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Kinetic Studies on the Aminolysis of 2-Phenyl-1-propyl Arenesulfonates in Methanol

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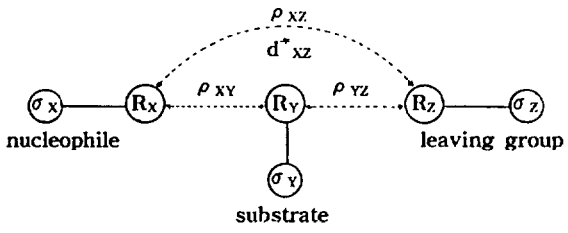
The results of kinetic studies on the reactions of 2-phenyl-1-propyl arenesulfonates with anilines and benzylamines in methanol at 55.0℃ are reported. The transition state variation with the substituents in the nucleophile (*X*) and leaving group (*Z*) is in accord with that expected from a negative ρ_{XZ} value : A stronger nucleophile and nucleofuge lead to a greater extent of bond-making and -breaking. Somewhat greater magnitude of ρ_{XZ} compared to the nearly constant value for the similar processes at a primary carbon atom has been interpreted to result from a partial contribution of the concurrent frontal displacement path.

Introduction

The cross-interaction constants, ρ_{ij} in Eq. (1) where *i* and *j* represent substituents in the nucleophile (*X*), substrate (*Y*) or leaving group (*Z*) in Scheme 1, are useful as a mechanistic tool for organic reactions in solution.[1]

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

We have shown for nucleophilic substitution reactions that: (i) The magnitudes of ρ_{XY} and ρ_{YZ} are directly proportional to the extent of bond-making and -breaking respectively in the transition state (TS), provided the fall-off of $|\rho_{ij}|$ (by *ca.* 2.8) due to an intervening nonconjugative group. *e.g.* CH_2 or CO, between the substituent and the reaction center is accounted for.[2] (ii) A positive [negative] ρ_{XZ}, which can be alternatively given as Eq. (2), leads to an earlier [later] TS along the

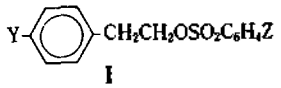


Scheme 1.

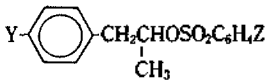
$$\rho_{XZ} = \frac{\partial\rho_z}{\partial\sigma_X} = \frac{\partial\rho_x}{\partial\sigma_z} \quad (2)$$

reaction coordinate for a stronger nucleophile ($\delta\sigma_X<0$) and/or a stronger nucleofuge, *i.e.*, a better leaving group ($\delta\sigma_Z>0$).[1] (iii) The magnitude of ρ_{XZ}, is a measure of the TS tightness; the greater the $|\rho_{XZ}|$, the tighter is the TS (the shorter is the d^*_{XZ} in Scheme 1).[1,3]

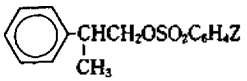
Previous works on the aminolysis (with anilines, $XC_6H_4NH_2$) of 2-phenylethyl arenesulfonate,[4] **I**, and its 1-methyl analogue,[5] **II**, have indicated that the overall reaction proceeds by an S_N2 mechanism with a relatively small degree of aryl participation for the substrate with an electron donating substituent, Y=*p*-CH_3O. The magnitude of ρ_{XZ} was, however, found to be somewhat large ($\rho_{XZ}=-0.45$[4] and 0.16[5] in MeOH at 65.0℃ for **I** and **II** with $Y=H$, respectively) compared with those for other corresponding reactions which are approximately constant for S_N2 processes with $\rho_{XZ}\cong0.33$ and 0.10 in MeCN at 65.0℃ at primary[6] and secondary carbon centers, respectively.[7]



I



II



III

Since the magnitude of ρ_{XZ} provides a measure of the tightness of the S_N2 TS, d^*_{XZ}, the anomalously high $|\rho_{XZ}|$ values for **I** and **II** have been interpreted as an indicative of the involvement of a frontal nucleophilic displacement in which the nucleophile (X) and leaving group (Z) come close together, *i.e.*, shorter d^*_{XZ}, leading to a greater magnitude of ρ_{XZ}.

In this work, we extend the aminolysis studies to the 2-methyl analogue of **I**, Eq. (3), in order to gain further information on such an anomaly in the reactions of **I** and **II**.

$$2XRNH_2 + C_6H_5CH(CH_3)CH_2OSO_2C_6H_4Z \xrightarrow[55.0℃]{MeOH} \underset{\textbf{III}}{} C_6H_5CH(CH_3)CH_2\cdot NHRX + XRNH_3^+ + {}^-OSO_2C_6H_4Z \quad (3)$$

$R=C_6H_4$ or $C_6H_4CH_2$
$X=p$-CH_3O, *p*-CH_3, H, *p*-Cl, *m*-NO_2 or *p*-NO_2
$Z=p$-CH_3, H, *p*-Cl or *p*-NO_2

Results and Discussion

The rate constants, k_2, for the reactions of 2-phenyl-1-propyl arenesulfonates, **III**, with anilines and benzylamines in methanol at 55.0℃ are summarized in Table 1. The rates are seen to increase with a stronger nucleophile ($\delta\sigma_X<0$) and nucleofuge ($\delta\sigma_Z>0$) as expected from a S_N2 type process. For the reactants with $X=Y=Z=$H, at 65.0℃, the rate becomes slower in the order **I** (11.0×10^{-5} $M^{-1}s^{-1}$)>**II** (3.55×10^{-5} $M^{-1}s^{-1}$>**III** (1.71×10^{-5} $M^{-1}s^{-1}$) reflecting steric effect of the methyl group in the last two, **II** and **III**. Efficient stabilization of the incipient cationic charge in the TS by the methyl group on C_α may also contribute to the greater reactivity of **II** compared to **III**.

The Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z) coefficients are collected in Table 2. The magnitude of these coefficients increases, and hence the TS shifts toward a later position along the reaction coordinate, *i.e.*, the extent of bond-making and -breaking increases, with a stronger nucleophile ($\delta\sigma_X<0$) and nucleofuge ($\delta\sigma_Z>0$). This type of TS variation with the substituents in the nucleophile (σ_X) and nucleofuge (σ_Z) is required by equation 2 when ρ_{XZ} is negative,[1] which is indeed observed as shown in Table 3. The trend of TS variation is also supported by the secondary kinetic isotope effects involving deuterated anilines. Reference to Table 4 reveals that a stronger nucleophile ($X=p$-CH_3O) and nucleofuge ($Z=p$-NO_2) leads to a smaller k_H/k_D value

Table 1. Second Order Rate Constants, $k_2\times10^6$ dm^3 mol^{-1} s^{-1}, for Reactions of *Z*-substituted 2-Phenyl-1-propyl Arenesulfonates with *X*-substituted Anilines and Benzylamines in MeOH at 55.0 ℃

Nucleophile	*X*	*Z*			
		p-CH_3	H	*p*-Cl	*p*-NO_2
Aniline	*p*-CH_3O	15.8	18.6	27.5	79.2
	p-CH_3	11.0	13.2	19.1	52.5
	H	6.03	7.76 (17.1)[a]	9.77	24.5
	p-Cl	2.75	3.16	4.37	9.77
	m-NO_2	0.501	0.562	0.692	1.12
	p-NO_2	0.388	0.437	0.550	0.832
Benzylamine	*p*-CH_3O	31.6	34.7	43.7	80.2
	p-CH_3	22.4	25.8	30.2	54.0
	H	15.1	16.2	19.5	28.9
	p-Cl	9.55	10.5	12.0	17.4
	p-NO_2	3.45	3.63	3.89	4.57

[a] At 65.0℃

Table 2. The Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z) coefficients for Reactions of *Z*-substituted 2-Phenyl-1-propyl arenesulfonates with *X*-substituted Anilines and Benzylamines

Nucleophile	*Z*	ρ_X[a]	β_X[b]	*X*	ρ_Z[a]	β_Z[b]
Aniline	*p*-CH_3O	−1.53	0.51	*p*-CH_3O	0.76	−0.25
	H	−1.57	0.53	*p*-CH_3	0.73	−0.24
	p-Cl	−1.63	0.53	H	0.63	−0.21
	p-NO_2	−1.89	0.64	*p*-Cl	0.59	−0.20
				m-NO_2	0.37	−0.12
				p-NO_2	0.35	−0.12
Benzylamine	*p*-CH_3	−0.89	0.76	*p*-CH_3O	0.44	−0.15
	H	−0.92	0.79	*p*-CH_3	0.40	−0.13
	p-Cl	−0.98	0.84	H	0.30	−0.10
	p-NO_2	−1.16	0.99	*p*-Cl	0.28	−0.09
				p-NO_2	0.13	−0.04

[a] The σ values were taken from J. A. Dean, "*Handbook of Organic Chemistry*" McGraw-Hill, New York, 1987, Table 7-1. The correlation coefficients were better than 0.994 in all cases. [b] The pK_a values were taken from: J. A. Dean, "*Handbook of Organic Chemistry*" McGraw-Hill, New York, 1987, Table 8 for anilines, and from R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.* **1986**, *108*, 5536 for arenesulfonates involving methyl transfers. $X=p$-CH_3O is excluded from the Brönsted plot for β_X (benzylamine) due to unreliable pK_a value listed. The correlation coefficients were better than 0.994 in all cases.

Table 3. Cross-interaction Constants, ρ_{XZ} and β_{XZ}, for Some Nucleophilic Substitution Reactions

Reaction	Solvent	Temp.℃	ρ_{XZ}	β_{XZ}
1. $XC_6H_4NH_2+CH_3CH_2OSO_2C_6H_4Z$[8]	MeOH	65	0.33	0.19
	MeCN	65	0.34	0.21
2. $XC_6H_4NH_2+(CH_3)_3SiCH_2OSO_2C_6H_4Z$[12]	MeOH	65	0.31	0.18
	MeCN	65	0.33	0.20
$XC_6H_4CH_2NH_2+(CH_3)_3SiCH_2OSO_2C_6H_4Z$[12]	MeCN	65	0.08	0.12
3. $XC_6H_4NH_2+(CH_3)_3CCH_2OSO_2C_6H_4Z$[13]	MeOH	55	0.31	0.18
$XC_6H_4CH_2NH_2+(CH_3)_3CCH_2OSO_2C_6H_4Z$[13]	MeOH	55	0.11	0.15
4. $XC_6H_4NH_2+C_6H_5CH(CH_3)OSO_2C_6H_4Z$[14]	MeOH	25	−0.56	−0.32
5. $XC_6H_4NH_2+C(CH_3)_3CHC_6H_5OSO_2C_6H_4Z$[15]	MeOH	35	0.0	0.0
6. $XC_6H_4NH_2+C_6H_5CH_2OSO_2C_6H_4Z$[16]	MeOH	30	−0.10	−0.06
7. $XC_6H_4NH_2+C_6H_5CH_2CH_2OSO_2C_6H_4Z$[4]	MeOH	65	−0.45	−0.28
8. $XC_6H_4CH_2NH_2+C_6H_5CH_2CH_2OSO_2C_6H_4Z$[17]	MeOH	65	−0.13	−0.21
9. $XC_6H_4NH_2+C_6H_5CH_2CH(CH_3)SO_2C_6H_4Z$[5]	MeOH	65	0.16	0.02
10. $XC_6H_4NH_2+C_6H_5CH(CH_3)CH_2OSO_2C_6H_4Z$[a]	MeOH	55	−0.39(0.999)[b]	−0.23(0.999)
$XC_6H_4CH_2NH_2+C_6H_5CH(CH_3)CH_2OSO_2C_6H_4Z$[a]	MeOH	55	−0.29(0.996)	−0.42(0.995)

[a]This work; [b]The values in parenthesis are the correlation coefficients at 99% confidence level.

Table 4. The Kinetic Isotope Effects (k_H/k_D) for the Reaction of 2-Phenyl-1-propyl *Z*-arenesulfonates with Deuterated *X*-anilines ($XC_6H_4ND_2$) in Deuterated Methanol (CH_3OD) at 55.0℃

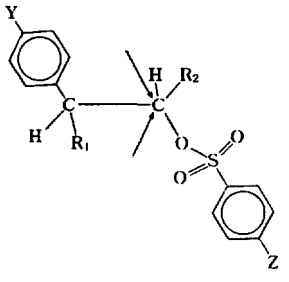
X	*Z*	MeOH (M^{-1} s^{-1})	MeOD (M^{-1} s^{-1})	k_H/k_D
p-CH_3O	*p*-NO_2	79.2 (± 1)[a] ×10^{-6}	88.6 (± 2) ×10^{-6}	0.894± 0.007[b]
p-CH_3O	*p*-CH_3	15.8 (± 0.6)×10^{-6}	17.5 (± 0.2)×10^{-6}	0.901± 0.008
p-Cl	*p*-NO_2	9.77(± 0.5)×10^{-6}	10.5 (± 0.7)×10^{-6}	0.924± 0.010
p-Cl	*p*-CH_3	2.75(± 0.4)×10^{-6}	2.94(± 0.5)×10^{-6}	0.935± 0.007

[a]Standard deviation, [b]Standard error.[18]

reflecting a greater degree of steric crowding due to a greater degree of bond formation.

It is interesting to note in Table 3 that the reaction type with a negative ρ_{XZ} value is rather rare, and occurs only in the S_N2 processes at a benzylic and primary 2-phenylethyl carbon centers. The magnitude of β_Z in Table 2, is relatively smaller, especially for the reactions with benzylamines, than those for the normal S_N2 processes, $\beta_Z \cong -0.30 \sim -0.45$,[8] suggesting a relatively low degree of bond cleavage in the TS. This is in line with a relatively greater magnitude of ρ_{XZ} and β_{XZ} for **III** in Table 3. For the reactions with anilines, the magnitude of ρ_{XZ} (= −0.39) and β_{XZ} (= −0.23) is somewhat greater than those for other S_N2 processes at a primary carbon center (ρ_{XZ}=0.31-0.33 and β_{XZ}=0.18-0.19). It is to be noted that very little change in $|\rho_{XZ}|$ may be expected for the 10℃ rise in temperature.[9] The magnitude of ρ_{XZ} and β_{XZ} is especially greater for the reactions with benzylamine; the magnitude is more than twice of that for other reactions at a primary carbon center, reactions 2, 3, and 8 in Table 3. Since the magnitude of ρ_{XZ} (and β_{XZ}) is a measure of the TS tightness, these larger values obtained in this work seem to reflect a somewhat tighter TS for the reactions studied in this work, Eq. (3). In view of our earlier results, however, the following alternative interpretation seems more plasusible.

The structure of the 2-phenylethyl arenesulfonate analogues, **IV**, suggests that the normal rear-side S_N2 attack by an aniline molecule must be sterically inhibited due to the relatively large size of the (*Y*) benzene ring (*e.g.* the Taft steric constants[10] are −0.07 and −0.38 for CH_3 and C_6H_5) lending probability to a front-side attack. In the front-side S_N2 attack the nucleophile and leaving group can come close together leading to a greater magnitude of ρ_{XZ} (and β_{XZ}). Indeed such a frontal attack has been predicted for the reactions of I based on the large magnitude of ρ_{XZ} (and β_{XZ}) observed.[4]



IV

I, $R_1=R_2=H$
II, $R_1=H$, $R_2=CH_3$
III, $R_1=CH_3$, $R_2=H$

For the 1-methyl analogue, **III**, however, the frontal attack should be somewhat limited by an extra methyl group on C_β. In any of the reactions of **I-III** it is hard to conceive of the total front-side attack process, since the normal rear-side attack process is intrinsically more favorable and can compete with the frontal process.[11] Therefore, the relatively

greater magnitude of ρ_{XZ} (β_{XZ}) obtained for **I-III** appears most likely to result from partial involvement of the frontal process. The extent of such contribution may decrease in the order **I>II>III**, considering an additional steric inhibition by the methyl group on C_α and C_β in **II** and **III** respectively. The increment of the magnitude, $\Delta\rho_{XZ}=\rho_{XZ(obsd)}-\rho_{XZ(normal)}$, is 0.14, 0.06 and 0.05 for the reactions of **I**, **II** and **III**, respectively, assuming the normal $|\rho_{XZ}|$ value in MeOH at 65.0℃ of 0.31[6] and 0.10[7] for the reactions at a primary and secondary carbon atom. The decrease in the increment, $\Delta\rho_{XZ}$, should reflect the decrease in the extent of the fronatal process contribution.

The greater increase in ρ_{XZ} and β_{XZ} for the reactions of **III** with benzylamines may arise from a greater contribution of the frontal process due to a greater degree of steric inhibition in the rear-side attack by the relatively larger nucleophile, benzylamine.

We therefore conclude that in the S_N2 reactioins of 2-phenylethyl arenesulfonates, **I-III**, with anilines and benzylamines the frontal attack process contribute partially. The contribution of the frontal process results in a greater magnitude of ρ_{XZ} and β_{XZ}, and the contribution is greater, the greater is the steric inhibition in the rear-side attack, and the lower is the steric requirement in the front-side attack.

Experimental

Materials. Merck analytical grade methanol was used without further purification. The nucleophiles, aniline, were Aldrich G.R. purchased, which were redistilled or recrystallized before use. Preparation of deuterated anilines were as described previously.[3,6] The analysis (NMR spectroscopy) of the deuterated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made.

Substrates, 2-phenyl-1-propyl arenesulfonates, were prepared by reacting Aldrich G.R. 1-phenyl-2-propanol with benzenesulfonyl chlorides.[19] The substrates synthesized were confirmed by spectral and elementary analyses as follows.

$C_6H_5CH(CH_3)CH_2OSO_2C_6H_5$. ν_{max} (neat) 1360, 1195 (SO_2), 1020 (SO) and 815 cm^{-1} (S-O-C); δ_H ($CDCl_3$) 1.2 (β-CH_3, 3H, d), 2.9 (CH, 1H, m), 4.1 (-CH_2-, 2H, d), 7.2-7.4 (phenyl, 10H, m). (Found: C, 73.7; H, 6.7. Calc. for $C_{15}H_{16}O_3S$: C, 73.8, H, 6.8%).

$C_6H_5CH(CH_3)CH_2OSO_2C_6H_4$-*p*-$CH_3$. mp. 45℃, ν_{max} (KBr) 1350, 1165 (SO_2), 1020 (SO) and 810 cm^{-1} (S-O-C); δ_H ($CDCl_3$) 1.3 (β-CH_3, 3H, d), 1.9 (*p*-CH_3, 3H, s), 2.8 (CH, 1H, m), 4.0 (-CH_2-, 2H, d), 7.2-7.8 (phenyl, 9H, m). (Found: C, 74.2; H, 7.1 Calc. for $C_{16}H_{18}O_3S$: C, 74.4; H, 7.0%).

$C_6H_5CH(CH_3)CH_2OSO_2C_6H_4$-*p*-Cl. mp. 74-75℃, ν_{max} (KBr) 1355, 1180 (SO_2), 1010 (SO) and 810 cm^{-1} (S-O-C); δ_H ($CDCl_3$) 1.3 (β-CH_3, 3H, d), 2.9 (CH, 1H, m), 4.2 (-CH_2-, 2H, d), 7.2-7.8 (phenyl, 9H, m). (Found: C, 74.2; H, 6.1 Calc. for $C_{15}H_{15}O_3S$: C, 74.1; H, 6.2%).

$C_6H_5CH(CH_3)CH_2OSO_2C_6H_4$-*p*-$NO_2$. mp. 108℃, ν_{max} (KBr) 1530, 1345 (NO_2), 1180 (SO_2) and 812 cm^{-1} (S-O-C); δ_H ($CDCl_3$) 1.3 (β-CH_3, 3H, d), 2.8 (CH, 1H, m), 4.2 (-CH_2-, 2H, d), 7.2-7.9 (phenyl, 9H, m). (Found: C, 62.4; H, 5.1 Calc. for $C_{15}H_{15}O_5NS$: C, 62.3; H, 5.2%).

Kinetic procedures. The rate measurements for the reactions of 2-phenyl-1-propyl arenesulfonates with anilines were attempted in acetonitrile but the rates were found to be too slow for our conductivity apparatus. Rates were measured conductimetically at 55.0± 0.05℃ in methanol. The conductivity bridge used in this work was a self-made cumputer interface automatic A/D converter conductivity bridge. Substrates were injected with a syringe. Pseudo-first order rate constants, k_{obs}, were determined by the Guggenheim method[20] with a large excess of aniline; [2-phenyl-1-propyl arenesulfonate]=10^{-3} mol dm^{-3} and [aniline]=0.025-0.50 mol dm^{-3}. Second-order rate constnat, k_2, were obtained from the slope of the plot of k_{obs} *vs.* [aniline] with more than four concentrations of aniline. The intercept of this plot was almost zero ranging from 1.6×10^{-7} to 7.1×10^{-11} s^{-1} indicating that many side reactions including methanolysis are insignificant during the rate measurements.

Product analysis. 2-phenyl-1-propyl arenesulfonate was reacted with excess aniline with stirring for more 15 half-lives at 55.0℃ in methanol, and the products were isolated by evaporating the solvent under reduced pressure. The TLC analysis of the product mixture gave three spots (silica gel, glass plate, 10% ethyl acetate/*n*-hexane).

R_f values. 0.62 ($C_6H_5CH(CH_3)CH_2NHC_6H_5$), 0.43 ($C_6H_5CH(CH_3)CH_2OSO_2C_6H_5$), 0.30 ($C_6H_5NH_2$), 0.02 ($C_6H_5NH_3^+$-$OSO_2C_6H_5$). The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate/*n*-hexane). Analysis of the products, $C_6H_5CH(CH_3)CH_2NHC_6H_5$: δ_H ($CDCl_3$) 1.2 (β-CH_3, 3H, d), 2.7 (CH, 1H, m), 3.0 (NH, 1H, broad), 4.2 (-CH_2-, 2H, d) and 7.2-7.6 (phenyl, 10H, m). $C_6H_5OSO_2$-NH_3^+-C_6H_5: δ_H ($CDCl_3$) 4.8 (NH_3^+, 3H, broad) and 7.1-7.7 (phenyl, 10H, m). The analysis of the reaction mixture, 2-phenyl-2-propyl arenesulfonate with aniline, by NMR at appropriate intervals for at least 15 half-lifes under exactly the same reaction conditions did not give any detectable change due to aryl participation.

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