Nucleophilic Substitution Reactions of Allyl Arenesulphonates with Anilines and *N,N*-Dimethylanilines

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Kinetic studies of the reactions of allyl arenesulphonates, **I**, with anilines and *N,N*-dimethylanilines in acetonitrile at 45.0 °C are reported. The sign and magnitude of the cross-interaction constants ρ_{xz} (and β_{xz}) between substituents in the nucleophile (X) and leaving group (Z) indicate that the transition state (TS) for **I** is relatively tight and is similar to that for the corresponding reactions of ethyl systems, rather than for benzyl systems. Variations of the simple Hammett (and Brønsted) coefficients ρ_x (β_x) and ρ_z (β_z) with substituents Z and X, respectively, are consistent with the trend expected from a positive ρ_{xz}, *i.e.*, that predicted by the potential energy surface diagram. The kinetic isotope effects involving *N*-deuteriated anilines support the mechanism proposed based on ρ_{xz} (β_{xz}) for the reactions of **I**, *i.e.*, an associative S_N2 process with an earlier TS for a stronger nucleophile and/or a better leaving group.

Studies of the solvolyses of allyl arenesulphonates,[1] **I** with LZ = $OSO_2C_6H_4Z$, have indicated that allyl systems are similar to the corresponding benzyl systems, **II**, in their solvolytic behaviour. However, the two systems do show some differences, the allyl being less reactive and more dependent on solvent nucleophilicity. On the other hand, *ab initio* MO calculations[2a] of the trigonal bipyramidal five-coordinate transition state (TS) structure at the 6 − 31 + + G* level[2b] for the identity exchange of hydride (H^-) have indicated that bond tightness in the TS for allyl, **I**, is similar to that for the ethyl system, **III**.

$CH_2{=}CH{-}CH_2LZ$	$C_6H_5CH_2LZ$	CH_3CH_2LZ
I	**II**	**III**

Recently, in a series of work on the application of cross-interaction constants,[3,4,8] ρ_{ij} and β_{ij}, as a measure of the TS structure [eqn. (1), *i,j* = X, Y or Z], the sign and magnitude of ρ_{ij} (and β_{ij}) have proved to be useful for predicting TS structures and their variations with the substituents in the nucleophile X, substrate Y, and/or leaving group (LG), Z. The definition of ρ_{xz},[3j,k] eqn. (2), postulates that if ρ_{xz} is negative a 'later' TS, ($\delta\rho_z > 0$ and/or $\delta\rho_x < 0$) is obtained with a stronger nucleophile ($\delta\sigma_x < 0$) and/or a better LG ($\delta\sigma_z > 0$), whereas the contrary is true for a positive ρ_{xz}, *i.e.*, an 'earlier' TS is obtained with a stronger nucleophile and/or a better LG. On the other hand, the magnitude of ρ_{ij} has been shown to be inversely proportional to the distance r_{ij} between two reaction centres.[3,4,8]

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

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

$$\rho_{xz} = \frac{\partial^2\log k_{xz}}{\partial\sigma_x\partial\sigma_z} = \frac{\partial\rho_z}{\partial\sigma_x} = \frac{\partial\rho_x}{\partial\sigma_z} \qquad (2)$$

In this work, we report the results of our kinetic studies on the reactions of allyl arenesulphonates (AAS) with anilines (AN) and *N,N*-dimethylanilines (DMA) in acetonitrile at 45.0 °C, (R1).

$$XC_6H_4NR_2 + CH_2{=}CH{-}CH_2OSO_2C_6H_4Z \xrightarrow[45.0\ ^\circ C]{MeCN} CH_2{=}CH{-}CH_2N^+R_2C_6H_4X + {}^-OSO_2C_6H_4Z \qquad (R1)$$

R = H or CH_3; X = *p*-CH_3O, *p*-CH_3, H, or *p*-Cl; Z = *p*-CH_3, H, *p*-Cl, or *p*-NO_2

We have characterized the TS structure for this reaction based on the sign and magnitude of ρ_{xz}, and shown that the reaction of AAS with AN (and DMA) is similar to that of the corresponding reactions of ethyl, **III**, rather than benzyl systems, **II**.

Table 1 Second-order rate constants, $k_2/10^3$ dm^3 mol^{-1} s^{-1}, for reactions of Z-substituted allyl arenesulphonates with X-substituted anilines and DMAs in MeCN at 45 °C

	Z			
X	*p*-CH_3	H	*p*-Cl	*p*-NO_2
R = H				
p-CH_3O	5.38	8.14	16.3	69.4
p-CH_3	3.48	5.64	11.2	48.0
H	1.82	2.82	6.04	27.0
p-Cl	0.618	1.00	2.20	11.8
R = CH_3				
p-CH_3O	3.14	5.25	9.77	49.0
p-CH_3	1.99	3.24	6.30	31.8
H	0.841	1.41	2.82	14.5
p-Cl	0.274	0.479	0.977	5.89

Results and Discussion

The second-order rate constants, k_2, for the reactions of AAS with ANs and DMAs are summarized in Table 1. The rates are seen to increase with a more electron-donating substituent (X = *p*-CH_3O) in the nucleophile and with a more electron-withdrawing substituent (Z = *p*-NO_2) in the LG, which is the reactivity behaviour expected for an S_N2 process.[6] The rates are greater with ANs rather than with the corresponding reactions of DMAs even through DMAs have slightly greater pK_a values (pK_a = 4.6 and 4.8 for AN and DMA, respectively).† This rate

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† The pK_a values of AN and DMA in water were taken from the same source as for footnote *b* in Table 2. The values are not available in acetonitrile.

Table 2 The Hammett (ρ_x and ρ_z)[a] and Brønsted (β_x[b] and β_z[c]) coefficients for reaction (R1)[d]

Z	ρ_x	β_x	X	ρ_z	β_z
$XC_6H_4NH_2$					
p-CH_3	−1.88	0.68	p-CH_3O	1.18	−0.32
H	−1.84	0.66	p-CH_3	1.20	−0.33
p-Cl	−1.75	0.63	H	1.24	−0.34
p-NO_2	−1.54	0.56	p-Cl	1.36	−0.37
$XC_6H_4N(CH_3)_2$					
p-CH_3	−2.15	0.59	p-CH_3O	1.25	−0.33
H	−2.10	0.57	p-CH_3	1.27	−0.34
p-Cl	−2.03	0.55	H	1.30	−0.35
p-NO_2	−1.87	0.51	p-Cl	1.39	−0.38

[a] The σ values were taken from R. D. Gilliom, *Introduction to Physical Organic Chemistry*, Addison-Wesley, Reading, 1970, p. 148. [b] The pK_a values were taken from W. C. Davis and W. Addis, *J. Chem. Soc.*, 1937, 1622; G. Thompson, *J. Chem. Soc.*, 1946, 1113. [c] The pK_a values are for methyl transfer: R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.*, 1986, **108**, 5536. [d] Correlation coefficients were better than 0.995 at the 99% confidence limit[14] in all cases.

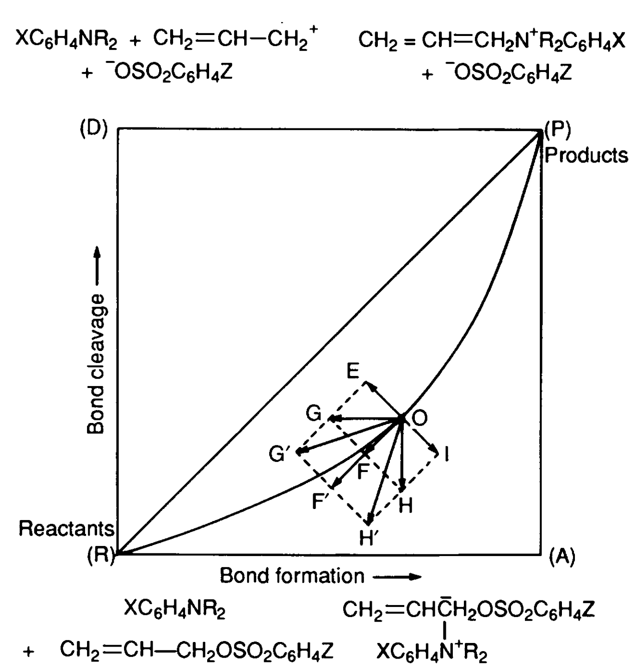

Fig. 1 Potential energy surface diagram showing variations with substituent changes (R = H or CH_3)

retardation for DMAs can be ascribed to the steric effect of the *N,N*-dimethyl group in the TS.[4] The simple Hammett and Brønsted coefficients are given in Table 2 for the variations of substituents in the nucleophile, ρ_x and β_x (= β_{nuc}), and in the LG, ρ_z and β_z (= β_{lg}).* The magnitude of ρ_x and β_x decrease with a more electron-withdrawing substituent in the LG (Z = p-NO_2) (*i.e.*, with a better LG) whereas the magnitude of ρ_z and β_z decreases with a more electron-donating substituent in the nucleophile (X = p-CH_3O) (*i.e.*, with a stronger nucleophile) for both nucleophiles, AN and DMA. These substituent effects on the TS variation are in accord with those predicted by the potential energy surface (PES) diagram,[5] Fig. 1. A better LG (stabilizes corners D and P) and a stronger nucleophile (stabilizes corners A and P) shift the TS, O, towards G (a decrease in bond formation) and H (a decrease in bond cleavage), respectively, as a result of vector sum of the Hammond[7] ($\overrightarrow{OF}$) and Thornton[5a] ($\overrightarrow{OE}$ and $\overrightarrow{OI}$, respectively) effects. An earlier TS predicted for a better LG and a stronger nucleophile based on the $\rho_x(\beta_x)$ and $\rho_x(\beta_x)$ values in Table 2 should mean that ρ_{xz} is positive in eqn. (2), as is indeed observed in Table 3. An examination of Table 3 reveals that the sign and magnitude of ρ_{xz} for AAS are quite similar to those of the ethyl series. This is in contrast to the similarity of the solvolysis mechanism proposed for allyl and benzyl arenesulphonates based on rather large values of both the sensitivity (*l*) to solvent nucleophilicity (*N*) and the sensitivity (*m*) to solvent ionizing power (*Y*) by Kevill *et al.*[1]

We note in Table 3 that the benzyl series[8] has a negative ρ_{xz} (β_{xz}) with a magnitude of approximately one third of that for the allyl as well as for the alkyl series.[4] In comparing the ρ_{xz} values for different solvent systems, we point out that the solvent change from MeOH to MeCN does not cause a significant difference in the magnitude of ρ_{xz} (β_{xz}). Thus, the positive sign as well as the greater magnitude of ρ_{xz} for the allyl system observed in this study clearly supports the view that the TS is relatively tight as expected from an associated S_N2 process;[3j,k,4] in contrast to the negative sign with a small magnitude of ρ_{xz} for the benzyl system which has been interpreted to provide evidence for a dissociative S_N2 process with a loose TS.[3j,k,8] For the dissociative S_N2 process, the TS variation is in accord with that predicted quantum mechanically, but not with that predicted by the PES diagram.[3j,k] Although reaction temperatures vary between the series, the conclusions reached based on the sign and magnitude of ρ_{xz} in Table 3 should not be affected.†

It is interesting to note that the magnitudes of β_x and β_z (Table 2)‡ as well as those of ρ_{xz} (and β_{xz}) (Table 3) suggest that the TS for the reaction with DMA is slightly looser than that for the reactions with AN. This may be attributed to a slightly greater basicity (nucleophilicity) of DMA resulting in a lesser degree of bond formation, as predicted by the PES diagram, provided the effect of bond formation outweighs that of bond breaking. It has been shown that in an associative-type S_N2 reaction[3j,k,4] bond formation progresses ahead of bond breaking so that bond formation has the dominant effect on the TS variation, whereas in a dissociative-type S_N2 process[3j,k,8] the reverse is true; *i.e.*, bond breaking has the dominant effect. This means that in the PES diagram, Fig. 1, the Hammond effect is greater than the Thornton effect, *i.e.*, instead of $\overrightarrow{OF}$ = $\overrightarrow{OE}$ = $\overrightarrow{OI}$, $\overrightarrow{OF}$ is greater than $\overrightarrow{OE}$ and $\overrightarrow{OI}$ so that the TS shifts to G′ and H′ instead of shifting to G and H, respectively. Thus, a stronger nucleophile, DMA, leads to a lesser degree of bond formation compared with AN.

A proposed relatively tight TS (based on the ρ_{xz} values for AAS) is supported by the kinetic isotope effects (KIE) involving *N*-deuteriated AN nucleophiles[9] in Table 4, where the secondary KIE involving *N*-deuteriated AN nucleophiles at the same temperature of 45.0 °C, are also included for the corresponding reactilons of benzyl and ethyl systems. First of

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* We included β values together with ρ values because β values are independent of the intervening non-conjugating group, *e.g.* CH_2 or CO, between the substituent and reaction centre.

† Temperature effects on ρ_{xz} (β_{xz}) should be relatively small, since the magnitudes of both ρ_x and ρ_z are an inverse function of temperature, *i.e.*, both bond-formation and bond-breaking decreases with higher temperature.

‡ The comparison of bond tightness based on $|\rho_x|$ between the AN and DMA series is, however, misleading, since the greater magnitudes of ρ_x for DMA do not reflect a greater degree of bond formation in the TS for DMA relative to AN. The magnitude of the simple ρ_x cannot be compared between two different reaction series due to a different degree of charge transmission depending on the reaction centre.[4]

Table 3 The cross-interaction constants, ρ_{xz} and β_{xz}, for nucleophilic substitution reactions

Reaction	Solvent	T/°C	$\rho_{xz}{}^{a}$	$\beta_{xz}{}^{b}$	Ref.
$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z$	MeOH	30.0	−0.10	−0.06	8(*d*)
$XC_6H_4NH_2 + CH_3OSO_2C_6H_4Z$	MeOH	65.0	0.30 (0.32)[c]	0.18 (0.20)[c]	4(*b*)
$XC_6H_4NH_2 + C_2H_5OSO_2C_6H_4Z$	MeOH	65.0	0.33 (0.34)	0.19 (0.21)	4(*b*)
$XC_6H_4N(CH_3)_2 + CH_3OSO_2C_6H_4Z$	MeOH	65.0	0.24 (0.25)	0.11 (0.12)	4(*c*)
$XC_6H_4N(CH_3)_2 + C_2H_5OSO_2C_6H_4Z$	MeOH	65.0	0.26 (0.27)	0.12 (0.13)	4(*c*)
$XC_6H_4NH_2 + CH_2{=}CHCH_2OSO_2C_6H_4Z$	MeCN	45.0	0.37[d]	0.21[d]	This work
$XC_6H_4N(CH_3)_2 + CH_2{=}CHCH_2OSO_2C_6H_4Z$	MeCN	45.0	0.30[d]	0.13[d]	This work

[a] The σ values were taken from the same source as footnote *a* in Table 2. [b] The pK_a values of DMAs were taken from the same source as footnote *b* in Table 2, and the pK_a values for sulphonic acid were taken from R. V. Hoffman and E. L. Befoure, *J. Am. Chem. Soc.*, 1982, **104**, 2183. [c] The values in parentheses are those in MeCN. [d] Multiple correlation coefficients were better than 0.994 at the 99% confidence limit[14] in all cases.

Table 4 The kinetic isotope effects observed for the reaction of Z-substituted allyl arenesulphonates with X-substituted *N*-deuteriated aniline nucleophiles in MeCN at 45.0 °C

X	Z	k_H/dm³ mol⁻¹ s⁻¹	k_D/dm³ mol⁻¹ s⁻¹	k_H/k_D
p-CH_3O	*p*-NO_2	6.894×10^{-2}	7.760×10^{-2}	
		6.970	7.698	$0.89_5 \pm 0.008^{b}$
		6.951	7.797	$(0.90_3)^{c}$
				$[0.86_1]^{d}$
		$6.93_8 \pm 0.04_0{}^{a}$	$7.75_2 \pm 0.05_1$	
p-CH_3O	*p*-CH_3	5.380×10^{-3}	6.155×10^{-3}	
		5.402	6.092	$0.87_6 \pm 0.008$
		5.376	6.203	(0.95_7)
				$[0.85_4]$
		$5.38_6 \pm 0.01_4$	$6.15_0 \pm 0.05_6$	
m-NO_2	*p*-NO_2	7.187×10^{-4}	8.179×10^{-4}	
		7.204	8.201	$0.87_3 \pm 0.007$
		7.136	8.288	(0.95_3)
				$[0.85_0]$
		$7.18_6 \pm 0.03_5$	$8.22_3 \pm 0.05_8$	
m-NO_2	*p*-CH_3	8.903×10^{-5}	10.12×10^{-5}	
		8.825	10.20	$0.86_7 \pm 0.009$
		8.799	10.28	(0.97_4)
				$[0.84_2]$
		$8.84_2 \pm 0.05_4$	$10.2_3 \pm 0.08_0$	

[a] Standard deviation. [b] Standard error.[15] [c] The values in parentheses are for the corresponding benzyl arenesulphonates in MeCN,[9a] converted to 45.0 °C. [d] The values in square brackets are for the corresponding ethyl arenesulphonates in MeCN,[9b] converted to 45.0 °C.

all, we note that the inverse KIE, $k_H/k_D < 1.0$, are obtained in all cases demonstrating that the N–H stretching[10] and bending[9,11] frequencies increase in the progress of reaction from the ground state to the TS due to steric congestion incurred by bond formation. Secondly, the effects of substituents, X and Z, on the degree of bond formation are consistent with those predicted by the sign of ρ_{xz};[3j,k] for the allyl and ethyl series ($\rho_{xz} > 0$), a stronger nucleophile and a better LG lead to a lesser degree of bond formation giving a larger k_H/k_D (< 1.0) value, whereas for the benzyl series ($\rho_{xz} < 0$) the trends are reversed, *i.e.*, they lead to a greater degree of bond formation with a smaller k_H/k_D (< 1.0) value.

We might consider the possibility of an S_N2' mechanism, in which the allylic system reacts with rearrangement of the double bond. This type of process is common to secondary and tertiary allylic halides, and is known to occur mainly by a carbonium ion-type mechanism.[16] In the present study, we have dealt with only the unsubstituted allylic systems and we do not think that the S_N2' mechanism is important. (i) There is no substituent to stabilize the carbonium ion; (ii) the ion-pair formation, $CH_2{\cdots}CH{\cdots}CH_2{}^{+}\,{}^{-}OSO_2C_6H_4Z$, is unlikely due to a large negative ion LG in which negative charge is delocalized and charge density is small so that the stabilization by solvation is very weak;[17] and (iii) our ρ_{xz} value is large indicating that the distance between N (on AN) and O (on benzenesulphonate) is relatively short in the TS compared with the corresponding distances in other reactions. In fact, $|\rho_{xz}|$ is similar to those for the corresponding reactions of methyl and ethyl benzenesulphonates as shown in Table 3. If the S_N2' were to occur in any significant amount the distance between N and O should be increased by two $C{\cdots}C$ bonds so that $|\rho_{xz}|$ should be reduced by *ca.* $\frac{1}{2}$–$\frac{1}{4}$ leading to a smaller value. The large $|\rho_{xz}|$ obtained in fact provides evidence against such a mechanism.[3j,k]

We conclude that the reactions of allyl arenesulphonates with ANs and DMAs proceed by an associative S_N2 process with a relatively tight TS which is similar to that involved in the corresponding reactions of ethyl systems rather than to that of benzyl systems. The TS variations with substituents in the nucleophile and leaving group are consistent with the trend expected from the positive ρ_{xz} values. The KIEs support these conclusions based on the sign and magnitude of ρ_{xz} (and β_{xz}).

Experimental

Materials.—Merck G.R. grade acetonitrile was purified before use as described previously.[4] Tokyo Kasei G. R. grade anilines were used after redistillation or recrystallization. *N,N*-dimethylanilines[12] and allyl arenesulphonates[1] were synthesized by well-known methods and the purity of the products was confirmed by IR and NMR spectroscopic analyses.

Determination of Rate Constants.—The conductivity method was used with a substrate concentration of 1.0×10^{-4} mol dm^{-3} and aniline (or DMA) concentration in excess, 0.03–0.18 mol dm^{-3} at 45 ± 0.05 °C. Pseudo-first-order rate constants, k_{obs}, obtained by the Guggenheim method[13] were plotted *vs.* [AN] or [DMA] to get the second-order rate constants, k_2, from the slope. Four or more AN concentrations were used in at least duplicate determinations of k_2, which was found to be reproducible to within ±2%.

Product Analysis.—Allyl arenesulphonate (0.05 mol) was reacted with an excess quantity of aniline (0.5 mol) and DMA (0.5 mol) for 2 days. After removal of solvent under reduced pressure, the products were washed with diethyl ether and water. The products obtained by column chromatography were analysed.

$C_6H_5NHCH_2CH{=}CH_2$: liquid, $R_f = 0.72$; δ 3.72 (H, broad, NH), 3.95 (2 H, d, CH_2), 5.16–5.32 (2 H, m, $CH_2{=}$), 5.80–6.03 (1 H, m, $=CH$) and 6.67–7.35 (5 H, m, aromatic).

$C_6H_5NH_3{}^{+}\,{}^{-}OSO_2C_6H_5$: m.p. 186–188 °C; $R_f = 0.02$; δ 7.2–7.8 (10, m, aromatic) and 8.2–8.7 (3 H, broad).

$C_6H_5N^{+}(CH_3)_2CH_2CH{=}CH_2\,{}^{-}OSO_2C_6H_5$: m.p. 67–68 °C; $R_f = 0.03$; δ 3.75 (6 H, s, CH_3), 4.80 (2 H, d, CH_2), 5.29–5.42 (2 H, m, $CH_2{=}$), 5.47–5.77 (1 H, m, $CH{=}$) and 7.32–7.97 (10 H, m, aromatic).

Acknowledgements

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