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CROSS INTERACTION CONSTANTS AS A MEASURE OF THE TRANSITION STATE STRUCTURE. 13. STERIC EFFECTS OF THE *N,N*-DIMETHYL GROUP ON THE TRANSITION STATE STRUCTURE IN AMINOLYSIS OF ALKYL BENZENESULPHONATES

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Kinetic studies on the reactions of methyl (MBS) and ethyl benzenesulphonates (EBS) with *N,N*-dimethylanilines (DMA) in methanol and acetonitrile are reported. The cross interaction constants ρ_{XZ} and β_{XZ}, between the substituents in the nucleophile (X) and the leaving group (Z) indicated that the transition states (TS) are looser than those for the reactions with anilines, but the relative tightness between the two substrates was the same; the TS was tighter for EBS despite the increase in steric effect leading to looser TSs for MBS and EBS alike. The TS variation between two different reaction series expected from the simple Hammett and Brønsted coefficients, ρ_X, ρ_Z, β_X and β_Z, was incompatible with that predicted by the cross interaction constants, demonstrating again the unreliability of the simple parameters.

INTRODUCTION

In previous work[1] on the characterization of transition state (TS) structures using cross interaction constants ρ_{ij} [equation (1)] and β_{ij} [equation (2)],[2] we showed that the magnitudes of cross interaction constants between substituents in the nucleophile (X) and the leaving group (Z) (Figure 1), ρ_{XZ} and β_{XZ}, are greater for the reactions of anilines with ethyl (EBS) than with methyl benzenesulphonates (MBS) in methanol and acetonitrile [equation (3)], indicating a tighter TS for ethyl rather than methyl derivatives. This unexpected trend was interpreted as the α-methyl substituent[3] in the ethyl compounds leading to a tighter TS structure.[1]

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

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

$$2XC_6H_4NH_2 + ROSO_2C_6H_4Z \xrightarrow[65\cdot0\,^\circ C]{MeOH\ or\ MeCN} RHNC_6H_4X + {}^-OSO_2C_6H_4Z + XC_6H_4NH_3^+ \quad (3)$$

$$R = CH_3 \text{ or } C_2H_5$$

This TS variation is in accord with that predicted by the potential energy surface (PES) diagram[4] (Figure 2). An electron-donating substituent (EDS) in the substrate ($Y = CH_3$) should stabilize the upper corners, D and P, so that the TS will shift to either G (decrease in bond formation) or G′ (decrease in both bond formation and cleavage), depending on whether the Hammond effect[5] is the same[6a] with (OF = OE) or greater[6b] (OF′ > OE) than the anti-Hammond effect.[4a] The kinetic isotope effects (KIE) in the nucleophilic substitution reaction involving deuterated aniline nucleophiles[7] indicated that the Hammond effect is in fact greater than the anti-Hammond effect[6] in all cases, so that an EDS in the substrate ($Y = CH_3$) should in fact lead to a looser TS with a greater decrease in bond formation than a relatively small decrease in bond breaking (see below).

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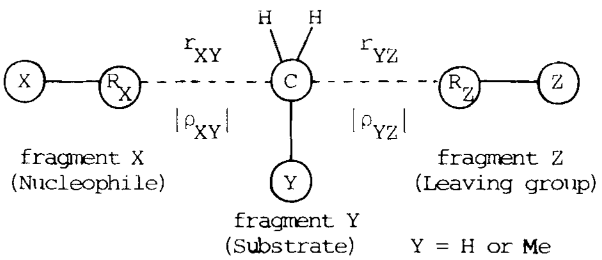

Figure 1. $r_{XZ} = r_{XY} + r_{YZ}$; R_X and R_Z are the reaction centres in the nucleophile and leaving group, respectively

The reactions of alkyl benzenesulphonates with anilines[1] [equation (3)] was found to proceed by an associative S_N2 mechanism with rate retardation for EBS originating not only from a steric origin[8] but also from the small secondary electron-donating polar effect of the α-methyl substitutent.[3] In this respect, it is of interest to see if a further increase in the steric effect in the TS can bring about the reversal in the relative tightness of the TS structure between EBS and MBS.

In this work, we carried out kinetic investigations on the reactions of alkyl benzenesulphonates with *N*,*N*-dimethylanilines (DMA), which should lead to a greater steric effect[2c] in the TS due to the two methyl groups on the reaction centre of the nucleophile:

$$XC_6H_4N(CH_3)_2 + ROSO_2C_6H_4Z \xrightarrow[65.0\,^\circ C]{MeOH\ or\ MeCN} R(CH_3)_2N^+C_6H_4X + {}^-OSO_2C_6H_4Z \quad (4)$$

$R = CH_3$ or C_2H_5; X = *p*-MeO, *p*-Me, H or *p*-Cl;

Z = *p*-Me, H, *p*-Cl or *p*-NO_2

and the cross interaction constants ρ_{XZ} and β_{XZ} were determined to compare the TS structure with that for the reactions of anilines[1] under the same reaction conditions [equation (3)].

RESULTS AND DISCUSSION

The second-order rate constants, k_2, for the reactions of MBS and EBS with DMA in methanol and acetonitrile are summarized in Table 1. The rates are lower by a factor of 1·2–3·6 for the reactions with DMAs than with anilines[1] under the same reaction conditions owing to a greater steric effect with DMAs. The average rate ratio for the two substrates, i.e. $k_2(MBS)/k_2(EBS)$, is *ca* 15 in methanol and *ca* 30 in acetonitrile.[9] This is greater than that (*ca* 10) for the reactions with anilines[1] [equation (3)], indicating that the relative rate for the two compounds depends on the size of the nucleophile. The ratio increases with increase in the size of the nucleophile so that the slow rate for EBS is mainly attributable to the greater effective bulk of a methyl group

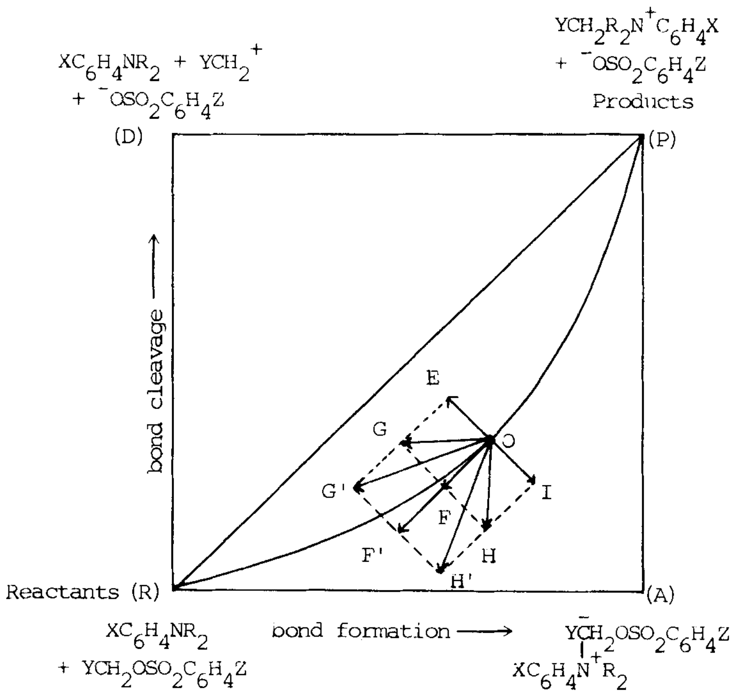

Figure 2. Potential energy surface diagram showing TS variations with substituent changes (Y, R = H or CH_3)

Table 1. Second-order rate constants, k_2 ($\times 10^4\ \mathrm{l\,mol^{-1}\,s^{-1}}$), for the reaction

$$XC_6H_4N(CH_3)_2 + ROSO_2C_6H_4Z \xrightarrow[65\cdot0\,^\circ C]{MeOH\ or\ MeCN} XC_6H_4N^+(CH_3)_2R + {}^-OSO_2C_6H_4Z$$

Solvent	R	X	Z: *p*-Me	H	*p*-Cl	*p*-NO2
MeOH	Me	*p*-MeO	57·3	78·0	157	488
		p-Me	34·6	48·1	90·9	324
		H	14·2	26·2	38·9	165
		p-Cl	3·84	5·13	11·1	41·7
	Et	*p*-MeO	3·79	5·39	8·49	28·1
		p-Me	2·01	3·51	5·22	17·1
		H	0·840	1·24	2·19	7·06
		p-Cl	0·241	0·409	0·671	2·51
MeCN	Me	*p*-MeO	14·9	24·7	54·9	264
		p-Me	8·62	14·6	31·8	165
		H	3·53	6·11	13·9	71·9
		p-Cl	1·05	1·81	4·32	24·6
	Et	*p*-MeO	0·512	0·846	1·88	8·86
		p-Me	0·293	0·502	1·14	5·49
		H	0·117	0·207	0·491	2·41
		p-Cl	0·0350	0·0600	0·149	0·818

sterically opposing the close approach of a nucleophilic reagent.[6b,8,10] Table 1 reveals that the reactivity trends are typical of those expected for S_N2 processes,[11] i.e. the rate increases with a more EDS in the nucleophile (X = *p*-MeO) and with a more electron-withdrawing substituent (EWS) in the leaving group (Z = *p*-NO_2) in all cases.

The Hammett[12] and Brønsted coefficients,[13] ρ_X and β_X ($=\beta_N$), for variation of substituent X in the nucleophile, and the corresponding parameters, ρ_Z and β_Z ($=\beta_{lg}$), for variation of substituent Z in the leaving group are summarized in Table 2. As we have noted for the reactions with anilines[1] [equation (3)], the magnitudes of ρ_X and β_X are substantially greater than those of ρ_Z and β_Z, suggesting a greater degree of bond formation than bond breaking in the TS, i.e. an associative S_N2 mechanism. The magnitudes of parameters for the reactions with DMAs are similar in general to those with anilines, except the $|\rho_X|$ values which are much greater for DMA than for anilines.[2h,14,15] The greater magnitude of ρ_X for DMA would normally be taken as an indication of a greater degree of bond formation[12] in the DMA reactions than in the reactions with anilines;[1] however this is misleading, as in fact bond formation is less with DMAs than with anilines as dis-

Table 2. Hammett (ρ_X and ρ_Z)[a] and Brønsted coefficients (β_X[b] and β_Z[c]) for reaction (4)

Solvent	R	Z	ρ_X[d]	β_X[e]	X	ρ_Z[d]	β_Z[d]
MeOH	Me	*p*-Me	−2·38	0·67	*p*-MeO	0·96	−0·33
		H	−2·36	0·66	*p*-Me	1·04	−0·35
			(−1·66)[f]	(0·60)[f]	H	1·09	−0·36
		p-Cl	−2·31	0·63		(1·16)[f]	(−0·39)[f]
		p-NO2	−2·16	0·59	*p*-Cl	1·12	−0·38
	Et	*p*-Me	−2·39	0·65	*p*-MeO	0·92	−0·31
		H	−2·30	0·63	*p*-Me	0·95	−0·32
			(−1·72)	(0·62)	H	0·98	−0·33
		p-Cl	−2·23	0·61		(1·11)	(−0·37)
		p-NO2	−2·12	0·58	*p*-Cl	1·05	−0·35
MeCN	Me	*p*-Me	−2·32	0·63	*p*-MeO	1·32	−0·44
		H	−2·29	0·62	*p*-Me	1·35	−0·45
			(−1·82)	(0·66)	H	1·38	−0·46
		p-Cl	−2·22	0·61		(1·33)	(−0·45)
		p-NO2	−2·08	0·57	*p*-Cl	1·45	−0·48
	Et	*p*-Me	−2·36	0·65	*p*-MeO	1·31	−0·44
		H	−2·32	0·63	*p*-Me	1·34	−0·45
			(−1·87)	(0·67)	H	1·38	−0·46
		p-Cl	−2·22	0·61		(1·32)	(−0·44)
		p-NO2	−2·09	0·57	*p*-Cl	1·45	−0·49

[a]The σ values were taken from R. D. Gilliom, *Introduction to Physical Organic Chemistry*, p. 148. Addison-Wesley, Reading, MA (1970).
[b]The pK_a values were taken from W. C. Davis and H. W. Addis, *J. Chem. Soc.* 1622 (1937) and G. Thompson, *J. Chem. Soc.* 1113 (1946).
[c]The pK_a values are for methyl transfer: R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.* **108**, 5536 (1986).
[d]Correlation coefficients were better than 0·998 with 99% confidence limit in all cases.
[e]Correlation coefficients > 0·993.
[f]Values in parentheses are those for the reactions with anilines [equation (3)].[1]

cussed below. This is another example of the unreliability of the Hammett coefficient[2f,g,16] as a measure of bond tightness involved in two different series of reactions due to the variable charge transmission when the reaction centre is varied [in this case from $—NH_2$ to $—N(CH_3)_2$]. The simple Hammett and Brønsted parameters can at best serve as a measure of the TS structure within a particular family of related reactions.[2k,16] The magnitudes of ρ_X and β_X in MeCN are in general smaller and those of ρ_Z and β_Z in MeCN are greater than the corresponding values in MeOH,[2h,17] suggesting a looser TS in MeCN than in MeOH. This comparison of the TS structure based on the simple Hammett and Brønsted parameters is again in contrast to the relative TS tightness predicted by the $|\rho_{XZ}|$ and $|\beta_{XZ}|$ values[2] (see below).

The cross interaction[2] constants ρ_{XZ} and β_{XZ} are summarized in Table 3. The sign of ρ_{XZ} (and β_{XZ}) is positive so that the PES diagram approach[2k,6a,18] to the predictions of the TS variation is applicable; a more EWS in the leaving group ($Z = p\text{-}NO_2$) stabilizes upper corners, D and P in Fig. 2, so that the TS will shift to G (or G′) predicting a smaller degree of bond formation as reflected in the smaller magnitudes of ρ_X and β_X (Table 2), whereas a more EDS in the nucleophile (X = *p*-MeO) stabilizes the right-hand corners P and A in Fig. 2, so that the TS shifts to H (or H′) predicting a smaller degree of bond breaking as reflected in the smaller $|\rho_Z|$ and $|\beta_Z|$ (Table 2).

The ρ_{XZ} and β_{XZ} values for EBS in Table 3 are greater than those for MBS, although the differences are small, suggesting a tighter TS for EBS than for MBS. This trend is identical with that found for reaction (3).[1] We note, however, that the magnitudes of ρ_{XZ} and β_{XZ} for the reactions with DMAs [equation (4)] are smaller by

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

Solvent	R	ρ_{XZ}[b]	SE[c]	β_{XZ}[d]	SE[c]
MeOH	Et	0·26 (0·33)	0·017	0·12 (0·19)	0·092
	Me	0·24 (0·30)	0·036	0·11 (0·18	0·078
MeCN	Et	0·27 (0·34)	0·022	0·13 (0·21)	0·113
	Me	0·25 (0·32)	0·016	0·12 (0·20)	0·102

[a]Multiple correlation coefficients were better than 0·993 at 99% confidence limit in all cases. The values in parentheses are those for the reactions with anilines[1] at 65·0 °C.
[b]The σ values were taken from the same source as for footnote a in Table 2.
[c]Standard errors; number of data points = 16.
[d]The pK_a values of *N,N*-dimethylanilines were taken from the same source as for footnote b in Table 2 and the pK_a values for sulphonic acid were taken from R. V. Hoffman and E. L. Belfoure, *J. Am. Chem. Soc.* **104**, 2183 (1982).

approximately the same amount (0·06–0·08 unit)[1] than the corresponding values for the reactions with aniline. The smaller magnitudes of ρ_{XZ} and β_{XZ} indicate that the TSs for the reactions of DMAs are looser than those for the reactions with anilines. Thus the bulky nucleophile DMA results in the formation of a looser TS than the relatively small aniline,[1] but a tighter TS is again obtained with EBS despite the overall increases in the steric effect;[2o,8] the relative tightness of the TS remains the same between EBS and MBS with net increases in the looseness for both alkyl compounds alike by a bulkier nucleophile.

Obviously, the dimethyl group is expected to exert both electronic (polar) and steric effects on the TS structure. The two effects will have opposing influences on the rate; electronically the dimethyl group increases the nucleophilicity of the N centre owing to an increased electron density (higher pK_a value[19]), but sterically it decreases the nucleophilicity of the reaction centre N.[8] An increased nucleophilicity due to the polar effect can increase bond formation when ρ_{XZ} is negative, whereas it decreases bond making when ρ_{XZ} is positive[2q,18] and the Hammond effect is greater than the anti-Hammond effect, which was found to be the case according to our results for KIE using deuterated aniline nucleophiles.[7] This is true, of course, when the steric effect does not overwhelm the relatively small electronic effect. Indeed, we found that in the reactions of 1-phenylethyl benzenesulphonates with DMA[2o] bond formation increases ($|\rho_{XY}|$ increases from 0·21 for aniline[2j] to 0·36 for DMA[2o]), since for this reaction ρ_{XZ} is negative.[2q] It is therefore reasonable that in the reactions of alkyl benzenesulphonates with DMA bond making is less in the TS than in the reactions with aniline,[1] since for these reaction series ρ_{XZ} is positive. We believe, however, that when the steric effect is very large, the small electronic effect becomes overwhelmed and the TS structure is mainly determined by the Hammond postulate,[5] i.e. increased steric hindrance leads to a later TS[20] for bond making, as has been observed in the Menshutkin reactions of methyl iodide with 2,6-dialkyl-substituted pyridines.[21] The smaller amount of bondmaking in the TS for the S_N2 reactions of the propionaldehyde compared with formaldehyde acetal derivatives[22] can, therefore, be attributed to electronic effects since in these reactions the TS is very loose and steric effects may not be too great.

The enhanced steric crowding with DMA, reflected in the rate retardation (Table 1), and the tighter TS obtained with EBS strongly suggest that this TS variation within a series (from Y = H to $Y = CH_3$) originates from the small electron-donating polar effect of the methyl group[3,8] (Figure 1).

The ρ_{XZ} and β_{XZ} values in Table 3 show that the magnitudes are greater in MeCN than in MeOH, although again the differences are small. This suggests a tighter TS in MeCN than in MeOH. This is in contrast to the higher $|\rho_X|$ and $|\beta_X|$ values, i.e. a greater degree of bond formation, and the lower $|\rho_Z|$ and $|\beta_Z|$ values, i.e. a lesser degree of bond breaking, in MeOH so that a tighter TS is expected in MeOH than in MeCN, as pointed out above. This shows again the unreliability of the simple Hammett and Brønsted parameters as a measure of the TS structure when TS structures are compared between two different reaction series.[2f,g,k,16]

EXPERIMENTAL

Materials. All materials used were as reported previously.[1,23]

Rate Measurements. The second-order rate constants, k_2, were determined as described.[1] The average deviations of k_2 were less than $\pm 3\%$ in more than triplicate determinations.[1]

Product analysis. Thin-layer chromotography (silica gel, glass plate, 30% ethylacetate–hexane eluent) of the reaction mixtures showed four spots corresponding to two reactants, $CH_3OSO_2C_6H_4Cl$ ($R_F = 0{\cdot}81$) and $C_6H_5N(CH_3)_2$ ($R_F = 0{\cdot}69$), one product $C_6H_5N^+(CH_3)_3^-OSO_2C_6H_4Cl$ ($R_F = 0{\cdot}34$) and a trace amount of unknown compound ($R_F = 0{\cdot}19$). In NMR, the cationic part of product $C_6H_5N^+(CH_3)_3$ had δ_H (60 MHz; $CDCl_3 + DMSO\text{-}d_6$) 3·70 [$(CH_3)_3$, 9H], 7.5–8.0 (C_6H_5, 5H, m).

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