interaction which leads to bond formation and bond breaking by the overlap of the incoming donor or occupied orbitals in the nucleophile, X^-, and the acceptor or empty orbitals of the substrate, CH_3–X. The stabilizing interaction energy, ΔE_{ct}, can be approximated[10a] as:

$$\Delta E_{ct} \approx (H_{ij}^2)/(\Delta\, \varepsilon_{FMO}) \qquad (7)$$

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* When the data were fitted to equation (3), multiple correlation coefficient[16] was little better (0.984) than the linearity, with r_O = 1.708 Å, f = 3.071 mdyn Å^{-1} and minimum energy of $\Delta E_{OO}^{\ddagger}$ = 9.8 kcal mol^{-1}.[6]

Table 3. The LUMO (σ^*_{CX}) levels for some CH_3X compounds together with r_X and $\Delta E_{XX}^{\ddagger}$ values.

CH_3-X	σ^*_{CX}/eV CNDO/2	σ^*_{CX}/eV *ab initio*	r_X/Å	$\Delta E_{XX}^{\ddagger}$/ kcal mol^{-1}
CH_3-F	9.88	—	1.827	11.7
CH_3-OH	11.13	13.06	1.909	21.2
CH_3-NH_2	12.17	14.91	2.008	38.0
CH_3-CH_3	—	15.56	2.161	—

where $\Delta\varepsilon_{FMO}$ is the energy gap between the highest occupied molecular orbital (HOMO) of the nucleophile, which is *n*, and the lowest unoccupied molecular orbital (LUMO) of the substrate CH_3X, which is σ^*_{CX}*, *i.e.*, $\Delta\varepsilon_{FMO}$ = LUMO (σ^*_{CX}) − HOMO (*n*), and H_{ij} is the matrix element which is proportional to the overlap, $H_{ij} \propto S_{ij}$. In the S_N2 reaction, variation in the energy gap, $\delta\Delta\varepsilon_{FMO}$, is known to have an overwhelming influence on changes in $\delta\Delta E_{ct}$ relative to δH_{ij}^2, *i.e.*, it is energy-gap controlled.[10a] The σ^*_{CX} levels of some substrates, CH_3X,[10a] are listed in Table 3 together with the r_X and $\Delta E_{XX}^{\ddagger}$ values[4,6] from Table 2. Inspection of Table 3 reveals that the higher the σ^*_{CX}, the higher the barrier, $\Delta E_{XX}^{\ddagger}$. This is reasonable since a higher σ^*_{CX} will give a greater $\Delta\varepsilon_{FMO}$ and hence a lower stabilizing energy $\Delta E_{ct}^{\ddagger}$. This means that the leaving ability of X is greater for lower σ^*_{CX}. Thus Table 3 shows that the reactivity (lower $\Delta E_{XX}^{\ddagger}$) follows the order of the leaving-group ability (lower σ^*_{CX}).[10] Consequently the degree of bond breaking of the C–X bond will be substantially greater than that of bond formation of the X–C bond, and the TBP-5C TS for this series is rather loose with a positive charge on the reaction centre carbon, as in (**1**). This also means that the HOMO, *n*, level of the nucleophile, X^-, will have little effect on ΔE_{ct} and hence on $\Delta E_{XX}^{\ddagger}$. Thus the degree of bond breaking *i.e.*, the increase in r_X, is the major degree of freedom[11] in the TBP-5C TS and constitutes a principal reaction co-ordinate, thus, is the only important contribution to the transition vector. Hence the greater the degree of bond breaking, the further the reaction has progressed along the reaction co-ordinate.[11]

According to the principle of narrowing of inter-frontier-level separation,[12] the LUMO level is lowered and the HOMO raised as the reaction progresses along the reaction co-ordinate, while the total energy of the reacting system rises until the TS is reached. Thus in order for the reaction to proceed, charge needs to be transferred from the *n* level of the nucleophile to the σ^*_{CX} level to effect bond-breaking and formation, which leads to a stabilizing orbital interaction but causes more deformation, increasing ΔE_{def}. The two opposing effects are optimized in the TS. By progressing along the reaction co-ordinate with increased stretching *i.e.*, a greater degree of bond breaking, the ε_{LU} is lowered further and the resulting decrease in $\Delta\varepsilon_{FMO}$ will give rise to a greater stabilizing interaction, ΔE_{ct}. Thus the higher the ε_{LU}, the greater will be the r_X and hence the greater will be $\Delta E_{XX}^{\ddagger}$.

A similar concept has been applied by Pross and Shaik[10b] in their valence-bond configuration-mixing approach to the prediction of the S_N2 TS structure. They concluded that the C–X bond in the good electron acceptor (CH_3X), for which the σ^*_{CX} is lower, has to stretch less than in the weak acceptor, for which the σ^*_{CX} is higher, in order for the reacting system to cross over the activation barrier.

(*b*) We now examine the reason why the force constant *f* appears to be invariant within the series. The variation of $\Delta E_{XX}^{\ddagger}$ can be attributed to two separate contributions as in equation (8).

$$\delta\Delta E_{XX}^{\ddagger} = \left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial f_X}\right)_{r_X}\delta f_X + \left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial r_X}\right)_{f_X}\delta r_X$$
$$= \tfrac{1}{2}(r_X - r_0)^2\,\delta f_X + f_X(r_X - r_0)\,\delta r_X \qquad (8)$$

The ratio of the two partial derivatives, R_d, is given by

$$R_d = \left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial r_X}\right)_{f_X}\Bigg/\left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial f_X}\right)_{r_X} = \frac{2f_X}{(r_X - r_0)} \qquad (9)$$

It has been shown for the TBP-5C TS of the reaction series (2) that Badger's rule,[13] equation (10), holds.

$$r_X = a - b\ln f_X \qquad (10)$$

where *a* and *b* are positive constants depending on the rows of the periodic table for the two bonding atoms. For the present series, the two atoms being bonded are the first-row elements, *i.e.*, 1–1 series, with $a = 7.985$ and $b = 0.478$.[6] This is why any correlation involving r_X and f_X should be considered in separate groups according to which rows of the periodic table the bonding atoms belong.[6] The variation of the two are therefore related by equation (10) as,

$$\delta r_X/\delta f_X = -b/f_X \qquad (11)$$

The ratio, Q_E, of the two energy contributions by r_X and f_X to the total changes in $\Delta E_{XX}^{\ddagger}$ can be given by,

$$Q_E = \left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial r_X}\right)_{f_X}\delta r_X\Bigg/\left(\frac{\partial\,\Delta E_{XX}^{\ddagger}}{\partial f_X}\right)_{r_X}\delta f_X = R_d\left(\frac{\delta r_X}{\delta f_X}\right)$$
$$= \left(\frac{2f_X}{r_X - r_0}\right)\left(\frac{-b}{f_X}\right) = \frac{-2b}{(r_X - r_0)} \qquad (12)$$

Substitution of r_X, r_0, and *b* leads to $R_d = 19.8$, $Q_E = -3.3$. The R_d value of *ca.* 20 indicates that the barrier change, $\delta\Delta E_{XX}^{\ddagger}$ (kcal mol^{-1}), due to the unit change in r_X(Å) is *ca.* 20 times greater than that due to the unit change in f_X(mdyn Å^{-1}). For the particular reaction series in Table 2, the total contribution from the increase in r_X to the increase in the intrinsic barrier, $\Delta E_{XX}^{\ddagger}$, is more than 3 times greater than that from the decrease in f_X($Q_E < 0$), and hence $\delta\Delta E_{XX}^{\ddagger}$ will be relatively insensitive to the variation in f_X. Thus the f_X values within the series appear to constitute a parameter which changes little within the small range of r_X change. Equation (12) indicates that the smaller $|r_X - r_0|$, or the greater $|b|$, the greater will be the magnitude of Q_E and hence the less variable a particular *f* value will become. Thus in the B region, where $|r_X - r_0| \simeq 0$, equation (3) will hold accurately and $\Delta E_{XX}^{\ddagger}$ will become a true quadratic function of $(r_X - r_0)$. We can summarize the results of the first example as follows.

(*a*) The reactivity follows the order of leaving group (LG) ability; a better LG has a lower barrier and hence is more reactive. Thus the degree of C–X bond breaking is substantially greater than that of X–C bond formation so that the TBP-5C TS has a loose structure with a positive charge on the reaction centre carbon, as in (**1**).

(*b*) There is approximate linearity between the intrinsic barrier, $\Delta E_{XX}^{\ddagger}$, and the C–X bond distance, r_X, in the TS with a positive slope, α.

$$\delta\Delta E_{XX}^{\ddagger} = \alpha(r_X - r_0) \qquad (5)$$
$$r_X > r_0 \text{ and } \alpha > 0$$

Table 4. Intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, for reaction (13) of example 2.

X	$\delta\Delta G_{XX}^{\ddagger}$/kcal mol^{-1}	σ
p-MeO	0.22	−0.27
p-Me	0.06	−0.17
H[a]	0.00	0.00
p-Cl	−0.28	0.23
3,4-Cl$_2$	−0.69	0.60

[a] $\Delta G_{XX}^{\ddagger}$ = 24.92 kcal mol^{-1}.

(*c*) A worse LG has a higher LUMO, σ^*_{CX}, and in order to lower the LUMO so that smaller inter-frontier level gap ($\Delta\varepsilon_{FMO}$) is obtained for a greater charge-transfer stabilization (ΔE_{ct}) in the TS, a greater degree of bond breaking is required as the reaction progresses. This results in a greater deformation energy of the TS giving a net increase in the intrinsic barrier.

Example 2. Solution-phase methyl-transfer reactions, (13), have been reported by Lewis *et al.*[1g] We obtained the intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, from their activation parameters,

$$\begin{aligned} & XC_6H_4SO_3^- + CH_3O_3SC_6H_4X \rightleftharpoons \\ & \qquad XC_6H_4SO_3CH_3 + {}^-O_3SC_6H_4X \quad (13) \end{aligned}$$

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as shown in Table 4. For this series, the Brønsted coefficients β_N and β_L were +0.37 and −0.63, respectively, giving a positive charge of +0.25 on the central carbon[1g,14] in the TBP–5C TS, (**2**). An electron withdrawing substituent

$$\begin{array}{ccc} -0.63 & +0.25 & -0.63 \\ XC_6H_4SO_3{-}{-}{-}{-} & C & {-}{-}{-}{-}O_3SC_6H_4X \end{array}$$

(**2**)

in the LG will stabilize the developing negative charge on the LG so that it will enhance the LG ability; in theoretical MO terms this corresponds to the lowering of the LUMO level by an electron-withdrawing substituent,[15] which will reduce the inter-frontier level gap, $\Delta\varepsilon_{FMO}$, and increase the charge-transfer stabilization, equation (7).[10a] Reference to Table 4 reveals that the LG with a more electron-withdrawing substituent, *i.e.*, a better LG, gives a lower barrier, $\Delta G_{XX}^{\ddagger}$; the reactivity trend is therefore in the order of LG ability.

A substantial positive charge on the central carbon (+0.25) together with this reactivity trend is a clear indication that this reaction series belongs to the E region ($r_X > r_0$) by analogy with example 1.

Thus the TBP–5C TS, (**2**), will be relatively loose and bond breaking will considerably exceed bond formation. Moreover the range of $\delta\Delta G_{XX}^{\ddagger}$ covered in this series is very small indeed, with only 0.9 kcal mol^{-1}. Therefore, the intrinsic barrier, $\Delta G_{XX}^{\ddagger}$, should be linearly related to r_X, by equation (5), with a positive slope α, Figure 5.

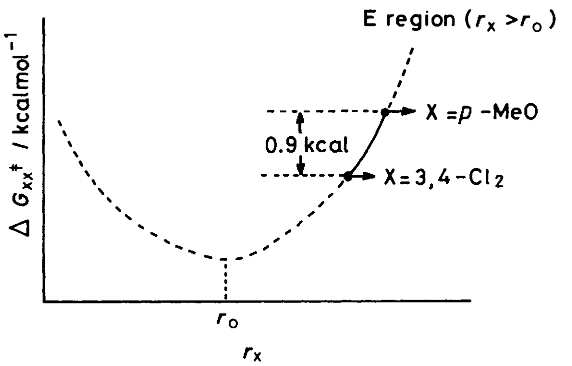

Figure 5. Approximate straight line covering small portions of the E region for the reaction (13) of example 2.

$$\delta\Delta G_{XX}^{\ddagger} = \alpha(r_X - r_0) \qquad (5)$$
$$r_X > r_0 \text{ and } \alpha > 0$$

On the other hand, plots of $\Delta G_{XX}^{\ddagger}$ *vs.* Hammett substituent constants σ[16] gave an excellent linear correlation, (14), with a

$$\delta\Delta G_{XX}^{\ddagger} = -1.02\,\sigma \qquad (14)$$

negative slope and correlation coefficient of 0.993. This is remarkable and gratifying in view of the uncertainties involved in the experimental determination of activation parameters.[1g] Comparison of equations (5) and (14) leads to

$$\left.\begin{array}{l} r_X = \lambda\sigma + r_0 \\ \text{or} \quad \Delta r = \lambda\sigma, \quad \lambda < 0 \end{array}\right\} \qquad (15)$$

where λ is a negative constant. This relation shows that the C–X bond stretch, r_X, in the TS is linearly related to σ. Since r_X is the principal reaction co-ordinate in this series belonging to the E region, we may conclude that σ is linearly related to the reaction co-ordinate, provided the change in the reaction co-ordinate, Δr, is not large.[17]

Example 3.—Solution-phase phenacyl-group transfer reactions (16) have been reported by Lewis *et al.*[3c] For this

$$\begin{aligned} & XC_6H_4SO_3^- + C_6H_5COCH_2O_3SC_6H_4X \rightleftharpoons \\ & \qquad XC_6H_4SO_3CH_2COC_6H_5 + {}^-O_3SC_6H_4X \quad (16) \end{aligned}$$

reaction, we calculated $\Delta G_{HX}{}^0$, $\Delta G_{HH}^{\ddagger}$, and $\Delta G_{HX}^{\ddagger}$ values from their kinetic data, and then estimated the intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, using the Marcus equation.* Neglect of the second-order term in equation (1) gave less accurate values of $\Delta G_{XX}^{\ddagger}$, but the mean difference between the two was only ±0.01 kcal mol^{-1} with a maximum difference of only ±0.03 kcal mol^{-1}, which is certainly negligible considering the experimental uncertainties in determination of $\Delta G_{HH}^{\ddagger}$ and $\Delta G_{HX}^{\ddagger}$ values. Nevertheless we used the values by the former method, which are summarized in Table 5.

For this reaction series, the Brønsted coefficients β_N and β_L were +0.74 and −0.26 respectively, giving a large negative charge of −0.48 on the reaction centre carbon in the TS, (**3**).[3c,14]

$$\begin{array}{ccc} -0.26 & -0.48 & -0.26 \\ XC_6H_4SO_3{-}{-}{-}{-} & C & {-}{-}{-}{-}O_3SC_6H_4X \end{array}$$

(**3**)

Furthermore, reference to Table 5 reveals that the reactivity trend follows the order of nucleophilicity; a more electron-

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* In the cross reaction [X $\neq$ Y in equation (2)], the intrinsic barrier is given by the average value, *i.e.*, $\Delta G_0^{\ddagger} = \Delta G_{XY}^{\ddagger} = \frac{1}{2}(\Delta G_{XX}^{\ddagger} + \Delta G_{YY}^{\ddagger})$. Introducing this with Y = H into equation (1), and solving for $\Delta G_{XX}^{\ddagger}$ in terms of ΔG^0_{HX}, $\Delta G_{HX}^{\ddagger}$, and $\Delta G_{HH}^{\ddagger}$ gives

$$\begin{aligned} \Delta G_{XX}^{\ddagger} = \\ & -\tfrac{1}{2}[-(2\Delta G_{HX}^{\ddagger} - 2G_{HH}^{\ddagger} - \Delta G^0_{HX}) \pm \{(2\Delta G_{HX}^{\ddagger} - 2\Delta G_{HH}^{\ddagger} - \Delta G^0_{HX})^2 \\ & + 4(2\Delta G_{HX}^{\ddagger}\,\Delta G_{HH}^{\ddagger} - \Delta G_{HH}^{\ddagger 2} - \Delta G^0_{HX}\,\Delta G_{HH}^{\ddagger} - 0.25\,\Delta G^0_{HX})^2\}^{\frac{1}{2}}] \end{aligned}$$

Neglect of the second-order term in equation (1) simplifies this to $\Delta G_{XX}^{\ddagger} = 2\Delta G_{HX}^{\ddagger} - \Delta G_{HH}^{\ddagger} - \Delta G^0_{HX}$.

Table 5. Intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, for reaction (16) of example 3.

X	$\delta\Delta G_{XX}^{\ddagger}$/kcal mol^{-1}	σ
p-MeO	-0.23	-0.27
p-Me[a]	-0.98	-0.17
H[b]	0.00	0.00
p-F	0.02	0.06
p-Cl	0.38	0.22
m-CF_3	0.76	0.43
3,4-Cl_2	0.89	0.60

[a] Excluded from our discussion of the Hammett-type plot. [b] $\Delta G_{HH}^{\ddagger}$ = 25.03 kcal mol^{-1}.

Table 6. Intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, for reaction (18) of example 4.

X	$\delta\Delta G_{XX}^{\ddagger}$/kcal mol^{-1}	σ
p-Bu^t	0.45	-0.20
p-Me	0.30	-0.17
H[a]	0.00	0.00
p-Cl	0.44	0.22
m-Cl	0.34	0.37
3,4-Cl_2	0.74	0.60

[a] $\Delta G_{HH}^{\ddagger}$ = 36.55 kcal mol^{-1}.

donating substituent in the nucleophile, increases nucleophilicity[18] which leads to a lower barrier, $\Delta G_{XX}^{\ddagger}$, and therefore a greater reactivity. This reactivity trend as well as the large negative charge on the reaction-centre carbon is quite contrary to those found for examples 1 and 2, and indeed indicates that in this reaction series bond-formation is ahead of bond-breaking and the TBP-5C TS, (**3**), is relatively tight so that the bond stretching r_X in the TS is shorter than r_0. Thus the reaction series belongs to the C region, in which a linear correlation (5) between $\Delta G_{XX}^{\ddagger}$ and $(r_X - r_0)$ should hold with a negative slope, α, since, again, the range covered by $\delta\Delta G_{XX}^{\ddagger}$ (*ca.* 1.10 kcal mol^{-1}) is small (Figure 6).

$$\delta\Delta G_{XX}^{\ddagger} = \alpha(r_X - r_0) \qquad (5)$$
$$r_X < r_0 \text{ and } \alpha < 0$$

Alternatively, plots of $\Delta G_{XX}^{\ddagger}$ *vs.* σ gave a good linearity with a positive slope and a correlation coefficient of 0.988. The slope being positive is an indication that this series belongs to the C region, unlike the series in the E region, example 2, where the slope was negative.

$$\delta\Delta G_{XX}^{\ddagger} = 1.89\,\sigma \qquad (17)$$

Comparison of equations (5) and (17) yields, equation (15) which is exactly the same relation as that obtained in example 2. Thus in this series also, r_X is greater $(\Delta r > 0)$ for a more electron-donating substituent $(\sigma < 0)$ than for a more electron-withdrawing substituent $(\sigma > 0)$, although all r_X values are smaller than r_0 in contrast with those in examples 1 and 2. We can rationalize this apparent contradiction as follows.

In this reaction series, the reactivity follows the order of nucleophilicity, and bond formation exceeds bond breaking, leading to a tight TS. This indicates that in this reaction series the degree of bond formation provides a principal reaction co-ordinate, *i.e.*, the greater the degree of bond formation, the further the reaction has progressed along the reaction co-ordinate. This means that the inter-frontier-level gap, ΔE_{FMO}, is mainly determined by the HOMO, n, of the nucleophile with the LUMO, σ^{*}_{CX}, of the substrate[10] having little effect. Since a more electron-withdrawing substituent in the nucleophile depresses the HOMO level,[15] elevation of the HOMO level is needed to gain the required charge-transfer stabilization by decreasing the inter-frontier-level gap, ΔE_{FMO}, in equation (7).[12] In order to elevate the HOMO of the nucleophile, further progress along the reaction co-ordinate, *i.e.*, a greater degree of bond formation, is necessary. Note that in this series bond formation is the principal reaction co-ordinate so that an increase in the reaction co-ordinate brings a greater degree of bond formation, *i.e.*, a shorter r_X in the TS.

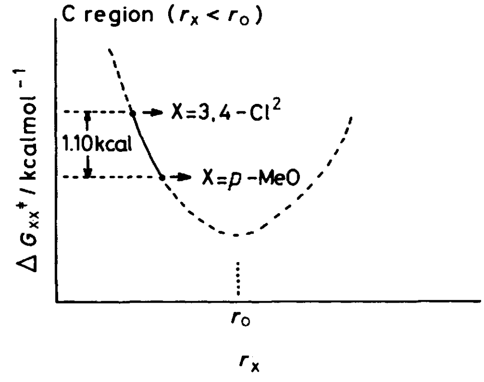

Figure 6. Approximate straight line covering small portion of the C region for reaction (16) of example 3.

Thus a more electron-withdrawing substituent in the nucleophile, reduces nucleophilicity, and requires a greater degree of bond formation, *i.e.*, a smaller r_X giving a greater $\Delta G_{XX}^{\ddagger}$ since the series belongs to the C region, *i.e.*, $r_X < r_0$.

Example 4.—Solution-phase methyl-transfer reactions have been studied with thiophenoxides, equation (18).[3a] From the reported rate constants, ΔG_{HX}°, $\Delta G_{HH}^{\ddagger}$, and $\Delta G_{HX}^{\ddagger}$ values were obtained and the intrinsic barriers, $\Delta G_{XX}^{\ddagger}$, were estimated using the Marcus equation as summarized in Table 6.

$$XC_6H_4S^- + CH_3SC_6H_4X \rightleftharpoons XC_6H_4SCH_3 + {}^-SC_6H_4X \qquad (18)$$

For this series, the Brønsted coefficients β_N and β_L were 0.54 and -0.46 respectively, giving a very small negative charge of -0.08 on the reaction centre carbon[5a,14] in the TS, (**4**).

$$\overset{-0.46}{XC_6H_4S}\text{----}\overset{-0.08}{C}\text{----}\overset{-0.46}{SC_8H_4X}$$

(**4**)

Inspection of Table 6 reveals that for this series there is no trend in the reactivity *vs.* nucleophilicity or LG ability as a whole; there is no linearity between $\Delta G_{XX}^{\ddagger}$ and $r_X - r_0$ so that this series does not belong to either the E or C region. The circumstances thus suggest that this series belongs to the B region, in which r_X values are near r_0 (Figure 7). Moreover the $\Delta G_{XX}^{\ddagger}$ values are not linearly related to σ but are a quadratic function of σ, equation (19), which suggests the same quadratic

$$\delta\Delta G_{XX}^{\ddagger} = \beta'\sigma^2 \qquad (19)$$

correlation between $\Delta G_{XX}^{\ddagger}$ and $r_X - r_0$, equation (3), for the series in the B region, (Figure 3).

$$\Delta G_{XX}^{\ddagger} = \tfrac{1}{2}f(r_X - r_0)^2 + \Delta G_{00}^{\ddagger} \qquad (3)$$

Comparison of equations (3) and (19) again leads to equation (5).

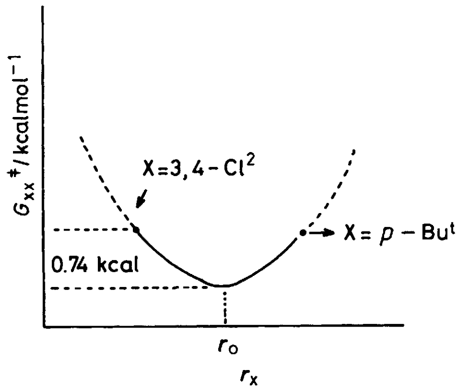

Figure 7. Parabolic curve covering the B region ($r_X \simeq r_0$) for reaction (18) of example 4.

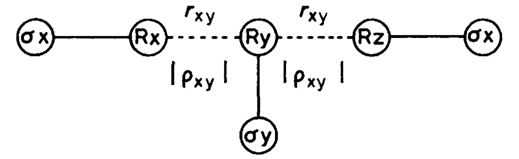

Figure 8. The S_N2 TS with three fragments, *i.e.*, nucleophile (X), substrate (Y), and LG (Z). R_X, R_Y, and R_Z represent reaction centres in each fragment.

$$\left.\begin{array}{l} r_X = \lambda\sigma + r_0 \\ \text{or} \quad \Delta r = \lambda\sigma, \quad \lambda < 0 \end{array}\right\} \qquad (5)$$

Since this series covers small portions of both the E and C regions, λ should be negative as it is in both the above regions. In the B region, $r_X \simeq r_0$ so that $|r_X - r_0|$ should be small; as a consequence, the range covered by $\Delta G_{XX}{}^{\ddagger}$ should also be small according to equation (3), as was found for this series, $\delta\Delta G_{XX}{}^{\ddagger}$ *ca.* 0.7 kcal mol^{-1}.

Another example of reaction series in the B region is the solution-phase methyl-transfer reactions with selenophenoxides,[5b] (20). We also found the same relations, (3), (5), and

$$XC_6H_4Se^- + CH_3SeC_6H_4X \rightleftharpoons XC_6H_4SeCH_3 + {}^-SeC_6H_4X \quad (20)$$

(19), although for this series the reaction-centre carbon had a substantial negative charge of −0.24.[3c] The range of $\Delta G_{XX}{}^{\ddagger}$ covered here was also found to be small, $\delta\Delta G_{XX}{}^{\ddagger}$ *ca.* 0.7 kcal mol^{-1}.

We conclude that (*i*) In the E and C regions, the intrinsic barrier, $\Delta G_{XX}{}^{\ddagger}$, is approximately linearly related to both r_X and σ, especially when the range covered is sufficiently small.

$$\delta\Delta G_{XX}{}^{\ddagger} = \alpha(r_X - r_0)$$
$$\delta\Delta G_{XX}{}^{\ddagger} = \beta\sigma$$

where $\alpha > 0$ and $\beta < 0$ in the E region, while the signs reverse to $\alpha < 0$ and $\beta > 0$ in the C region. The sign of β provides, in fact, a criterion for determining the region between E and C.

(*ii*) In the B region, no such linearities are expected but quadratic relations hold instead.

$$\Delta G_{XX}{}^{\ddagger} = \alpha'(r_X - r_0)^2 + \Delta G_{00}{}^{\ddagger}$$
$$\delta\Delta G_{XX}{}^{\ddagger} = \beta'\sigma^2$$

where α′ and β′ are positive constants. Again the quadratic relation between $\Delta G_{XX}{}^{\ddagger}$ and σ provides a criterion for the B region.

(*iii*) In all regions, the bond length r_X in the TS is linearly related to the Hammett substituent constant σ, with a negative slope, λ. This correlation should be a fundamental one for the intrinsic-barrier controlled reaction series,* in which the effect of thermodynamic contribution on activation barriers is negligible.

$$\begin{array}{l} r_X = \lambda\sigma + r_0 \\ \text{or} \quad \Delta r = \lambda\sigma, \quad \lambda < 0 \end{array}$$

(*iv*) A corollary of conclusion (*iii*) is that for a more electron-donating substituent in the nucleophile ($\sigma_X < 0$), *i.e.*, a stronger nucleophile, a greater degree of bond breaking, ($\Delta r_{YZ} > 0$), is obtained whereas for a more electron-withdrawing substituent ($\sigma_Z > 0$) in the LG, *i.e.*, a better LG, a greater degree of bond formation ($\Delta r_{XY} < 0$) is obtained. These predictions of the TS variation are consistent with those of the quantum-mechanical (QM) model.[10b] Thus,

$$\begin{array}{l} \Delta r_{YZ} = \lambda\sigma_X \\ \Delta r_{XY} = \lambda\sigma_Z, \quad \text{with } \lambda < 0 \end{array} \qquad (21)$$

where subscripts X, Y, and Z denote substituents in the nucleophile, substrate, and LG respectively[19] (Figure 8).

Finally, use of our recently derived relationship between the cross interaction constant, ρ_{ij}, and r_{ij}, equation (22),[17b] together with equation (21) leads to a useful set of relations, equation (23).

$$r_{ij} = A - B\log|\rho_{ij}| \qquad (22)$$

where *A* and *B* are positive constants depending on the rows of the periodic table for the two bonding atoms.[13]

$$\left.\begin{array}{l} \Delta\log|\rho_{XY}| = k\sigma_Z \\ \Delta\log|\rho_{YZ}| = k\sigma_X \end{array}\right\} \; k > 0 \qquad (23)$$

Since in the ordinary cross-reaction series it is difficult to discern whether a particular series is intrinsically controlled or not,[20] equation (23) provides useful criteria for such purposes.

Examples of the intrinsic-barrier controlled series are found in the results of our recent kinetic studies, series (i)–(iv), for which *k* values were indeed positive and all substituents effects were in agreement with the predictions of the QM model.

(*i*)[21] $XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z \rightleftharpoons YC_6H_4CH_2{}^+NH_2C_6H_4X + {}^-OSO_2C_6H_4Z$

(*ii*)[22] $XC_6H_4NH_2 + YC_6H_4CHCH_3OSO_2C_6H_4Z \rightleftharpoons YC_6H_4CHCH_3{}^+NH_2C_6H_4X + {}^-OSO_2C_6H_4Z$

(*iii*)[23] $XC_6H_4NH_2 + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \rightleftharpoons YC_6H_4CH_2CH_2{}^+NH_2C_6H_4X + {}^-OSO_2C_6H_4Z$

(*iv*)[24] $XC_6H_4N(CH_3)_2\ YC_6H_4CHCH_3OSO_2C_6H_4Z \rightleftharpoons YC_6H_4CHCH_3{}^+N(CH_3)_2C_6H_4X + {}^-OSO_2C_6H_4Z$

(*v*)[25] $XC_6H_4NH_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \rightleftharpoons YC_6H_4COCH_2{}^+NH_2C_6H_4X + {}^-OSO_2C_6H_4Z$

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* The Marcus equation, (1), shows that either the intrinsic barrier, $\Delta G_0{}^{\ddagger}$, or the thermodynamic barrier, ΔG^0, can be dominant in determining the activation barrier, $\Delta G^{\ddagger}$, and hence the reactivity, since the second-order term is normally negligible (see example 3 in the text) and see footnote * above. A cross reaction series (X ≠ Y) will be intrinsic-barrier controlled when (*i*) $\Delta G^0 = 0$, (*ii*) $\delta\Delta G^{\ddagger} \simeq 0$, or (*iii*) $\delta\Delta G^{\ddagger} \propto \delta\Delta G^0$. We have dealt with in this work only the case (*i*). Likewise, for the thermodynamically controlled series there will be three cases equivalent to those above.

In contrast with these reaction series, reaction (*v*) had a negative *k* so that the series can be ruled out as an intrinsic-barrier controlled one. This series is in fact known to be thermodynamically controlled. The negative sign of λ in the thermodynamically controlled series leads to a positive λ in the following relations

$$\Delta r_{XY} = \lambda\sigma_Z$$
$$\Delta r_{YZ} = \lambda\sigma_X \quad \text{with } \lambda > 0$$

These relations indicate that a more electron-withdrawing substituent ($\sigma_Z > 0$) in the LG will give a greater bond distance r_{XY}, *i.e.*, less bond formation and a more electron-donating substituent in the nucleophile, ($\sigma_X < 0$), will give a less bond-breaking, *i.e.*, a smaller r_{YZ}; this is consistent with the predictions of the TS variation by the potential-energy surface (PES) model.[15b,20,25] It has been shown that the PES model applies to the thermodynamically controlled reaction series.[20] Thus two sets of equations (21) and (23) provide useful criteria for determining the nature of the reaction series, *i.e.*, whether a series is intrinsically controlled in which case the QM model applies, or thermodynamically controlled in which case the PES model applies.[10b,20] There will be many reaction series for which no clear-cut classification of the nature of the reaction series is possible.[20]

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