Nucleophilic Substitution Reactions of Thiopheneethyl Arenesulfonafes with Anilines and N,N-Dimethylanilines

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Nucleophilic substitution reactions of 2-thiopheneethyl benzenesulfonates (2-TEB) and 3-thiopheneethyl benzenesulfonates (3-TEB) with anilines and N,N-dimethylanilines (DMA) are investigated in acetonitrile at 60.0 °C. The cross-interaction constants ρ_{XZ} determined for the reactions with anilines are large negative (-0.50) which are comparable to those for the similar predominantly frontside-attack S_N2 reactions of 1-phenylethyl (1-PEB), 2-phenylethyl (2-PEB) and cumyl benzenesulfonates. A large negative ρ_{XZ} value ($-0.4 \sim -0.8$) is considered to provide a mechanistic criterion for the frontside-attack S_N2 mechanism with a four-center transition state. In agreement with this proposal the kinetic isotope effects, k_H/k_D, involving deuterated aniline nucleophiles are all greater than one reflecting partial N-H(D) bond cleavage in the transition state. The MO theoretical reactant structures of 1-PEB, 2-PEB and 2-TEB based on the PM3 calculation show that the benzene ring blocks the backside nucleophile approach to the reaction center carbon (C_α) enforcing the frontside-attack S_N2 mechanism.

Introduction

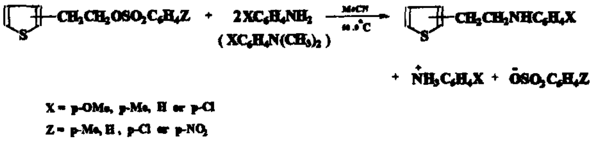
Cross-interaction constant ρ_{XZ}, eq. 1, where σ_X and σ_Z refer to substituents in the nucleophile and leaving group, respectively, has been shown to be useful as a mechanistic tool for organic reactions in solution.[1] The ρ_{XZ} can alternatively be defined by eq. 2.[1] According to this expression, a stronger nucleophile ($\delta\sigma_X<0$)

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (1)$$

$$\rho_{XZ} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \qquad (2)$$

and/or a stronger nucleofuge ($\delta\sigma_Z>0$) lead to a later transition state (TS) when ρ_{XZ} is negative ($\delta\rho_Z>0$ and $\delta\rho_X<0$), whereas they lead to an earlier TS when ρ_{XZ} is positive $\delta\rho_Z<0$ and $\delta\rho_X>0$). On the other hand, the magnitude of ρ_{XZ} is a measure of the TS tightness;[1] the greater the magnitude of ρ_{XZ}, the stronger is the interaction between the necleophile and leaving group and hence the tighter is the TS. We found that a relatively large negative ρ_{XZ} value is in general related to an S_N2 reaction *via* the frontside nucleophilic attack; thus for the S_N2 reactions of anilines with 1-phenylethyl (1-PEB), 2-phenylethyl (2-PEB) and cumyl benzenesulfonates, all of which are believed to proceed predominantly by the frontside-attack mechanism, the ρ_{XZ} values obtained were -0.55 (in MeOH at 25.0 °C),[2] -0.45 (in MeOH at 65.0 °C)[3] and -0.75 (in MeCN at 55.0 °C)[4] respectively. The magnitudes of these ρ_{XZ} values for the frontside-attack S_N2 reactions are considerably greater than that for the similar but pure backside-attack S_N2 reactions of benzyl benzenesulfonates ($\rho_{XZ}=-0.10$ in MeOH at 35.0 °C);[5] in fact they are greater than the ρ_{XZ} values ($\rho_{XZ}\cong 0.3$) for the similar reactions with a relatively tight TS at primary carbon centers.[6]

In view of the importance of the sign and magnitude of the ρ_{XZ} value as a mechanistic tool, it is of interest to extend the mechanistic studies to the aminolyses of 2-thiopheneethyl benzenesulfonates (2-TEB) and 3-thiopheneethyl benzenesulfonates (3-TEB) using anilines and N,N-dimethylanilines (DMA), eq. 3. Our interests in this work are twofold: (i) Do they also proceed by the frontside-attack S_N2 mechanism? *i.e.*, are the ρ_{XZ} large negative as we found for 2-PEB? (ii) What are the effects of thiophene rings (2- and 3-thiophene-) on the TS structure?



(3)

Results and Discussion

The second-order rate constants, k_2, for the reactions of 2-TEB and 3-TEB with anilines and N,N-dimethylanilines in acetonitrile at 60.0 °C are summarized in Tables 1 and 2. The rates are faster for a stronger nucleophile ($\delta\sigma_X<0$) and nucleofuge ($\delta\sigma_Z>0$) as expected from typical S_N2 reactions. The rates are retarded with N,N-dimethylanilines due to steric effect of the N,N-dimethyl groups. The effect of 2-thiophene (in 2-TEB) and 3-thiophene (in 3-TEB) ring on the rate differs a little from that of the benzene ring (in 2-PEB)[3] when rates are compared after differences in solvent and reaction temperature are taken into account, *e.g.*, $k_2 = 3.49 \times 10^{-5}\ dm^3mol^{-1}s^{-1}$ in MeCN at 60.0 °C for 2-TEB (with X=Z=H) whereas $k_2=11.0 \times 10^{-5}\ dm^3mol^{-1}s^{-1}$ in MeOH at 65.0 °C for 2-PEB (with X=Y=Z=H).[3]

The Hammett (ρ_X and ρ_Z) and **Brönsted** (β_X and β_Z) coefficients are listed in Tables 3 and 4. Reference to these Tables reveals that the magnitudes of $|\rho_X|$ and β_X are in general greater for 3-TEB than for 2-TEB whereas ρ_Z and $|\beta_Z|$ are greater for 3-TEB than those for the corresponding 2-TEB, albeit differences are small. These trends suggest that

Table 1. The second order rate constants, k_2(x 10^5) $M^{-1}s^{-1a}$, for the reactions of Z-substituted 2-thiopheneethyl arenesulfonates with X-substituted anilines (AN) and N,N-dimethylanilines (DMA) in Acetonitrile at 60.0 °C

		Z			
Nucleophile	X	p-Me	H	p-Cl	p-NO_2
AN	p-OMe	5.73	8.87	17.2	62.0
	p-Me	4.28	6.10	10.4	38.4
	H	2.39	3.49	5.43	18.2
	p-Cl	1.02	1.38	2.17	6.26
DMA	p-OMe	1.45	2.31	3.70	12.9
	p-Me	0.997	1.57	2.36	7.94
	H	0.589	0.800	1.27	3.98
	p-Cl	0.229	0.342	0.501	1.51

[a] The k_2 values were reproducible to ± 3%.

Table 2. The second order rate constants, k_2(x 10^5) $M^{-1}s^{-1a}$, for the reactions of Z-substituted 3-thiopheneethyl arenesulfonates with X-substituted anilines and N,N-dimethylanilines in acetonitrile at 60.0 °C

		Z			
Nucleophile	X	p-Me	H	p-Cl	p-NO_2
AN	p-OMe	4.47	7.08	12.9	56.2
	p-Me	3.55	5.37	9.33	36.3
	H	2.19	3.47	5.62	19.5
	p-Cl	1.12	1.59	2.57	7.94
DMA	p-OMe	0.840	1.42	2.92	13.9
	p-Me	0.708	1.06	2.19	9.55
	H	0.409	0.641	1.30	5.37
	p-Cl	0.230	0.333	0.646	2.49

[a] The k_2 values were reproducible to ± 3%.

Table 3. The Hammett (ρ_X and ρ_Z) and Brфnsted(β_X and β_Z) coefficients for the reactions of Z-substituted 2-thiopheneethyl arenesulfonates with X-substituted anilines and N,N-dimethylanilines[a]

Nucleouhile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	p-Me	-1.52	0.55	p-OMe	1.09	- 0.30
	H	-1.62	0.58	p-Me	1.01	- 0.27
	p-Cl	-1.79	0.64	H	0.93	-0.25
	p-NO_2	-2.00	0.72	p-Cl	0.84	-0.23
DMA	p-Me	-1.59	0.57	p-OMe	1.00	-0.27
	H	-1.68	0.61	p-Me	0.94	-0.25
	p-Cl	-1.73	0.62	H	0.88	-0.24
	p-NO_2	-1.86	0.67	p-Cl	0.85	-0.23

[a] Correlation coefficients: >0.994.

Table 4. The Hammett (ρ_X and ρ_Z) and Brфnsted (β_X and β_Z) coefficients for the reactions of Z-substituted 3-thiopheneethyl arenesulfonates with X-substituted anilines and N,N-dimethylanilines[a]

Nucleophile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	p-Me	-1.22	0.44	p-OMe	1.16	-0.31
	H	-1.30	0.47	p-Me	1.07	-0.29
	p-Cl	-1.41	0.51	H	0.99	-0.27
	p-NO_2	-1.70	0.61	p-Cl	0.90	-0.24
DMA	p-Me	-1.10	0.40	p-OMe	1.30	-0.35
	H	-1.27	0.46	p-Me	1.26	-0.34
	p-Cl	-1.33	0.48	H	1.18	-0.32
	p-NO_2	-1.52	0.54	p-Cl	1.10	-0.30

[a] Correlation coefficients: >0.994.

Table 5. The Cross Interaction Constants, ρ_{XZ} and ρ_{XZ}

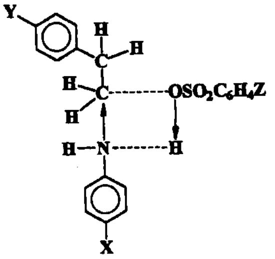
Substrate	Nucleophile	ρ_{XZ}	β_{XZ}
2-Thiopheneethyl	AN	- 0.50(0.999)[a]	- 0.30(0.995)[a]
	DMA	- 0.27(0.999)	- 0.16(0.994)
3-Thiopheneethyl	AN	- 0.50(0.999)	- 0.30(0.994)
	DMA	- 0.28(0.999)	- 0.17(0.993)

[a] Correlation coefficients.

bond-making is greater but bond cleavage is smaller and hence the TS is slightly tighter for 2-TEB than for 3-TEB. Excellent linearities obtained in the plots of log k_2 *vs* σ_Z including Z=p-NO_2 may be an indication that there is very little aryl participation since the aryl-assisted path should become important for a strong nucleofuge (Z=p-NO_2).[7]

The cross-interaction constants, ρ_{XZ} (and β_{XZ}), are determined by subjecting the rate data in Tables 1 and 2 to multiple regression analysis using equation 1.[1] The results in Table 5 reveal that the sign of ρ_{XZ} (and also of β_{XZ}) is negative and the magnitude is large which is comparable to those for the similar reactions of 1-PEB[2] and 2-PEB.[3] For these reactions of 1-PEB and 2-PEB we obtained large negative ρ_{XZ} values (– 0.56 and – 0.45 in MeOH at 25.0 °C and 65.0 °C respectively) and based on these and various other evidence[8] including stereochemical studies[8d] the reactions were concluded to proceed predominantly by the frontside attack S_N2 pathway. The large negative ρ_{XZ} value therefore suggests that the reactions of anilines with 2- and 3-thiopheneethyl arenesulfonates in MeCN at 60.0 °C proceed predominantly by the frontside-attack S_N2 mechanism.

At first we were puzzled to find that 2-phenylethyl benzenesulfonates (2-PEB) react with anilines predominantly by the frontside-attack S_N2 mechanism since there is another CH_2 group between the reaction center (C_α) and the benzene ring, which may not cause steric crowding for the C_α carbon to interfere with the backside-attack.[3] The frontside-attack mechanism was based on the large negative ρ_{XZ} and primary kinetic isotope effects (k_H/k_D>1.0) observed with deuterated aniline nucleophiles.[1C] These two rather unusual results can be nicely accommodated by a four-center TS in Scheme 1.[2,3] This TS structure shows that two substituents X and Z can interact strongly via two routes (thus a large magnitude of ρ_{XZ}) and one of the N-H(D) bond partially breaks to give primary kinetic isotope effects (k_H/k_D>1.0) involving deuterated aniline nucleophiles. In fact the magnitude of k_H/k_D observed is smaller than would be expected from only N-H(D) bond breaking effect, since vibrational frequencies of another N-H(D) bond, which is not cleaved, increases and hence gives inverse secondary kinetic isotope effect, k_H/k_D<1.0, due to steric crowding in the TS and the observed k_H/k_D value is the result of the two contributions.[9] Since the four-center TS of the type in Scheme 1 is not possible for the reactions with N,N-dimethylanilines, the smaller magnitude of the ρ_{XZ} values observed, *ca.* one-half of that for the reactions with anilines, provides evidence in sup-



Scheme 1.

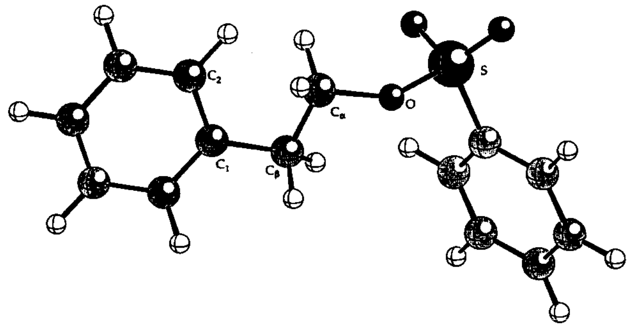


Figure 1. The PM3 optimized reactant structure of 2-phenylethyl benzenesulfonate (2-PEB). [$\rho_{XZ} = -0.45$ in MeOH at 65.0 °C: $\angle C_\alpha C_\beta C_1 = 111.62°$, $\angle C_\alpha C_\beta C_1 C_2 = 42.47°$, d($C_\alpha$-$C_2$)=2.932 Å].

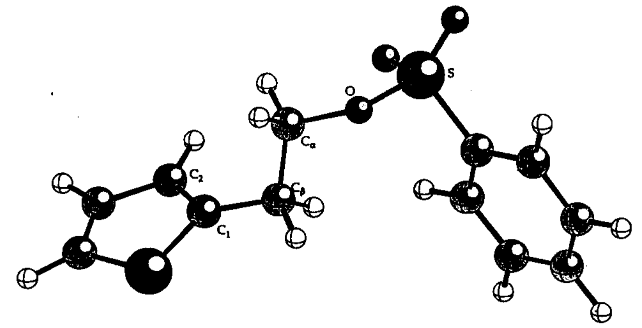


Figure 2. The PM3 optimized reactant structure of 2-phenylethyl benzenesulfonate (2-TEB). [$\rho_{XZ} = -0.50$ in MeCN at 60.0 °C: $\angle C_\alpha C_\beta C_1 = 110.60°$, $\angle C_\alpha C_\beta C_1 C_2 = 67.47°$, d($C_\alpha$-$C_2$=3.160 Å].

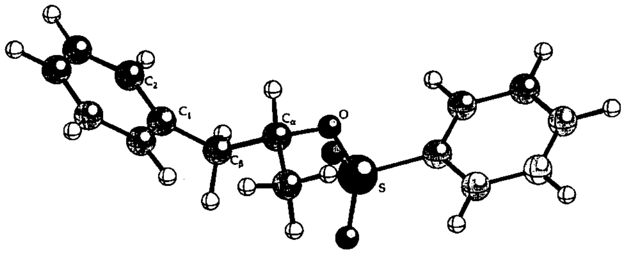
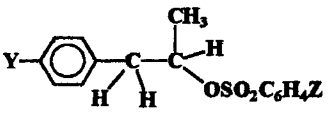


Figure 3. The PM3 optimized reactant structure of 1-phenyl-2-propyl benzenesulfonate (PPB). [$\rho_{XZ} = +0.16$ in MeOH at 65.0 °C: $\angle C_\alpha C_\beta C_1 = 111.60°$, $\angle C_\alpha C_\beta C_1 C_2 = 84.33°$, d($C_\alpha$-$C_2$)=3.553 Å].

port of the frontside-attack S_N2 mechanism with the four-center TS.[10] Another puzzling result observed in a previous work was that the reactions of anilines with 1-phenyl-2-propyl benzenesulfonates (PPB) gave $\rho_{XZ} = +0.11$ for Y=p-CH_3O and +0.16 for Y=H.[11] These ρ_{XZ} values are close to those for the similar backside-attack S_N2 reactions at the secondary carbon centers ($\rho_{XZ} \cong 0.12$).[1C,6] This means that PPBs react with anilines by the normal backside-attack mechanism for a benzenesulfonate with the secondary carbon center.



PPB

Our MO theoretical reactant structures based on the PM3 calculations[12] reveal that for 2-PEB (and also for 2-TEB) the backside approach of the aniline nucleophile to the reaction center carbon is made diffilcult by the benzene ring whereas for PPB the benzene ring is not likely to cause such an interference to the backside approach. The three PM3 optimized reactant structures are presented in Figures (l)-(3); the ring plane in 2-PEB and 2-TEB bisects the angle formed by the two H atoms at C_α (dihedral angle $C_\alpha C_\beta C_1 C_2$ is relatively small) and thereby partially blocks the backside approach, while PPB has a structure in which the benzene ring is rotated *ca.* 90° (dihedral angle of $C_\alpha C_\beta C_1 C_2$ is now approximately, 90°) and thereby clears the space for the backside approach of the nucleophile to C_α. It is interesting to note that the ρ_{XZ} observed for the reactions of anilines with phenacyl benzenesulfonates, which have primary carbon reaction centers, in MeOH at 45.0 °C is 0.32,[13] the average value for the similar reactions at primary carbon centers.[6] This means that the intervening carbonyl group does not cause steric blocking of the backside approach of the nucleophile.

In accordance with the four-center TS proposed for the reactions of 2-TEB and 3-TEB, the kinetic isotope effects observed with deuterated aniline nucleophiles are the primary effects, $k_H/k_D > 1.0$,[1c,9] as shown in Table 6. The k_H/k_D values are all greater than one (1.28-2.30) and the magnitudes of k_H/k_D are slightly greater for 2-TEB than those corresponding values for 3-TEB. This can be interpreted as a somewhat tighter TS for the former, since the four-center TS structure in Scheme 1 indicates that the closer approach of the nucleophile should cause a greater degree of N-H(D) bond cleavage resulting in a greater k_H/k_D value.

We conclude that the reactions of 2-TEB and 3-TEB with anilines proceeds by the frontside-attack S_N2 mechanism with the four-center TS (Scheme 1). The frontside-attack S_N2 mechanism is characterized by a large negative ρ_{XZ} ($\rho_{XZ} = -0.4 \sim -0.8$) and the primary kinetic isotope effect, $k_H/k_D > 1.0$, involving deuterated aniline nucleophiles. For 2-phenylethyl-, 2-thiopheneethyl- and 3-thiopheneethyl- benzenesutionates the backside approach of the aniline nucleophile is blocked by the benzene ring so that the frontside approach S_N2 mechanism is enforced, but for 1-phenyl-2-propyl- and phenacylbenzenesulfonates no such interference to the backside approach of the nucleophile is caused by the ring leading to the normal backside-attack S_N2 mechanism.

Table 6. Secondary kinetic isotope effects for the reactions of Z-substituted 2-thiopheneethyl and 3-thiopheneethyl arenesulfonates with X-substituted deuterated anilines in acetonitrile at 60.0 °C

Substrate	X	Z	k_H($M^{-1}s^{-1}$)	k_D($M^{-1}s^{-1}$)	k_H/k_D
2-Thiophene	p-OMe	p-Me	$(5.73 \pm 0.02^a) \times 10^{-5}$	$(2.05 \pm 0.24) \times 10^{-5}$	2.30 ± 0.22^b
	p-Cl	p-Me	$(1.02 \pm 0.04) \times 10^{-5}$	$(0.530 \pm 0.005) \times 10^{-5}$	1.92 ± 0.23
	p-OMe	p-NO_2	$(6.20 \pm 0.09) \times 10^{-4}$	$(3.65 \pm 0.17) \times 10^{-4}$	1.70 ± 0.08
	p-Cl	p-NO_2	$(6.26 \pm 0.05) \times 10^{-5}$	$(4.78 \pm 0.16) \times 10^{-5}$	1.31 ± 0.05
3-Thiophene	p-OMe	p-Me	$(4.47 \pm 0.06) \times 10^{-5}$	$(2.93 \pm 0.19) \times 10^{-5}$	1.53 ± 0.10
	p-Cl	p-Me	$(1.12 \pm 0.05) \times 10^{-5}$	$(0.681 \pm 0.005) \times 10^{-5}$	1.64 ± 0.18
	p-OMe	p-NO_2	$(5.62 \pm 0.05) \times 10^{-4}$	$(4.39 \pm 0.07) \times 10^{-4}$	1.28 ± 0.02
	p-Cl	P-NO_2	$(7.94 \pm 0.04) \times 10^{-5}$	$(6.14 \pm 0.48) \times 10^{-5}$	1.29 ± 0.10

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

Experimental

Materials. 2-(2-Thienyl)ethanol, 2-(3-thienyl)ethanol and benzenesulfonyl chloride used for synthesis of the substrates were Aldrich G.R. grade. Anilines were Tokyo Kasei G.R. grade and N,N-dimethylanilines were prepared by the known method. Merck G.R. grade acetonitrile solvent was distilled 3 times before use.

Preparation of thiopheneethyl benzenesulfonates. 2-(2-Thienyl)ethanol (3 m mol) and pyridine (5 mL) were mixed and refluxed at 0 °C. To this mixture, benzenesulfonyl chloride (1 equivalent) was added and refluxed until salt is formed. The reaction mixture was checked by TLC for the progress of the reaction and ice was added. The mixture was extracted with ether twice and the unreacted pyridine was removed. The extract was washed twice with brine and dried over $MgSO_4$, after which ether was removed with rotary evaporator. The product was purified by either column chromatography (silica gel 70-230 mesh) or recrystallization. NMR (400 MHz) data are as follows.

2-Thiopheneethyl tosylate. liquid, δ_H($CDCl_3$), 7.68 (2H, d, ortho, J=8.79 Hz), 7.25 (2H, d, meta, J=8.79 Hz), 7.07 (1H, d, J=5.86 Hz), 6.84 (1H, dd, J=4.88 Hz, J'=2.93 Hz), 6.74 (1H, d, J=2.93 Hz), 4.15 (2H, t, CH_2, J=6.84 Hz), 3.11 (2H, t, CH_2, J=6.84 Hz), 2.37 (3H, s, CH_3). IR (cm^{-1}) 1459, 1597 (Ar C=C), 1177, 1358 ($\nu_{S=O}$), 1096 (ν_{C-O}), 816 (ν_{S-O}), 737, 901 (phenyl).

2-Thiopheneethyl benzenesulfonate. liquid, δ_H ($CDCl_3$), 7.86 (2H, dd, ortho, J=7.33 Hz, J'=1.47 Hz), 7.63 (1H, dd, para, J=8.06 Hz, J'=1.47 Hz), 7.52 (2H, t, meta, J= 8.06 Hz, J'=7.33 Hz), 7.13 (1H, dd, J=5.12 Hz, J'=4.17 Hz), 6.89 (1H, dd, J=5.12 Hz, J'=2.93 Hz), 6.79 (1Hz, t, J=2.20 Hz, J'=1.47 Hz), 4.24 (2H, t, CH_2, J=7.33 Hz, J'=6.59 Hz), 3.17 (2H, t, CH_2, J=7.33 Hz, J'=6.59 HZ). IR (cm^{-1}) 1446, 1580 (Ar C=C), 1182, 1380 ($\nu_{S=O}$), 1064 (ν_{C-O}), 832 (ν_{S-O}), 754, 901 (phenyl).

2-Thiopheneethyl p-chlorobenzenesulfonate. liquid, δ_H($CDCl_3$), 7.76 (2H, d, ortho, J=8.79 Hz), 7.48 (2H, d, meta, J=8.79 Hz), 7.14 (1H, d, J=5.13 Hz), 6.90 (1H, dd, J=5.13 Hz, J'=3.67 Hz), 6.79 (1H, d, J=2.19 Hz), 4.25 (2H, t, CH_2, J=6.60 Hz), 3.19 (2H, t, CH_2, J=6,60 Hz). IR (cm^{-1}) 1477, 1583 (Ar C=C), 1181, 1363 ($\nu_{S=O}$), 1090 (ν_{C-O}), 828 (ν_{S-O}), 748, 902 (phenyl).

2-Thiopheneethyl p-nitrobezenesulfonate. mp 89-91 °C, δ_H($CDCl_3$), 8.33 (2H, d, ortho, J=8.79 Hz), 7.98 (2H, d, meta, J=8.79 Hz), 7.14 (1H, d, J=6.84 Hz), 6.89 (1H, dd, J=5.86 Hz, J'=2.93 Hz), 6.79 (1H, d, J=2.93 Hz), 4.33 (2H, t, CH_2, J=6.84 Hz), 3.22 (2H, t, CH_2, J=6.84 Hz). IR (cm^{-1}) 1473, 1590 (Ar C=C), 1184, 1355 ($\nu_{S=O}$), 1095 (ν_{C-O}), 858 (ν_{S-O}), 740, 906 (phenyl).

3-Thiopheneethyl tosylate. liquid, δ_H($CDCl_3$), 7.62 (2H, d, ortho, J=8.78 Hz), 7.23 (2H, d, meta, J=8.78 Hz), 7.13 (1H, dd, J=4.88 Hz, J'=2.93 Hz), 6.88 (1H, d, J=2.93 Hz), 6.79 (1H, d, J=4.88 Hz), 4.14 (2H, t, CH_2, J=6.83 Hz), 2.90 (2H, t, CH_2, J=6.83 Hz), 2.35 (3H, s, CH_3). IR (cm^{-1}) 1459, 1597 (Ar C=C), 1177, 1359 ($\nu_{S=O}$), 1097 (ν_{C-O}), 816 (ν_{S-O}), 739, 905 (phenyl).

3-Thiopheneethyl benzenesulfonate. liquid, δ_H ($CDCl_3$), 7.83 (2H, d, ortho, J=8.79 Hz), 7.62 (1H, t, meta, J=7.81 Hz, J'=6.84 Hz), 7.50 (2H, t, para, J=7.81 Hz), 7.21 (1H, dd, J=4.88 Hz, J'=2.93 Hz), 6.96 (1H, s), 6.86 (1H, d, J=4.88 Hz), 4.22 (2H, t, CH_2, J=6.84 Hz), 2.98 (2H, t, CH_2, J=6.84 Hz). IR (cm^{-1}) 1456, 1589 (Ar C=C), 1183, 1359 ($\nu_{S=O}$), 1096 (ν_{C-O}), 822 (ν_{S-O}), 786, 906 (phenyl).

3-Thiopheneethyl p-chlorobenzenesulfonate. mp 58-59 °C, δ_H($CDCl_3$), 7.75 (2H, d, ortho, J=8.79 Hz), 7.48 (2H, d, meta, J=7.82 Hz), 7.25 (1H, dd, J=4.88 Hz, J'=2.92 Hz), 6.98 (1H, d, J=2.92 Hz), 6.85 (1H, d, J=4.89 Hz), 4.24 (2H, t, CH_2, J=6.83 Hz), 3.01 (2H, t, CH_2, J=6.83 Hz). IR (cm^{-1}) 1477, 1583 (Ar C=C), 1182, 1362 ($\nu_{S=O}$), 1090 (ν_{C-O}), 826 (ν_{S-O}), 784, 906 (phenyl).

3-Thiopheneethyl p-nitrobenzenesulfonate. mp 104-105 °C, δ_H($CDCl_3$), 8.32 (2H, d, ortho, J=8.79 Hz), 7.96 (2H, d, meta, J=8.79 Hz), 7.22 (1H, dd, J=4.88 Hz, J'= 2.93 Hz), 6.98 (1H, s), 6.83 (1H, d, J=4.88 Hz), 4.32 (2H, t, CH_2, J=6.83 Hz), 3.04 (2H, t, CH_2, J=6.83 Hz). IR (cm^{-1}) 1477, 1583 (Ar C=C), 1184, 1355 ($\nu_{S=O}$), 1090 (ν_{C-O}), 827 (ν_{S-O}), 784, 906 (phenyl).

Kinetic procedure. Rates were measured conductimetrically at 60.0 ± 0.05 °C in acetonitrile. The kinetic procedures for determinations of k_{obs} were as described previously.[2~5,14] In general, linearities for the plot of k_{obs} *vs* [amine] were excellent with more than 4 excess amine concentrations, eq. 4. The k_2 values were reproducible to ± 3%. In MeCN, k_1 was negligible.

$$k_{obs} = k_1 + k_2[\text{amine}] \tag{4}$$

Product analysis. The substrate, 2- and 3-thiopheneethyl p-nitrobenzenesulfonate (0.05 mole) and aniline (0.5 mole) or N,N-dimethylaniline (0.5 mole) were reacted under the same reaction condition for more than 15 half-lives. The salt was filtered and solvent was removed from the filtrate. The aniline was isolated by column chromatography. The analytical data are as follows.

$2\text{-}C_4H_3SCH_2CH_2NHC_6H_4\text{-}p\text{-}CH_3$. liquid, δ_H($CDCl_3$), 7.16 (1H, dd, ortho, *J* =5.13 Hz, *J′* =1.47 Hz), 7.00 (2H, d, ortho, *J* =8.79 Hz), 6.95 (1H, dd, *J* =5.13 Hz, *J′* =3.66 Hz), 6.85 (1H, dd, *J* =3.66 Hz, *J′* =1.47 Hz), 6.55 (2H, d, meta *J* = 8.79 Hz), 3.66 (1H, broad, s, NH), 3.42 (2H, t, CH_2, *J* =7.33 Hz, *J′* =6.59 Hz), 3.12 (2H, t, CH_2, *J* =6.59 Hz), 2.24 (3H, s, CH_3).

$3\text{-}C_4H_3SCH_2CH_2NHC_6H_4\text{-}p\text{-}CH_3$. liquid, δ_H($CDCl_3$), 7.26 (1H, dd, *J* =5.13 Hz, *J′* =2.93 Hz), 6.98 (2H, d, ortho, *J* = 8.06 Hz), 6.97 (1H, s), 6.95 (1H, d, *J* =5.12 Hz), 6.53 (2H, d, meta *J* =8.06 Hz), 3.65 (1H, broad, s, NH), 3.35 (2H, t, CH_2, *J* =7.33 Hz, *J′* =6.59 Hz), 2.92 (2H, t, CH_2, *J* =6.59 Hz), 2.23 (3H, s, CH_3).

$p\text{-}CH_3C_6H_4NH_3^{+}\text{-}OSO_2C_6H_4\text{-}p\text{-}NO_2$. mp 235-237 °C, δ_H($CDCl_3$), 8.25 (2H, d, ortho, *J* =8.79 Hz), 7.90 (2H, d, meta, *J* =8.79 Hz), 7.25 (2H, d, ortho, *J* =7.82 Hz), 7.17 (2H, d, meta, *J* =7.82 Hz), 2.26 (3H, s, CH_3).

$2\text{-}C_4H_3SCH_2CH_2N^{+}(CH_3)_2C_6H_4\text{-}p\text{-}CH_3\,^{-}OSO_2C_6H_4\text{-}p\text{-}NO_2$. mp 171-172 °C, δ_H($CDCl_3$), 8.24 (2H, d, ortho, SArH, *J* =8.79 Hz), 7.88 (2H, d, meta, SArH, *J* =8.79 Hz), 7.53 (2H, dd, ortho, NArH, *J* =9.52 Hz, *J′* =2.93 Hz), 7.33 (2H, t, meta, NArH, *J* =8.06 Hz), 7.18 (1H, dd, *J* =5.13 Hz, *J′* =1.46 Hz), 6.84 (1H, dd, *J* =5.13 Hz, *J′* =2.94 Hz), 6.69 (1H, dd, *J* =2.94 Hz, *J′* =1.46 Hz), 4.02 (2H, t, CH_2, *J* =8.06 Hz), 3.51 (6H, s, $N(CH_3)_2$), 2.91 (2H, t, CH_2, *J* =8.06 Hz), 2.28 (3H, s, $ArCH_3$).

$3\text{-}C_4H_3SCH_2CH_2N^{+}(CH_3)_2C_6H_4\text{-}p\text{-}CH_3\,^{-}OSO_2C_6H_4\text{-}p\text{-}Cl$. mp 156-157 °C, δ_H($CDCl_3$), 7.93 (2H, dd, ortho, SArH, *J* =7.33 Hz, *J′* =2.93 Hz), 7.59 (2H, d, meta, SArH, *J* = 8.80 Hz), 7.34 (4H, m, NArH), 7.18 (1H, dd, *J* =5.13 Hz, *J′* = 2.93 Hz), 7.10 (1H, s), 6.94 (1H, dd, *J* =5.13 Hz, *J′* =1.47 Hz), 4.45 (2H, t, CH_2, *J* =8.06 Hz), 3.78 (6H, s, $N(CH_3)_2$), 2.74 (2H, t, CH_2, *J* =8.06 Hz), 2.41 (3H, s, $ArCH_3$).

MO Calculation. The structures of reactants, 1-PEB, 2-PEB, 2-TEB, 3-TEB, PPB and cumyl benzenesulfonate, were determined by full optimization using the PM3 method.[12] The structures correspond to the most stable forms, which were confirmed by identifying all positive eigenvalues in the Hessian matrix.[15]

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