Competitive Reaction Pathways in the Nucleophilic Substitution Reactions of Aryl Benzenesulfonates with Benzylamines in Acetonitrile

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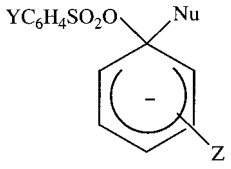
The reactions of aryl benzenesulfonates ($YC_6H_4SO_2OC_6H_4Z$) with benzylamines ($XC_6H_4CH_2NH_2$) in acetonitrile at 65.0 °C have been studied. The reactions proceed competitively by S−O (k_{S-O}) and C−O (k_{C-O}) bond scission, but the former provides the major reaction pathway. On the basis of analyses of the Hammett and Brönsted coefficients together with the cross-interaction constants ρ_{XY}, ρ_{YZ}, and ρ_{XZ}, stepwise mechanisms are proposed in which the S−O bond cleavage proceeds by rate-limiting formation of a trigonal-bipyramidal pentacoordinate (TBP-5C) intermediate, whereas the C−O bond scission takes place by rate-limiting expulsion of the sulfonate anion ($YC_6H_4SO_3^-$) from a Meisenheimer-type complex.

Introduction

Nucleophilic substitution reactions of aryl benzenesulfonate, **1**, exhibit interesting mechanistic variations depending on the substrate (i.e., on substituents Y and Z), nucleophile, and solvent.[1] For example, thiophenoxide nucleophiles ($XC_6H_4S^-$) have been reported to react exclusively by the C−O bond cleavage (k_{C-O}) involving a Meisenheimer complex, **2**, while nitrogen and oxygen base nucleophiles react through complex S−O (k_{S-O}) and C−O bond cleavage (k_{C-O}) paths[1b] (Scheme 1). The S−O bond cleavage path is a simple nucleophilic displacement at sulfur with a phenoxide leaving group, whereas the C−O bond cleavage path is a nucleophilic aromatic substitution (S_NAr) with sulfonate leaving group. The rate of C−O bond cleavage should be influenced by the substituent Z, since the stability of the complex **2** depends strongly on the electron-withdrawing power of the substituent Z and also on the nucleofugality of the leaving group, $YC_6H_4SO_3^-$ in **2**, which in turn should depend on the substituent on the ring Y. There have been no systematic kinetic studies involving the effects of substituents on phenoxides (Z), sulfonate rings (Y), and nucleophiles (X).



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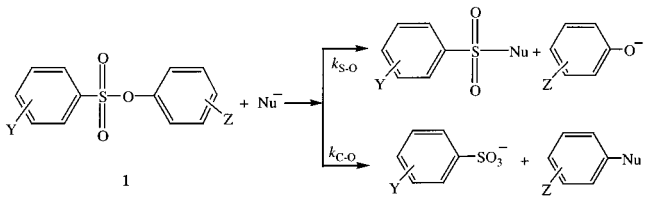
To investigate various mechanistic possibilities in the nucleophilic substitution reaction of aryl benzenesulfonates, we have carried out kinetic studies on the reaction of aryl benzenesulfonates ($YC_6H_4SO_3C_6H_4Z$) with excess amounts of benzylamines ($XC_6H_4CH_2NH_2$) in acetonitrile at 65.0 °C, Nu = $XC_6H_4CH_2NH_2$ in Scheme 1. Under excess amine reaction conditions, a benzylammonium cation, $XC_6H_4CH_2NH_3^+$, is formed additionally in Scheme 1. We have varied all three substituents, X, Y, and Z, and reaction mechanisms are discussed by determining the Hammett coefficients ρ_X, ρ_Y, and ρ_Z, together with the cross-interaction constants[2] ρ_{XY}, ρ_{YZ}, and ρ_{XZ}, eq 1a,b, where i and j represent X, Y, or Z.

Scheme 1



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

$$\rho_{ij} = \partial\rho_j/\partial\sigma_i = \partial\rho_i/\partial\sigma_j \quad (1b)$$

Results and Discussion

The reactions were first order (k_{obs}) in both substrate, [S], and benzylamine, [N], eqs 2 and 3. Plots of k_{obs} against [N] were linear in accordance with eq 3

$$\text{rate} = k_{obs}[S] \quad (2)$$

$$k_{obs} = k_0 + k_N[N] \quad (3)$$

where k_0 and k_N are the rate constants for solvolysis and aminolysis, respectively. The solvolysis was negligible

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Table 1. Second-Order Rate Constants, k_N ($\times 10^4$ $M^{-1}s^{-1}$), for the Reactions of $YC_6H_4SO_2OC_6H_4Z$ with $XC_6H_4CH_2NH_2$ in Acetonitrile at 65.0 °C

		Y			
Z	X	*p*-CH_3	H	*p*-Cl	*p*-NO_2
p-CH_3	*p*-OCH_3	3.20	3.88	4.57	6.40
	p-CH_3	2.29	2.89	3.70	5.51
	H	1.35	1.88	2.45	3.80
	p-Cl	0.614	0.764	0.933	1.33
H	*p*-OCH_3	2.79	3.20	3.87	5.19
	p-CH_3	2.41	2.80	3.33	4.55
	H	2.11	2.50	3.01	4.14
	p-Cl	1.11	1.50	1.90	2.90
p-Cl	*p*-OCH_3	2.79	3.13	3.49	4.45
	p-CH_3	2.23	2.57	3.04	4.22
	H	1.88	2.16	2.55	3.40
	p-Cl	1.48	1.81	2.16	3.12
p-NO_2	*p*-OCH_3	3.00	3.80	4.54	5.27
	p-CH_3	2.63	3.05	3.52	4.60
	H	2.21	2.55	2.98	3.94
	p-Cl	1.65	1.89	2.25	3.10

Table 2. Hammett ρ_X and ρ_Y Values[a] Determined with the Total Rate Constants, k_N, for the Reactions of $YC_6H_4SO_2OC_6H_4Z$ with $XC_6H_4CH_2NH_2$ in Acetonitrile at 65.0 °C

ρ_X

	Y			
Z	*p*-CH_3	H	*p*-Cl	*p*-NO_2
p-CH_3	-1.43 ± 0.02	-1.40 ± 0.10	-1.38 ± 0.16	-1.37 ± 0.22
H	-0.78 ± 0.15	-0.64 ± 0.11	-0.59 ± 0.09	-0.49 ± 0.06
p-Cl	-0.52 ± 0.06	-0.47 ± 0.06	-0.41 ± 0.04	-0.33 ± 0.06
p-NO_2	-0.51 ± 0.02	-0.58 ± 0.05	-0.58 ± 0.07	-0.45 ± 0.02

ρ_Y

	X			
Z	*p*-OCH_3	*p*-CH_3	H	*p*-Cl
p-CH_3	0.31 ± 0.03	0.39 ± 0.04	0.45 ± 0.06	0.34 ± 0.04
H	0.28 ± 0.02	0.29 ± 0.02	0.30 ± 0.03	0.42 ± 0.05
p-Cl	0.21 ± 0.01	0.29 ± 0.02	0.27 ± 0.02	0.33 ± 0.03
p-NO_2	0.24 ± 0.07	0.25 ± 0.02	0.26 ± 0.02	0.28 ± 0.02

[a] The σ values were taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

under the reaction conditions ($k_0 \cong 0$). The second-order rate constants for aminolysis (k_N) were obtained from the slopes of the plots (eq 3) and are summarized in Table 1. The rates are faster with a stronger nucleophile ($\delta\sigma_X < 0$) and nucleofuge ($\delta\sigma_Z > 0$; not consistently but generally, vide infra) as expected from a typical nucleophilic substitution reaction. The rate is faster also with a stronger electron-withdrawing group in the substrate ($\delta\sigma_Y > 0$), indicating negative charge development (on the sulfur center) in the transition state (TS). These results suggest that the major reaction is substitution at the sulfur, k_{S-O} path, with minor k_{C-O} contribution to the k_N values, eq 4.

$$k_N = k_{S-O} + k_{C-O} \quad (4)$$

This is supported by the Hammett coefficients ρ_X and ρ_Y, determined using the overall rate constants k_N in Table 2. The ρ_X values listed in Table 2 consist of two components: $\rho_X = \rho_{X(S-O)} + \rho_{X(C-O)}$. In both cases, the electronic charge on the nitrogen atom of the nucleophile is transferred to the substrate (to S and/or C), and hence, the sign of ρ_X should be negative as observed. The ρ_X values range from -0.3 to -1.4, which are rather low because the benzene ring is insulated from the reaction site by a methylene unit, the falloff factor due to one CH_2 unit being ca. 2.2.[3] The relatively wide range covered seems to result from complex competitive contributions of k_{S-O} and k_{C-O} values to the k_N. Although the sign of ρ_Y is positive, the size is small ($\rho_Y \cong 0.2 \sim 0.5$). The low ρ_Y values obtained with the neutral, benzylamine nucleophiles in MeCN at 65.0 °C in this work are in contrast to the much larger $\rho_{Y(S-O)}$ value of +2.52 for the reactions with phenoxide anion nucleophiles in ethanol at 25.0 °C.[1d] Anionic nucleophiles seem to transfer much larger negative charge to the sulfur center than the neutral amines.

Table 3. Contributions[a] of S−O and C−O Bond Cleavage for the Reactions of $YC_6H_4SO_2OC_6H_4Z$ with $XC_6H_4CH_2NH_2$ in Acetonitrile at 65.0 °C

X =[b]	% S−O	$k_{S-O} \times 10^4$	% C−O	$k_{C-O} \times 10^4$	$k_N \times 10^4$
p-OCH_3	60	1.92	40	1.28	3.20
p-CH_3	69	1.93	31	0.868	2.80
H	81	2.03	19	0.475	2.50
p-Cl	90	1.35	10	0.150	1.50

	$\rho_{X(S-O)} = -0.29 \pm 0.16$ ($r = 0.788$)		$\rho_{X(C-O)} = -1.85 \pm 0.07$ ($r = 0.996$)		
Z =[c]	% S−O	$k_{S-O} \times 10^4$	% C−O	$k_{C-O} \times 10^4$	$k_N \times 10^4$
p-CH_3	72	1.35	28	0.526	1.88
H	81	2.03	19	0.475	2.50
p-Cl	89	1.92	11	0.238	2.16
p-NO_2	93	2.37	7	0.179	2.55

	$\rho_{Z(S-O)} = -0.20 \pm 0.10$a ($r = 0.820$)		$\rho_{Z(C-O)} = -0.51 \pm 0.14$ ($r = 0.933$)		
Y = Z =[d]	% S−O	$k_{S-O} \times 10^4$	% C−O	$k_{C-O} \times 10^4$	$k_N \times 10^4$
p-CH_3	87	1.17	13	0.176	1.35
H	81	2.03	19	0.475	2.50
p-Cl	86	2.19	14	0.357	2.55
p-NO_2	86	3.39	14	0.552	3.94

[a] The sum of the areas of the two gas chromatographic peaks corresponding to the two products, $YC_6H_4SO_2NHCH_2C_6H_4X$ and $XC_6H_4CH_2NHC_6H_4Z$, is used as the total yield. [b] For Y = Z = H. [c] For X = Y = H. [d] For X = H.

The percentage contributions of the two paths are determined for three cases as shown in Table 3. Reference to Table 3 reveals that the contribution of k_{C-O} path increases with a stronger nucleophile ($\delta\sigma_X < 0$)[1d] and with a stronger electron-donating substituent Z on the phenoxide ring ($\delta\sigma_Z < 0$). The $\rho_{X(C-O)}$ determined for Y = Z = H is large negative ($\rho_{X(C-O)} = -1.85$). For benzylamines, the magnitude of the Brönsted coefficient β_X ($= \beta_{nuc}$) and Hammett coefficient ρ_X ($= \rho_{nuc}$) values are almost the same (albeit the sign is opposite) because the slope of the plot of pK_a's for benzylammonium ions in water versus σ is close to unity ($\cong 1.06$).[4] This means that the high $\rho_{X(C-O)}$ value obtained nearly corresponds to a large $\beta_{X(C-O)}$ value ($\cong 1.85$). Much smaller $\rho_{X(C-O)}$ (and hence similar magnitude of $\beta_{X(C-O)}$) of -0.76 was obtained for the reactions of 1-chloro-2,4-dinitrobenzene in ethanol at 45.0 °C,[1a] for which formation of the Meisenheimer complex is the rate-limiting step. The large β_X value obtained in the present work is an indication that the C−O bond cleavage path proceeds through an intermediate **2** with rate-limiting

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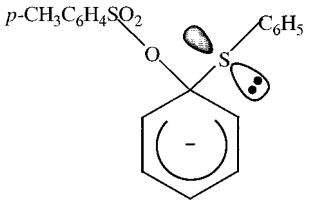
expulsion of the leaving group, $YC_6H_4SO_3^-$. This is supported by the ρ_Z value for the C−O bond cleavage path, $\rho_{Z(C-O)} = -0.51$, in Table 3. The negative $\rho_{Z(C-O)}$ value reflects positive charge development on the reaction center carbon in the TS, which should mean that the C−O bond cleavage as the $YC_6H_4SO_3^-$ group departs from **2** is rate-limiting. If the nucleophilic attack of benzylamine were the rate-determining step, the sign of $\rho_{Z(C-O)}$ should have been reversed ($\rho_{Z(C-O)} > 0$). Liotta et al.[5] have reported a ρ_Z value of +4.41 for the nucleophilic aromatic substitution reactions of *p*-Z-substituted chlorobenzenes ranging from Z = *p*-NO_2 to Z = *p*-CH_3 with piperidine in diethylene glycol at 194.5 °C. Greizerstein et al.[6] obtained $\rho_Z = +3.80$ for the similar reactions of 4-Z-1-chloro-2-nitrobenzene with piperidine in benzene at 45.0 °C. In these reactions, the chloro substituent is replaced by piperidine. These reactions are believed to proceed through an intermediate (Meisenheimer complex) with rate-limiting *addition* of the nucleophile, and exalted substituent constants, σ^-, gave better correlations. Bunnett et al.[1b] have shown that the percentage of the C−O bond cleavage increases with the polarizability of the nucleophile in the reactions of 2,4-dinitrophenyl *p*-toluenesulfonate. The nucleophiles that gave the most C−O scission (92∼93%) are those with a high polarizability reaction center, a thiophenoxide anion ($C_6H_5S^-$), and a carbanion ($CH_3CO\bar{C}HCO_2C_2H_5$). In contrast, the nucleophiles that gave the most S−O scission are those with a low polarizability reaction center, oxyanions (CH_3O^-, $C_6H_5O^-$, and glycine ethyl ester). These results are consistent with the rate-limiting expulsion of *p*-toluenesulfonate anion from the Meisenheimer complex, **2**. In complex **3**, there is a strong vicinal $n_S-\sigma^*_{C-O}$ (interaction between the lone pair orbital on the S atom (n_S) and the antibonding σ^* orbital of the C−O bond) charge-transfer interaction[7] with weakening of the C−O bond. In general, in the vicinal (σ_{A-B})-antibond



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(σ^*_{C-D}) type interaction, the bond orders of the A−B and C−D bonds decrease and hence are weakened so that the facile C−D bond scission occurs.[7] The greater this effect, the higher the level of bond orbital (*n* or σ) and the lower the level of antibonding orbital (σ^*). It is well-known that the lone pair levels on sulfur and carbanion are much higher than those on the oxygen.[7c] Thus, the strong $n_S-\sigma^*_{C-O}$ and $n_{carbanion}-\sigma^*_{C-O}$ charge-transfer interactions lead to facile C−O bond cleavage and increase the percentage C−O bond scission. Bunnett et al.[1b] have also shown that neither k_{S-O} nor k_{C-O} for the nucleophiles studied can be correlated with the Swain and Scott eq 5.[8]

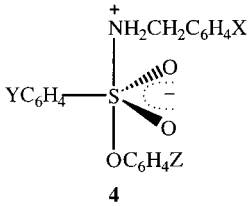
$$\log k_{S-O} = s_{S-O}n + \text{constant} \quad (5a)$$

$$\log k_{C-O} = s_{C-O}n + \text{constant} \quad (5b)$$

This is reasonable since the Swain and Scott equation applies only to the concerted nucleophilic substituion (S_N2) reactions,[8] not to the stepwise reaction series. We therefore conclude that the C−O bond cleavage path proceeds stepwise with rate-limiting expulsion of the sulfonate group from the Meisenheimer complex **2**.

We can now understand why the $\rho_X(k_N)$ values ($\cong -1.4$) for Z = *p*-CH_3 are much larger than those for other Z substituents ($\cong -0.3$ to -0.8); since the contribution of k_{C-O} path is the largest for Z = *p*-CH_3 (28%), the large magnitude of $\rho_{X(C-O)}$ ($=-1.85$) leads to the large overall $\rho_X(k_N)$ in Table 2. Somewhat larger $\rho_{X(C-O)}$ ($=-2.52$) values are observed in the reactions of 2,4-dinitrophenyl benzenesulfonates with substituted phenoxide nucleophiles ($XC_6H_4O^-$) ranging from X = *p*-CH_3O to X = *p*-CN in ethanol at 25.0 °C.[1d] The large magnitude is of course due to the phenoxide nucleophiles used, for which a direct conjugation between the phenoxide oxygen and electron acceptor para substituent can occur, and hence, the exalted constant (σ^-) gives better correlation.[9]

Consideration of the large contribution of the k_{C-O} path for Z = *p*-CH_3 gives us a relatively low average $\rho_{X(S-O)}$ value of ca. −0.3, which in turn gives us $\beta_{X(S-O)}$ of ca. 0.3. This value falls in the range of β_X values ($\beta_X \cong 0.1-0.4$),[10] which are usually obtained for a stepwise reaction with rate-limiting formation of an intermediate. An approximate $\rho_{Z(S-O)}$ value obtained for X = Y = H is ca. +0.2 in Table 3. This is also in line with the rate-limiting formation of a zwitterionic bipyramidal pentacoordinate (TBP-5C) intermediate, **4**, where the nucleophile and leaving group (phenoxide) are known to occupy apical site.[11] The overall $\rho_Z(k_N)$ and $\beta_Z(k_N)$ values are indeterminate due largely to the opposing contribution of $\rho_{Z(S-O)} > 0$ and $\rho_{Z(C-O)} < 0$. For X = *p*-Cl, the k_{C-O} contribution is only 10%. We have found an approximate $\beta_Z(k_N)$ value for X = *p*-Cl and Y = *p*-CH_3 using the pK_a (MeCN) values,[12] $\beta_Z(k_N) = -0.19 \pm 0.05$ ($r = 0.960$ except for Z = *p*-NO_2), which should correspond to $\beta_{Z(S-O)}$ considering the low (10%) contribution of k_{C-O} path. We have also determined approximate estimate of $\rho_{Z(S-O)}$ for X = Y = H, $\rho_{Z(S-O)} \cong 0.20$ ($r = 0.820$). Admittedly, both values are not very reliable; nevertheless, they suggest very low



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magnitude of the $\rho_{Z(S-O)}$ as well as $\beta_{Z(S-O)}$ value; the low values of β_Z (β_{lg}) have been considered to indicate a rate-limiting bond formation in the stepwise processes of carbonyl, thiocarbonyl, dithiocarbonyl, and phosphoryl group transfer reactions.[10] Based on the magnitudes of β_X and β_Z values, we can conclude that the k_{S-O} reaction path proceeds by a stepwise mechanism in which bond formation of the TBP-5C intermediate is rate limiting. A similar mechanism has been proposed also by Uhm et al. for the S−O bond cleavage path.[1d]

Finally, we have correlated the overall rate constants, k_N, with combinations of two substituent constants and determined the cross-interaction constants, ρ_{XY}, ρ_{YZ}, and ρ_{XZ}, eqs 6a−c. Since the k_N values used ($k_N = k_{S-O} + k_{C-O}$) are composite values with major contribution of k_{S-O}

$$\log(k_{XY}/k_{HH}) = -(0.68 \pm 0.06)\sigma_X + (0.34 \pm 0.03)\sigma_Y + (\mathbf{0.28} \pm 0.14)\sigma_X\sigma_Y \quad (r = 0.980, n = 16) \quad (6a)$$

$$\log(k_{YZ}/k_{HH}) = +(0.35 \pm 0.04)\sigma_Y - (0.11 \pm 0.04)\sigma_Z - (\mathbf{0.16} \pm 0.10)\sigma_Y\sigma_Z \quad (r = 0.933, n = 16) \quad (6b)$$

$$\log(k_{XZ}/k_{HH}) = -(0.90 \pm 0.11)\sigma_X + (0.15 \pm 0.05)\sigma_Z + (\mathbf{0.63} \pm 0.27)\sigma_X\sigma_Z \quad (r = 0.928, n = 16) \quad (6c)$$

path, the cross-interaction constants obtained are not very accurate with relatively large standard deviations but can be taken as mechanistic indications for the major pathway, k_{S-O}. We note that the signs ($\rho_{XY} > 0$, $\rho_{YZ} < 0$, and $\rho_{XZ} > 0$) are all in line with a stepwise mechanism[2,13] through an intermediate, and the concerted (S_N2 type) nucleophilic displacement at sulfur can be precluded safely since the signs of $\rho_{XY}(<0)$ and $\rho_{YZ}(>0)$ are reversed in such a concerted process.[13] The small magnitude of ρ_{YZ} ($\cong -0.16$) is also consistent with the rate-limiting formation of the intermediate, since in the TBP-5C adduct formation the change in the intensity of interaction between substituents Y and Z should be small. The indeterminate nature of the ρ_Z value noted earlier is apparent in eqs 6, where ρ_Z is negative in eq 6b but is positive in eq 6c (vide supra).

For variations of substituents X and Y, a faster rate is accompanied by a lower selectivity; i.e., the reactivity-selectivity principle (RSP) holds.[14] This adherence to the RSP together with a positive ρ_{XZ} value is also considered to constitute a mechanistic criterion for a stepwise mechanism through an intermediate.[15]

Conclusion

The nucleophilic substitution reactions of aryl benzenesulfonates with benzylamines in acetonitrile are complex with two distinct competing reaction pathways, $k_N = k_{S-O} + k_{C-O}$. The C−O bond cleavage path is favored by a stronger nucleophile (X = *p*-CH_3O) and by an electron donor substituent (Z = *p*-CH_3) on the phenoxide ring. The S−O bond cleavage path, k_{S-O}, proceeds by a stepwise mechanism in which nucleophilic attack is rate limiting, while the C−O bond cleavage path, k_{C-O}, proceeds through a Meisenheimer complex in which the expulsion of the sulfonate leaving group is rate limiting. The overall rate constants, k_N, in which the major contribution is the S−O bond cleavage path, k_{S-O}, lead to the sign of the cross-interaction constants, $\rho_{XY} > 0$, $\rho_{YZ} < 0$, and $\rho_{XZ} > 0$, which are consistent with a stepwise mechanism through an intermediate. The adherence to the RSP is also in line with the proposed mechanism for the k_{S-O} path.

Experimental Section

Materials. Benzylamines were Merck GR grades and aryl benzenesulfonates were prepared by Tipson method[16] using phenols and benzenesulfonyl chlorides. The prepared substrates were confirmed by melting points, IR and NMR spectroscopy, and elemental analysis as follows:

***p*-$CH_3C_6H_4SO_2OC_6H_4$-*p*-CH_3:** mp 64 °C; IR (KBr)/cm^{-1} 1595, 1515 (C−C aromatic), 1355, 1170 (SO_2), 805 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 2.3 (CH_3, 3H, s), 2.5 (CH_3, 3H, s), 6.8−7.8 (phenyl, 8H, m). Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.1; H, 5.4. Found: C, 63.8; H, 5.1.

***p*-$CH_3C_6H_4SO_2OC_6H_5$:** mp 76 °C; IR (KBr)/cm^{-1} 1610, 1510 (CC aromatic), 1355, 1180 (SO_2), 805 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 1.3 (CH_3, 3H, s), 6.8−7.8 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.9; H, 4.9. Found: C, 62.6.; H, 4.7.

***p*-$CH_3C_6H_4SO_2OC_6H_4$-*p*-Cl:** mp 88 °C; IR (KBr)/cm^{-1} 1610, 1515 (CC aromatic), 1355, 1170 (SO_2), 805 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, s), 2.3 (CH_3, 3H, d), 6.7−7.8 (phenyl, 8H, m). Anal. Calcd for $C_{13}H_{11}ClO_3S$: C, 55.2; H, 3.9. Found: C, 54.8; H, 4.1.

***p*-$CH_3C_6H_4SO_2OC_6H_4$-*p*-NO_2:** mp 98 °C; IR (KBr)/cm^{-1} 1610, 1515 (CC aromatic), 1525,1345 (NO_2), 1355, 1180 (SO_2), 805 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, s), 2.3 (CH_3, 3H, d), 6.8−7.6 (phenyl, 8H, m). Anal. Calcd for $C_{13}H_{11}NO_5S$: C, 53.2; H, 3.8.; N, 4.8. Found: C, 52.9; H, 3.7; N, 4.4.

***p*-$CH_3C_6H_4SO_2OC_6H_5$:** mp 102 °C; IR (KBr)/cm^{-1} 1595, 1490 (CC aromatic), 1340, 1165 (SO_2), 1020 (SO), 810 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, d), 2.4 (*p*-CH_3, 3H, d), 6.8−7.8 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.9; H, 4.9. Found: C, 63.0; H, 4.9.

***p*-$ClC_6H_4SO_2OC_6H_5$:** oil form.; IR (KBr)/cm^{-1} 1600, 1495 (CC aromatic), 1355, 1180 (SO_2), 1020 (SO); ^{1}H NMR (60 MHz, $CDCl_3$) 6.8−7.8 (phenyl, 10H, m). Anal. Calcd for $C_{12}H_{10}O_3S$: C, 61.5; H, 4.3. Found: C, 61.4; H, 4.3.

***p*-$ClC_6H_4SO_2OC_6H_4$-*p*-Cl:** mp 69 °C; IR (KBr)/cm^{-1} 1585, 1495 (CC aromatic), 1355, 1180 (SO_2), 1010 (SO); ^{1}H NMR (60 MHz, $CDCl_3$) 6.9−7.9 (phenyl, 9H, m). Anal. Calcd for $C_{12}H_9ClO_3S$: C, 53.6; H, 3.4. Found: C, 54.0; H, 3.6.

***p*-$ClC_6H_4SO_2OC_6H_4$-*p*-NO_2:** mp 74 °C; IR (KBr)/cm^{-1} 1605, 1495 (CC aromatic), 1530, 1345 (NO_2), 1360, 1180 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 6.9−8.0 (phenyl, 9H, m). Anal. Calcd for $C_{12}H_9NO_5S$: C, 51.6; H, 3.2; N, 5.0. Found: C, 51.8; H, 3.4; N, 5.2.

***p*-$ClC_6H_4SO_2OC_6H_4$-*p*-CH_3:** mp 75 °C (lit. 74.8−76.0 °C); IR (KBr)/cm^{-1} 1610, 1515 (CC aromatic), 1355, 1180 (SO_2), 805 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, d), 2.3 (*p*-CH_3, 3H, s), 6.8−7.5 (phenyl, 8H, m). Anal. Calcd for $C_{13}H_{11}ClO_3S$: C, 55.2; H, 3.9. Found: C, 55.6; H, 4.1.

***p*-$ClC_6H_4SO_2OC_6H_5$:** mp 82 °C; IR (KBr)/cm^{-1} 1585, 1495 (CC aromatic), 1355, 1180 (SO_2), 1010 (SO); ^{1}H NMR (60 MHz, $CDCl_3$) 6.9−7.6 (phenyl, 9H, m). Anal. Calcd for $C_{12}H_9ClO_3S$: C, 53.6; H, 3.4. Found: C, 53.5.; H, 3.3.

***p*-$ClC_6H_4SO_2OC_6H_4$-*p*-Cl:** mp 84 °C; IR (KBr)/cm^{-1} 1600, 1510 (CC aromatic), 1360, 1170 (SO_2), 840 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 6.9−7.5 (phenyl, 8H, m). Anal. Calcd for $C_{12}H_8Cl_2O_3S$: C, 47.5; H, 2.7. Found: C, 47.4.; H, 2.9.

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***p*-ClC$_6$H$_4$SO$_2$OC$_6$H$_4$-*p*-NO$_2$:** mp 114 °C; IR (KBr)/cm^{-1} 1605, 1510 (CC aromatic), 1515, 1345 (NO_2), 1365, 1175 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 6.8−8.2 (phenyl, 8H, m). Anal. Calcd for $C_{12}H_8ClNO_5S$: C, 45.9; H, 2.6; N, 4.5. Found: C, 45.7; H, 2.6; N, 4.4.

***p*-NO$_2$C$_6$H$_4$SO$_2$OC$_6$H$_4$-*p*-CH$_3$:** mp 98 °C; IR (KBr)/cm^{-1} 1600, 1538 (CC aromatic), 1510, 1340 (NO_2), 1360, 1170 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, d), 2.4 (*p*-CH_3, 3H, s), 7.0−8.0 (phenyl, 8H, m). Anal. Calcd for $C_{13}H_{11}NO_5S$: C, 53.2; H, 3.8; N, 4.8. Found: C, 53.0; H, 3.6; N, 4.5.

***p*-NO$_2$C$_6$H$_4$SO$_2$OC$_6$H$_5$:** mp 92 °C; IR (KBr)/cm^{-1} 1600, 1510 (CC aromatic), 1500, 1340 (NO_2), 1360, 1170 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 1.4 (CH_3, 3H, d), 2.4 (*p*-CH_3, 3H, s), 7.0−8.0 (phenyl, 8H, m). Anal. Calcd for $C_{12}H_9NO_5S$: C, 51.6; H, 3.2; N, 5.0. Found: C, 51.3; H, 3.3; N, 5.3.

***p*-NO$_2$C$_6$H$_4$SO$_2$OC$_6$H$_4$-*p*-Cl:** mp 114 °C; IR (KBr)/cm^{-1} 1605, 1510 (CC aromatic), 1515, 1345 (NO_2), 1365, 1175 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 7.1−8.1 (phenyl, 8H, m). Anal. Calcd for $C_{12}H_8ClNO_5S$: C, 45.9; H, 2.6; N, 4.5. Found: C, 46.2; H, 2.8; N, 4.6.

***p*-NO$_2$C$_6$H$_4$SO$_2$OC$_6$H$_4$-*p*-NO$_2$:** mp 139 °C; IR (KBr)/cm^{-1} 1605, 1510 (CC aromatic), 1525, 1345 (NO_2), 1370, 1180 (SO_2), 850 (SOC); ^{1}H NMR (60 MHz, $CDCl_3$) 7.1−8.2 (phenyl, 8H, m). Anal. Calcd for $C_{12}H_8N_2O_7S$: C, 44.4; H, 2.5; N, 8.6. Found: C, 44.4; H, 2.6; N, 8.8.

Kinetic Procedure. Rates were measured conductometrically at 65.0 °C. The conductivity due to cation (benzylammoinum ion) and anions ($ZC_6H_4O^-$ and $YC_6H_4SO_3^-$) produced increases with the progress of reaction. Pseudo-first-order rate constants, k_{obs}, were determined by the Guggenheim method with a large excess of benzylamine; [aryl benzenesulfonate] = 10^{-3}M and [benzylaime] = 0.1−0.25 M. Second-order rate constants, k_N, were obtained from the slope of a plot of k_{obs} vs [N] (eq 3) with more than four concentrations of benzylamine. The reported values of k_N are the averages of more than duplicate runs and were reproducible to within ±3%.

Product Analysis. Upon completion of rate measurements, the products were separated using HP5890A gas chromatograph. A HP-1 (5 m × 0.53 mm × 2.65 μm) column and FID (350 °C) detector were used. The injector temperature was 250 °C. The oven temperature was 100 °C initially and was increased to 140 °C at a rate of 10 °C/min and to 200 °C at the rate of 2 °C/min. The flow rate of carrier gas, He, was 20 mL/min. The two possible benzylamides products, $YC_6H_4SO_2NHCH_2C_6H_4X$ and $XC_6H_4CH_2NHC_6H_4Z$, were prepared by the Tipson method and recrystallized over ethanol. These standards were then used to identify the reaction products from the kinetic measurements. The areas of the two peaks were used to determine percentage (or fraction) contributions of k_{S-O} and k_{C-O} paths, which are listed in Table 3. The individual rate constants, k_{S-O} and k_{C-O}, were then obtained by multiplying the fractions to k_N. Analysis of the products gave the following results:

C$_6$H$_5$SO$_2$NHCH$_2$C$_6$H$_4$-*p*-OCH$_3$: IR (KBr)/cm^{-1} 1600, 1510 (CC aromatic), 1350, 1175 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.7 (CH_2, 2H, s), 3.5 (*p*-OCH_3, 3H, s), 3.9 (NH, H, s), 6.5−7.6 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.6; H, 5.5; N, 5.1. Found: C, 60.7; H, 5.4; N, 5.1.

C$_6$H$_5$SO$_2$NHCH$_2$C$_6$H$_4$-*p*-CH$_3$: IR (KBr)/cm^{-1} 1590, 1490 (CC aromatic), 1345, 1160 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.4 (*p*-CH_3, 3H, s), 2.8 (CH_2, 2H, s), 3.8 (NH, H, s) 6.8−7.8 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.3; H, 5.8; N, 5.4. Found: C, 64.4; H, 5.6; N, 5.4.

C$_6$H$_5$SO$_2$NHCH$_2$C$_6$H$_5$: IR (KBr)/cm^{-1} 1600, 1490 (CC aromatic), 1350, 1175 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.8 (NH, H, s) 6.8−7.8 (phenyl, 10H, m). Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.1; H, 5.3; N, 5.7. Found: C, 63.4; H, 5.3; N, 5.7.

C$_6$H$_5$SO$_2$NHCH$_2$C$_6$H$_4$-*p*-Cl: IR (KBr)/cm^{-1} 1580, 1495 (CC aromatic), 1350, 1175 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.9 (NH, H, s), 6.9−7.9 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}ClNO_2S$: C, 55.4; H, 4.3; N, 5.0. Found: C, 55.2; H, 4.2; N, 5.0.

***p*-CH$_3$C$_6$H$_4$SO$_2$NHCH$_2$C$_6$H$_5$:** IR (KBr)/cm^{-1} 1595, 1510 (CC aromatic), 1350, 1170 (SO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.3 (*p*-CH_3, 3H, s), 2.8 (CH_2, 2H, s), 3.8 (NH, H, s), 6.8−7.8 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.3; H, 5.8; N, 5.4. Found: C, 64.4; H, 5.7; N, 5.3.

C$_6$H$_5$NHCH$_2$C$_6$H$_4$-*p*-OCH$_3$: IR (KBr)/cm^{-1} 1600, 1500 (CC aromatic); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.8 (NH, H, s), 6.9−7.9 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}NO$: C, 78.8; H, 7.1; N, 6.6. Found: C, 78.9; H, 7.0; N, 6.6.

C$_6$H$_5$NHCH$_2$C$_6$H$_4$-*p*-CH$_3$: IR (KBr)/cm^{-1} 1590, 1495 (CC aromatic); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.8 (NH, H, s), 6.9−7.8 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}N$: C, 85.2; H, 7.7; N, 7.1. Found: C, 85.3; H, 7.6; N, 7.1.

C$_6$H$_5$NHCH$_2$C$_6$H$_5$: IR (KBr)/cm^{-1} 1600, 1490 (CC aromatic); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.9 (NH, H, s), 6.9−7.9 (phenyl, 10H, m). Anal. Calcd for $C_{13}H_{13}N$: C, 85.2; H, 7.2; N, 7.6. Found: C, 85.3; H, 7.0; N, 7.7.

C$_6$H$_5$NHCH$_2$C$_6$H$_4$-*p*-Cl: IR (KBr)/cm^{-1} 1575, 1490 (CC aromatic); ^{1}H NMR(60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.8 (NH, H, s), 6.9−7.9 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}ClN$: C, 71.7; H, 5.6; N, 6.4. Found: C, 71.9; H, 5.5; N, 6.3.

***p*-CH$_3$C$_6$H$_4$NHCH$_2$C$_6$H$_5$:** IR (KBr)/cm^{-1} 1590, 1515 (CC aromatic); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.9 (NH, H, s), 6.9−7.9 (phenyl, 9H, m). Anal. Calcd for $C_{14}H_{15}N$: C, 85.2; H, 7.7; N, 7.1. Found: C, 85.3; H, 7.6; N, 7.1.

***p*-ClC$_6$H$_4$NHCH$_2$C$_6$H$_5$:** IR (KBr)/cm^{-1} 1590, 1495 (CC aromatic); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.8 (NH, H, s), 6.9−8.0 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}ClN$: C, 71.7; H, 5.6; N, 6.4. Found: C, 71.9; H, 5.5; N, 6.6.

***p*-NO$_2$C$_6$H$_4$NHCH$_2$C$_6$H$_5$:** IR (KBr)/cm^{-1} 1590, 1500 (CC aromatic), 1515, 1300 (NO_2); ^{1}H NMR (60 MHz, $CDCl_3$) 2.8 (CH_2, 2H, s), 3.9 (NH, H, s), 7.1−8.0 (phenyl, 9H, m). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.4; H, 5.3; N, 12.3. Found: C, 68.4; H, 5.5; N, 12.3.

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