Cross Interaction Constants as a Measure of the Transition State Structure. (Part 10), Mechanism of Reactions between Phenacyl Benzenesulfonates with N,N-Dimethylanilines

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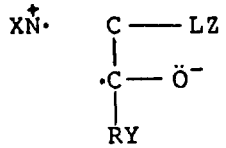
The transition state (TS) structure for the reactions of phenacyl benzenesulfonates with N,N-dimethylanilines (DMA) is investigated using various selectivity parameters, especially with cross-interaction constants, ρ_{ij}, β_{ij} and λ_{ij}. The trends in reactivity were similar to aniline series but the TS was found to be somewhat looser than that for aniline series. It was found that the RSP and BEP principle hold within the DMA series but are violated between two different reaction series with DMA and aniline.

Introduction

It has been sown that the α-carbonyl group in phenacyl compound provides a "shunt" in the resonance in the resonance in the transition state(TS)[1], which resulted in a remarkable decrease in the cross interaction between substituents in the nucleophile (X) and those in the substrate (Y), as can be



(I)

represented by the valence-bond configuration,[2] (I), where X, Y and Z are substituents in the nucleophile, substrate and leaving group (LG) respectively. The magnitude of the Hammett type cross interaction constants[3], in ρ_{XY}, eq. 1a, where $i,j = X$, Y or Z, between substituents X and Y was unusually small compared to the normal values ($|\rho_{XY}| \cong 0.6$–0.8) for the S_N2 type reactions. Similarly the magnitudes of the Brønsted type[4] (β_{ij} in eq. 1b) and mixed Hammett-

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

$$\log (k_{ij}/k_{HH}) = \beta_i\Delta pK_i + \beta_j\Delta pK_j + \beta_{ij}\Delta pK_i\Delta pK_j \quad (1b)$$

$$\log (k_{ij}/k_{HH}) = \rho_i\sigma_i + \beta_j\Delta pK_j + \lambda_{ij}^{(i)}\sigma_i\Delta pK_j \quad (1c)$$

Brønsted type[4] (λ_{ij} in eq. 1c) cross-interaction constants also indicated the resonance shunt phenomenon due to the contribution of structure (I) in the TS.

We report here the results of our kinetic investigations of the nucleophilic substitution reactions of phenacyl benzenesulfonates with N,N-dimethylanilines in methanol at 55.0 °C, eq. (2).

$$XC_6H_4N(CH_3)_2 + YC_6H_4COCH_2OSO_2C_6H_4Z \xrightarrow[55.0℃]{MeOH} YC_6H_4COCH_2N(CH_3)_2C_6H_4X + {}^-OSO_2C_6H_4Z \quad (2)$$

X = p-CH_3O, p-CH_3, H, or p-Br

Y = H, p-Cl, or p-NO_2

Z = p-CH_3, H, p-Cl, or p-NO_2

Table 1. Second Order Rate Constants, $k_2(\times 10^4 l\ mol^{-1}sec^{-1})$, for the Reaction of Phenacyl Benzenesulfonates with N,N-dimethylanilines in Methanol at 55.0 °C

Y	X/Z	p-CH_3	H	p-Cl	p-NO_2
H	p-OCH_3	6.69	10.3	19.3	77.1
	p-CH_3	4.24	7.03	11.9	51.8
	H	2.13	3.31	6.04	27.7
	p-Br	0.640	1.11	2.21	10.0
p-Cl	p-OCH_3	9.45	15.2	21.7	82.0
	p-CH_3	6.26	9.76	16.2	57.6
	H	2.99	4.60	7.84	30.3
	p-Br	1.00	1.68	2.62	11.4
p-NO_2	p-OCH_3	52.6	63.7	72.0	116
	p-CH_3	35.7	41.2	51.3	84.5
	H	17.7	21.5	26.1	45.6
	p-Br	6.25	7.91	9.68	17.5

Our aims in this work are two-fold: confirmation of the resonance shunt phenomena and unravelling of the effect of nucleophilicity on the TS structure, by using N,N-dimethylanilines (DMA) as nucleophiles.

Results and Discussion

The second order rate constants, k_2, for the reaction of phenacyl benzenesulfonates with DMA in methanol at 55.0 °C, eq. 2, are given in Table 1. The reaction rates are less than one-half of those of similar reactions with anilines.[1b] Table 1 reveals that the rate of nucleophilic substitution increases when nucleophile or nucleofuge becomes stronger, *e.g.*, $X = p$-CH_3O or $Z = p$-NO_2 for a given substrate. The rate is also seen to increase with a more electron-withdrawing substituent in the substrate, *e.g.*, $Y = p$-NO_2, indicating that negative charge developed in the TS at the reaction center, C_α, is stabilized; this also suggests that formation of the N-C_α bond is more advanced than bond breaking of the C_α-LG bond in the TS. All these reactivity trends are in accord with those of the aniline reactions.

The Hammett and Brønsted coefficients involving substituent changes in the nucleophile, ρ_X and β_X, are summarized

Table 2. Hammett's ρ_X and Bronsted β_X Values for Reaction (2)[a]

Y \ Z	ρ_X[b]				β_X[c]			
	p-CH_3	H	*p*-Cl	*p*-NO_2	*p*-CH_3	H	*p*-Cl	*p*-NO_2
H	-2.02	-1.95	-1.86	-1.76	0.43	0.41	0.39	0.37
	(-2.08)	(-1.99)	(-1.95)		(0.75)	(0.72)	(0.70)	
p-Cl	-1.97	-1.92	-1.87	-1.70	0.41	0.40	0.33	0.36
	(-2.01)	(-1.95)	(-1.88)		(0.73)	(0.70)	(0.68)	
p-NO_2	-1.85	-1.80	-1.76	-1.65	0.39	0.38	0.37	0.35
	(-1.89)	(-1.81)	(-1.80)		(0.68)	(0.66)	(0.65)	
Corr. Coeff.	>0.999				>0.990			

[a]The values in parenthesis are those for the reactions with aniline nucleophiles. [b]The σ values were taken from R. D. Gilliom, "Introduction to Phys. Org. Chem." Addison-Wesley, Reading, 1970, p. 148. [c]The pK_a values were taken from W. C. Davis and H. W. Addis, *J. Chem. Soc.*, 1622 (1937); G. Thompson *ibid.*, 1113 (1946).

Table 3. Hammett's ρ_Z and Bronsted β_Z Values for Reaction (2)[a]

Y \ X	ρ_Z[b]				β_Z[c]			
	p-OCH_3	*p*-CH_3	H	*p*-Br	*p*-OCH_3	*p*-CH_3	H	*p*-Br
H	1.10	1.14	1.18	1.25	-0.37	-0.38	-0.39	-0.42
	(1.14)	(1.19)	(1.24)		(-0.28)	(-0.40)	(-0.41)	
p-Cl	0.97	1.00	1.06	1.10	-0.32	-0.34	-0.35	-0.37
	(1.03)	(1.03)	(1.09)		(-0.34)	(-0.34)	(-0.36)	
p-NO_2	0.35	0.39	0.43	0.46	-0.12	-0.13	-0.14	-0.15
	(0.42)	(0.43)	(0.47)		(-0.14)	(-0.14)	(-0.16)	
Corr. Coeff.	>0.997				>0.983			

[a,b]The same as in Table 2. [c] pK_a values used are for methyl transfer reactions taken from R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.*, **108**, 5536 (1986).

in Table 2. The magnitudes of ρ_X are somewhat smaller, but those of β_X are substantially smaller than those of the corresponding values for aniline nucleophiles, indicating less degree of bond formation with DMA than with anilines. This constitutes a violation of reactivity-selectivity principle (RSP)[5], since the less reactive DMAs have less selectivity *i.e.*, small $|\rho_X|$ or $|\beta_X|$ values. Comparison of the magnitudes of ρ_X or β_X with the relative rates between DMA and aniline indicates that the BEP principle[6] dose not hold since a less reactive reactant (DMA) with a higher activation barrier has an earlier TS (a less degree of bond formation).

The magnitudes of both ρ_X and β_X, and hence the extent of bond formation, decrease with a better leaving group (Z= *p*-NO_2) and with a more electron-withdrawing substituent in the substrate (Y = *p*-NO_2). These trends are in contrast with those found in the rate variation. Thus the rate increases observed with a stronger nucleofuge and with a more electron-withdrawing substituent in the substrate are accompanied by less charge transfer and hence less selecivity, which is in accord with the RSP.[5] Thus within the family of related reactions with DMA the RSP holds but between two different families of reactions *i.e.*, DMA *vs* aniline series, the RSP is violated.[5]

The ρ_Z and β_Z values obtained for substituent changes in the LG are presented in Table 3. The magnitudes of both parameters are slightly smaller than those for the corresponding aniline series, suggesting slightly less degree of bond breaking in the TS for the reactions with DMA. The magnitudes of ρ_Z and β_Z are, however, considerably smaller than those of ρ_X and β_X, which suggests much less bond breaking than bond formation in the TS. Here again the RSP holds within the series of DMA reactions but it is violated between the two different series of DMA and aniline nucleophiles. The faster rate (lower activation barrier) with the earlier TS, *i.e.*, less bond-making and -breaking exhibited by a stronger nucleophile or nucleofuge demonstrates adherence to the BEP principle[6]; within the family of DMA reactions, thus, both the RSP[5] and BEP principle hold. This is in accord with

Table 4. Hammett's ρ_Y Values for Reaction (2)[a,b]

X/Z	*p*-CH_3	H	*p*-Cl	*p*-NO_2
p-OCH_3	0.70	0.61	0.47	0.14
	(0.67)	(0.57)	(0.44)	
p-CH_3	0.73	0.61	0.49	0.15
	(0.70)	(0.60)	(0.46)	
H	0.74	0.64	0.50	0.17
	(0.72)	(0.61)	(0.48)	
p-Br	0.77	0.66	0.52	0.19
Corr. Coeff.	>0.998			

[a,b]The same as in Table 2.

Table 5. The Cross Interaction Constants, ρ_{ij} Values, for Reaction (2)[a,b]

Z	ρ_X	ρ_Y	ρ_{XY}	Corr. Coeff.
p-CH_3	-2.02	0.74	0.12	0.999
			(0.14)	
H	-1.94	0.64	0.11	0.999
			(0.11)	
p-Cl	-1.87	0.50	0.09	0.999
			(0.10)	
p-NO_2	-1.75	0.17	0.08	0.999
X	ρ_Y	ρ_Z	ρ_{YZ}	Corr. Coeff.
p-OCH_3	0.60	1.11	-0.59	0.999
			(-0.63)	
p-CH_3	0.62	1.14	-0.59	0.999
			(-0.65)	
H	0.63	1.18	-0.59	0.999
			(-0.66)	
p-Br	0.66	1.25	-0.62	0.999
Y	ρ_X	ρ_Z	ρ_{XZ}	Corr. Coeff.
H	-1.96	1.18	0.28	0.999
			(0.32)	
p-Cl	-1.97	1.05	0.30	1.000
			(0.31)	
p-NO_2	-1.81	0.42	0.21	0.999
			(0.23)	

[a,b]The same as in Table 2.

Table 6. Cross Interaction Constants λ_{XY} and λ_{YZ} Values for Reaction (2)[a,b]

Z	β_X	ρ_Y	λ_{XY}[c]	X	ρ_Y	β_Z	λ_{YZ}[d]
p-CH_3	0.43	0.73	-0.027	*p*-OCH_3	0.64	-1.87	1.00
			(-0.05)				(0.99)
H	0.41	0.63	-0.024	*p*-CH_3	0.70	-2.09	1.03
			(-0.04)				(1.02)
p-Cl	0.40	0.49	-0.019	H	0.67	-2.00	1.00
			(-0.04)				(1.04)
p-NO_2	0.37	0.17	-0.017	*p*-Br	0.70	-2.09	1.04
Corr. Coeff.		>0.992				>0.993	

[a,b,c]The same as in Table 2. [d]The pK_a values used are for benzenesulfonic acids taken from R. V. Hoffman and E. L. Belfore, *J. Am. Chem. Soc.* **104,** 2183 (1982).

Table 7. Cross Interaction Constants, β_{XZ} Values, for Reaction (2)[a]

Y	β_X[b]	β_Z[c]	β_{XZ}
H	0.42	-1.96	0.098
			(0.20)
p-Cl	0.41	-1.74	0.097
			(0.19)
p-NO_2	0.38	-0.69	0.071
			(0.14)
Corr. Coeff.		>0.992	

[a]The same as in Table 2. [b]The pK_a values are taken from the same source as for foot note [c]in Table 2. [c]The pKa values are taken from the same source as for foot note [d]in Table 6.

the thermodynamically controlled reaction series, since a stronger nucleophile or nucleofuge should lead to an increased exothermicity within a series of analogous reactions as thermodynamical stabilities of products formed would require.[1b]

Hamett ρ_Y values determined with three substituents (*Y*) in the substrate are summarized in Table 4. The ρ_Y values are positive and decrease with a stronger nucleophile or nucleofuge.

The ρ_{ij}, λ_{ij} and β_{ij} values[4] obtained by multiple linear regression analysis of the second-order rate constants, k_2, in Table 1, for substituents *i* and *j* by using equations 1a-1c are summarized in Tables 5~7. We note that the magnitude of ρ_{XY} is slightly smaller but that of λ_{XY} is considerably smaller than that of the corresponding value for the aniline series. The smaller value, especially of λ_{XY}, suggests that bond formation is less in the TS for DMA series than that in the TS for aniline nucleophiles.

The size of both parameters are, again, much less than that expected from an S_N2 reaction[3k,7] so that the resonance shunt phenomena should operate in the DMA series also as we found in the aniline series.

The magnitudes of ρ_{YZ} and λ_{YZ} in Tables 5 and 6 are again slightly less than those corresponding values with aniline nucleophiles, indicating slight increase in the bond breaking with DMA. This is, however, in contrast to the trends found with the magnitudes of ρ_Z and β_Z, which indicated slight decrease in the degree of bond cleavage in the TS. This anomaly can be rationalized by the less degree of bond formation found with DMA; the less degree of bond formation should lead to the less degree of charge transfer with a less contribution from the resonance shunt, which in turn will give a longer C_α-C_β bond for the DMA[1b] series. Hence the decrease in ρ_{YZ} or λ_{YZ} (and of $|\rho_X|$ and $|\beta_X|$) with the decrease in $|\rho_Z|$ or $|\beta_Z|$ can be accommodated. Thus the TS in the DMA reaction has a looser structure than that in the aniline reaction, *i.e.*, bond formation is substantially less but bond breaking is slightly greater in the TS with DMA as compared with aniline.

This should lead to smaller values of ρ_{XZ} and β_{XZ}, since the TS is looser with DMA than with aniline; this expectation is borne out in the smaller values of both ρ_{XZ} and β_{XZ} for DMA than for aniline, in Table 7.

It has been shown that a reaction series may be classified into the intrinsic- and the thermodynamic-controlled reactions[8] depending on the sign of constants *k* and *k'*, eq. 3;[1h,8] both are positive for the intrinsic-controlled series in which the TS variation follows predictions by the quantum-mechanical (QM) model,[9] whereas they are negative in the thermodynamic-controlled reaction series in which the TS variation follows predictions by the potential energy surface (PES) diagram model.[10]

$$\log|\rho_{XY}| = k\sigma_Z \tag{3a}$$

$$\log|\rho_{YZ}| = k'\sigma_X \tag{3b}$$

Reference to Table 5 reveals that correlation (3*a*) hodls with $k<0$, as required from a thermodynamically controlled reactons.[8] However, the relation (3*b*) does not hold, since, as noted above, the contribution of resonance shunt increases with the greater degree of bond formation for a more electron-withdrawing substituent in the nucleophile *e.g.*, $X = p-Br$, as evidenced by a greater magnitude of ρ_{YZ} and β_{YZ} for the nucleophiles with these substituents. Thus the correction of the deviations due to complications arising from a varying degree of resonance shunt[1b] will make the reaction with DMA consistent with eq. 3b also.

We conclude that:

(i) The trends in the reactivity of the reactions of phenacyl benzenesulfonates with DMA are similar to those of the reactions with aniline.

(ii) The RSP and BEP principle are found to hold within the DMA series, but not between two series of DMA and aniline.

(iii) Selectivity parameters, ρ_{XY} and β_{XY}, indicated that the resonance shunt phenomena operate in the TS for the DMA series also.

(iv) The TS for the DMA series is somewhat looser than that for the aniline series.

Experimental

Materials. Materials were as described in the previous reports.[1b,1h] GR grade commercial para-Br-N,N-dimethylaniline was purified by the known method and had mp. 54 °C.[11]

Rate constans. Rates were measured conductometrically at 55.0 °C. Pseudo-first order rate constants, k_1^{obs}, were de-

termined by the Guggenheim method[12] with a large excess (over 10^2 times) of DMA and second order rate constants, k_2, were obtained from the slope of a plot of k_1^{obs} *vs* [DMA], eq. (4).

$$k_1^{obs} = k_1 + k_2[\text{DMA}] \quad (4)$$

k_1 is the rate constant for methanolysis, which was found to be negligible as evidenced by zero intercept ($k_1 = 0$) in all cases. The k_2 values were averages of at least duplicate runs. Good second order kinetics with linear correlation coefficients of better than 0.999 for the plot of equation (4) indicated that the reaction is free from an ionic strength effect or from the base catalysis by DMA.

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