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NUCLEOPHILIC SUBSTITUTION REACTIONS OF METHALLYL ARENESULPHONATES WITH ANILINES AND *N*, *N*-DIMETHYLANILINES

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Kinetic studies of the reactions of methallyl arenesulphonates (II) 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) suggest that the transition state (TS) is slightly tighter than that for the corresponding reactions of allyl arenesulphonates (I). This is also supported by the observation that the magnitudes of ρ_X and ρ_Z for II are uniformly greater than those for the reactions of I. These results are in line with the simple MO theory that the 2-position of the allyl system is inactive electronically. The steric effect of the 2-methyl group in II causes a rate retardation and a shift of the TS toward a later position along the reaction coordinate with a slight increase in the overall tightness of the TS structure. The large $|\rho_{XZ}|$ value obtained eliminates the possibility of an S_N2' mechanism.

INTRODUCTION

Recently we have been involved with the application of cross-interaction constants, ρ_{ij} and β_{ij}, as a measure of the transition-state (TS) structure [equation (1), $i, j = X, Y$ or Z]:

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

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

It has been shown that the sign and magnitude of ρ_{ij} (and β_{ij}) are 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}:

$$\rho_{XZ} = \frac{\partial^2 \log k_{XZ}}{\partial\sigma_X\,\partial\sigma_Z} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \quad (2)$$

postulates that if ρ_{XZ} is negative a stronger nucleophile ($\delta\sigma_X < 0$) and/or a better LG ($\delta\sigma_Z > 0$) lead to a 'later' TS ($\delta\rho_Z > 0$ and/or $\delta\rho_X < 0$), 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_{XZ} is inversely proportional to the distance r_{XZ} between the two reaction centres of the nucleophile and LG, a greater $|\rho_{XZ}|$ indicating a tighter TS.[1]

In a previous work,[2] we applied these criteria to the TS structure for the nucleophilic substitution reactions of allyl arenesulphonates (**I**) with anilines (ANs) and *N*,*N*-dimethylanilines (DMAs). We concluded that the TS structure for the allyl system is similar to that of the corresponding reactions of ethyl rather than benzyl systems, in constrast to the similarity reported in the solvolytic behaviour between the allyl and benzyl systems.[3]

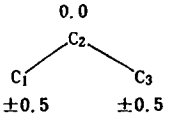
In this paper, we report on kinetic studies of the reactions of methallyl arenesulphonates (MAAs) (**II**) with ANs and DMAs in acetonitrile at 45·0 °C. The choice of MAAs as the substrate was partly dictated by its importance in the test of Hückel molecular orbital (HMO) theory that a substituent on the central carbon (C-2) of the allyl system should be inactive, i.e. a substituent

$CH_2{=}CH{-}CH_2OSO_2C_6H_4Z$

I

$CH_2{=}C(CH_3){-}CH_2OSO_2C_6H_4Z$

II



III

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should have practically no effect electronically on the reactivity,[4] and hence on the TS structure, as HMO formal charge distribution of an allylic ion (cation or anion) indicates (**III**).

RESULTS AND DISCUSSION

The second-order rate constants, k_2, for the reactions of MAAs (**II**) with ANs and DMAs are reported in Table 1. The reactivity trends are in accord with those expected for an S_N2 process; the rates are greater with a more electron-donating substituent in the nucleophile and with a more electron-withdrawing substituent in the *LG*. The rate retardation for DMAs (relative to ANs) due to the steric effect of the *N,N*-dimethyl group is greater for **II** than for the corresponding reactions of allyl systems, **I**;[2] typically $k_{DMA}/k_{AN} = 0{\cdot}50$ and $0{\cdot}44$ for **I** and **II** respectively, with X=Z=H. This enhanced rate retardation for **II** may simply be ascribed to the additional steric effect of the 2-methyl group in the TS for **II**.

One might expect a rate increase from the 2-methyl substitution, provided the reaction centre carbon, C-1, is positively charged in the TS, since such a TS will be partially stabilized by an electron-donating group, CH_3.

On the contrary, however, the 2-methyl group is seen to cause a rate retardation, $k_{II}/k_I = 0{\cdot}47$ and $0{\cdot}42$ for AN and DMA with X=Z=H, respectively. This rate retardation due to the 2-methyl substitution leaves us with two alternative interpretations: (i) the reaction centre carbon is negatively charged in the TS so that an electron-donating group destabilizes the TS leading to a rate decrease; or (ii) the substituent in the 2-position has no effect on the TS electronically, as the HMO theory predicts,[4] but the rate is decreased owing to the steric effect of the 2-methyl group in the TS. The decision as to which of these two interpretations is more likely can be made by considering the change in the TS structure due to the 2-methyl substitution; if the former explanation holds, the TS should become looser since the additional supply of negative charge in the TS by the 2-methyl group should lead to a decrease in bond formation and an increase in bond cleavage. On the other hand, if the latter interpretation is more likely, then we should obtain a later TS by the 2-methyl substitution in accordance with the Hammond postulate;[5] as a result, both the degree of bond formation and bond cleavage will increase, which will leave the overall tightness of the TS approximately the same.

Table 1. Second-order rate constants, k_2 (10^3 dm^3 mol^{-1} s^{-1}) for reactions of Z-substituted methallyl arenesulphonates with X-substituted anilines and *N,N*-dimethylanilines in acetonitrile at 45·0 °C

	Z			
X	*p*-CH_3	H	*p*-Cl	*p*-NO_2
R = H				
p-CH_3O	2·81	4·62	11·1	56·3
p-CH_3	1·63	2·55	7·02	33·8
H	0·795	1·33	3·74	18·7
p-Cl	0·291	0·512	1·41	8·93
R = CH_3				
p-CH_3O	1·24	2·17	6·01	36·3
p-CH_3	0·647	1·11	3·00	19·7
H	0·280	0·485	1·38	9·46
p-Cl	0·069	0·139	0·429	3·06

The TS structure or its variation is reflected in the magnitude of various selectivity parameters, such as the simple Hammett, ρ_i, and Brønsted coefficients, β_i, and the cross-interaction constants, ρ_{ij} and β_{ij}.[1] We have collected the ρ_X (and $\beta_X = \beta_{nu}$) and ρ_Z (and $\beta_Z = \beta_{lg}$) values in Table 2 for the variations of substituents in the nucleophile and LG, respectively.

The magnitude of ρ_X (and β_X) decreases with a more electron-withdrawing substituent in the LG (i.e. with a better LG) whereas the magnitude of ρ_Z (and β_Z) decreases with a more electron-donating susbstituent in the nucleophile (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[10] (Figure 1). A better LG and a stronger nucleophile shift the TS, O, towards G and H, respectively, leading to an earlier TS. An earlier TS predicted for a better LG and/or a stronger nucleophile based on the variation of ρ_X (β_X) and ρ_Z (β_Z) values in Table 2 requires a positive ρ_{XZ} in equation (2),[1] as is indeed observed in Table 3. Reference to Table 3 reveals that the sign is similar, $\rho_{XZ} > 0$, but the magnitudes of ρ_{XZ} (and β_{XZ}) for MAAs are slightly greater than those for the corresponding reactions of the allyl and ethyl series.

The greater magnitude of ρ_{XZ} for the MAAs than that for the allyl system supports the suggestion that the 2-methyl substitution in an allyl system has virtually no effect electronically on the TS structure as the HMO theory predicts.[4] In particular, the greater magnitude of ρ_{XZ} obtained indicates that the TS has become tighter by the 2-methyl substitution in contrast to a looser TS expected from the electron-donating effect of the 2-methyl group if interpretation (i) holds.[1] The effect of the 2-methyl group is only reflected in the rate retardation as a result of steric interference which causes to shift the TS to a later position along the reaction coordinate.[5] This will have little effect on the magnitude of ρ_{XZ}, since an increase in the degree of bond formation (a shorter Nu—C distance with a greater $|\rho_X|$) will be approximately cancelled by an increase in bond cleavage (a longer C-1—*LG* distance with a greater $|\rho_Z|$), leading to little change in r_{XZ} and hence in $|\rho_{XZ}|$.

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

Compound	Z	ρ_X	β_X	X	ρ_Z	β_z
$XC_6H_4NH_2$	*p*-CH_3	−1·96	0·71	*p*-CH_3O	1·38	−0·37
		(−1·88)[e]	(0·68)[e]		(1·18)	(−0·32)
	H	−1·88	0·68	*p*-CH_3	1·41	−0·38
		(−1·84)	(0·66)		(1·20)	(−0·33)
	p-Cl	−1·79	0·64	H	1·46	−0·40
		(−1·75)	(0·63)		(1·24)	(−0·34)
	p-NO_2	−1·58	0·57	*p*-Cl	1·58	−0·43
		(−1·54)	(0·56)		(1·36)	(−0·37)
$XC_6H_4N(CH_3)_2$	*p*-CH_3	−2·49	0·68	*p*-CH_3O	1·56	−0·42
		(−2·15)	(0·59)		(1·25)	(−0·33)
	H	−2·37	0·65	*p*-CH_3	1·58	−0·43
		(−2·10)	(0·57)		(1·27)	(−0·34)
	p-Cl	−2·26	0·62	H	1·63	−0·44
		(−2·03)	(0·55)		(1·30)	−(0·35)
	p-NO_2	−2·13	0·58	*p*-Cl	1·74	−0·47
		(−1·87)	(0·51)		(1·39)	(−0·38)

[a] The σ values were taken from Ref. 6
[b] The pK_a values were taken from Refs 7 and 8.
[c] The pK_a values are for methyl transfer.[9]
[d] Multiple correlation coefficients were better than 0·994 at the 99% confidence limit.
[e] The values in parentheses are those for the corresponding reactions of allyl arenesulphonates.[2]

We in fact observed that the magnitudes of ρ_X and ρ_Z for the reactions of the MAA series (**II**) are uniformly greater than those for the corresponding reactions of the allyl series (**I**)[2] (Table 2). However, as in the case of a greater ρ_{XZ} with a tighter TS in the reactions of ethyl arenesulphonates with anilines compared with the corresponding reactions of the methyl system, the increase in bond formation seems to exceed that in bond breaking in the TS variation owing to steric effects leading to a net increase in overall tightness of the TS.[12]

We conclude, therefore, that the 2-methyl group has no significant effect electronically on the TS structure as the simple HMO theory requires, the rate retardation observed for MAA relative to the allyl system originating purely from the steric effect.

The magnitudes of β_X and β_Z (Table 2) and those of ρ_{XZ} (and β_{XZ}) (Table 3) again suggest[2] a slightly looser TS for the reactions with DMAs than that for the reactions with ANs, which can be attributed to a slightly greater basicity of DMAs.[13] As to the possi-

Table 3. Cross-interaction constants, ρ_{XZ} and β_{XZ}, for nucleophilic substitution reactions

Reaction	Solvent	T(°C)	ρ_{XZ}[a]	β_{XZ}[b]
$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z$	MeOH	30·0	−0·10	−0·06
$XC_6H_4NH_2 + CH_3OSO_2C_6H_4Z$	MeOH	65·0	0·30	0·18
			(0·32)[c]	(0·20)[c]
$XC_6H_4NH_2 + C_2H_5OSO_2C_6H_4Z$	MeOH	65·0	0·33	0·19
			(0·34)	(0·21)
$XC_6H_4N(CH_3)_2 + CH_3OSO_2C_6H_4Z$	MeOH	65·0	0·24	0·11
			(0·25)	(0·12)
$XC_6H_4N(CH_3)_2 + C_2H_5OSO_2C_6H_4Z$	MeOH	65·0	0·26	0·12
			(0·27)	(0·13)
$XC_6H_4NH_2 + CH_2{=}CHCH_2OSO_2C_6H_4Z$	MeCN	45·0	0·37	0·21
$XC_6H_4N(CH_3)_2 + CH_2{=}CHCH_2OSO_2C_6H_4Z$	MeCN	45·0	0·30	0·13
$XC_6H_4NH_2 + CH_2{=}C(CH_3)OSO_2C_6H_4Z$	MeCN	45·0	0·40[d]	0·24[d]
$XC_6H_4N(CH_3)_2 + CH_2{=}C(CH_3)CH_2OSO_2C_6H_4Z$	MeCN	45·0	0·37[d]	0·17[d]

[a] The σ values were taken from Ref. 6. References are given in Refs 1 and 2.
[b] The pK_a values of DMAs were taken from Refs 7 and 8 and the pK_a values for sulphonic acids from Ref. 11. References are given in Refs 1 and 2.
[c] The values in parentheses are those in acetonitrile.
[d] Multiple correlation coefficients were better than 0·992 at the 99% confidence limit in all cases (this work).

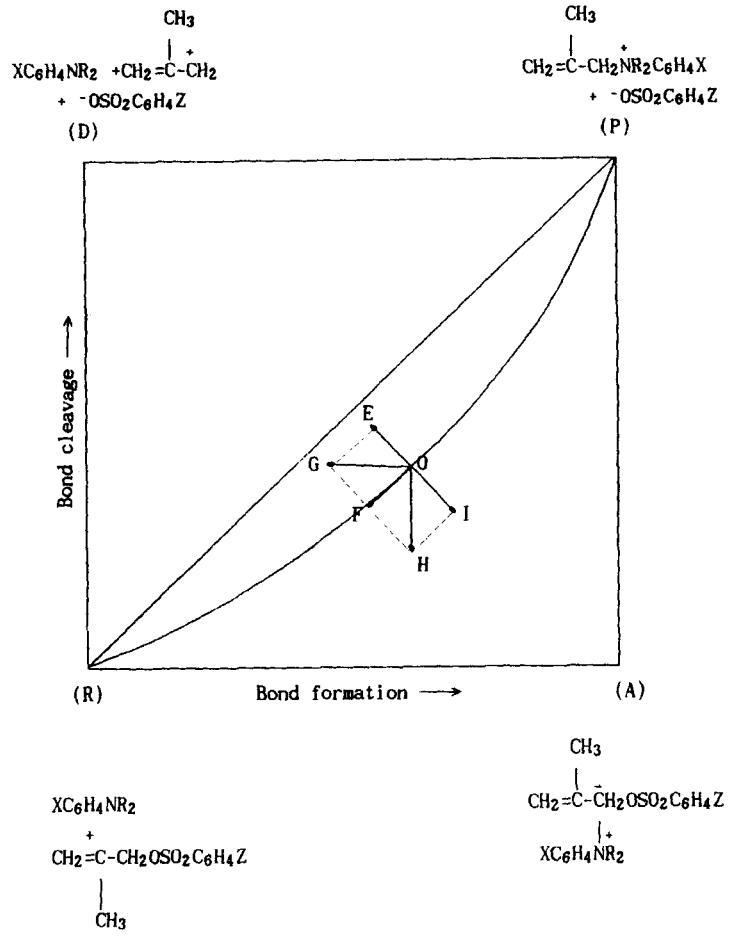
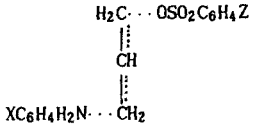


Figure 1. Potential energy surface diagram showing TS variations with substituent changes (R=H or CH_3)

bility of an S_N2' mechanism,[14] in which the allylic system reacts with rearrangement of double bond, essentially the same argument that was used for the allyl system applies:[2] carbonium ion and/or ion-pair formation in the TS is unlilkely, as the relatively large ρ_{XZ} value suggests a tight TS with negative charge development at the reaction centre carbon in the TS.[15] An S_N2' mechanism is important when rearrangement can take place in the allylic cation,[14] or when the nucleophile can attack the other end (C-3) of the allylic system (**IV**), in



(IV)

which case the distance between N and O should be increased by two C····C bonds so that $|\rho_{XZ}|$ should be reduced by ca 1/2–1/4, leading to a smaller value.[2] The large $|\rho_{XZ}|$ observed (reflecting a short N····O distance) in fact provides a novel mechanistic criterion for rejecting the S_N2' mechanism.

EXPERIMENTAL

Materials. Methallyl arenesulphonates were synthesized by well known methods and the purity of the products was confirmed by IR and NMR spectroscopic analyses.[2,3b] All other materials used are as reported previously.[2]

Determination of rate constants. The procedure adopted is as described previously.[2] Rates were repro-

ducible to within ±3%. We did not perform product analyses since the reaction systems and mechanisms in this work are similar to those for the allyl system for which the product analyses were carried out and confirmed that no unexpected products are formed.[2]

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