ciak, A. M.; Ziolkowski, J. J. *J. Mol. Catal.* **1983**, *18*, 193. (f) Landis, C. R.; Halpern, J. *Organometallics* **1983**, *2*, 840. (g) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (h) Pertici, P.; Vitulli, G.; Carlini, C.; Ciardelli, F. *J. Mol. Catal.* **1981**, 353. (i) Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 556. (j) Bennett, M. A. *Chemtech.* **1980**, 444. (k) Bennett, M. A.; Huang, T.-N.; Smith, A. K.; Turney, T. W. *Chem. Commun.* **1978**, 582.

20. (a) Baralt, E.; Smith, S. J; Hurwitz, J.; Horvath, I. T.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187. (b) Fish, R. H.; Baralt, E.; Kim, H.-S. *Organometallics* **1991**, *101*, 1965. (c) Lynch, T. J.; Banah, M.; Kaesz, H. D,; Porter, C. R. *J. Org. Chem.* **1984**, 1266.
21. (a) Johnston, R. A. W.; Wilby, A. H. *Chem. Rev.* **1985**, *85*, 129 and references therein. (b) Okano, T.; Tsukiyama, K.; Konishi, H. *Chem. lett.* **1982**, 603. (c) Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 5253. (d) Eckhard, I. F.; Fielden, R.; Summers, L. A. Aust. *J. Chem.* **1975**, *28*, 1149. (e) Nishimura, S.; Shu, T.; Hara, T.; Takagi, Y. *Bull. Chem. Soc. Jpn.* **1966**, *33*, 329.
22. (a) Chin, C. S.; Lee, B.; Kim, S. *Organometallics* **1993**, *12*, 1462. (b) Chin, C. S.; Lee, B.; Kim, Y. *Bull. Korean Chem. Soc.* **1993**, *14*, 374. (c) Chin, C. S.; Lee, S. *Catalysis Lett.* **1992**, *14*, 135. (d) Chin, C. S.; Lee, B.; Chun, J. *J. Chem. Soc. Dalton Trans.* **1991**, 443.
23. Unpublished results.
24. Cole, T.; Ramage, R.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6182.
25. Theodoridis, G.; Manfredi, M. C.; Krebs, J. D. *Tetrahedron Lett.* **1990**, 6141.
26. Chin, C. S.; Shin, J.H.; Kim, J. B. *J. Organomet. Chem.* **1988**, *356*, 381.
27. Nishimura, S.; Onoda, T.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1356.
28. (a) Chin, C. S.; Lee, B.; Park, S. P. *J. Organomet. Chem.* **1990**, *393*, 131. (b) Farnetti, E.; Kaspar, J.; Spogliarchi, R.; Graziani, M. *Chem. Commun.* **1988**, 947.
29. Blaser, H.-U. *Tetrahedron: Asymmetry* **1991**, *2*, 843.
30. Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 1620.
31. Blum, J.; Amer, I.; Zoran, A.; Sasson, Y. *Tetrahedron Lett.* **1983**, *24*, 4139.
32. Ham, G. E.; Coker, W. P. *J. Org. Chem.* **1964**, *24*, 194.
33. Cordier, G. in: *Heterogeneous Catalysis and Fine Chemicals*; Eds. Guinset, M. vol. 41 (Elsevier, 1988) p 19.
34. See (a) *J. Chem. Educ.* **1978**, *55*, A355. (b) *Chem. Eng. News* **1979**, 61 (Dec. 4) and **1963**, 47 (July 8).
35. (a) Vrieze, K.; Collman, J. P.; Sears, Jr., C. T. *Inorg. Synth.* **1968**, *11*, 101. (b) Herde, J. L.; Hanbert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.
36. (a) Uson, R.; Oro, L. A.; Artigas, J.; Sariego, R. J. *Organomet. Chem.* **1979**, *179*, 65. (b) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1787.

The Isoparametricity and Non-Interaction Phenomena in the Reactions of Benzyl Benzenesulfonates with Anilines

Igor V. Shpanko[†], Seung Il Kim, Han Joong Koh, and Ikchoon Lee*

Department of Chemistry, Inha University, Inchon 402-751, Korea
[†]*Leave of absence from Department of Chemistry, Donetsk State University, Donetsk, Ukraine*

Received March 3, 1995

The nucleophilic substitution reactions of benzyl benzenesulfonates with anilines have been studied in dimethylsulfoxide-tetrahydrofuran mixtures (1 : 3 and in part 1 : 1, v/v) with varying substituents in the nucleophile (X), substrate (Y) and leaving group (Z). Total second-order interactions between variable factors provide experimental evidence for the isoparametricity phenomenon : at the isoparametric points (IPPs), $\hat{\sigma}_X$, $\hat{\sigma}_Z$ and $\hat{T}$ (isokinetic temperature) the rate of nucleophilic displacement does not change with variation in substituents Y, *i.e.* $\rho_Y=0$; after passing through these IPPs, the order of reactivity for the substrate is reversed. Significant third-order interaction ($Q_{XYT}=-1.66$) provides realization of the non-interaction phenomenon: at critical values of $\hat{\sigma}_{Y(XT)}=0.08$ and $\hat{\sigma}_{X(YT)}=-0.26$ corresponding second-order interactions between temperature and substituents X (Q_{XT}) as well as substituents Y (Q_{YT}) vanish; after passing through these critical values the sign reversals for Q_{XT} and Q_{YT} are observed. The first- and second-order sensitivity coefficients as well as the IPPs were used for characterization of the transition state structure.

Introduction

Interactions between structural factors, *i.e.* their non-additive effects, have been of interest in the studies of the reaction mechanism and have been used for characterization of transition state (TS) structure.[1-4] In the simplest case cumulative effects of substituents, *i* and *j*, on the reactivity are described by Eq. (1). The cross-interaction coefficient, ρ_{ij}, can be determined from Eqs (1-3).

$$\log k_{ij}=\log k_{00}+\rho_i^\circ\sigma_i+\rho_j^\circ\sigma_j+\rho_{ij}\sigma_i\sigma_j \tag{1}$$

$$\rho_i=\rho_i^\circ+\rho_{ij}\sigma_j \tag{2}$$

$$\rho_j = \rho_j^{\circ} + \rho_{ij}\sigma_i \qquad (3)$$

The ρ_i and ρ_j values can serve as a relative measure of the TS structure within a particular family of the similar reactions,[3,5] which forms a cross-reaction series. According to eqs (2) and (3) the cross-interaction coefficient, ρ_{ij}, is a quantitative measure of changes in ρ_i and ρ_j accompanying structural changes in the reactants, and hence ρ_{ij} can reflect the variations in TS structure at least to the degree of approximation with which the ρ_i and ρ_j values define structural properties of the TS.

Owing to the cross term, ρ_{ij}, such intriguing feature as the isoparametricity emerges.[6] At the critical, $\hat{\sigma}_i = -\rho_j^{\circ}\rho_{ij}^{-1}$ and $\hat{\sigma}_j = -\rho_i^{\circ}\rho_{ij}^{-1}$, values called the isoparametric points (IPPs), the magnitude of log k_{ij} is the same, log $\hat{k}_{ij} = \log k_{oo} - \rho_i^{\circ}\rho_j^{\circ}\rho_{ij}^{-1}$, and remains constant when either substituent i at the IPP, $\hat{\sigma}_j$, or substituent j at the IPP, $\hat{\sigma}_i$, are varied. In other words the ρ_i in eq. (2) and ρ_j in eq. (3) are equal to zero at the IPPs, $\hat{\sigma}_j$ and $\hat{\sigma}_i$, respectively. After passing through the IPP, $\hat{\sigma}_i$ or $\hat{\sigma}_j$, sign inversion for the sensitivity coefficient, ρ_j or ρ_i, is predicted.[2,6]

Being trivial from mathematical point of view the isoparametricity as a real phenomenon is a challenge to the traditional concepts of organic chemistry because it provides for reversal of the order of reactivity for the reactants within a framework of a single cross-reaction series (the paradox of the isoparametricity).

During studies of cumulative structural effects on the rate of the S_N2 reactions of Y-substituted benzoyl halides and benzyl bromides with X-substituted anilines significant cross-interaction, ρ_{XY}, was found.[2] This provided experimental evidence for the existence of the isoparametricity phenomenon in these reactions. A number of the IPPs, $\hat{\sigma}_X$, was demonstrated. In accordance with mathematical prediction sign reversals were observed for sensitivity coefficient, ρ_Y, after passing through the IPPs, $\hat{\sigma}_X$, in all cases. The IPPs, $\hat{\sigma}_X$, were used for characterization of the TS structure.

In this work we extend studies on the isoparametricity phenomenon to the reactions of benzyl benzenesulfonates (BBSs) with anilines at 20.0, 30.0 and 40.0 ℃, eq. (4). The dimethylsulfoxide-tetrahydrofuran (DMSO-THF) mixtures were found more suitable for our studies than CH_3OH and CH_3CN used formerly.[7~10]

$$\text{Y-}C_6H_4CH_2OSO_2C_6H_4\text{-Z} + 2\text{X-}C_6H_4NH_2 \rightarrow$$

$$\text{Y-}C_6H_4CH_2NHC_6H_4\text{-X} + \text{X-}C_6H_4NH_3^+ + {}^-OSO_2C_6H_4\text{-Z} \qquad (4)$$

X=*p*-NH_2, *p*-OCH_3, H
Y=H, *m*-Cl, *p*-NO_2
Z=*p*-CH_3, H, *p*-Cl, *m*-NO_2

Results and Discussion

Dimethylsulfoxide reacts slowly with BBSs forming dimethylbenzyloxysulfonium benzenesulfonates,[11] eq. (5). The pseudo-first-order rate constants, k_1^{solv}, for the solvolysis of BBSs in DMSO-THF mixtures are reported in Table 1 together with Hammett coefficients, ρ_Y and ρ_Z. The rate is seen to increase with the DMSO content of the solvent mixtures and decrease (increase) with electron withdrawing substituent (EWS) in the benzyl moiety, $\rho_Y<0$ [leaving group (LG), $\rho_Z>0$].

Table 1. Pseudo-first-order Rate Constants, k_1^{solv}($\times 10^5$ s^{-1}), and Hammett coefficients, ρ_Y and ρ_Z, for the Solvolysis of Y-benzyl Z-benzenesulfonates in DMSO-THF

DMSO-THF (v/v)	Temp. ℃	Z	Y			ρ_Y[a]
			H	*m*-Cl	*p*-NO_2	
1 : 3	20.0	*p*-CH_3	1.01	0.581	0.155	−1.06
		H	2.26	0.825	0.345	−1.06
		p-Cl	7.35	2.93	1.58	−0.85
		m-NO_2	104	38.8	18.2	−0.97
		ρ_Z[b]	2.29	2.15	2.39	
	30.0	H	6.59	3.54	2.06	−0.65
	40.0	H	17.1	9.63	4.94	−0.69
1 : 1	20.0	H	6.67	2.38	0.861	−1.14

[a] Correlation coefficients; $r \geq 0.980$. [b] Correlation coefficients; $r \geq 0.994$.

Table 2. Second-order Rate Constants ($k_2 \times 10^3$ $dm^3 \cdot mol^{-1} \cdot s^{-1}$), for the Reactions of Y-benzyl Z-benzenesulfonates with X-anilines in DMSO-THF (1 : 1, 1 : 3, v/v) Mixtures at 20.0, 30.0 and 40.0 ℃

DMSO-THF (v/v)	Temp. ℃	Z	X	Y		
				H	*m*-Cl	*p*-NO_2
1 : 1	20.0	H	*p*-NH_2	24.6	24.9	26.1
			p-OCH_3	4.04	3.65	3.23
			H	1.11	0.888	0.701
1 : 3		*p*-CH_3	*p*-NH_2	8.17	8.99	11.2
			p-OCH_3	1.37	1.25	1.13
			H	0.332	0.276	0.227
		H	*p*-NH_2	16.1	17.3	19.7
			p-OCH_3	2.73	2.46	2.21
			H	0.725	0.588	0.473
		p-Cl	*p*-NH_2	50.9	51.8	53.1
			p-OCH_3	8.48	7.31	6.32
			H	2.01	1.58	1.29
		m-NO_2	*p*-NH_2	407	377	353
			p-OCH_3	65.2	56.1	46.4
			H	18.6	14.5	10.2
	30.0	H	*p*-NH_2	29.5	29.8	30.1
			p-OCH_3	5.03	4.71	4.33
			H	1.46	1.21	1.05
	40.0	H	*p*-NH_2	57.6	55.9	53.1
			p-OCH_3	8.95	8.14	7.46
			H	2.51	2.19	1.90

The second-order rate constants, k_2, obtained by eq. (6) for the reactions of BBSs with anilines are collected in Table 2. Inspection of Table 2 reveals that the rate increases with an electron donating substituent (EDS), X, in a nucleophile and EWS, Z, in a LG and decreases with an EWS, Y, in a substrate, except for a number of the reactions of *p*-phenylenediamine (X=*p*-NH_2) in which a slight rate increase is noted with a more Y=EWS (Y=*p*-NO_2). Such inverse of substrate reactivity is usual for the S_N2 reactions, in which the

Table 3. Hammett ρ_i values[a] for the Reactions of Y-benzyl Z-benzenesulfonates with X-anilines in DMSO-THF (1 : 3, v/v) Mixture at 20.0, 30.0 and 40.0 ℃

(1) ρ_X

Temp. ℃	Z	Y=H	*m*-Cl	*p*-NO$_2$
20	*p*-CH$_3$	−2.10	−2.29	−2.56
	H[b]	−2.04	−2.19	−2.38
	H	−2.04	−2.22	−2.45
	p-Cl	−2.12	−2.29	−2.44
	m-NO$_2$	−2.03	−2.14	−2.33
30	H	−1.98	−2.10	−2.21
40	H	−2.06	−2.13	−2.19

[a] Correlation coefficients; $r \geq 0.999$. [b] In DMSO-THF (1 : 1, v/v).

(2) ρ_Y

Temp. ℃	Z	X=*p*-NH$_2$	*p*-OCH$_3$	H
20	*p*-CH$_3$	0.18	−0.11	−0.21
	H[b]	0.03	−0.13	−0.26
	H	0.11	−0.12	−0.24
	p-Cl	0.02	−0.16	−0.25
	m-NO$_2$	−0.08	−0.19	−0.34
30	H	0.01	−0.08	−0.18
40	H	−0.04	−0.10	−0.15

[a] Correlation coefficients; $r \geq 0.980$. [b] In DMSO-THF (1 : 1, v/v).

(3) ρ_Z

Temp. ℃	X	Y=H	*m*-Cl	*p*-NO$_2$
20	*p*-NH$_2$	1.95	1.86	1.72
	p-OCH$_3$	1.92	1.89	1.84
	H	1.99	1.96	1.88

[a] Correlation coefficients; $r \geq 0.999$.

IPPs, $\hat{\sigma}_X$, are passed through.[2]

$$\text{Y-C}_6\text{H}_4\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-Z} + (\text{CH}_3)_2\text{SO} \rightarrow \text{Y-C}_6\text{H}_4\text{CH}_2\text{OS}^+(\text{CH}_3)_2 + {}^-\text{OSO}_2\text{C}_6\text{H}_4\text{-Z} \tag{5}$$

$$k_1^{obs} = k_1^{solv} + k_2[\text{aniline}] \tag{6}$$

Substituent Effects. Hammet coefficients, ρ_X, ρ_Y and ρ_Z, are collected in Table 3. The $|\rho_X|$ values gradually increase with a stronger EWS in a substrate that indicates increasing electron transfer in the TS from the attacking N atom of aniline to the reaction center of the substrate with a greater degree of bond formation with a stronger Y=EWS. The ρ_Z values increase with a more EWS, Y, in a substrate and less EDS, X, in a nucleophile indicating the increase in bond breaking.

The negative ρ_Y values obtained in all reactions of aniline (X=H) and *p*-anisidine (X=*p*-OCH$_3$) become positive in most reactions of *p*-phenylenediamine (X=*p*-NH$_2$). This result testifies change in the charge at the benzylic carbon at the TS from positive to negative with a stronger nucleophile (X=*p*-NH$_2$) and indicates the transition through the IPPs, $\hat{\sigma}_X$, accompanying change in the order of reactivity for the substrate. The same situation is observed in the reactions of *p*-phenylenediamine with Z-substituted BBSs: positive ρ_Y coefficient (Z=*p*-CH$_3$, H, *p*-Cl) becomes negative with a better LG (Z=*m*-NO$_2$). In this case the transition through the IPP, $\hat{\sigma}_Z$, takes place.

Considered trends of changes in sensitivity coefficients, ρ_X, ρ_Y and ρ_Z, indicate total interaction between substituents X, Y and Z. The experimental data (k_2) in Table 2 were subjected to multiple regression analysis[12] using eq. (1), which coefficients together with calculated values of the IPPs, are given in Table 4. Obtained regressions show second-order interactions, ρ_{XY}, ρ_{XZ} and ρ_{YZ} in all cross-reaction series. Significant interaction between substituents X and Y, ρ_{XY}, provides experimental evidence for the existence of the isoparametricity phenomenon in reactions (4). In most reaction series the IPPs, $\hat{\sigma}_X$, are observable and the transitions through the isoparametric values of $\hat{\sigma}_X$ were realized with predicted reversals of the order of substrate reactivity (see also Table 3). The magnitude of the IPP, $\hat{\sigma}_X$, depends on substituents Z in LG, temperature and solvent.

It should be emphasized that the IPP, $\hat{\sigma}_Z$, was realized in the reactions of *p*-phenylenediamine with Y, Z-substituted BBSs (ρ_{YZ} interaction) in DMSO-THF (1 : 3) mixture at 20.0 ℃. After passing through the isoparametric value $\hat{\sigma}_Z = 0.38$ the order of substrate reactivity is reversed ($\rho_Y = 0.18$, 0.11, 0.02 and −0.08 for Z=*p*-CH$_3$, H, *p*-Cl and *m*-NO$_2$; Table 3).

The ρ_{XY}, ρ_{YZ} and ρ_{XZ} values depend on effects of substituents Z, X and Y respectively. Thus the $|\rho_{XY}|$ decreases with a more EWS in a LG (Z=*m*-NO$_2$), ρ_{XZ} increases with a more EWS in the benzyl moiety (Y=*p*-NO$_2$) and $|\rho_{YZ}|$ shows the trend of increase with a more EDS in a nucleophile (X=*p*-NH$_2$). Hence there is a complete non-additivity in the simultaneous effects of substituents X, Y and Z on the investigated process, *i.e.* the third-order interaction ρ_{XYZ} takes place, which can be determined by means of Eqs. (7-8).

$$\log k_{XYZ} = \log k_{000} + \rho^\circ{}_X\ \sigma_X + \rho^\circ{}_Y\ \sigma_Y + \rho^\circ{}_Z\ \sigma_Z + \rho^\circ{}_{XY}\ \sigma_X\sigma_Y + \rho^\circ{}_{XZ}\ \sigma_X\sigma_Z + \rho^\circ{}_{YZ}\ \sigma_Y\sigma_Z + \rho_{XYZ}\ \sigma_X\sigma_Y\sigma_Z \tag{7}$$

$$\rho_{ij} = \rho^\circ{}_{ij} + \rho_{ijk}\sigma_k \tag{8}$$

According to eq. (8) the plots ρ_{XY} *vs* σ_Z and ρ_{XZ} *vs* σ_Y show linear relations with the nearly equal slopes (ρ_{XYZ}) in eqs. (9) and (10).

$$\rho_{XY} = -0.51 + 0.19\sigma_Z, \ r = 0.905 \tag{9}$$

$$\rho_{XZ} = 0.05 + 0.20\sigma_Y, \ r = 0.995 \tag{10}$$

According to eqs. (8-10) at the critical values $\hat{\sigma}_{Z(XY)} = -\rho^\circ{}_{XY} \cdot \rho_{XYZ}{}^{-1} = 2.68$ and $\hat{\sigma}_{Y(XZ)} = -\rho^\circ{}_{XZ} \cdot \rho_{XYZ}{}^{-1} = -0.25$ corresponding interaction coefficients, ρ_{XY} and ρ_{XZ}, should be equal to zero, *i.e.* interaction between substituents X and Y on the one hand and X and Z on the other hand will vanish. This prediction agrees with influence of substituents Z and Y on the values of ρ_{XY} and ρ_{XZ} (Table 4).

Temperature Effects. The reactions of Y-substituted BBSs (Z=H) with X-substituted anilines in DMSO-THF (1 : 3) mixture were studied at 20.0, 30.0 and 40.0 ℃. The activation parameters, $\Delta H^\dagger$ and $\Delta S^\dagger$, derived from the Arrhenius equation, are summarized in Table 5.

The values of $\Delta H^\dagger$ and $\Delta S^\dagger$ depend on substituents X

Table 4. Coefficients ρ^o_i, ρ^o_j, ρ_{ij} and Values of the IPPs, $\hat{\sigma}_i$ and $\hat{\sigma}_j$, for Reactions of Y-benzyl Z-benzenesulfonates with X-anilines in DMSO : THF (1 : 3, v/v) Mixture

(1) ρ_{XY} values[a]

Z	Temp. ℃	log k_{oo}	ρ^o_X	ρ^o_Y	ρ_{XY}	$\hat{\sigma}_X$	$\hat{\sigma}_Y$
p-CH$_3$	20.0	−3.46	−2.09	−0.23	−0.55	−0.42[c]	−3.80
H[b]		−2.95	−2.03	−0.25	−0.44	−0.57[c]	−4.61
H		−3.13	−2.03	−0.25	−0.53	−0.47[c]	−3.83
p-Cl		−2.68	−2.12	−0.26	−0.41	−0.63[c]	−5.17
m-NO$_2$		−1.73	−2.02	−0.32	−0.38	−0.84	−5.31
H	30.0	−2.84	−1.99	−0.17	−0.28	−0.61[c]	−7.11
H	40.0	−2.60	−2.06	−0.15	−0.17	−0.88	−12.1

(2) ρ_{XZ} values [a]

Y	Temp. ℃	log k_{oo}	ρ^o_X	ρ^o_Z	ρ_{XZ}	$\hat{\sigma}_X$	$\hat{\sigma}_Z$
H	20.0	−3.13	−2.08	1.97	0.05	41.6	−39.4
m-Cl		−3.22	−2.26	1.94	0.14	16.4	−13.8
p-NO$_2$		−3.32	−2.48	1.89	0.21	11.8	−9.0

(3) ρ_{YZ} values[a]

X	Temp. ℃	log k_{oo}	ρ^o_Y	ρ^o_Z	ρ_{YZ}	$\hat{\sigma}_Y$	$\hat{\sigma}_Z$
p-NH$_2$	20.0	−1.77	0.10	1.95	−0.26	7.50	0.38[c]
p-OCH$_3$		−2.54	−0.12	1.92	−0.10	19.2	−1.20
H		−3.15	−0.23	1.99	−0.14	14.2	−1.64

[a] Correlation coefficients; $r \geq 0.999$. [b] In DMSO-THF (1 : 1, v/v) [c] Experimentally observed IPP.

Table 5. The Values of the Activation Parameters, $\Delta H^{\dagger}$ (kcal·mol^{-1}) and $\Delta S^{\dagger}$ (cal·mol^{-1}K^{-1}), Calculated at 303.0 K, for the Reactions of Y-benzyl Benzenesulfonates (Z=H) with X-anilines in DMSO-THF (1 : 3) Mixture at 20.0, 30.0 and 40.0 ℃

Y	X	$\Delta H^{\dagger}$	$-\Delta S^{\dagger}$
H	*p*-NH$_2$	10.2	29.3
	p-OCH$_3$	9.41	35.4
	H	9.94	36.1
m-Cl	*p*-NH$_2$	9.28	32.3
	p-OCH$_3$	9.53	35.2
	H	10.6	34.5
p-NO$_2$	*p*-NH$_2$	7.72	37.5
	p-OCH$_3$	9.68	34.8
	H	11.3	32.4

and Y indicating interactions between structural factors and temperature. These interactions were determined by eq. (11), where $\tau_T = (1/T - 1/303) \cdot 10^3$.

$$\log k_{iT} = \log k_{oo} + \rho^{\circ}_i \sigma_i + b''_T \tau_T + Q_{iT} \sigma_i \tau_T \qquad (11)$$

The obtained regressions which reflect combined effects of temperature and substituents X as well as Y are given in Table 6. The parameters log k_{oo} and ρ°_i are estimated at $T=303.0$ K (the accepted standard temperature) and are in good agreement with the experimental data (Tables 2 and 3). The only IPP $\hat{T}=307$ K (isokinetic temperature) falls within the measurable region in the reactions of *p*-phenylenediamine (X=*p*-NH$_2$) with Y-substituted BBSs (Z=H). For these reactions sensitivity coefficients, ρ_Y, are as large as 0.11 (20.0 ℃), 0.01 (30.0 ℃) and -0.04 (40.0 ℃), *i.e.* the reversal of the order of substrate reactivity occurs due to change in temperature. The same isokinetic temperature ($\hat{T}=307$ K) is derived from temperature dependence $\rho_Y = 0.025 + 0.69\tau_T$, $r=0.985$. Cross-interaction coefficients Q_{XT} and Q_{YT} depend on substituents Y and X respectively. Furthermore the sign inversions of both Q_{XT} and Q_{YT} are observed with variations of Y and X. This result demonstrates clearly the total non-additivity in the simultaneous effects of substituents X, Y and temperature, *i.e.*, their third-order interaction, Q_{XYT}, which can be determined using eqs. (12-15).

$$\log k_{XYT} = \log k_{ooo} + \rho^{\circ}_X \sigma_X + \rho^{\circ}_Y \sigma_Y + b^o_T \tau_T + \rho^{\circ}_{XY} \sigma_X \sigma_Y + Q^o_{XT} \sigma_X \tau_T + Q^{\circ}_{YT} \sigma_Y \tau_T + Q_{XYT} \sigma_X \sigma_Y \tau_T \qquad (12)$$

$$\rho_{XY} = \rho^{\circ}_{XY} + Q_{XYT} \tau_T \qquad (13)$$

$$Q_{XT} = Q^o_{XT} + Q_{XYT} \sigma_Y \qquad (14)$$

$$Q_{YT} = Q^o_{YT} + Q_{XYT} \sigma_X \qquad (15)$$

According to eqs. (13-15) the plots ρ_{XY} *vs* τ_T, Q_{XT} *vs* σ_Y and Q_{YT} *vs* σ_X show linear relations with the equal slope ($Q_{XYT} = -1.66$) in eqs (16-18).

$$\rho_{XY} = -0.32 - 1.66\tau_T, \quad r = 0.980 \qquad (16)$$

$$Q_{XT} = 0.14 - 1.66\sigma_Y, \quad r = 0.997 \qquad (17)$$

$$Q_{YT} = -0.43 - 1.66\sigma_X, \quad r = 0.990 \qquad (18)$$

As it follows out of eqs. (13-18) at the critical values $\hat{\tau}_{T(XY)} = -\rho^{\circ}_{XY} \cdot Q_{XYT}^{-1} = -0.19$ ($T=321$ K or 48 ℃), $\hat{\sigma}_{Y(XT)} = -Q^o_{XT}$

Table 6. Coefficients ρ^o_i, b^o_T and Q_{iT} of Eq. (11) for the Reactions of Y-benzyl Benzenesulfonates (Z=H) with X-anilines in DMSO-THF (1 : 3) Mixture

(1) Q_{XT} values[a]

Y	log k_{oo}	ρ^o_X	b^o_T	Q_{XT}
H	−2.84	−2.02	−2.42	0.11
m-Cl	−2.92	−2.15	−2.57	−0.41
p-NO_2	−3.00	−2.28	−2.76	−1.18

[a] Correlation coefficients; $r \geq 0.999$.

(2) Q_{YT} values[b]

X	log k_{oo}	ρ^o_Y	b^o_T	Q_{YT}
p-NH_2	−1.52	0.03	−2.56	0.70
p-OCH_3	−2.30	−0.10	−2.36	−0.08
H	−2.85	−0.19	−2.48	−0.38

[b] Correlation coefficients; $r \geq 0.997$.

$Q_{XYT}^{-1} = 0.08$, and $\hat{\sigma}_{X(YT)} = -Q^o_{YT} Q_{XYT}^{-1} = -0.26$ corresponding cross-terms ρ_{XY}, Q_{XT} and Q_{YT} disappear, *i.e.*, the second-order interactions between structural factors as well as structural factors and temperature should be vanished. This non-interaction phenomenon is indeed observed in the reactions under studied with the transitions through the noted critical values $\hat{\sigma}_{Y(XT)}$ and $\hat{\sigma}_{X(YT)}$, accompanied structural changes in the reactants (Table 6).

Isoparametric Points and Transition State Structure. The first-, second-, and third-order sensitivity coefficients, ρ_i, ρ_{ij}, ρ_{ijk}, Q_{iT} and Q_{ijT}, testify radical changes in the S_N2 TS, the structure of which depends on all structural variables as well as temperature. At the IPP, $\hat{\sigma}_i$, the simple coefficient, ρ_i, becomes equal to zero that provides a mechanistic significance of the IPP as a test of the TS structure.

The second-order interaction coefficient, ρ_{ij}, have been shown to be useful tool for characterization of the TS structures[1]. A decrease in the magnitude of $|\rho_{XY}|$ (Table 4) with a better LG and higher temperature reflects a decrease in bond formation in the TS. An increase in the ρ_{XZ} value with a more EWS, Y, reflects an increase in a tightness of the TS. A decrease in the ρ_{YZ} value with a more EDS, X, shows a decrease in bond breaking.

The TS variations can be illustrated by the potential energy surface (PES) diagram, Figure 1. Relatively small negative and positive ρ_Y values (−0.22-0.15) as well as $\rho_Y = 0$ (Table 3) indicate that the TSs should be on or near the border line, RP, separating the dissociative ($\rho_Y < 0$) and associative ($\rho_Y > 0$) reactions. Relatively large $|\rho_X|$ (−1.99-−2.53) and ρ_Z (1.74-1.98) values indicate that the TSs are more advanced along the reaction coordinate toward the products than the reactants.

At the IPPs, $\hat{\sigma}_X$, observed for ρ_{XY} interaction (Table 4), $\rho_Y = 0$, hence the TS should be symmetrical (bond formation=bond breaking). Its position on the PES diagram is denoted by the point *C*. An EDS, *X*, in the nucleophile with $|\sigma_X| > |\hat{\sigma}_X|$ will stabilize the right-hand corners, *A* and *P*, so that the TS will shift to *F*, which is obtained as a sum of the two vectors, CE and CG, in accordance with the Hammond and anti-Hammond (or Thornton) effects, assumed the same (the simplest version). Bond breaking is predicted to decrease, so that the TS should be associative (bond formation>bond breaking). This prediction is supported by positive ρ_Y values observed for X=*p*-NH_2 (Table 3). On the other hand decrease in electron donating ability of X ($|\sigma_X| < |\hat{\sigma}_X|$) leads to the dissociative TS (the point *J*) with the result that $\rho_Y < 0$.

At the IPP, $\hat{\sigma}_Z$, observed in the reactions of *p*-phenylenediamine (X=*p*-NH_2) for ρ_{YZ} interaction (Table 4), $\rho_Y = 0$, *i.e.* the TS is symmetrical (the point *C*). Substituent Z in the LG with $\sigma_Z > \hat{\sigma}_Z$ (Z=*m*-NO_2) will stabilize the upper corners, *D* and *P*, so that the TS shifts to K with decrease in bond formation with the result that it becomes dissociative ($\rho_Y < 0$). On the other hand substituent Z with $\sigma_Z < \hat{\sigma}_Z$ (Z=H or *p*-CH_3) will shift the TS to L so that it becomes associative ($\rho_Y > 0$). In fact the sign inversion of the ρ_Y is observed after passing through the IPPs, $\hat{\sigma}_X$ and $\hat{\sigma}_Z$ (Tables 3 and 4).

It should be noted that all changes in the sensitivity coefficients ρ_X, ρ_Y and ρ_Z caused by dual substituent variables X and Y, Y and Z, X and Z respectively as well as the signs of the second-order coefficients, ρ_{ij}, are in complete agreement with the predictions based on the PES model, *i.e.* the TS variations follow that predicted by this model.

The value of the IPP, $\hat{\sigma}_{i(j)}$, obtained by ρ_{ij} interaction between substituent *i* and *j*, proved to be dependent linearly on effect of substituent *k*, eq. (19). This relationship indicates that realization of the TS when $\rho_j = 0$ at the IPP $\hat{\sigma}_{i(j)}$, should be connected with effect of substituent *k* as well. For example, eqs. (20-21) for the reaction (4) in DMSO-THF (1 : 3) at 20.0 ℃ show that realization of the symmetrical TS when $\rho_Y = 0$ at the IPP, $\hat{\sigma}_{X(Y)}$ [$\hat{\sigma}_{Z(Y)}$], which is obtained by interaction between substituents X and *Y* (Y and Z), depends on substituent Z in the LG (X in the nucleophile). The values $\hat{\sigma}_{X(Y)}$ and $\hat{\sigma}_{Z(Y)}$ become more negative with more EWSs, Z and X (σ_Z, $\sigma_X > 0$).

$$\hat{\sigma}_{i(j)} = \hat{\sigma}_{o(j)} + q\sigma_k \tag{19}$$

$$\hat{\sigma}_{X(Y)} = -0.49 - 0.49\sigma_Z, \; r = 0.994 \tag{20}$$

$$\hat{\sigma}_{Z(Y)} = -1.79 - 3.13\sigma_X, \; r = 0.978 \tag{21}$$

Analogous temperature dependence for the IPP, $\hat{\sigma}_{X(Y)}$, is given by eq. (22) for the reactions (4) in DMSO-THF (1 : 3) at 20.0, 30.0 and 40.0 ℃. The value of the IPP, $\hat{\sigma}_{X(Y)}$, at which $\rho_Y = 0$, becomes less negative with decrease in temperature (Table 4). Thus the symmetrical TS occurs along the reaction coordinate with a weaker nucleophile at lower temperature.

$$\hat{\sigma}_{X(Y)} = -0.66 + 1.87 \cdot \left(\frac{1}{T} - \frac{1}{303}\right) \cdot 1000, \; r = 0.980 \tag{22}$$

Solvent Effects. In spite of significant interactions between substituents X and Y in reactions of BBSs with anilines in CH_3OH, CH_3CN and their mixtures, the IPPs, $\hat{\sigma}_X$, were not realized in these media. The $\hat{\sigma}_X$ value (Z=H) is −1.21(1) in CH_3OH at 35.0 ℃ and −0.98(10) in CH_3CN at 20.0 ℃. These IPPs lie outside the measurable region as opposed to experimentally observed ones in DMSO-THF mixtures (Table 4).

Such solvent effects on the value of the IPP, $\hat{\sigma}_X$, can be ascribed to different solvation behavior of CH_3OH and CH_3CN on the one hand and DMSO and THF on the other hand. In fact high polarity (ε) and large solvent hydrogen-bond donor acidity (α)[13] of CH_3OH ($\varepsilon=32.7$, $\alpha=0.93$) and CH_3CN ($\varepsilon=35.9$, $\alpha=0.19$) provide better solvation of the LG in the TS as compared with DMSO ($\varepsilon=46.5$, $\alpha=0$)-THF ($\varepsilon=7.58$, $\alpha=0$) mixtures (1 : 1, 1 : 3, v/v), *i.e.* the TS should be more dissociative in CH_3OH and CH_3CN. That is why the symmetrical TS ($\rho_Y=0$) at the IPP, σ_X, in these solvents should be realized with stronger nucleophile than *p*-phenylenediamine ($X=p\text{-}NH_2$, $\sigma_X=-0.66$). At the same time large solvent hydrogen-bond donor basicity (β)[13] of DMSO ($\beta=0.76$) and THF ($\beta=0.55$) enhances in their mixtures the reactivity of anilines due to hydrogen bonding with amino groups, so that the symmetrical TS will realize with weaker nucleophile as compared with that in CH_3OH and CH_3CN, that provides experimental observations of the IPPs, $\hat{\sigma}_X=-0.63$---0.42 (Table 4).

Conclusion

Total interactions between variable factors, *i.e.* their general non-additive effects, in the reactions of BBSs with anilines provide experimental evidence for the isoparametricity phenomenon and non-interaction phenomenon. The first- and second-order sensitivity coefficients, ρ_i, ρ_{ij}, and Q_{iT} as well as the IPPs, $\hat{\sigma}_i$, are useful mechanistic tool in the study of TS, especially the IPPs can be used as a direct test of the TS structure.

Experimental

Materials. Dimethyl sulfoxide was dried with molecular sieves (4 Å) by prolonged contact and then fractionally distilled at low pressure. Tetrahydrofuran was purified by refluxing with, and fractionally distilling from $LiAlH_4$. Anilines (Aldrich G.R.) were redistilled or recrystallized before use. Benzyl benzenesulfonates were prepared by reacting silver Z-substituted benzenesulfonates with Y-substituted benzyl bromides.[14] The substrates were recrystallized more than twice from anhydrous benzene-petroleum ether (30-70 ℃) mixtures and confirmed by spectral and melting point in accordance with literature data.[7~9,14~16]

Kinetic Procedures. Rates were measured conductimetrically. Pseudo-first-order rate constants, k_1^{obs}, were determined by the Guggenheim method with a large excess of aniline: [benzyl benzenesulfonate]$=10^{-4}$ mol dm^{-3} and [aniline]$=0.06$-0.50 mol dm^{-3}. Second-order rate constants, k_2, were obtained from the slope of a plot of k_1^{obs} *vs* [aniline] eq. (5). The linearity of the plots, eq. (5), was good in general, with correlation coefficients of better than 0.998 (k_1^{obs} values for four or more [aniline] and k_1^{solv} values were used).

Solvolysis Products. Products $[Y\text{-}C_6H_4CH_2O(CH_3)_2S^+\cdot{}^-SO_3C_6H_4\text{-}Z$, $Y=p\text{-}NO_2$, $Z=p\text{-}CH_3$, $m\text{-}Cl$, $m\text{-}NO_2]$ of the solvolysis reactions of BBSs with excess DMSO were isolated under kinetic conditions as oil after addition of ether-ethyl acetate (1 : 1, v/v) mixture. In NMR the cationic part of products $[p\text{-}NO_2\text{-}C_6H_4CH_2OS^+(CH_3)_2]$ had δ_H (60 MHz) 3.80 $[(CH_3)_2S^+$, 6H, s],[17] 5.48 [CH_2, 2H, s], 7.40-7.56 [$p\text{-}NO_2\text{-}C_6H_4$, 4H, m].

Acknowledgment. We thank the Korea Science and Engineering Foundation and the Inha University for support of this work.

References

1. Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57.
2. Shpan'ko, I. V. *Mendeleev Commum.* **1991**, *119*.
3. Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.
4. Dubois, J.-E.; Ruasse, M.-F.; Argile, A. *J. Am. Chem. Soc.* **1984**, *106*, 4840.
5. McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331.
6. Palm, V. A., In *Fundamentals of Quntitative Theory of Organic Reactions* 2nd ed.; Khimiya: Leningrad, 1977; chaps. 1 and 7.
7. Lee, I.; Lee, W. H.; Sohn, S. C.; Kim, C. S. *Tetrahedron* **1985**, *41*, 2635.
8. Lee, I.; Sohn, S. C.; Oh, Y. J.; Lee, B. C. *Tetrahedron* **1986**, *42*, 4713.
9. Lee, I.; Sohn, S. C.; Oh, Y. J. *J. Chem. Soc. Perkin 2*, **1986**, 1631.
10. Lee, I.; Lee, W. H.; Jung, H.-J. *Bull. Inst. Basic Sci. Inha Univ.* **1991**, *12*, 69.
11. Smith, C. G.; Winstein S. *Tetrahedron* **1958**, *3*, 317.
12. Shorter, J., In *Correlation Analysis of Organic Reactivity*; Research Studies Press: New York 1982; chap. 2.
13. Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
14. Yoh, S. D., *J. Korean. Chem. Soc.* **1975**, *19*, 116, 449.
15. Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3443.
16. Fang, F. T.; Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1958**, *80*, 563.
17. Khuddus, M. A.; Swern, D. *J. Am. Chem. Soc.* **1973**, *95*, 8393. [$p\text{-}CH_3$, $m\text{-}Cl$, $m\text{-}NO_2$] of the solvolysis reactions of BBSs with excess DMSO were isolated under kinetic conditions as oil after addition of ether-ethyl acetate (1 : 1, v/v) mixture. In NMR the cationic part of products $[p\text{-}NO_2\text{-}C_6H_4CH_2OS^+(CH_3)_2]$ had δ_H (60 MHz) 3.80 $[(CH_3)_2S^+$, 6H, s][17], 5.48 [CH_2, 2H, s], 7.40-7.56 [$p\text{-}NO_2\text{-}C_6H_4$, 4H, m].