Cross Interaction Constants As a Measure of Transition State Structure. Part 7. Aminolysis of Alkyl Benzenesulphonates

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Kinetic studies of the reactions of methyl and ethyl benzenesulphonates with anilines and benzylamines in methanol and acetonitrile at 65.0 °C have been reported. The magnitudes of cross-interaction constants between substituents in the nucleophile (X) and the leaving group (Z), ρ_{XZ} and β_{XZ}, were found to be greater for the ethyl series which indicates a tighter transition state for ethyl rather than methyl derivatives. This unexpected trend has been rationalized by making the assumption that the small electron-donating polar effect, of the α-methyl substituent in the ethyl compounds, requires a tighter transition-state structure in addition to the major effect of steric repulsion on the activation barrier which is present in all S_N2 reactions taking place at a carbon centre.

It is well known that ethyl compounds give virtually no elimination products even with a strong base mainly because the S_N2 process is rapid.[1] The S_N2 reactions of ethyl derivatives, however, occur *ca.* 30 times less readily than those of methyl compounds.[2] This decrease in reactivity has been attributed to the electron-donating polar effect of the α-methyl group[3] and the non-bonding steric interaction in the transition state (TS) between the substituent, methyl group, and the entering and leaving group (LG).[2,4,5] Although it has been suggested that the two effects are of comparable importance,[5] the currently accepted view is in favour of an over-riding steric hindrance as the cause of the relative rate retardation in the ethyl system.[2,4,5]

In our previous reports,[6] we have provided some examples of characterizing TS structures using various cross interaction constants, ρ_{ij} [equation (1)] and β_{ij} [equation (2)]. We found

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

$$\log(k_{ij}/k_{HH}) = \beta_i\Delta pK_i + \beta_j\Delta pK_j + \beta_{ij}\Delta pK_i\Delta pK_j \qquad (2)$$

that the magnitudes of these parameters are normally inversely proportional to the bond distances r_{ij} in the TS (Figure 1, where subscripts *i,j*, or k = X, Y, or Z).[7]

In this work, we report the results of our kinetic investigations on the reactions of methyl (MBS) and ethyl benzenesulphonates (EBS) with anilines (AN) and benzylamines (BA) in methanol and acetonitrile, equation (3).

$$2XRNH_2 + R'OSO_2C_6H_4Z \xrightarrow{\text{MeOH or MeCN}} R'HNRX + {}^-OSO_2C_6H_4Z + XRNH_3^+ \qquad (3)$$

$R = C_6H_4$ or $C_6H_4CH_2$
$R' =$ Me or Et

Here we are primarily interested in the application of cross interaction constants to the characterization of the TS structure making special reference to the TS variation accompanied with an α-methylation of the substrate.

Results and Discussion

For the aminolysis carried out in methanol, complications may arise from the methanolysis, equation (4), which proceeds in parallel with the aminolysis, equation (3). One of the products (sulphonic acid) produced in the methanolysis will, however, be present in excess in the amine solution as the same, two ionic products, $XC_6H_4NH_3^+$ and ${}^-OSO_2C_6H_4Z$, from the aminolysis. Furthermore, the hydrolysis rates of MBS and EBS in *ca.* 10^{-3} mol dm^3 aqueous sulphuric acid have been shown to decrease by less than *ca.* 0.03%.[8] We have compared the two methanolysis rate constants k_1, which were determined (*i*) by an extrapolation (k_1^{ex}) of pseudo-first-order rate constants, k_1^{obs}, to zero amine concentration, equation (5), and (*ii*) by a direct

$$ROSO_2C_6H_4Z + MeOH \longrightarrow ROMe + HOSO_2C_6H_4Z \qquad (4)$$

$$k_1^{obs} = k_1 + k_2[\text{Amine}] \qquad (5)$$

rate measurement (k_1) carried out independently, as shown in Table 1. For both substrates with Z = *p*-Me and *p*-NO$_2$, k_1^{ex}

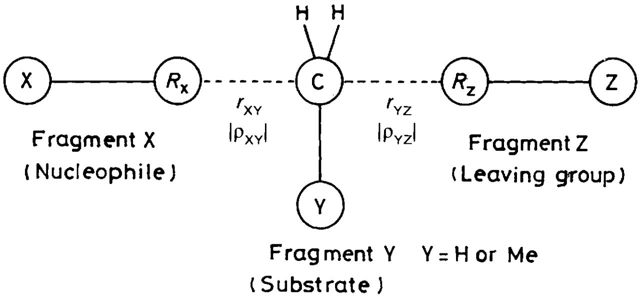

Figure 1. $r_{XZ} = r_{XY} + r_{YZ}$; R_X and R_Z are the reaction centres in the nucleophile and leaving group, respectively.

Table 1. Methanolysis rate constants, k_1^{ex} and $k_1/10^{-5}$ s^{-1} of methyl and ethyl benzenesulphonates obtained by extrapolation and by direct measurement (in parentheses) at 65.0 °C, respectively.[a]

	R	
Z	Me	Et
p-Me	6.55 ± 0.71 (7.06 ± 0.19)	3.88 ± 0.23 (3.41 ± 0.16)
H	8.63 ± 0.42	4.36 ± 0.21
p-Cl	20.7 ± 1.01	8.69 ± 0.33
p-NO$_2$	63.8 ± 1.60 (64.2 ± 0.41)	32.1 ± 1.05 (34.3 ± 0.93)

[a] The error limits show the range of values for the four determinations; see text.

Table 2. The second-order rate constants, $k_2/10^{-4}$ dm^3 mol^{-1} s^{-1} for the reaction: $2XRNH_2 + R'OSO_2C_6H_4Z \xrightarrow{65\,^{\circ}C} R'HNRX + XRNH_3^+ + {}^-OSO_2C_6H_4Z$. The values in parentheses are those at 55.0 °C.

			Z			
Nucleophile	R′	X	*p*-CH_3	H	*p*-Cl	*p*-NO_2
$XC_6H_4NH_2$[a]	Et	*p*-MeO	8.46	12.1	20.9	75.5
		p-Me	5.50	8.32	14.7	55.7
		H	2.88 (1.51)	4.50 (2.24)	7.76 (3.89)	32.5 (16.3)
		p-Cl	1.07	1.69	3.24	13.9
	Me	*p*-MeO	73.0	105	191	709
		p-Me	47.5	69.0	138	513
		H	24.0 (13.5)	35.5 (19.8)	72.4 (38.4)	296 (153)
		p-Cl	9.96	15.8	31.4	136
$XC_6H_4NH_2$[b]	Et	*p*-MeO	1.35	2.14	3.98	19.6
		p-Me	0.870	1.26	2.96	13.4
		H	0.417	0.676	1.36	7.34
		p-Cl	0.141	0.244	0.550	3.01
	Me	*p*-MeO	14.1	22.5	45.7	209
		p-Me	8.68	14.9	31.1	147
		H	4.56	7.47	15.2	83.2
		p-Cl	1.62	2.82	5.89	35.0
$XC_6H_4CH_2NH_2$[b]	Et	*p*-MeO	1.65	2.66	5.07	23.8
		p-Me	1.31	2.17	4.12	20.6
		H	0.932	1.48	2.95	14.6
		p-Cl	0.538	0.951	1.83	9.89
	Me	*p*-MeO	51.5	84.9	155	754
		p-Me	42.1	67.6	128	650
		H	29.3	47.3	88.1	473
		p-Cl	18.0	29.6	58.7	318

[a] In MeOH. [b] In MeCN.

and k_1 obtained by the two methods agree satisfactorily within experimental accuracy. The error limits shown in Table 1 reflect the range of values for the four extrapolated k_1^{ex} obtained with X = *p*-MeO, *p*-Me, H, and *p*-Cl. The Hammett coefficients[9] $\rho_Z (= \rho_{1g})$ determined with these extrapolated k_1^{ex} values were 1.06 ($R = 0.991$) and 1.02 ($R = 0.993$) for MBS and EBS respectively; these are indeed reasonable values in view of the ρ_Z values obtained for the aminolysis processes (see below).

In contrast with the average rate ratio of *ca.* 30 reported for the two substrates, *i.e.*, *k*(MBS)/*k*(EBS) *ca.* 30,[2] (*ca.* 10 for the aminolysis, see below), the relative rate is only 2 for the methanolysis (*ca.* 1.0 for hydrolysis).[8] Thus, the relative rate of the two compounds depends on the size of the nucleophile, the ratio increases with an increase in the size of the nucleophile. This conforms to the view that the slow rate of EBS is due mainly to the greater effective bulk of a methyl group sterically opposing the close approach of a nucleophilic reagent.[1,2,4,5]

The second-order rate constants k_2 for the aminolysis of MBS and EBS are summarized in Table 2. Rates of EBS are seen to be *ca.* 10–30 times less than those of MBS. Reactivity trends are typical of those expected for S_N2 processes; the rate increases with a more electron-donating group in the nucleophile (X = *p*-MeO) and with a more electron-withdrawing substituent in the LG[10] (Z = *p*-NO_2) in all cases.

The Hammett and Brønsted coefficients, ρ_X and β_X $(= \beta_N)$, obtained by varying substituent X in the nucleophile, and the corresponding parameters, ρ_Z and β_Z $(= \beta_{1g})$, for variation of substituent Z in the LG are summarized in Table 3. Reference to Table 3 reveals that the magnitudes of β_X are substantially greater than those of β_Z, indicating a greater degree of bond formation than bond breaking in the TS, *i.e.*, the reaction proceeds by an associative S_N2 mechanism. The smaller magnitude of ρ_X values for the reactions with benzylamines compared with those for the reactions with anilines reflects the fall off of susceptibility due to a CH_2 group between the interacting centres in benzylamine. The selectivity parameters $|\rho_X|$ and $|\beta_X|$ are smaller with a more electron-withdrawing substituent in the LG, while $|\rho_Z|$ and $|\beta_Z|$ are greater with a more electron-withdrawing group in the nucleophile; thus a greater reactivity is accompanied by a smaller selectivity (Table 2), so that the reactivity–selectivity principle[11] (RSP) is found to hold. Moreover, the selectivity trends are completely in line with the predictions of the TS variation based on the potential-energy surface (PES) diagram approach of More O'Ferrall[12a] and Jencks[6g,12b] (Figure 1). In the PES diagram, Figure 2, a stronger nucleophile (X = *p*-MeO) will stabilize the corners P and A, and hence, the TS will shift to the point C resulting in a decrease in bond breaking, *i.e.*, smaller $|\rho_Z|$ and $|\beta_Z|$. Likewise a stronger nucleofuge (Z = *p*-NO_2) will stabilize the corners P and D, and the TS will now move to the point E resulting in a decrease in bond formation, *i.e.*, smaller $|\rho_X|$ and $|\beta_X|$.

The Hammett[1a–i] and Brønsted[1j] type cross interaction constants ρ_{XZ} and β_{XZ} [*i,j* = X,Z in equations (1) and (2)] are shown in Table 4. The sign of ρ_{XZ} (and β_{XZ}) is positive, in agreement with the predictions of the TS variation based on the PES diagram approach; since bond breaking decreases ($d\rho_Z < 0$) with a more electron-donating group in the nucleophile ($d\sigma_X < 0$), and bond formation decreases ($d\rho_X > 0$ *i.e.*, $d|\rho_X| < 0$) with a more electron-withdrawing substituent in the LG ($d\sigma_Z > 0$), we obtain a positive ρ_{XZ}.

Table 3. The Hammett, ρ_X and ρ_Z,[a] and Brønsted coefficients, β_X ($=\beta_N$)[b] and β_Z ($=\beta_{lg}$)[c] for reaction (3).

Nucleophile	R′	Z	ρ_X[f]	β_X[f]	X	ρ_Z[f]	β_Z[f]
$XC_6H_4NH_2$[d]	Et	*p*-Me	−1.80	0.65	*p*-MeO	1.01	−0.34
		H	−1.72	0.62	*p*-Me	1.06	−0.35
		p-Cl	−1.64	0.59	H	1.11	−0.37
		p-NO_2	−1.48	0.54	*p*-Cl	1.18	−0.39
	Me	*p*-Me	−1.74	0.63	*p*-MeO	1.05	−0.35
		H	−1.66	0.60	*p*-Me	1.10	−0.37
		p-Cl	−1.59	0.58	H	1.16	−0.39
		p-NO_2	−1.49	0.52	*p*-Cl	1.20	−0.40
$XC_6H_4NH_2$[e]	Et	*p*-Me	−1.98	0.71	*p*-MeO	1.23	−0.41
		H	−1.87	0.67	*p*-Me	1.28	−0.43
		p-Cl	−1.77	0.64	H	1.32	−0.44
		p-NO_2	−1.64	0.59	*p*-Cl	1.40	−0.47
	Me	*p*-Me	−1.87	0.67	*p*-MeO	1.24	−0.41
		H	−1.82	0.66	*p*-Me	1.29	−0.43
		p-Cl	−1.80	0.65	H	1.33	−0.45
		p-NO_2	−1.56	0.56	*p*-Cl	1.41	−0.47
$XC_6H_4CH_2NH_2$[e]	Et	*p*-Me	−0.97	0.97	*p*-MeO	1.22	−0.41
		H	−0.91	0.89	*p*-Me	1.26	−0.42
		p-Cl	−0.89	0.88	H	1.27	−0.42
		p-NO_2	−0.78	0.79	*p*-Cl	1.33	−0.44
	Me	*p*-Me	−0.93	0.92	*p*-MeO	1.23	−0.40
		H	−0.90	0.89	*p*-Me	1.26	−0.42
		p-Cl	−0.85	0.84	H	1.28	−0.43
		p-NO_2	−0.77	0.73	*p*-Cl	1.32	−0.44

[a] The σ values were taken from ref. 9. [b] The pK_a values were taken from ref. 1, p. 1131. [c] The pK values are for methyl transfers: R. V. Hoffman; J. M. Shankweiler, *J. Am. Chem. Soc.*, 1986, **108**, 5536. [d] In MeOH. [e] In MeCN. [f] Correlation coefficients were better than 0.997 with 99% confidence limit in all cases.

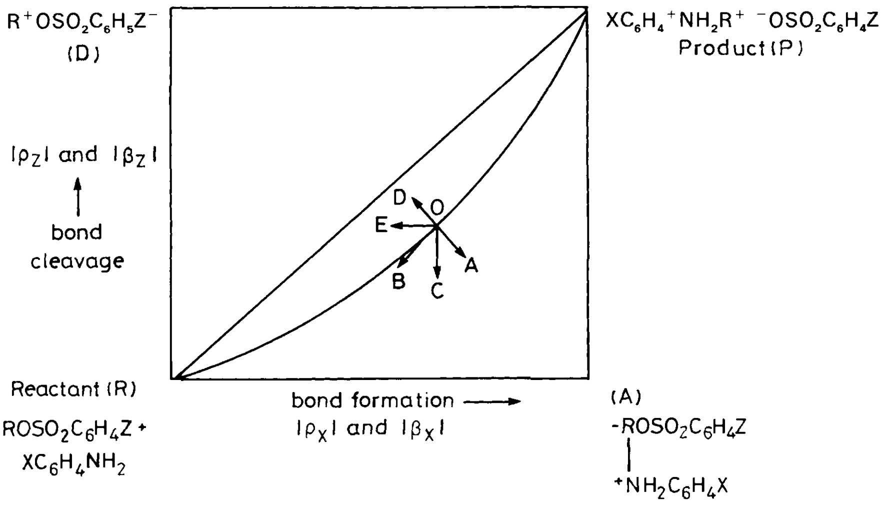

Figure 2. Potential-energy-surface diagram showing TS variations with substituent changes in the nucleophile and the leaving group.

$$\rho_{XZ} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} > 0 \qquad (6)$$

$$\Delta r_{XY} = \lambda \sigma_Z \qquad \Delta r_{YZ} = \lambda' \sigma_X \qquad (7)$$

In terms of bond lengths in the TS (Figure 1), these correspond to the following relations with positive constants λ and λ′.[13] An interesting feature of the reactions of alkyl benzenesulphonates with anilines, equation (3), is that the magnitude as well as the sign of ρ_{XZ} (and β_{XZ}) is strikingly similar to that for the corresponding reactions of phenacyl benzenesulphonates (Table 5),[1g] which has been found to constitute a typical thermodynamically controlled reaction series;[1g,14] the RSP is valid for the series, and the TS variation can be correctly predicted by the PES-diagram approach in

Table 4. Cross-interaction constants ρ_{XZ}[a] and β_{XZ}[b] for reaction (3).

	ρ_{XZ}[e]			β_{XZ}[e]		
R′	$XC_6H_4NH_2$		$XC_6H_4CH_2NH_2$	$XC_6H_4NH_2$		$XC_6H_4CH_2NH_2$
Et	0.33[c]	0.34[d]	0.19[d]	0.19[c]	0.21[d]	0.28[d]
Me	0.30[c]	0.32[d]	0.18[d]	0.18[d]	0.20[d]	0.26[d]

[a] The σ values were taken from ref. 9. [b] The pK_a values of anilines were taken from ref. 1, p. 1131 and the pK_a values for sulphonic acids were taken from R. V. Hoffman, and E. L. Belfoure, *J. Am. Chem. Soc.*, 1982, **104**, 2183. [c] In MeOH. [d] In MeCN. [e] Multiple correlation coefficients were better than 0.992 at 99% confidence limit in all cases.

Table 5. Cross interaction constants ρ_{XZ} and β_{XZ} for the reactions of phenacyl benzenesulphonates ($YC_6H_4COCH_2OSO_2C_6H_4Z$) with anilines ($XC_6H_4NH_2$) and benzylamines ($XC_6H_4CH_2NH_2$) in MeOH at 45.0 °C.[6g,n]

Nucleophile	Y	ρ_{XZ}	β_{XZ}	*R*
$XC_6H_4NH_2$	H	0.32	0.20	
	p-Cl	0.31	0.19	>0.999
	p-NO_2	0.23	0.14	
$XC_6H_4CH_2NH_2$	H	0.12	0.20	
	p-Cl	0.11	0.18	>0.997
	p-NO_2	0.09	0.15	

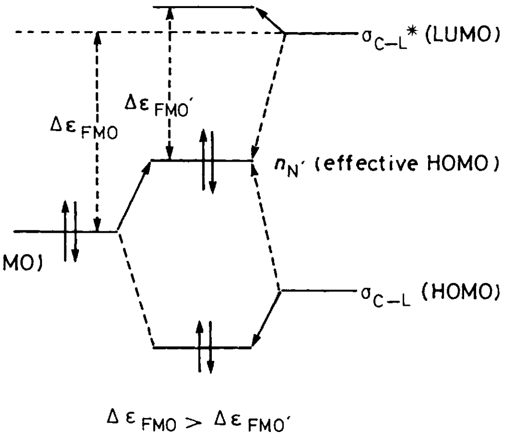

Figure 3. Orbital interactions between the HOMO of the nucleophile (n_N) and the frontier orbitals of the substrate, σ_{C-L}* and σ_{C-L}. The n_N′ and $\Delta\varepsilon_{FMO}$′ are the nucleophile HOMO and the inter-frontier energy gap after the orbital interaction, respectively.

contrast to the TS variation expected from the predictions based on the quantum-mechanical approach.[14]

Inspection of Table 4 reveals that $|\rho_{XZ}|$ and $|\beta_{XZ}|$ for EBS are greater than those for MBS, albeit that the differences are small, suggesting that the TS for EBS is somewhat tighter than that for MBS, as is also evident from a somewhat greater $|\beta_X|$ and a somewhat smaller $|\beta_Z|$ for the former. This is in accord with the Hammond postulate since the rate retardation with EBS is considered to result mainly from the steric crowding of the α-methyl group,[4] which will increase the activation energy and lead to a later TS. Activation parameters, $\Delta H^‡$ and $\Delta S^‡$, determined with limited rate data for two temperatures are 12.2 and −33.9 and 14.7 kcal mol^{-1} † and −30.6 cal K^{-1} mol^{-1} for MBS and EBS respectively, indicating that the effects of α-methyl substitution show up predominantly in the energy of activation. Thus the steric crowding in the TS for EBS raises the activation energy and the rate is retarded, nevertheless a tighter TS is obtained *i.e.*, r_{XZ}(EBS) < r_{XZ}(MBS) in Figure 1. This seemingly contradictory result can be resolved by taking the electron-donating polar effect of the α-methyl group into account. The α-methyl substitution of MeL to EtL (L = $OSO_2C_6H_4Z$) raises the frontier MO (FMO) levels of the latter in general[15] due to the electron-donating polar effect of the methyl group. In particular, the lowest unoccupied MO (LUMO) level, which is sigma antibonding with respect to the cleaving bond C–L (σ_{CL}*),[16] is raised resulting in less charge transfer stabilization, $\Delta E_{ct}(<0)$ in equation (8),[14a,16] where H_{ij}

$$\Delta E_{ct} \cong \frac{H_{ij}^2}{\Delta\varepsilon_{FMO}} \qquad (8)$$

is an interaction matrix element and $\Delta\varepsilon_{FMO} = \varepsilon_{LU}$(substrate) − ε_{HO}(nucleophile) = $\sigma_{CL}^* - \sigma_n$ (Figure 3). In order to raise the highest occupied (HO) level of the nucleophile σ_n (non-bonding, *n*, orbital) so that a smaller gap, $\Delta\varepsilon_{FMO}$, with a greater charge transfer, ΔE_{ct}, is obtained, further progress along the reaction co-ordinate (RC) is necessary.[13,15] According to the principle of inter-frontier level narrowing,[15a,b] the HOMO is raised and the LUMO lowered while the total energy of the reacting system is elevated as the reaction proceeds along the RC until the TS is reached.

In nucleophilic substitution reactions where the HOMO of the nucleophile (n_N) lies closer in energy to the substrate LUMO (σ_{C-L}*) (*e.g.* a reaction between a strong nucleophile and, possibly, a substrate with a good LG), the energy gap, $\Delta\varepsilon_{FMO}$, is small so that a large stabilizing charge transfer, $\Delta E_{ct}(<0)$, is expected at an incipient orbital interaction. In this situation, the transition point is reached at an early stage along the RC since little inter-frontier level narrowing is needed, with a relatively low concomitant activation energy, $\Delta E^‡$.

When the HOMO of the nucleophile is too low (say due to an electron-withdrawing substituent X) and/or the FMOs, σ_{C-L}* and σ_{C-L}, of the substrate are very high (possibly due to an electron-donating substituent Y and/or Z), the initial charge transfer is minimal due to an excessive energy gap, $\Delta\varepsilon_{FMO}$ (Figure 3). In this case, however, a strong repulsive HOMO-(n_N) − HOMO(σ_{C-L}) interaction elevates the nucleophile HOMO to a level (n_N′) which is high enough to give a smaller energy gap, $\Delta\varepsilon_{FMO}$′ (Figure 3), required to initiate the charge-transfer interaction. As the reaction proceeds along the RC, this charge transfer into the empty σ_{C-L}* orbital induces a C–L (or C–Rz) bond elongation which is attended by a lowering of the σ_{C-L}* level.[13,17] Thus even when an initial energy gap is large, the repulsive HOMO–HOMO interaction allows the required level of charge transfer to take place at a later transition point as a result of the inter-frontier orbital narrowing to a smaller $\Delta\varepsilon_{FMO}$′. The transition point will be reached, therefore, at a later stage along the RC, since the extent of the inter-frontier orbital narrowing parallels the progress of reaction.[13]

In S_N2-type reactions, two limiting cases may arise: in the type I TS, the degree of bond breaking greatly exceeds that of bond

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† 1 cal = 4.184 J.

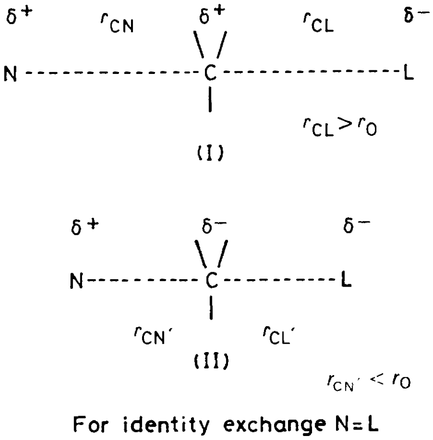


Figure 4.

formation, whereas in the type II TS, the reverse is true, (Figure 4). In the former the reactivity trend follows the LG ability and the extent of bond cleavage, r_{CL}, may serve as a progress variable reflecting the extent of reaction progress along the RC, while in the latter the reactivity trend parallels the nucleophilicity with the extent of bond formation, r_{CN}', providing a progress variable.[13] These two limiting types of reaction series were indeed found; a loose (tight) TS of type I (type II) had a reactivity trend paralleling the LG ability (nucleophilicity), which had a looser (tighter) TS with a more electron-donating (electron-withdrawing) substituent (X, Y, or Z) requiring a greater activation energy $\Delta E^{\ddagger}$.[13]

In fact the changes in the bond length in the TS, Δr, follow a linear relation [equation (9)] with the Hammett substituent constant σ within a small range of TS variation.[13]

$$\Delta r_{ij} = \beta\sigma_k \qquad i,j, \text{ and } k = \text{X, Y, and Z} \qquad (9)$$

$$r_{XY} = r_{YZ}$$

where β is a negative constant in contrast to λ in relations (7) where it is positive. We have pointed out that in the intrinsically controlled reaction series, such as the thermoneutral identity reactions, the slope (β) is negative, whereas in the non-identity, thermodynamically controlled reaction series the slope (λ) is positive.[13]

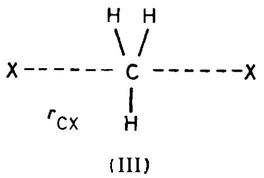
What do we mean, then, by a tight or loose TS? In this respect, the results of our recent work on the nature of the intrinsic barrier in the methyl transfer reactions, equation (10), is quite

$$X^- + MeX \rightleftharpoons XMe + X^- \qquad (10)$$

relevant.[7,18] Our *ab initio* MO theoretical studies on the stretching force constants, f_{CX}, dependence of bond length, r_{CX}, in the trigonal bipyramidal five-co-ordinate (TBP-5C) TS, III, have shown that Badger's rule,[19] equation (11), is also

$$r_{CX} = a_{ij} - b_{ij} \log f_{CX} \qquad (11)$$

applicable to the stretching bond in the TS, where a_{ij} and b_{ij} are the constants dependent only on the rows, *i* and *j*, of the periodic table for the two atoms being bonded, *e.g.*, C and X = F in III for which $i = j = 1$. It has been shown that a_{ij} corresponds to a standard bond length (at $f_{CX} = 1.0$) for a series of bonds involving atoms belonging to the *i*- and *j*-th rows in the periodic table; in fact the experimental a_{ij} values corresponded closely to the median non-polar covalent bond radii for the normal diatomics of *i–j*th row.[20,21] The a_{ij} value determined for the TBP-5C TS of reaction,[10] with X = F, OH, Me, CN *etc.*, *i.e.*, for 1–1 series of atoms, had the value corresponding to that for 1–4 series;[18] this means that in the TBP-5C TS, the carbon centre has a covalent-bond radius similar to that of fourth-row elements, *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. Since the methyl transfer reaction (10) is thermoneutral, the activation barrier is an intrinsic one,[13,18] which is non-thermodynamic in origin. Thus the intrinsic barrier[22] needed in the thermoneutral reaction is shown to originate in the dramatic stretching of the covalent radius of the carbon centre in the TBP-5C TS.[23,24,25]



(III)

Furthermore, we found that within a family of reaction series, the intrinsic barrier, $\Delta E_{XX}^{\ddagger}$, varied within a very small range and was linearly correlated,[13] equation (12), with either positive ($\alpha > 0$) or negative ($\alpha < 0$) slope for which r_X ($= r_{CX}$) in III is

$$\delta\Delta E_{XX}^{\ddagger} = \alpha(r_X - r_o) \qquad (12)$$

greater ($r_X > r_0$), or shorter ($r_X < r_0$) than the median value r_0 (for which the median intrinsic barrier is $\Delta E_{00}^{\ddagger}$). For the former case of $r_X > r_0$, the longer the bond length r_X, the greater the intrinsic barrier indicating that further expansion beyond the median length r_0 requires more energy; for $r_X < r_0$ case, the greater intrinsic barrier is required for the shorter bond length than r_0 indicating that compression to less than the median length of r_0 also costs more energy. It is, therefore, necessary to account for both components of the intrinsic barrier, *i.e.*, $\Delta E_{00}^{\ddagger}$ which is for the median or optimum bond length of r_0 for a series and constitutes a major component, and a minor variation, $\delta\Delta E_{XX}^{\ddagger} = \Delta E_{XX}^{\ddagger} - \Delta E_{00}^{\ddagger}$ which is needed to expand or compress beyond r_0. This variation of intrinsic barriers, $\delta\Delta E_{XX}^{\ddagger}$, for expansion or compression beyond r_0 was due to a small variation of an electron-donating or electron-withdrawing polar effect present in the nucleophile, substrate or LG.[13] It is precisely to the latter category *i.e.*, $r_X < r_0$ that the reactions, equation (3), of the present work belong albeit that the TS is not symmetrical, since EBS has a tighter TS with a higher activation barrier relative to MBS due to an electron-donating polar effect of a methyl group in the substrate.

Conclusions

The rate retardation (and hence the higher activation barrier) found with EBS is not only of steric origin but also of the small, secondary electron-donating polar effect of the α-methyl substitution. After all, the two effects are contributing additively in determining the TS structure, notwithstanding that they may not be of comparable importance.

Experimental

Materials.—Anilines and benzylamines were purified as described previously.[6j] G.R. grade solvent MeOH was used without further purification. Alkylbenzenesulphonyl halides. Solid esters were recrystallized from ether and dried in a vacuum oven. Liquid esters were distilled.

Ethyl toluene-p-*sulphonate*. M.p. 32–33 °C (lit.,[26] 32 °C), δ 1.2 (Me, 3 H, t), 2.4 (CH_2, 2 H, q), and 7.6 (C_6H_4, 4 H, q); ν_{max} 1 360 cm^{-1} (SO_2) (Found: C, 53.7; H, 7.0. Calc. for $C_9H_{12}O_3S$: C, 53.98; H, 7.05%).

Ethyl benzenesulphonate. Liquid, δ 1.3 (Me, 3 H, t), 3.2 (CH_2, 2 H, q), and 7.8 (C_6H_5, 5 H, m); ν_{max} 1 355 (SO_2) and 1 185 cm^{-1} (SO_2).

Ethyl Chlorobenzene-p-*sulphonate.* M.p. 19–20 °C, δ 1.4 (Me, 3 H, t), 4.2 (CH_2, 2 H, q), and 7.8 (C_6H_4, 4 H, q); ν_{max} 1 360 (SO_2) and 1 180 cm^{-1} (SO_2).

Ethyl nitrobenzene-p-*sulphonate.* M.p. 82–83 °C, δ 1.4 (CH_3, 3 H, t), 4.3 (CH_2, q), and 8.4 (C_6H_4, 4 H, q); ν_{max} 1 370 (SO_2) and 1 180 cm^{-1} (SO_2) (Found: C, 41.44; H, 3.88; N, 6.09. Calc. for $C_8H_9O_5NS$: C, 41.56; H, 3.92; N, 6.06%).

Methyl toluene-p-*sulphonate.* M.p. 26–27 °C (lit.,[27] 27.5 °C), 2.5 (Me, 3 H, s), 3.7 (OMe, 3 H, s), and 7.6 (C_6H_4, 4 H, m); ν_{max} 1 355 (SO_2) and 1 180 cm^{-1} (SO_2) (Found: C, 51.55; H, 5.4. Calc. for $C_8H_9O_5NS$: C, 51.60; H, 5.41%).

Methyl benzenesulphonate. Liquid, δ 3.1 (OMe, 3 H, s) and 7.8 (C_6H_5, 5 H, m); ν_{max} 1 360 (SO_2) and 1 185 cm^{-1} (SO_2).

Methyl chlorobenzene-p-*sulphonate.* M.p. 44–45 °C, 4.0 (OMe, 3 H, s) and 7.8 (C_6H_4, 4 H, q); ν_{max} 1 360 (SO_2) and 1 180 cm^{-1} (SO_2) (Found: C, 40.5; H, 3.3. Calc. for $C_7H_7O_3SCl$: C, 40.69; H, 33.41%).

Methyl nitrobenzene-p-*sulphonate.* M.p. 90–93 °C (lit.,[28] 90–92 °C), 3.8 (OMe, 3 H, s) and 8.3 (C_6H_4, 4 H, m); ν_{max} 1 370 (SO_2) and 1 180 cm^{-1} (SO_2) (Found: C, 38.55; H, 3.2; N, 6.5. Calc. for $C_7H_7O_5NS$: C, 38.71; H, 3.25; N, 6.45%).

Product Analysis.—$CH_3CH_2NHC_6H_5$. δ 1.2 (Me, 3 H, t), 3.1 (CH_2, 2 H, q), 3.4 (NH, 1 H, br), and 6.9 (C_6H_5, 5 H, m); ν_{max} 3 400 (N–H, secondary aromatic amine) and 1 335 cm^{-1} (C–N, secondary aromatic amine); $R_f = 0.52$.

$CH_3NHC_6H_5$. δ 2.7 (Me, 3 H, s), 3.5 (NH, 1 H, br), and 6.9 (C_6H_5, 5 H, m); ν_{max} 3 450 (N–H, secondary aromatic amine) and 1 316 cm^{-1} (C–N, secondary aromatic amine); $R_f = 0.45$.

$C_6H_5NH_3^+$ $^-SO_3C_6H_4CH_3$. M.p. 210–215 °C, ν_{max} 3 400 cm^{-1} (N–H, NH_3^+), 2 600 (N–H, NH_3^+), 1 600 (bending, N–H, NH_3^+), 1 500 (bending, N–H, NH_3^+), 1 200 (S=O, SO_3), 1 150 (S=O, SO_3^-), 560 (ν, scissor, SO_2, SO_3^-), and 480 cm^{-1} (wagging, SO_2, SO_3^-); (Found: C, 58.3; H, 5.75; N, 5.3. Calc. for $C_{13}H_{15}O_3NS$: C, 58.63; H, 6.06; N, 5.26%).

Rate Measurements.—The second-order rate constants k_2 were determined as described previously.[6f–l] Average deviations of k_2 were less than ±3% in the more than duplicate determinations.

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