the shape of the Franck–Condon envelopes.

Elementary theory is less successful in predicting the effects of geometrical constraint. In VI$^-$, $\pi(6) \rightarrow \pi(7)$ occurs at higher energy than in IV$^-$, consistent with the existence of a geometrical constraint that limits c by preventing the rings from becoming coplanar. However, such a constraint should have the effect of lowering the energy of $\pi(7) \rightarrow \pi(10)$, so that the sum of the energies of these two transitions remains constant. This is contrary to what is found.

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Supplementary Material Available: First-order electron densities, orbital energies, and one-electron transition energies in 2,2′-bipyridine and 4,4′-bipyridine and electronic absorption spectra of some additional bipyridines (7 pages). Ordering information is given on any current masthead page.

Cross-Interaction Constants as a Measure of the Transition-State Structure. 14. Nucleophilic Substitution Reactions of 1-Phenyl-2-propyl Benzenesulfonates with Anilines in Methanol

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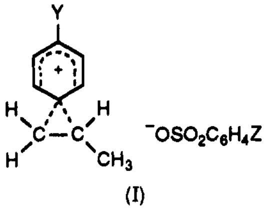
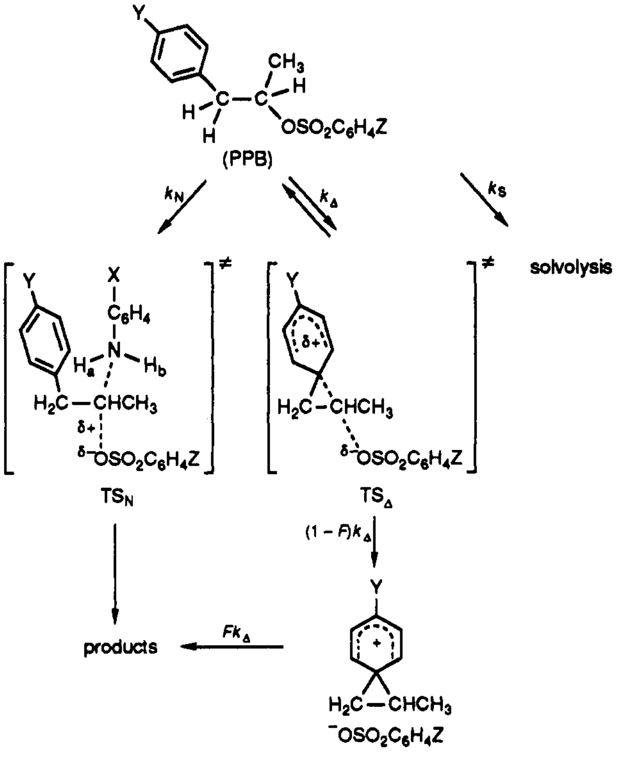
The kinetics of the reactions between 1-phenyl-2-propyl benzenesulfonates (PPB) and anilines in methanol at 65.0 °C are investigated, and the mechanism is discussed on the basis of various selectivity parameters, especially on the cross-interaction constants, ρ_{ij}. The aryl participation is significant only with the p-CH_3O-substituted substrate. ρ_{XZ} is positive, and accordingly the transition state (TS) variations with substituents are consistent with those predicted by the potential energy surface diagram. The TS is of an intermediate type between that for an associated (tight) and a dissociated (loose) S_N2 process; it is rather tight, but bond breaking is ahead of bond making with positive charge development at the reaction center in the TS. The possibility of front-side attack with a four-center TS is precluded because of strong steric hinderance in a close approach of the two bulky groups, the nucleophile and leaving group, on the same side in the front-side attack.

In a previous work,[1] we have shown that in the solvolysis of 1-phenyl-2-propyl benzenesulfonates (PPB) in methanol–acetonitrile mixtures the solvent-assisted path, k_S in Scheme I,[2,3] is more favored in the competition with the aryl-assisted path, k_Δ (for solvolysis, only these two paths are available), and the transition-state (TS) structure shifts toward that resembling the ion pair like intermediate,[4] I, as the solvent nucelophilicity decreases with the concomitant increase in the solvent polarity.[5] It was concluded that the aryl-assisted pathway prevails over the solvent-assisted path when the nucleophilicity of solvent[6] is low,



(I)

Scheme I



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[1] Lee, I.; Lee, W. H.; Lee, H. W.; Lee, B. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 785.

[2] (a) Schadt, F. L., III; Lancelot, C. J.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1978**, *100*, 228. (b) Brown, H. C.; Bernheimer, R.; Kim, C. J.; Scheppele, S. E. *J. Am. Chem. Soc.* **1967**, *89*, 370. (c) Brown, H. C.; Morgan, K. J.; Chloupek, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 2137. (d) Cram, D. J. *J. Am. Chem. Soc.* **1964**, *86*, 3767. (e) Cram, D. J.; Thompson, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 6766. (f) Winstein, S.; Morse, B. K. *J. Am. Chem. Soc.* **1952**, *74*, 1133.

[3] (a) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 5919. (b) Snyder, E. I. *J. Am. Chem. Soc.* **1970**, *92*, 7529. (c) Schoeller, W. W.; Schenck, G. E. *Tetrahedron* **1973**, *29*, 425. (d) Schoeller, W. W.; Dahm, J. *Tetrahedron* **1973**, *29*, 3237. (e) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1974**, 872.

[4] Fornarini, S.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *110*, 34.

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Table I. Second-Order Rate Constants ($k_2 \times 10^5$ M^{-1} s^{-1}) for the Reactions between $YC_6H_4CH_2CH(CH_3)OSO_2C_6H_4Z$ and $XC_6H_4NH_2$ in Methanol at 65.0 °C

		Z[a]			
Y	X	p-CH_3	H	p-Cl	p-NO_2
p-CH_3O	p-CH_3O	7.23 ± 0.02	11.5 ± 0.2	22.1 ± 0.2	105 ± 2.0
	p-CH_3	6.61 ± 0.09	10.5 ± 0.02	20.4 ± 0.6	97.7 ± 0.6
	H	5.81 ± 0.01	9.12 ± 0.07	17.4 ± 0.2	88.2 ± 0.2
	p-Cl	4.66 ± 0.04	7.59 ± 0.05	15.1 ± 0.2	75.9 ± 1.1
p-CH_3	p-CH_3O	5.25 ± 0.07	7.78 ± 0.02	14.1 ± 0.2	55.0 ± 1.0
	p-CH_3	4.07 ± 0.04	6.17 ± 0.06	10.7 ± 0.3	43.7 ± 0.6
	H	2.57 ± 0.06	4.09 ± 0.03	7.30 ± 0.02	29.7 ± 0.3
	p-Cl	1.53 ± 0.02	2.40 ± 0.05	4.37 ± 0.02	18.8 ± 0.3
H	p-CH_3O	4.99 ± 0.06	7.55 ± 0.06	13.1 ± 0.3	47.9 ± 1.2
	p-CH_3	3.82 ± 0.02	5.62 ± 0.10	9.77 ± 0.04	37.2 ± 0.5
	H	2.42 ± 0.02	3.55 ± 0.10	6.61 ± 0.08	25.1 ± 0.5
	p-Cl	1.30 ± 0.03	2.04 ± 0.05	3.66 ± 0.07	14.8 ± 0.4
p-Cl	p-CH_3O	4.79 ± 0.10	6.72 ± 0.07	11.9 ± 0.12	43.7 ± 0.34
	p-CH_3	3.47 ± 0.08	4.91 ± 0.14	8.63 ± 0.18	32.4 ± 0.45
	H	2.04 ± 0.05	3.03 ± 0.04	5.50 ± 0.14	20.7 ± 0.30
	p-Cl	1.01 ± 0.03	1.55 ± 0.04	2.84 ± 0.05	11.2 ± 0.33
p-NO_2	p-CH_3O	3.81 ± 0.04	5.50 ± 0.14	9.18 ± 0.17	30.4 ± 0.6
	p-CH_3	2.32 ± 0.04	3.32 ± 0.06	5.68 ± 0.07	19.7 ± 0.5
	H	1.24 ± 0.01	1.82 ± 0.02	3.19 ± 0.06	11.5 ± 0.2
	p-Cl	0.498 ± 0.011	0.758 ± 0.017	1.35 ± 0.03	5.01 ± 0.08

[a] The error limits shown are average deviations based on triplicate runs.

and accordingly, in hexafluoroisopropyl alcohol (HFIP), which has extremely low nucleophilicity with high ionizing power, the solvolysis was found to proceed entirely by the aryl-assisted pathway. These conclusions were reached on the basis of various selectivity parameters, notably the cross-interaction constants, ρ_{ij}, in eq 1.[7,8]

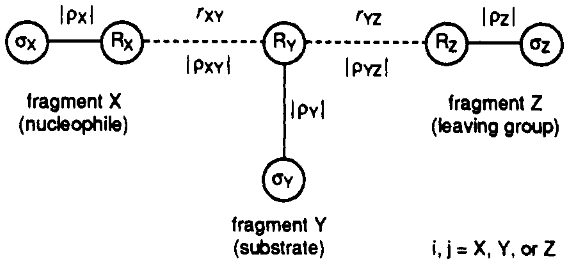
$$\log (k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

The cross-interaction constants between substituents in the nucleophile (X) and leaving group (Z), ρ_{XZ} defined in eq 2, have an important significance as to the type of TS variation with substituents.[9]

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

Thus, a negative ρ_{XZ} indicates that a more electron-donating substituent (EDS) in the nucleophile (i.e., a stronger nucleophile), $\delta\sigma_X < 0$, leads to a greater positive ρ_Z, $\delta\rho_Z > 0$ (i.e., a greater degree of bond breaking). In effect, the negative ρ_{XZ} value predicts a "later TS" for a stronger nucleophile or a better LG. This prediction is precisely what we would expect from the quantum-mechanical (QM) model for prediction of TS variation.[8g,10]

Chart I



Conversely, if ρ_{XZ} is positive, a stronger nucleophile and a better LG lead to an "earlier TS" with a lesser degree of bond making and breaking. In this case, the TS variation can be predicted with the potential energy surface (PES) model,[8p,11] and the effects of substituents on the TS variation are in complete agreement with what we would expect thermodynamically. A stronger nucleophile and a better LG will give thermodynamically more stable products so that the reaction will become more exothermic. An increase in exothermicity will lead to an earlier TS according to the Hammond postulate,[12] which is also based on thermodynamic stabilities of reactants and products. Thus, a reaction series becomes thermodynamically controlled when ρ_{XZ} is positive and the TS variation follows that predicted by the PES model.[11]

On the other hand, it has been shown that the distance r_{ij} between two reaction centers R_i and R_j (Chart I),[9] i.e.,

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(5) Lee, I.; La, S.-M.; Lee, B.-S.; Sohn, S. C. *J. Korean Chem. Soc.* **1984**, *28*, 210.

(6) (a) Bentley, T. W. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Ed.; *Advances in Chemistry Series 215*; American Chemical Society: Washington, DC, 1987; p 255. (b) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.

(7) Shorter, J. *Correlation Analysis of Organic Reactivity*; Research Studies Press: Chichester, 1982; Chapter 2.

(8) (a) Lee, I.; Sohn, S. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1055. (b) Lee, I.; Shim, C. S.; Chung, S. Y.; Lee, H. W. *Bull. Korean Chem. Soc.* **1987**, *8*, 350. (c) Lee, I. *Bull. Korean Chem. Soc.* **1987**, *8*, 426. (d) Lee, I.; Kim, H. Y.; Kang, H. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1216. (e) Lee, I.; Kang, H. K. *Tetrahedron Lett.* **1987**, *28*, 1183. (f) Lee, I.; Kang, H. K.; Lee, H. W. *J. Am. Chem. Soc.* **1987**, *109*, 7472. (g) Lee, I.; Shim, C. S.; Chung, S. Y.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 975. (h) Lee, I.; Kim, H. Y.; Kang, H. K.; Lee, H. W. *J. Org. Chem.* **1988**, *53*, 2678. (i) Lee, I.; Shim, C. S.; Kim, H. Y.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1919. (j) Lee, I.; Kim, I. C. *Bull. Korean Chem. Soc.* **1988**, *9*, 133. (k) Lee, I.; Huh, C.; Koh, H. J.; Lee, H. W. *Bull. Korean Chem. Soc.* **1988**, *9*, 376. (l) Lee, I.; Kim, H. Y.; Lee, H. W.; Kim, I. C. *J. Phys. Org. Chem.* **1989**, *2*, 35. (m) Lee, I.; Shim, C. S.; Lee, H. W. *J. Phys. Org. Chem.* **1989**, *2*, 484. (n) Lee, I.; Shim, C. S.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1205. (o) Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1989**, 943. (p) Lee, I.; Choi, Y. H.; Rhyu, K. W.; Shim, C. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1881. (q) Lee, I.; Rhyu, K. W.; Shim, C. S.; Oh, H. K. *J. Phys. Org. Chem.* **1990**, *3*, 751. (r) Lee, I.; Lee, W. H.; Lee, H. W. *J. Phys. Org. Chem.* **1990**, *3*, 545. (s) Lee, I.; Koh, H. J.; Huh, C.; Lee, H. W. *J. Phys. Org. Chem.* **1990**, *3*, 550. (t) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317.

(9) (a) Lee, I. *Bull. Korean Chem. Soc.* **1987**, *8*, 200. (b) Lee, I. *Bull. Korean Chem. Soc.* **1988**, *9*, 179.

(10) (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702. (b) Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642.

(11) (a) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915. (b) More O'Ferrall, R. A. *J. Chem. Soc. B*, **1970**, 274. (c) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705. (d) Harris, J. M.; Kurz, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 349. (e) Critchlow, J. E. *J. Chem. Soc., Faraday Trans. 1*, **1972**, *68*, 1774. (f) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(12) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) le Noble, W. J.; Asano, T. *J. Am. Chem. Soc.* **1975**, *97*, 1778. (c) le Noble, W. J.; Miller, A. R. *J. Org. Chem.* **1979**, *44*, 889. (d) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7900.

Table II. Comparison of Methanolysis Rate Constants Obtained by Extrapolation, k_1^{ext}, and by Independent Measurements, k_1^{sol}, for the Reactions of $YC_6H_4CH_2CH(CH_3)OSO_2C_6H_4Z$ and $XC_6H_4NH_2$ in Methanol at 65.0 °C

X	Y	Z	aniline concn (M)	k_{obsd} (s^{-1})	k_1^{sol} (s^{-1})	k_2 (M^{-1} s^{-1})
p-CH_3	p-CH_3O	p-NO_2	0.6003	3.44×10^{-3}		
			0.4497	3.31×10^{-3}		
			0.3002	3.17×10^{-3}		
			0.1504	3.00×10^{-3}		
			0.00	2.86×10^{-3} (k_1^{ext})	2.88×10^{-3}	9.74×10^{-4} ($r = 0.998$)[a]
p-CH_3	p-NO_2	p-CH_3	0.6003	3.02×10^{-5}		
			0.4497	2.66×10^{-5}		
			0.3002	2.34×10^{-5}		
			0.1504	1.97×10^{-5}		
			0.00	1.63×10^{-5} (k_1^{ext})	1.65×10^{-5}	2.32×10^{-5} ($r = 0.999$)[a]

[a] Correlation coefficient for the plot of k_{obsd} vs [aniline].

the degree of bond making or breaking in the TS is a logarithmic inverse function of the magnitude of cross-interaction constants. Thus, other conditions being equal, r_{ij} is inversely related to $|\rho_{ij}|$ so that a greater (smaller) magnitude of cross-interaction constants reflects a tighter (looser) TS.

In this work, we carried out kinetic studies of the reactions between PPB and anilines in methanol, eq 3, with a view to elucidating the TS structure using various selectivity parameters, especially, the cross interaction constants.

$$2XC_6H_4NH_2 + YC_6H_4CH_2CH(CH_3)OSO_2C_6H_4Z \xrightarrow[MeOH]{65.0\ ^\circ C} YC_6H_4CH_2CH(CH_3)NHC_6H_4X + XC_6H_4NH_3^+ + {}^-OSO_2C_6H_4Z \quad (3)$$

$X = p\text{-}CH_3O, p\text{-}CH_3, H, \text{or } p\text{-}Cl$

$Y = p\text{-}CH_3O, p\text{-}CH_3, H, p\text{-}Cl, \text{or } p\text{-}NO_2$

$Z = p\text{-}CH_3, H, p\text{-}Cl, \text{or } p\text{-}NO_2$

Results and Discussion

The reaction of PPB can proceed through three pathways: solvolysis, k_S, aryl-assisted, k_Δ, and direct bimolecular nucleophilic substitution by aniline, k_N, which can be either front-side (k_f) or back-side (k_r) attack (Scheme I). The pseudo-first-order rate constants for methanolysis, eq 4,[1] are relatively large and comparable to the second-order rate constants, k_2, summarized in Table I. However, the acid formed in the methanolysis will be present in the reaction medium as the anilinium ion pair since the aniline concentration was kept in excess (ca. 150–600×) of the substrate in all cases. This means that the solvolysis, or the product of it, in no way interferes with the bimolecular substitution pathways, k_Δ and k_N (Scheme I), in view of the fact that the product ether is relatively inert and only undergoes an acid-catalyzed reaction under fairly strenuous condition.[13] That the methanolysis constituted merely a parallel path to the main reaction was confirmed with methanolysis rate constants determined by extrapolation, k_1^{ext}, with eq 5, and by independent measurements, k_1^{sol}.

$$YC_6H_4CH_2CH(CH_3)OSO_2C_6H_4Z + CH_3OH \xrightarrow{65.0\ ^\circ C} YC_6H_4CH_2CH(CH_3)OCH_3 + H^+ + {}^-OSO_2C_6H_4Z \quad (4)$$

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

The two values, k_1^{ext} and k_1^{sol}, agree very well as shown in Table II for the two representative cases of fast and slow reactions. Any olefin-forming β-elimination is also precluded by our product analysis.

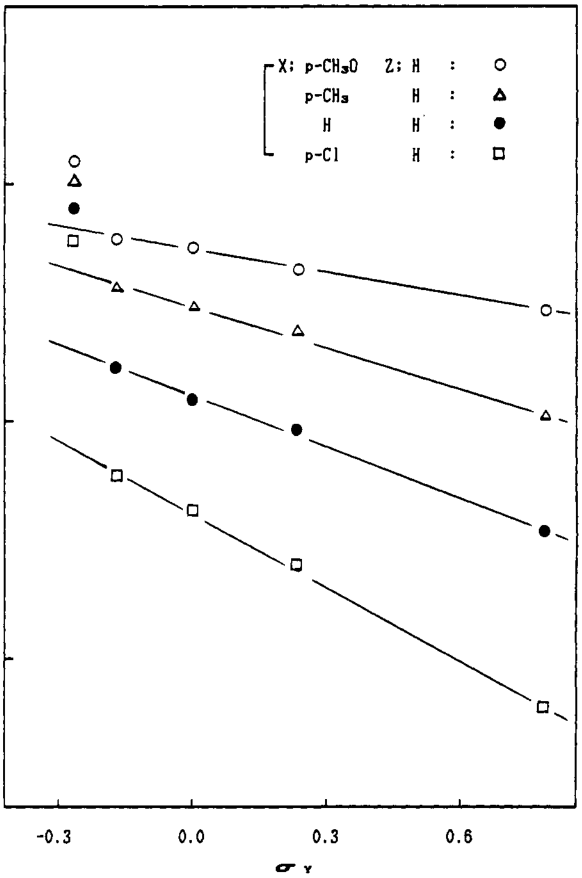

Figure 1. Hammett ρ_Y plots for reaction 3.

Table III. Hammett ρ_Y Values[a,b] for Reaction 3

	Z			
X	p-CH_3	H	p-Cl	p-NO_2
p-CH_3O	−0.15	−0.16	−0.20	−0.27
p-CH_3	−0.26	−0.29	−0.29	−0.36
H	−0.35	−0.37	−0.39	−0.43
p-Cl	−0.52	−0.53	−0.54	−0.60

[a] Correlation coefficients; $r > 0.990$. [b] $Y = p$-CH_3O is expected.

Reference to Table I reveals that reactivity trends are typical of those expected for S_N2 processes;[14] the rate increases with a more EDS in the nucleophile ($X = p$-CH_3O) and with a more EWS in the leaving group ($Z = p$-NO_2). The rate increases also with a more EDS in the substrate

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[13] Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan Publishing Co.: New York, 1981; p 262.

[14] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; Chapter 4.

Table IV. Percent Aryl-Assisted Reaction ($100\,[Fk_\Delta/(k_s + k_N + k_\Delta)]$)[a] As Determined by Hammett Plot Method for PPB

	Z			
X	p-CH$_3$	H	p-Cl	p-NO$_2$
p-CH$_3$O	21	26	30	40
p-CH$_3$	29	32	38	46
H	43	44	46	55
p-Cl	52	53	56	62

[a] The k_s values are obtained from ref 1 and converted to second-order rate constants by dividing by [MeOH].

($Y = p\text{-CH}_3O$), suggesting a positive charge development at the reaction center in the TS. This is also supported by the negative slopes, ρ_Y, of the Hammett[15] plots (Figure 1) for variations of substituent Y in the substrate in Table III. The enhanced reactivity for $Y = p\text{-CH}_3O$, which deviates positively from the straight-line plot, can be ascribed to an extensive aryl participation in the reactions of PPB with this relatively strong EDS. The linearities of the plots, excluding $Y = p\text{-CH}_3O$, are, however, found to be better with σ rather than σ^+, which is the same trend as in the solvolysis of PPB in methanol–acetonitrile mixtures.[1] This suggests that positive charge development at the reaction-center carbon in the TS for reaction 3 is relatively small, as the relatively small magnitude of the ρ_Y values indicates (Table III), or alternatively, there is little direct conjugation between the substituent and the reaction center. Understandably, the degree of aryl participation as expressed by $100[k_\Delta/(k_\Delta + k_S + k_N)]$ for $Y = p\text{-CH}_3O$ in Table IV, where k_Δ is obtained by the difference between k_2 observed and the extrapolated rate constant from the Hammett plot for k_N in Figure 1 and k_S is the measured value in our previous work,[1] is lower than that for the solvolysis.[1] The percentage increases and hence the aryl participation, k_Δ, increases as the nucleophilicity of the nucleophile decreases (nucleophilicity is lower with $X = p\text{-Cl}$) in reaction 3 or with solvent mixture of lower methanol content in the solvolysis[1]). A large negative ρ_Y, i.e., a greater positive charge development in the TS for a weaker nucleophile ($X = p\text{-Cl}$) in Table III, is also in line with the contention that the aryl-assisted pathway, k_Δ, becomes more important as the nucleophilicity of the nucleophile gets lower. The main reason why the aryl participation is lower than that in the methanolysis is that the nucleophilicity of aniline is greater than that of methanol.[6]

The Hammett and Brönsted[16] coefficients, ρ_X and β_X ($=\beta_N$), obtained by varying substituent X in the nucleophile, and the corresponding parameters, ρ_Z and $\beta_Z(=\beta_{lg})$, for variation of substituent Z in the leaving group are summarized in Table V. We note in this table that bond formation ($|\rho_X|$ or $|\beta_X|$) is unusually low and bond breaking ($|\rho_Z|$ or $|\beta_Z|$) is relatively large for $Y = p\text{-CH}_3O$, demonstrating an extensive contribution of the aryl-assisted pathway. For other substituents (Y) in the substrate, $|\beta_X|$ appears to be somewhat greater than $|\beta_Z|$, implying a relatively tight structure of the TS. This is an interesting implication, since the negative ρ_Y indicates positive charge development in the TS;[15] i.e., bond breaking is relatively more advanced than bond formation; thus, the TS is relatively tight but bond breaking is relatively ahead of bond-making. Normally, bond breaking is ahead of bond making in a relatively loose TS (dissociative S_N2)[17,18] when ρ_Y is negative, whereas the opposite holds in a relatively tight TS (associative S_N2)[8g,p] when ρ_Y is positive. Thus, the reaction of PPB with anilines in methanol (eq 3) constitutes an intermediate type of reaction between the two extreme cases. This intermediate character is also evident in the sign of the cross-interaction constants, ρ_{XY}, ρ_{YZ}, and ρ_{XZ} in Table VI. Our previous works[8] have shown that the sign of the constants ρ_{XZ} usually agrees with that of ρ_{XY} but differ from that of ρ_{YZ}; for an associative S_N2 type,[8g,p] ρ_{XY} and ρ_{XZ} were positive and ρ_{YZ} was negative, while for a dissociative S_N2 type,[17,18] the signs reversed to negative for ρ_{XY} and ρ_{XZ} and positive for ρ_{YZ}. Examination of Table VI shows that for reaction 3, ρ_{XY} is negative but ρ_{XZ} is positive, i.e., the signs of the two constants differ.

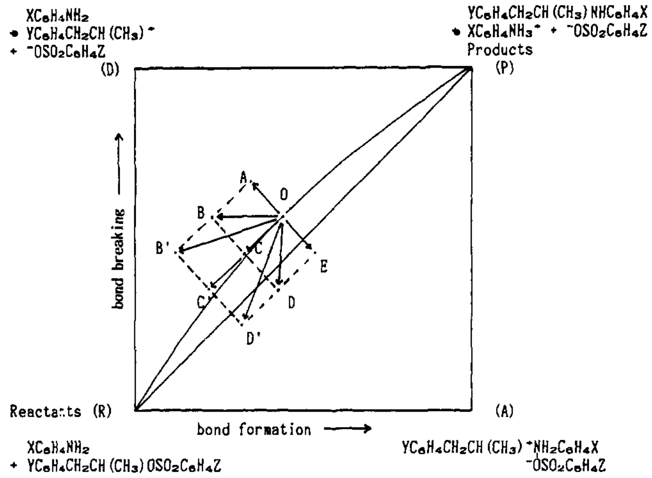

Figure 2. Potential energy surface diagram showing TS variations with substituent changes.

The magnitudes of the three cross-interaction constants also suggest a relatively tight TS; $|\rho_{XY}| \cong 0.7$ is very large; i.e., bond formation is relatively advanced, considering an extra CH_2 group present in the substrate that normally reduces ρ values by about a factor of 2.4–2.8[19] compared to that of a normal S_N2 reaction for which $|\rho_{XY}| = 0.6–0.7$. Similarly, the magnitudes of ρ_{YZ} and ρ_{XZ} are also large so that bond cleavage is less and the TS is tighter compared to those in a dissociative S_N2 reaction (Table VII).[8a]

The positive ρ_{XZ} values obtained for reaction 3, however, require that the TS variations with substituents be consistent with those predicted by the potential energy surface (PES) diagram[10c,20] (Figure 2). Indeed, we find that a stronger nucleophile ($X = p\text{-CH}_3O$) and/or a better leaving group ($Z = p\text{-NO}_2$) leads to an earlier TS as the PES model requires; a stronger nucleophilic stabilizes the right-hand corners, P and A, so that the TS will shift to either D (decrease in bond formation) or D′ (decrease in both bond formation and bond breaking) depending on whether the Hammond effect is the same as (OE = OC) or is greater than the anti-Hammond effect (OC′ > OE). The kinetic isotope effects[21] involving the deuterated aniline nucleo-

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[15] (a) Gilliom, R. D. *Introduction to Physical Organic Chemistry*; Addison-Wesly: Reading, 1970; Chapter 9. (b) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: Cambridge, 1973; p 7.

[16] Brönsted, J. N.; Pederson, K. J. *Z. Phys. Chem.* **1924**, *108*, 185.

[17] (a) Lee, I.; Lee, W. H.; Sohn, S. C.; Kim, C. S. *Tetrahedron* **1985**, *41*, 2635. (b) Lee, I.; Sohn, S. C.; Kang, C. H.; Oh, Y. J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1631. (c) Lee, I.; Sohn, S. C.; Oh, Y. J.; Lee, B. C. *Tetrahedron* **1986**, *42*, 4713.

[18] (a) Han, G. L.; Park, J. H.; Lee, I. *Bull. Korean Chem. Soc.* **1987**, *8*, 393. (b) Lee, I.; Choi, Y. H.; Lee, H. W.; Lee, B. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1537.

[19] (a) Reference 14a, p 146. (b) Jacobson, B. M.; Lewis, E. S. *J. Org. Chem.* **1988**, *53*, 446. (c) Siggel, M. R. F.; Streitwieser, A., Jr.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022.

[20] (a) Lee, I.; Seo, H. S. *Bull. Korean Chem. Soc.* **1986**, 7, 448. (b) Lee, I.; Song, C. H. *Bull. Korean Chem. Soc.* **1986**, *7*, 186.

Table V. Hammett (ρ_X and ρ_Z)[a] and Brönsted Coefficients (β_X[b] and β_Z[c] in Parentheses) for Reaction 3

	$\rho_X(\beta_X)$[d] Z =				$\rho_Z(\beta_Z)$[e] X =			
Y	*p*-CH_3	H	*p*-Cl	*p*-NO_2	*p*-CH_3O	*p*-CH_3	H	*p*-Cl
p-CH_3O	–0.38 (0.14)	–0.36 (0.13)	–0.34 (0.12)	–0.28 (0.10)	1.23 (–0.41)	1.24 (–0.41)	1.25 (–.42)	1.28 (–0.43)
p-CH_3	–1.09 (0.39)	–1.03 (0.37)	–1.02 (0.37)	–0.94 (0.34)	1.08 (–0.36)	1.09 (–0.36)	1.12 (–0.37)	1.15 (–0.38)
H	–1.18 (0.42)	–1.14 (0.41)	–1.11 (0.40)	–1.02 (0.37)	1.03 (–0.35)	1.05 (–0.35)	1.08 (–0.36)	1.11 (–0.37)
p-Cl	–1.36 (0.49)	–1.28 (0.46)	–1.24 (0.45)	–1.19 (0.43)	1.02 (–0.34)	1.03 (–0.34)	1.07 (–0.36)	1.10 (–0.37)
p-NO_2	–1.76 (0.63)	–1.70 (0.61)	–1.65 (0.59)	–1.55 (0.56)	0.95 (–0.32)	0.98 (–0.33)	1.02 (–0.34)	1.06 (–0.35)

[a] The σ values were taken from ref 15a, p 147. [b] The pK_a values were taken from ref 13, p 737. [c] The pK_a values are for methyl transfers: Hoffman, R. V.; Shankweiler, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 5536. [d] Correlation coefficients, $r > 0.996$. [e] Correlation coefficients, $r > 0.998$.

Table VI. Hammett-Type Cross-Interaction Constants[a] for Reaction 3

Z	ρ_{XY}	r[b]	X	ρ_{YZ}	r[b]	Y	ρ_{XZ}	r[b]
p-CH_3	–0.72	0.998	*p*-CH_3O	–0.13	0.999	*p*-CH_3O	0.11	0.999
H	–0.71	0.999	*p*-CH_3	–0.10	0.999	*p*-CH_3	0.14	0.999
p-Cl	–0.68	0.998	H	–0.09	0.999	H	0.16	0.999
p-NO_2	–0.66	0.999	*p*-Cl	–0.09	0.999	*p*-Cl	0.17	0.999
						p-NO_2	0.21	0.998

[a] The k_2 values for Y = *p*-CH_3O are excluded. [b] Correlation coefficients at 99% confidence level.

Table VII. Comparison of Cross-Interaction Constants for the Reactions between $ROSO_2C_6H_4Z$ and $XC_6H_4NH_2$ in Methanol

R	ρ_{XY}	ρ_{YZ}	ρ_{XZ}
$YC_6H_4CH_2$–[8a] (BBS)	–0.62	0.11	–0.10
$YC_6H_4CH(CH_3)$–[8h] (1-PEB)	–0.21	0.11	–0.56
$YC_6H_4CH_2CH_2$–[18b] (2-PEB)	–0.12	0.07	–0.45
$YC_6H_4CH_2CH(CH_3)$– (PPB)	–0.71	–0.09	0.16

Table VIII. Comparison of the Kinetic Isotope Effects (k_H/k_D) for the Reactions of 1-Phenyl-2-propyl Benzenesulfonates (PPB) with Deuterated Anilines in Acetonitrile at 65.0 °C with Those for Other Reaction Series

X	Y	Z	PPB	BBS[a]	EBS[b]	2-PEB[c]
p-CH_3O	H	*p*-NO_2	0.93_8	0.90_8	0.86_9	0.97_6
p-CH_3O	H	*p*-CH_3	0.92_8	0.96_0	0.86_2	0.96_1
p-Cl	H	*p*-NO_2	0.90_6			1.03_1
p-Cl	*p*-CH_3O	*p*-NO_2	0.98_7			
m-NO_2	H	*p*-CH_3		0.97_6	0.85_1	

[a] Data for the corresponding reactions of benzyl benzenesulfonates[22a,c] converted to the value at 65.0 °C using the relation $k_H/k_D = \exp[-0.1865(\omega^* - \omega)/T]$. [b] Data for the corresponding reactions of ethyl benzenesulfonates at 65.0 °C.[22b] [c] Data for the corresponding reactions of 2-phenylethyl benzenesulfonates at 65.0 °C.[22d]

philes[22] have shown that the Hammond effect is invariably greater than the anti-Hammond effect.[10b,23] This means that the TS will shift to D′ so that both bond making and breaking are reduced. This prediction is borne out in the decreased $|\rho_Z|$ and increased $|\rho_{YZ}|$ with a more EDS in the nucleophile. Likewise, a better leaving group shifts the TS to B′ so that again both bond making and breaking are reduced as demonstrated by a decrease in $|\rho_X|$ and $|\rho_{XY}|$. On the other hand, a more EDS in the substrate (Y = *p*-CH_3O) will stabilize the upper left corner, D, and the TS will move to A so that bond breaking will increase but bond making will decrease, i.e., a looser TS will be obtained, as indeed evidenced by a decrease in $|\rho_X|$, an increase in $|\rho_Z|$, and a decrease in $|\rho_{XZ}|$.

Comparison of the magnitude of ρ_{XZ} (=0.16) with those for the similar reactions of methyl (ρ_{XZ} = 0.30),[8p] ethyl (ρ_{XZ} = 0.33),[8p] and phenacyl (ρ_{XZ} = 0.32)[8g] benzenesulfonates indicates that the TS (for reaction 3) is substantially looser than that for typical associative S_N2 reactions, but is significantly tighter than that for a typical dissociative S_N2 reaction of benzyl benzenesulfonates ($|\rho_{XZ}|$ = 0.10).[8a] Somewhat looser TS for PPB with smaller $|\rho_{XZ}|$ compared to the TS for a typical associative S_N2 reaction can be partly attributed to the aryl participation; in the aryl-assisted path $|\rho_{XZ}|$ should vanish since no bond making occurs in TS_Δ.

The magnitude of ρ_{XY} is much greater for PPB than that for 2-phenylethyl[18b] derivatives (2-PEB, Table VII), suggesting that the TS becomes tighter by an α-methyl substitution.[24] This means that increased steric hindrance results in a later TS for bond making, which is in accord with the Hammond postulate.[12] In contrast, if the electronic effect were prevailing, the α-methyl substitution would have led to a lesser amount of bond making in the TS since the energy of the carbocation species in the top left-hand corner, D, of Figure 2 is lowered when an α-hydrogen in the 2-phenylethyl system (2-PEB) is replaced by a methyl group to form the 1-phenyl-2-propyl system so that the TS moves toward the corner, D, resulting in a lesser amount of bond making and a greater degree of bond breaking, i.e., a looser TS.

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(21) (a) Seltzer, S.; Zavitsas, A. A. *Can. J. Chem.* **1967**, *45*, 2023. (b) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1354. (c) Westaway, K. C.; Lai, Z.-G. *Can. J. Chem.* **1988**, *66*, 1263. (d) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980. (e) Lai, Z.-G.; Westaway, K. C. *Can. J. Chem.* **1989**, *67*, 21.

(22) (a) Lee, I.; Koh, H. J.; Lee, B.-S.; Lee, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 335. (b) Lee, I.; Koh, H. J.; Lee, B.-S.; Lee, H. W.; Choi, J. H. *Bull. Korean Chem. Soc.* **1990**, *11*, 435. (c) Lee, I.; Koh, H. J.; Lee, H. W. *J. Chem. Res., Synop.* **1990**, 282. (d) Lee, I.; Koh, H. J.; Lee, H. W. *J. Phys. Org. Chem.* **1991**, *4*, 101.

(23) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1989; Chapter 2.

(24) (a) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; Chapter 3. (b) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361. (c) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238. (d) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952**, *74*, 1113. (e) Loudon, G. M.; Berke, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 4508.

The TS structures proposed is supported by the kinetic isotope effects (KIE) observed with deuterated aniline nucleophiles in Table VIII. We note that all the k_H/k_D values are less than one; this means that the possibility of an involvement of the four-center TS (TS$_f$)[25] is tenuous or TS$_f$ may contribute only a minor fraction to the reaction, as the small ρ_{XZ} indicated, so that the inverse secondary KIE is prevailing; in the TS$_f$ bond stretching of N–H$_a$ due to hydrogen bonding by H$_a$ should give primary KIE (>1.0), as in the reactions of 1-PEB and 2-PEB with anilines.[22] The size of k_H/k_D is in line with the expected trend from the positive ρ_{XZ}. A greater degree of bond formation leads to a greater inverse secondary KIE; i.e., a smaller k_H/k_D (<1.0) value is obtained with a weaker nucleophile (X = *p*-Cl) and/or a worse leaving group (Z = *p*-CH$_3$). Aryl participation with Y = *p*-CH$_3$O is again demonstrated by a considerable increase in the k_H/k_D value; as noted previously in this pathway, k_Δ, there will be no KIE (especially no inverse KIE) with the deuterated aniline nucleophile since the TS$_\Delta$ does not contain the aniline nucleophile.

The actual size of the k_H/k_D values for PPB tends to be intermediate between that for a loose dissociative (BBS)[22a] and a tight associative (EBS)[22c] S$_N$2 TS (Table VIII), as has been concluded on the basis of the sign and magnitude of ρ_{XZ}.[8a,p,17] α-Methyl substitution of 2-PEB into PPB appears to lead to a tighter TS since the k_H/k_D values are smaller for the latter. This is similar to a tighter TS for ethyl (EBS) rather than for methyl benzenesulfonates[8p,q] and, as noted above, can be considered a demonstration of the Hammond postulate;[12] the steric hindrance due to the α-methyl group elevates the activation barrier (k_H and k_D are smaller) leading to a later TS (more bond formation) that resembles the endoergic product more.[8p,q,22b]

We conclude that in the reactions of PPB with anilines in methanol the k_r pathway is predominant with some contribution of k_Δ only for Y = *p*-CH$_3$O. The involvement of the k_f path is insignificant.

Experimental Section

Materials. Anilines were purified as described previously.[8i] Merck G.R. grade methanol was used without further purification. In the preparation of substituted 1-phenyl-2-propyl benzenesulfonates (PPB), the corresponding benzyl bromide or phenylacetone was reacted with Grignard reagent[26] or appropriate reducing agent[27] (LiAlH$_4$ or LiBH$_4$) to produce 1-phenyl-2-propyl alcohol, which was then converted to benzenesulfonates by reacting with benzenesulfonyl chloride using the Tipson's method[28] and recrystallized from *n*-hexane and ethyl ether more than twice. Melting points and spectral data for compounds synthesized are as reported previously.[1]

Kinetic Procedures. Rates were measured conductimetrically at 65.0 °C in methanol. The conductivity cell used in this work was placed in a Pyrex pressure bottle with a tightly sealed cap to prevent leak of methanol vapor. Substrates were injected by a syringe. The vapor pressure inside the bottle is excepted to rise with a corresponding rise of the boiling point. The rise of external pressure (max. ~2 atm), however, is not significant to affect the observed rates. Pseudo-first-order rate constants, k_1^{obs}, were determined by the Guggenheim method[29] with a large excess of aniline; [PPB] $\cong 10^{-3}$ M and [aniline] $\cong$ 0.15–0.60 M. Second-order rate constants, k_2, were obtained from the slope of a plot of k_1^{obs} versus [aniline] with a greater than 4-fold excess of aniline (eq 5). The methanolysis rate constants, k_1^{ext}, given as an intercept of the plot, agreed with the methanolysis rate constants determined independently. The linearity of the plot (eq 5) was good with correlation coefficients of better than 0.998 with 99% confidence limit.[30] The k_2 values listed in Table I are the averages obtained by more than triplicate runs and were reproducible to within ±3%.[30]

Product Analysis. 1-Phenyl-2-propyl *p*-methylbenzenesulfonate was reacted with excess aniline with stirring for 7 days at 65.0 °C in methanol, and the products were isolated by evaporating solvent under reduced pressure. A solid precipitate I and a compound in gel state II were obtained by filteration. I was washed with ethyl ether and II was treated with a column chromatograph (silica gel, 20% ethyl acetate/*n*-hexane). The TLC analysis of the previous product mixture gave 4 spots (silica gel, glass plate, 20% ethyl acetate/*n*-hexane). R_f values: 0.66 ($C_6H_5CH_2CH(CH_3)NHC_6H_5$), 0.48 ($C_6H_5CH_2CH(CH_3)OSO_2C_6H_4$-*p*-CH$_3$), 0.31 ($C_6H_5NH_2$), 0.03 ($C_6H_5NH_3^{+-}OSO_2C_6H_4$-*p*-CH$_3$).

Analysis of the products, $C_6H_5CH_2CH(CH_3)NHC_6H_5$ and $C_6H_5NH_3^{+-}OSO_2C_6H_4$-*p*-CH$_3$, gave the following results.

$C_6H_5CH_2CH(CH_3)NHC_6H_5$: ν_{max} (NaCl) 3390 (secondary aromatic NH), 1600, 1500 (C–C aromatic), 1450 (–CH$_2$–), 1380 (CH$_3$), 1320 (C–N secondary aromatic amine), 1255 (CO aromatic) cm^{-1}; δ (60 MHz, CDCl$_3$), 1.1 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 3.2 (NH, 1 H, s), 3.6 (CH, 1 H, q), 6.5–7.2 (phenyl, 10 H, m). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.12; H, 8.19; N, 6.60.

$C_6H_4NH_3^{+-}OSO_2C_6H_4$-*p*-CH$_3$: mp 212–217 °C (lit.[17b] mp 210–215 °C); ν_{max} (KBr) 3390, 2600 (NH, NH$_3^+$), 1200, 1150, 560, 480 (SO, SO$_3^-$) cm^{-1}; δ (60 MHz, DMSO) 2.3 (*p*-CH$_3$, 3 H, s), 7.0–7.6 (phenyl, 9 H, m), 8.1–8.8 (NH$_3$, 3 H, br). Anal. Calcd for $C_{13}H_{15}O_3NS$: C, 58.85; H, 5.70; N, 5.28. Found: C, 58.79; H, 5.81; N, 5.21.

The UV peak ($\lambda_{max} \cong$ 282, 244 nm) corresponding to any olefin by β-elimination reaction was not detected.

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(25) Okamoto, K.; Takeuchi, K.; Inoue, T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 842 and references cited therein.

(26) Overberger, C. G.; Saunders, J. H.; Allen, R. E.; Gander, R. In *Organic Syntheses*; Horning, E. C., Ed.; John Wiley and Sons: New York, 1960; Collect. Vol. III, p 200.

(27) Sroog, C. E.; Woodburn, H. M. In *Organic Syntheses*; Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963; Collect. Vol. IV, p 271.

(28) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.

(29) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.

(30) (a) Moroney, M. J. *Facts from Figures*; Penguin Books, Harmonds Worth: Middlesex, 1956; p 295. (b) Wold, S.; Sjöström, M. *Correlation Analysis in Chemistry*, recent advances ed.; Plenum: New York, 1978; Chapter 1.