

Kinetics and Mechanism of Reactions between 2-Phenylethyl Benzenesulphonates and Anilines in Methanol

Ikchoon Lee,* Yong Hoon Choi, and Hai Whang Lee
Department of Chemistry, Inha University, Incheon, 160 Korea
Byung Choon Lee

Department of Science Education, Choongbuk National University, Chongju, 310 Korea

Kinetics of reactions between 2-phenylethyl benzenesulphonates and anilines in methanol at 65.0 °C have been studied; the mechanism is discussed on the basis of cross interaction constants, ρ_{ij} . The overall reaction was found to proceed by a dissociative S_N2 mechanism with a relatively small degree of aryl participation. The fraction of the phenonium ion intermediate captured by the nucleophile, aniline, in the aryl-assisted pathway has been shown to increase with a stronger nucleophile, and a four-centre transition state in an intermolecular S_Ni mechanism is suggested for the aryl-unassisted pathway.

Solvolyses of 2-phenylethyl compounds have been the subject of many studies in connection with the involvement of an aryl-assisted pathway.¹ It is now well established that such solvolyses proceed through discrete aryl-assisted (k_A) and aryl-unassisted (k_N) pathways (Scheme 1), *i.e.* solvent and neighbouring aryl group compete in rate-determining displacement of the leaving group.^{1c}

Recently we have introduced mechanistic criteria for organic reactions in solution based on cross interaction constants, ρ_{ij} [equation (1)].² The cross interaction constants reflect the

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

strength of indirect interaction between substituents in fragments i and j through reaction centres R_i and R_j in the transition state (TS) as illustrated in Scheme 2. Note that the fragments comprising the TS are the nucleophile, the substrate, and the leaving group in a nucleophilic substitution reaction.^{2a} The individual cross interaction constants ρ_{ij} can be obtained by varying substituents (with constants σ_i and σ_j) simultaneously and subjecting the series of k_{ij} values determined to a multiple linear regression analysis using equation (1). According to equation (1) ρ_{ij} can be defined mathematically as in equation (2), indicating, for example, that a more electron-withdrawing

$$\rho_{ij} = \frac{\partial^2 \log k_{ij}}{\partial \sigma_i \partial \sigma_j} = \frac{\partial \rho_j}{\partial \sigma_i} = \frac{\partial \rho_i}{\partial \sigma_j} \quad (2)$$

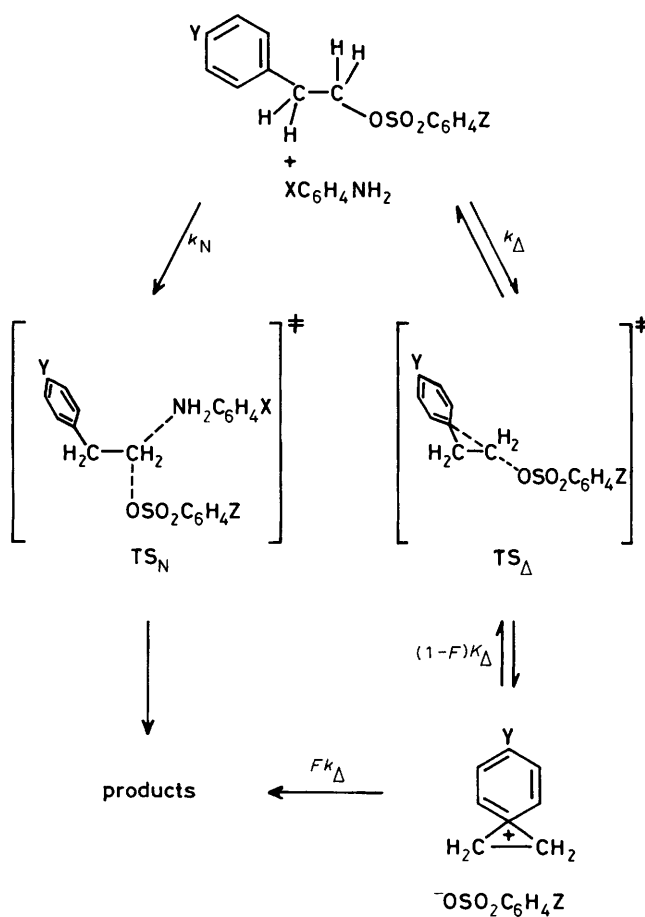
substituent (EWS) in fragment i ($d\sigma_i > 0$), leading to a greater negative ρ_j value ($d\rho_j < 0$), will give a negative ρ_{ij} value, and so on.

It has been shown that the distance r_{ij} between two reaction centres R_i and R_j (Scheme 2), *i.e.* the degree of bond-making or -breaking in the TS, is a logarithmic inverse function of $|\rho_{ij}|$ ^{3,4} [equation (3), where α and β are universal constants which

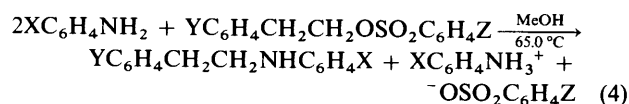
$$r_{ij} = \alpha + \beta \log (1/|\rho_{ij}|) \quad (3)$$

depend only on the rows of the Periodic Table for the two atoms being bonded⁴]. Other conditions being equal, r_{ij} will be inversely related to the magnitude of ρ_{ij} ; a greater (smaller) $|\rho_{ij}|$ will indicate a tighter (looser) TS.

We have carried out kinetic studies of the reactions between 2-phenylethyl benzenesulphonates and anilines in methanol at 65.0 °C [equation (4)], and determined three kinds of cross



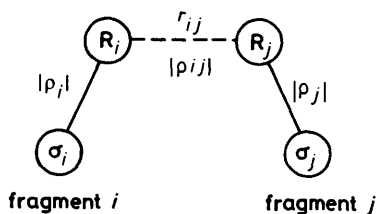
Scheme 1.



X = *p*-MeO, *p*-Me, H, or *p*-Cl
Y = *p*-MeO, *p*-Me, H, *p*-Br, or *p*-NO₂
Z = *p*-Me, H, *p*-Cl, or *p*-NO₂

Table 1. Second-order rate constants ($10^4 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the reactions between $\text{YC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$ and $\text{XC}_6\text{H}_4\text{NH}_2$ in methanol at 65.0 °C

Z	X	Y				
		<i>p</i> -MeO	<i>p</i> -Me	H	<i>p</i> -Br	<i>p</i> -NO ₂
<i>p</i> -Me	<i>p</i> -MeO	2.18	1.75	1.61	1.49	1.32
	<i>p</i> -Me	1.76	1.38	1.24	1.16	1.02
	H	1.14	0.902	0.776	0.708	0.616
H	<i>p</i> -Cl	0.628	0.490	0.427	0.380	0.315
	<i>p</i> -MeO	3.22	2.69	2.47	2.35	2.12
	<i>p</i> -Me	2.44	1.93	1.76	1.65	1.45
<i>p</i> -Cl	H	1.54	1.27	1.10	1.05	0.891
	<i>p</i> -Cl	0.891	0.671	0.603	0.550	0.452
	<i>p</i> -MeO	5.73	5.22	4.89	4.74	4.37
<i>p</i> -NO ₂	<i>p</i> -Me	4.47	3.96	3.63	3.48	3.02
	H	2.79	2.29	2.11	1.98	1.68
	<i>p</i> -Cl	1.41	1.15	1.05	1.00	0.891
<i>p</i> -NO ₂	<i>p</i> -MeO	23.0	21.7	20.9	20.6	20.0
	<i>p</i> -Me	17.8	15.7	14.8	14.4	13.3
	H	9.26	8.00	7.45	7.05	6.31
	<i>p</i> -Cl	4.53	3.79	3.45	3.31	2.81



Scheme 2.

interaction constants, ρ_{XY} , ρ_{YZ} , and ρ_{XZ} . We discuss here various mechanistic details of the reactions based on the signs and magnitudes of these cross interaction constants.

Results and Discussion

Second-order rate constants, k_2 , for the reactions of 2-phenylethyl benzenesulphonates with anilines in methanol are summarized in Table 1. The values lie in the range 10^{-5} – $10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 10–20 times greater than those of the methanolysis rate constants.⁵

The rate is seen to increase with a more electron-withdrawing substituent in the leaving group ($Z = \text{EWS}$) and with a more electron-donating substituent (EDS) in the nucleophile ($X = \text{EDS}$). It is however relatively insensitive to substituent variation in the substrate (Y); only a slight rate enhancement is induced by $Y = \text{MeO}$ ($k_{p\text{-MeO}}/k_{\text{H}} \approx 1.4$ for $X = Z = \text{H}$). This is in contrast with the behaviour of the same compound in methanol at 55.0 °C ($k_{p\text{-MeO}}/k_{\text{H}} \approx 2.0$).⁵ Since the MeO substituent is a strong phenyl group activator for the aryl-assisted process, k_{Δ} ,^{1c} such a small rate increase must indicate that the aryl-assisted pathway is less important in the nucleophilic displacement reaction (4) than in the solvolysis. This means that the fraction F represents only one of the three possible ways of phenonium ion capture, *i.e.* displacement by the nucleophile aniline, by the solvent methanol, with reversion to the reactants, whereas in the solvolysis the solvent competes only with the third path (reverse reaction).

The k_2 values in Table 1 were subjected to a multiple linear regression analysis⁶ using equation (1), and three kinds of cross interaction constant, ρ_{XY} , ρ_{YZ} , and ρ_{XZ} , were determined,

Table 2. Hammett coefficients, ρ_X , ρ_Y , ρ_Z , and cross interaction constants ρ_{ij} for reaction (4) ($R = \text{multiple correlation coefficient}$)⁶

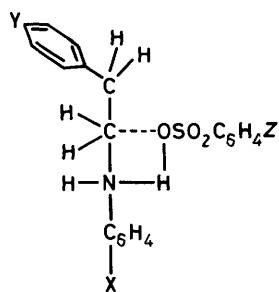
(a) ρ_X , ρ_Y , and ρ_{XY}				
Z	ρ_X	ρ_Y	ρ_{XY}	R
<i>p</i> -Me	-1.16	-0.17	-0.11	0.998
H	-1.22	-0.15	-0.12	0.998
<i>p</i> -Cl	-1.34	-0.12	-0.13	0.999
<i>p</i> -NO ₂	-1.58	-0.10	-0.17	0.999
(b) ρ_Y , ρ_Z , and ρ_{YZ}				
X	ρ_Y	ρ_Z	ρ_{YZ}	R
<i>p</i> -MeO	-0.11	1.17	0.10	1.000
<i>p</i> -Me	-0.14	1.14	0.08	0.999
H	-0.16	1.03	0.07	0.999
<i>p</i> -Cl	-0.18	0.96	0.07	0.999
(c) ρ_X , ρ_Z , and ρ_{XZ}				
Y	ρ_X	ρ_Z	ρ_{XZ}	R
<i>p</i> -MeO	-1.14	0.99	-0.38	1.000
<i>p</i> -Me	-1.19	1.04	-0.45	0.999
H	-1.23	1.06	-0.45	0.999
<i>p</i> -Br	-1.26	1.08	-0.44	0.999
<i>p</i> -NO ₂	-1.33	1.10	-0.49	0.999

together with ρ_X , ρ_Y , and ρ_Z values. The results are summarized in Table 2.

The magnitude of ρ_X in Table 2(a) increases with a more electron-withdrawing substituent in the leaving group, indicating an increase in charge transfer from the nucleophile, and hence an increase in bond formation, as the leaving ability of the leaving group increases. This is supported by the observation of a parallel increase in the magnitude of ρ_{XY} with a more electron-withdrawing substituent in the leaving group. All the ρ values in Table 2(a) (ρ_X , ρ_Y , and ρ_{XY}) are negative, correctly reflecting a somewhat dissociative TS structure of the normal intrinsic-controlled reaction.^{7,8} Of the two factors comprising the activation energy of a reaction (ΔG^\ddagger), the intrinsic (ΔG_o^\ddagger) and thermodynamic (ΔG°) barriers^{7,8} in the Marcus equation $\Delta G^\ddagger = \Delta G_o^\ddagger + \Delta G^\circ/2 + (\Delta G^\circ)^2/16\Delta G_o^\ddagger$,⁹ either can be dominant; when the intrinsic barrier is dominant (intrinsic-controlled reaction) effects of substituents on TS variation follow the quantum mechanical (QM) model.¹⁰ Thus a stronger nucleophile and/or nucleofuge is predicted to lead to a greater degree of bond-breaking and/or -formation, resulting in a 'late' TS, in contrast to thermodynamic control. For example, according to the Bell-Evans-Polanyi (BEP) principle,¹¹ activation energy is proportional to energy (or heat) of reaction; a lower activation barrier is obtained for a more exothermic reaction with the TS nearer to the reactants in structure. Thus a stronger nucleophile or nucleofuge should lead to an 'early' TS; TS variation of this type can be predicted by the potential energy surface (PES) model.^{10a,12}

A negative value of ρ_{XY} implies that a more electron-withdrawing substituent ($d\sigma_Y > 0$) in the substrate leads, according to equation (2), to greater degree of bond formation ($d\rho_X < 0$). A slight decrease in the magnitude of ρ_Y with $Z = \text{EWS}$ in the leaving group suggests that the increase in bond formation is somewhat greater than that in bond breaking as the substituent Z becomes more electron-withdrawing.

The values of $|\rho_{XY}|$ (0.10–0.17) are relatively small, in general slightly greater than those for phenacyl benzenesulphonates ($\text{YC}_6\text{H}_4\text{COCH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$; 0.07–0.14),⁸ but is smaller than those for 1-phenylethyl benzenesulphonates ($\text{YC}_6\text{H}_4\text{CHMeOSO}_2\text{C}_6\text{H}_4\text{Z}$; 0.20–0.25)^{2c} under similar reaction conditions. These unusually small $|\rho_{XY}|$ values can be attributed to the



Scheme 3.

participation of the aryl-assisted pathway in the reaction of 2-phenylethyl benzenesulphonates; in the aryl-assisted pathway we expect no interaction, *i.e.* $\rho_{XY} \approx 0$, between substituents X in the nucleophile and Y in the substrate at the TS, since the TS for the aryl-assisted path (TS_A in Scheme 1) does not include the nucleophile. Another reason for the small $|\rho_{XY}|$ values could be the extra CH₂ group in the substrate, which extends the distance between the substituent Y and the reaction centre R_Y, causing a decrease in the intensity of interaction between the two substituents X and Y in the aryl-unassisted pathway. This is also reflected in the small $|\rho_{YZ}|$ values in Table 2(b). The values of $|\rho_{YZ}|$ (0.06–0.09) are smaller than for the similar reactions of benzyl benzenesulphonates (YC₆H₄CH₂OSO₂C₆H₄Z; 0.11–0.35)^{2a,13} but similar to those for the methanolysis of 2-phenylethyl benzenesulphonates (0.07–0.11).⁵

Reference to Table 2(b) reveals that the magnitude of ρ_Y decreases and that of ρ_Z increases as the nucleophile becomes stronger (X = EDS); the increases in the degree of bond-formation ($\Delta|\rho_Y| < 0$) and bond-breaking ($\Delta\rho_Z > 0$) with a stronger nucleophile are again manifestations of the intrinsic-controlled nature of the reaction.¹⁰

The value of ρ_{YZ} is, however, seen to increase, indicating that bond breaking is less, with a more electron-donating substituent in the nucleophile. This contradictory result may also be rationalized by the participation of an aryl-assisted pathway: interaction between substituents Y and Z will be enhanced in TS_A, since a by-pass bridge is formed providing an additional interaction route³ as well as shortening the distance between the two substituents. A stronger nucleophile should have a greater chance of capturing the phenonium-ion intermediate resulting in a greater fraction *F*. Thus the stronger the nucleophile, the greater will be the fraction *F*, which should increase the proportion of reaction proceeding through the aryl-assisted pathway.

Finally in Table 2(c) we see that ρ_X and ρ_{XZ} are both negative, and their magnitudes as well as those of ρ_Z increase with a more electron-withdrawing substituent in the substrate. The negative sign of the ρ_{XZ} values, again, reflects correctly the observation that a stronger nucleophile and/or nucleofuge leads to a 'late' TS with a greater degree of bond-breaking and/or -making, in accord with the predictions of the QM model.¹⁰ Here again we witness a parallel increase in the magnitudes of ρ_X , ρ_Z , and ρ_{XZ} , which may be simply interpreted as a result of a greater degree of bond-making as compared with bond-breaking.

We find, however, that the ρ_{XZ} values are anomalously large, and similar to those for the similar reactions of 1-phenylethyl benzenesulphonates.^{2c} Thus it seems likely that the two reactions proceed by the same mechanism, *i.e.* a four-centre TS in an intermolecular S_Ni mechanism¹⁴ (Scheme 3). In this mechanism the nucleophile is required to approach from the front, forming a by-pass hydrogen bridge, which greatly enhances the interaction between substituents X and Z. A molecular model indeed indicates that frontal approach of the

nucleophile is preferred to the rear-side attack. We are attempting to confirm this by MO calculations.

Somewhat smaller $|\rho_{XZ}|$ values for compounds with Y = EDS constitute further support for the involvement of the aryl-assisted path, since $|\rho_{XZ}|$ should be zero in the absence of the nucleophile.

The results of the present studies can be summarized as follows.

(i) The nucleophilic substitution reactions of 2-phenylethyl benzenesulphonates with anilines proceed through discrete aryl-assisted and -unassisted pathways.

(ii) The fraction of the phenonium-ion intermediate captured by the nucleophile, aniline, leading to the products increases with a stronger nucleophile.

(iii) The aryl-unassisted pathway proceeds *via* a four-centre TS in an intermolecular S_Ni mechanism.

(iv) The overall reaction proceeds by a dissociative, frontal nucleophilic displacement with a relatively small degree of aryl participation.

Experimental

Materials.—Methanol and anilines were used after appropriate purification as described previously.^{5,8,13} 2-Phenylethyl benzenesulphonates were prepared following Tipson's method¹⁵ and purified before use as described.

2-*p*-Tolylethyl toluene-*p*-sulphonate had m.p. 66–68 °C (lit.,¹⁶ 69–70 °C); ν_{\max} . 1 595 (C–C), 1 360 (SO₂), 1 175 (SO₂), 1 020 (SO), and 815 cm⁻¹ (S–O–C); δ 2.3 (CH₃, 3 H, s), 2.4 (CH₃, 3 H, s), 2.9 (β-CH₂, 2 H, t), 4.2 (α-CH₂, 2 H, t), and 7.4 (aromatic, 8 H, m) (Found: C, 66.1; H, 6.3. Calc. for C₁₆H₁₈O₃S: C, 66.2; H, 6.25%).

2-*p*-Tolylethyl benzenesulphonate had m.p. 61–62.5 °C (lit.,¹⁶ 61.5–62.5 °C); ν_{\max} . 1 600 (C–C), 1 315 (SO₂), 1 175 (SO₂), 1 015 (SO), and 820 cm⁻¹ (S–O–C); δ 2.3 (CH₂, 3 H, s), 2.9 (β-CH₂, 2 H, t), 4.2 (α-CH₂, 2 H, t), 7.0 (aromatic, 4 H, s), and (aromatic, 4 H, m) (Found: C, 65.1; H, 5.8. Calc. for C₁₅H₁₆O₃S: C, 65.2; H, 5.8%).

2-*p*-Tolylethyl *p*-chlorobenzenesulphonate had m.p. 56–57 °C; ν_{\max} . 1 590 (C–C), 1 355 (SO₂), 1 180 (SO₂), 1 010 (SO), and 1 005 cm⁻¹ (C–Cl); δ 2.3 (CH₃, 3 H, s), 2.8 (β-CH₂, 2 H, t), 4.2 (α-CH₂, 2 H, t), and 7.3 (aromatic, 8 H, m) (Found: C, 57.9; H, 4.9. C₁₅H₁₅ClO₃S requires C, 58.0; H, 4.9%).

2-*p*-Tolylethyl *p*-nitrobenzenesulphonate had m.p. 84–86 °C (lit.,¹⁶ 84–85 °C); ν_{\max} . 1 605 (C–C), 1 545 (NO₂), 1 360 (NO₂), 1 310 (SO₂), 1 180 (SO₂), and 1 030 cm⁻¹ (SO); δ 2.3 (CH₃, 3 H, s), 2.9 (β-CH₂, 2 H, t), 4.4 (α-CH₂, 2 H, t), 7.1 (aromatic 4 H, s), and 8.2 (aromatic, 4 H, m) (Found: C, 55.9; H, 4.35; N, 4.35. Calc. for C₁₅H₁₅NO₅S: C, 56.1; H, 4.7; N, 4.4%).

Rate Constants.—Rates were measured conductimetrically at 65.0 °C in methanol. Pseudo-first-order rate constants, k_1^{obs} , were determined by the Guggenheim method¹⁷ with a large excess of aniline, and second-order rate constants, k_2 , were then obtained from the slope of a plot of k_1^{obs} versus [aniline] with a greater than four-fold excess of aniline [equation (5)]. The

$$k_1^{\text{obs}} = k_1 + k_2[\text{aniline}] \quad (5)$$

methanolysis rate constants, k_1 , given as an intercept of the plot, were 10–20 times less than the k_2 values.⁵ These k_1 values agreed with the methanolysis rate constants determined independently. The linearity of the plot [equation (5)] was good in general, with correlation coefficients of better than 0.998 with 99% confidence limits.¹⁸ The k_2 values listed in Table 1 are the averages obtained by more than duplicate runs, and were reproducible to within $\pm 5\%$.

Product Analysis.—Products of the reaction of 2-phenylethyl tosylate with aniline ($\text{PhCH}_2\text{CH}_2\text{NHPh}$ and $\text{MeC}_6\text{H}_4\text{OSO}_2^- \text{NH}_3^+\text{Ph}$) were identified by t.l.c., i.r., n.m.r., and elemental analyses. T.l.c. analysis showed three spots, corresponding to two reactants [$\text{PhCH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Me}$ (R_F 0.26) and aniline (R_F 0.19)] and one product [$\text{PhCH}_2\text{CH}_2\text{NHPh}$ (R_F 0.52)]; the solvent was cyclohexane–ethyl acetate (9:1).

N-(2-Phenylethyl)aniline showed ν_{max} 3 400 (secondary aromatic NH) and 1 320 cm^{-1} (C–N of secondary aromatic amine); δ 7.0 (Ph, 10 H, m), 4.4 (NH, 1 H, m), 3.3 (α -CH₂, 2 H, t), and 2.8 (β -CH₂, 2 H, t).

Anilinium toluene-p-sulphonate, insoluble in organic solvents (benzene, chloroform, diethyl ether, or light petroleum) had m.p. 210–215 °C; ν_{max} 3 400, 2 600, 1 600, and 1 500 (NH_3^+), and 1 200, 1 150, 560, and 480 cm^{-1} (SO_2) (Found: C, 58.3; H, 5.7; N, 5.3. $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$ requires C, 58.6; H, 6.1; N, 5.3%).

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