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Application of correlation interaction coefficients. Part 1. Structure–reactivity relationship of phenylethyl arenesulfonates under high pressure

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ABSTRACT: The rates for the reaction of (Z)-phenylethyl (X)-benzenesulfonates with (Y)-pyridines under pressure in acetonitrile at 60 °C were measured by an electrical conductivity method. From the values of ρ_X, ρ_Y and ρ_Z, it was concluded that bond formation between the nucleophile and reaction center is more advanced in the transition state (TS). The magnitude of the correlation interaction term, ρ_{ij}, was used to determine the structure of the transition state for the S_N reaction. As the pressure increases, the Hammett reaction constants ρ_X and ρ_Y decrease, but the correlation interaction coefficients, ρ_{XZ} and ρ_{YZ}, increase. The results indicate that the reaction of (Z)-phenylethyl (X)-benzenesulfonates with (Y)-pyridines probably proceeds via a dissociative S_N2 reaction and with increasing pressure the TS moves to an early position. This result agrees with the MOFJ diagram interpretation and shows that the correlation interaction term, ρ_{ij}, can be a useful tool for determining the structure of the TS. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: correlation interaction coefficients; phenylethyl arenesulfonates; structure–reactivity.

INTRODUCTION

There has been considerable interest in determining the transition-state (TS) structure for S_N reactions using multiple Hammett plots.[1] Previous works[2] showed that the magnitude of the correlation interaction coefficient (CIC), $\rho_{ij,}$ between substituents *i* and *j* is expressed by

$$\log(k_{ij}/k_{00}) = p_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j$$

and therefore ρ_{XZ} (ρ_{ZX}) and ρ_{YZ} (ρ_{ZY}) are represented by the following equations:

$$\log(k_{XZ}/k_{00}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (1)$$

$$\log(k_{YZ}/k_{00}) = \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{YZ}\sigma_Y\sigma_Z \qquad (2)$$

where X, Y and Z are the substituents of the leaving group (L), nucleophile (Nu) and substrate (S), respectively. ρ_{ij} (ρ_{XZ} or ρ_{YZ}) depends on the change in the distance between the reaction centers, which can express the sensitivity of ρ_i to σ_j (or ρ_j to σ_i). That is, ρ_{XZ} and ρ_{YZ} influence the degree of Cα—L bond fission and that of Nu—Cα bond formation, respectively. For benzylic derivatives,[2b] the TS structure of the nucleophilic substitution reaction is predicted both by the sign of ρ_Z and by comparing the relative values of ρ_{XZ} and $|\rho_{YZ}|$.

The effects of pressure on Menschutkin reactions, which are typical S_N2 reactions of alkyl halides with tertiary amines to form quaternary ammonium salts, have been widely studied.[3,4] We have reported[5] that the kinetic study of the Menschutkin-type reaction of benzyl benzenesulfonate with pyridine in acetone was carried out by an electric conductivity method at pressures from 1 to 2000 bar. The enthalpy, entropy and volume of activation indicated that this reaction proceeds via the S_N2 mechanism in which the rate of the reaction is determined by Cα—Nu bond formation in the TS. Under atmospheric pressure, the substituent effect of the phenylethyl system was not as significant as expected, but the electron-donating substituents still showed a slight acceleration to give a small negative ρ value and the Hammett plot curved slightly towards the activating substituents. This result represents a more favorable bond-breaking in the TS by the electron-donating substituents. However, the effect is not as great as that of the benzyl system.[6]

In this paper, we report the results of kinetic investigations of the nucleophilic substitution reactions

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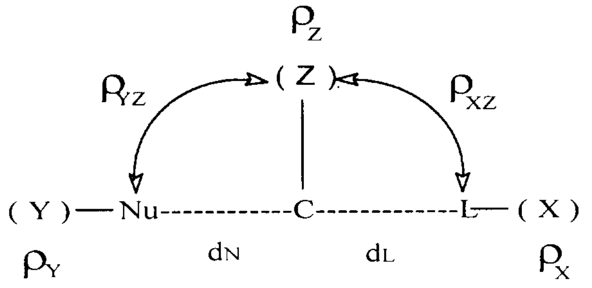
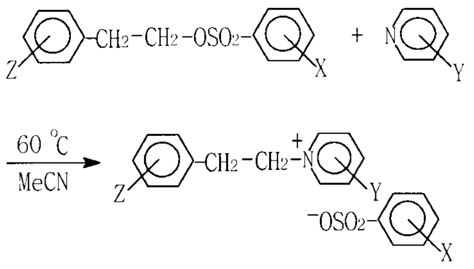


Scheme 1



X = H, 4-Br, 3-NO$_2$
Y = 3,4-(CH$_3$)$_2$, 3-CH$_3$, H, 3-Cl
Z = 4-CH$_3$, H, 4-Cl

Scheme 2

of phenylethyl arenesulfonates with pyridines in acetonitrile under various pressures, building on previous successful applications of substitution effects.[7] The TS for the S_N reaction can be represented by three components: the leaving moiety (L) with substituent X. the nucleophile (Nu) with Y and the substrate (S) with Z. These are attached to each reaction center, as shown in Scheme 1, where d_N (or d_L) is the distance between Nu (or L) and C.

We discuss the changes in the TS structures with increasing pressure for the reaction of phenylethyl arenesulfonates with pyridines in acetonitrile.

RESULTS AND DISCUSSION

The kinetic reaction for the nucleophilic displacement that yields the salts of phenylethyl derivatives is depicted in Scheme 2. The reaction rates were determined by monitoring the changes in the electrical conductance resulting from the formation of the salt in the reaction of phenylethyl benzenesulfonate with pyridine in acetonitrile at 60 °C.

The second-order rate constants, k_2, are summarized in Tables 1 and 2 for this reaction at various pressures.

The reaction rate was increased by electron-donating substituents in pyridine, which acts as a nucleophile. The rate increased with both increasing electron-donating ability of the substrate and leaving ability of the leaving moiety. However, the change in the rate constants is less sensitive to the nature of the substituents with the phenylethyl substrate than with a benzyl substrate, because of the additional CH$_2$ group. The Hammett plots (with Hammett substituent constants taken from Ref. 8) generally show good linear correlations (correlation coefficients $\geq$0.997) and the ρ_X, ρ_Y and ρ_Z values are listed in Tables 3–6.

Table 1. Second-order rate constants, $10^4\ k_2$ (l mol^{-1} s^{-1}), for the reactions of (Z)-phenylethyl brosylates with (Y)-pyridines in acetonitrile at 60 °C at different pressures

		Y			
Z	Pressure, (bar)	3,4-(CH$_3$)$_2$	3-CH$_3$	H	3-Cl
4-CH$_3$	1	2.931	1.541	0.9112	0.1883
	1000	3.921	2.219	1.345	0.2739
	2000	6.221	3.721	2.454	0.5011
H	1	2.793	1.462	0.8512	0.1708
	1000	3.809	2.130	1.273	0.2510
	2000	6.071	3.630	2.353	0.4671
4-Cl	1	2.641	1.355	0.7901	0.1521
	1000	3.633	1.998	1.191	0.2255
	2000	5.916	3.466	2.234	0.4209

Table 2. Second-order rate constants, $10^4\ k_2$ (l mol^{-1} s^{-1}), for the reactions of (Z)-phenylethyl (X)-benzenesulfonates with pyridine in acetonitrile at 60 °C at different pressures

		X		
Z	Pressure, (bar)	H	4-Br	3-NO$_2$
4-CH$_3$	1	0.4093	0.9112	4.604
	1000	0.5978	1.345	6.135
	2000	0.9908	2.454	9.184
H	1	0.3819	0.8512	4.361
	1000	0.5568	1.273	5.890
	2000	0.9331	2.353	8.934
4-Cl	1	0.3531	0.7901	4.105
	1000	0.5168	1.191	5.582
	2000	0.8738	2.234	8.656

Table 3. Reaction constants (ρ_Y) and correlation interaction coefficients (ρ_{YZ}) for the reactions of (Z)-phenylethyl brosylates with (Y)-pyridines in acetonitrile at 60 °C at different pressures

	ρ_Y		
Z	1 bar	1000 bar	2000 bar
4-CH$_3$	−1.94	−1.89	−1.80
H	−1.98	−1.93	−1.83
4-Cl	−2.02	−1.98	−1.89
ρ_{YZ} (r^a)	−0.21 (0.998)	−0.22 (0.999)	−0.24 (0.997)

[a] Multiple correlation coefficient.

Table 4. Reaction constants (ρ_X) and correlation interaction coefficients (ρ_{XZ}) for the reactions of (Z)-phenylethyl (X)-benzenesulfonates with pyridine in acetonitrile at 60 °C at different pressures

	ρ_X		
Z	1 bar	1000 bar	2000 bar
4-CH_3	1.48	1.42	1.34
H	1.49	1.43	1.36
4-Cl	1.50	1.45	1.38
ρ_{XZ} (r^a)	0.04 (0.980)	0.07 (0.988)	0.09 (0.986)

[a] Multiple correlation coefficient.

Table 5. Reaction constants (ρ_Z) and correlation interaction coefficients (ρ_{ZY}) for the reactions of (Z)-phenylethyl brosylates with (Y)-pyridines in acetonitrile at 60 °C at different pressures

	ρ_Z		
Y	1 bar	1000 bar	2000 bars
3,4-$(CH_3)_2$	−0.112	−0.083	−0.054
3-CH_3	−0.134	−0.114	−0.078
H	−0.154	−0.132	−0.102
3-Cl	−0.231	−0.207	−0.188
ρ_{ZY} (r^a)	−0.21 (0.989)	−0.23 (0.996)	−0.24 (0.999)

[a] Multiple correlation coefficient.

Table 6. Reaction constants (ρ_Z) and correlation interaction coefficients (ρ_{ZX}) for the reactions of (Z)-phenylethyl (X)-benzenesulfonates with pyridine in acetonitrile at 60 °C at different pressures

	ρ_Z		
X	1 bar	1000 bar	2000 bar
H	−0.173	−0.159	−0.138
4-Br	−0.154	−0.132	−0.102
3-NO_2	−0.140	−0.108	−0.070
ρ_{ZX} (r^a)	0.05 (0.989)	0.08 (0.999)	0.10 (0.989)

[a] Multiple correlation coefficient.

Effect of substituent

In Table 3, the value of ρ_Y increases when there is an electron-withdrawing substituent in the substrate ($Z = 4\text{-}Cl$), which indicates that charge transfer from the nucleophile is increased. In other words, bond formation is increased. This trend is reasonable, because an electron-withdrawing substituent facilitates the charge transfer from the nucleophile to the reaction center, C α, enhancing the positive charge on the N atom of pyridine and increasing Nu—Cα bond formation. The value of ρ_X is positive and increases with increasing electron-withdrawing ability of the substituents on the substrate (Table 4). However, the effect of changing the substituent from $Z = 4\text{-}CH_3$ to 4-Cl is greater on ρ_Y than on ρ_X. This indicates that the variation in bond formation between the nucleophile and the substrate reaction center is larger than that of bond cleavage between the leaving moiety and the reaction center. In Tables 5 and 6, the sign of ρ_Z is negative, which indicates that the reaction center of the substrate (Cα) develops a positive charge, and also means that the degree of bond breaking is greater than that of bond formation in the TS for the reaction series. Since the change in the magnitude of ρ_Y is larger than that of ρ_X with various substituents, the change in bond formation is greater than that in bond breaking. These results will affect the ρ_{ij} values. The magnitudes of ρ_{ij} imply advanced bond formation (in the case of ρ_{YZ}) or imminent departure of the leaving moiety (in the case of ρ_{XZ}). The magnitudes of ρ_{YZ} and ρ_{XZ} indicate the degree of Nu—Cα bond formation and Cα—L bond fission, respectively. The magnitude of ρ_{YZ} obtained from the plot of ρ_Y against σ_Z (ρ_Z with σ_Y) is larger than that of ρ_{XZ}. When the substituent (Z) is 4-CH_3, the Cα—L bond in the TS is as long as, or slightly longer than, the Nu—Cα bond, because the sign of ρ_Z is negative, which means that the reaction center of the substrate develops a positive charge. When the substituent (Z) is changed from 4-CH_3 to 4-Cl, the Nu—Cα bond formation is greatly increased, but Cα—L bond fission is slightly increased. The magnitudes of ρ_Y are comparable to those found for the reactions of benzyl benzenesulfonates with pyridines in acetone[2b] ($\rho_{YZ} = -0.52$, $\rho_{XZ} = 0.15$). The values of ρ_Z for the reactions of a phenylethyl substrate are smaller than that for the benzyl substrate because the phenylethyl system has an extra CH_2 group between the substituent Z and the reaction center of the β-carbon atom. An extra CH_2 group will increase the distance between Z and reaction center, hence it is expected to decrease the $|\rho_{YZ}|$ value in comparison with that of the benzyl system. However, the ratio of $|\rho_{YZ}|$ to ρ_{XZ} is larger than that for the benzyl system. When ρ_{XZ} is smaller than $|\rho_{YZ}|$ for a different substituent, it indicates that the leaving moiety is already at a distance from the substrate reaction center, so there is less variation in the distance from the reaction center, but more variation in ρ_{YZ}. Since we expect both benzyl and phenylethyl systems to react by a dissociative S_N2 mechanism, from the sign of ρ_Z and the comparison of ρ_{ij} ($|\rho_{YZ}| > \rho_{XZ}$), the reactions suggest a dissociative S_N2 mechanism.[7b]

Effect of Pressure

In Tables 3 and 4, the magnitudes of $|\rho_Y|$ and ρ_X decrease when the pressure increases, which suggests that the degrees of bond formation and breaking are decreased. A change of pressure from 1 to 2000 bar seems to cause a smaller decrease in $|\rho_Y|$ than in ρ_X, because the magnitude of ρ_Z decreases with increasing pressure, which indicates that the degree of bond breaking is more advanced than that of bond formation in the TS for this reaction series. Therefore, in this reaction, the pressure leads to the formation of the TS in an earlier position, which is more similar to a concerted S_N2-type reaction pathway. From comparison of the activation volume ($\Delta V^{\ddagger}$) for benzyl and phenylethyl systems, the $\Delta V^{\ddagger}$ of benzyl benzenesulfonate with pyridine at 40 °C in acetone was $-12.97\,\mathrm{cm^3\,mol^{-1}}$ and that of the phenylethyl system was $12.30\,\mathrm{cm^3\,mol^{-1}}$. These two $\Delta V^{\ddagger}$ values are very similar, suggesting that the reaction mechanisms resemble each other under high pressure.

These results accord with the comparison of ρ_{ij}; the magnitude of ρ_{YZ} is larger than that of ρ_{XZ} under low pressure, since the degree of Cα—L bond cleavage is enhanced and the Nu—Cα bond is poorly formed in the TS. As the pressure is increased, the formation of the Nu—Cα bond is decreased less than the breaking of the Cα—L bond in the TS, because with an increase in pressure the degree of variation of ρ_{XZ} is greater than that of $|\rho_{YZ}|$. This indicates that the leaving moiety is closer to the substrate reaction center, so the degree of variation in the distance from the reaction center becomes large, but bond formation with the nucleophile decreases slightly. Hence the TS moves from a dissociative S_N2 to more concerted S_N2 type with increase in pressure. This result accords with the sign and the variation of $|\rho_Z|$ values, where $|\rho_Z|$ decreases with increasing pressure. In Menschutkin-type reactions, the concerted S_N2 reaction has a smaller negative ρ_Z value than the dissociative S_N2 reaction.

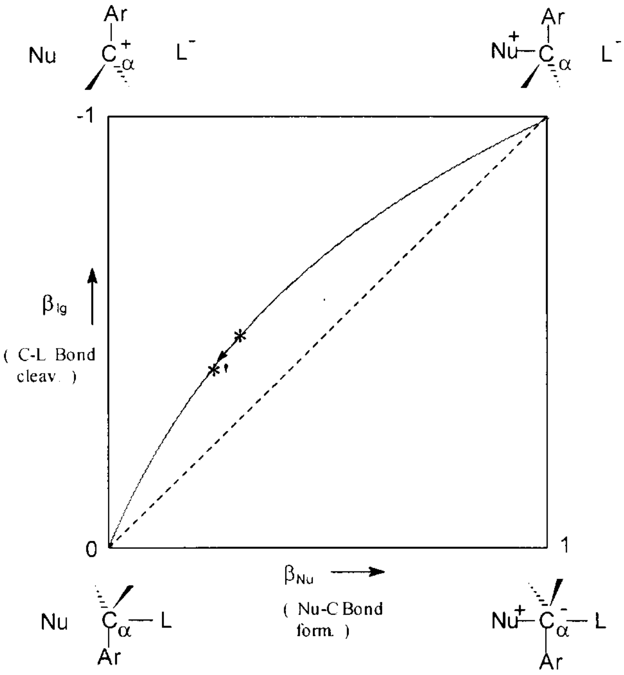


Figure 1. MOFJ diagram based on structure–reactivity coefficient for the reaction of (Z)-phenylethyl (X)-arenesulfonates with (Y)-pyridines. The energy contours are not shown. With higher pressure, the transition state* moves towards*′, lowering the energy of the intermediate

Table 7. Brønsted β_{Nu} values for the reactions of (Z)-phenylethyl brosylates with pK_as[a] of pyridines in acetonitrile at 60 °C at different pressures

	β_{Nu}		
Z	1 bar	1000 bar	2000 bar
4-CH_3	0.268	0.262	0.250
H	0.273	0.268	0.254
4-Cl	0.279	0.274	0.262

[a] pK_as were evaluated from 1.199pK_a (water) + 5.630 ($r = 0.986$) in acetonitrile; see Ref. 9a, correlation coefficient ≥0.996).

Table 8. Brønsted β_{lg}[a] values for the reactions of (Z)-phenylethyl (X)-arenesulfonates with pyridine in acetonitrile at 60 °C under at different pressures

	β_{lg}		
Z	1 bar	1000 bar	2000 bar
4-CH_3	−0.476	−0.457	−0.430
H	−0.480	−0.462	−0.437
4-Cl	−0.483	−0.466	−0.443

[a] pK_as were taken from Ref. 9b, correlation coefficient ≥0.996.

The sign of the product $\rho_{XZ}\,\rho_{YZ}$ can also predict the movement of TS.[2b] In other words, if the sign of the product $\rho_{XZ}\,\rho_{YZ}$ is positive, the TS movement agrees with the Thornton effect, but if it is negative, the TS movement obeys the Hammond effect. In this reaction series, a negative sign of $\rho_{XZ}\,\rho_{YZ}$ means that the TS works in harmony with the Hammond effect. This is in good accord with the prediction of the More O'Ferrall–Jencks (MOFJ) diagram in Fig. 1. The MOFJ diagram can predict the changes that occur in the structure of the TS when the substituent in the substrate, nucleophile or leaving group is changed. The energies of the reactants, products and the two possible intermediates (the carbonium ion and the pentavalent complex) are represented at the corner of the energy surface. The *x* and *y* axes represent changes in the length of the Nu—Cα and Cα—L bonds, respectively. The energy contour shows the lowest energy pathway, the reaction coordinate, through the energy surface. The Brønsted β_{Nu} and β_{lg} are summarized in Tables 7 and 8. When the substituent (Z) is changed from 4-CH_3 to 4-Cl, the values of β_{Nu} are smaller than those of β_{lg}. Thus, Nu—Cα bond formation proceeds poorly compared with Cα—L bond cleavage. By comparing β_{Nu} and β_{lg} with increase in pressure, the TS movement on the MOFJ diagram can be monitored. At atmospheric pressure, the TS predicted by the β_{Nu} and β_{lg} values is designated with an asterisk (*). With increasing pressure, both of the absolute β values decrease, indicating that the formation of the Nu—Cα bond and the breaking of the Cα—L bond were decreased in the TS. Therefore, the TS moves to a more reactant-like (* → *′) pathway. This result means that the change in the TS agrees with Hammond's effect, as was also shown by the negative sign for the product ρ_{XZ} ρ_{YZ}.

In conclusion, the Hammett ρ values of the nucleophile, leaving group and substrate can be used to estimate the structure of the TS. The magnitude of ρ_{ij} is a useful tool for determining the structure of the TS. In particular, the comparison of ρ_{XZ} with ρ_{YZ} and the sign of ρ_Z can indicate the type of S_N reaction. Under low pressure, $|\rho_Z|$ is slightly larger than that at high pressure and the fact that $|\rho_{YZ}|$ is greater than ρ_{XZ} at low pressure indicates that this reaction series proceeds via a dissociative S_N2 process. However, with increasing pressure, $|\rho_{YZ}|$ value is slightly larger than ρ_{XZ}, while the magnitude of ρ_Z is smaller than that at low pressure, which indicates that the TS of this reaction moves from a dissociative S_N2 to a somewhat concerted and more early-type S_N2 process. This result is in good accord with the MOFJ model. A negative sign of ρ_{XZ} ρ_{YZ} means that the TS works in harmony with the Hammond effect.

EXPERIMENTAL

Instruments. The conductivity meter was a TOA 60-V equipped with a Fisher 9010 circulator. The conductivity cell has two parts, a glass cylinder with a volume of 5 cm^3, in which two Pt circular plate electrodes are sealed, and a one-branch Teflon tube 8 cm long and 1 cm in diameter. The former part is the conducting cell and the latter serves as the pressure conductor. This cell was placed in the pressure vessel.

Materials. All materials were purchased from Wako (Osaka, Japan) or Merck (Darmstadt, Germany). Acetonitrile was purified by distillation, after adding anhydrous potassium carbonate and letting it stand for 3 days at room temperature. Commercial pyridine was purified by several distillations through potassium hydroxide. Other liquid pyridines were used without further purification, but solids recrystallized before use. All the purified pyridines were stored in brown ampoules under a nitrogen atmosphere.

The preparation of the substrate and the product analysis were as described previously.[10] Phenylethyl brosylate was prepared by Tipson's procedure as follows: Phenylethyl alcohol (2.73 g, 0.022 mol) was dissolved in pure pyridine (*ca* 40 cm^3) and subsequently *p*-bromobenzenesulfonyl chloride (5.71 g, 0.022 mol) was gradually added with stirring at 0 °C. After 3 h at 0 °C, the mixture was poured into ice–water and crystals were collected, yield 63%, m.p. 57 °C (recrystallized from *n*-hexane) (lit.[10] 58–59 °C).

To prepare *N*-phenylethylpyridinium 4-bromobenzenesulfonate, pyridine (0.554 g, 0.007 mol) was added to a solution of phenylethyl 4-bromobenzenesulfonate (2.387 g, 0.007 mol) in anhydrous acetonitrile (80 cm^3). The mixture was heated under reflux for 4 h and then left overnight at room temperature. The product was separated from the solvent and washed with anhydrous diethyl ether, crystalline (45%), m.p. 156 –157 °C (recrystallized from propan-2-ol). Found: C, 54.3; H, 4.80; N, 3.45. Calc. for $C_{19}H_{18}BrNO_3$: C, 54.3; H, 4.30; N, 3.30%. ^1H NMR (300 MHz, DMSO): δ 3.2 (2 H, t, β-H), 4.7 (2 H, t, α-H), 8.7 (2 H, d, α-H of pyridine), 8.2 (2 H, t, β-H of pyridine), 7.5 (9 H, m, phenyl).

Kinetics. The reaction of phenylethyl brosylate with pyridine at different pressures was followed by a conductometric method. As the reaction proceeds, the electrical conductance increases because of the formation of the salt. The conductivity cell was suspended in a high-pressure vessel with an electrode lead and the vessel was placed in a thermostat (±0.01 °C). Solvolysis related to nucleophilic addition was always negligible.

Kinetic runs were carried out under pseudo-first-order conditions with pyridine in which the amine concentration is over 100 times larger than that of substrate. Guggenheim plots were used for determining the pseudo-first-order rate constant, from which the second-order rate constants were calculated. Rate constants were reproducible to ±5% at 1–2000 bar. The rate constants, k_{obs}, are linearly correlated with the nucleophile concentration, which indicates that the reaction is second order. The following rate law expresses the pseudo-first-order relationship with respect to each reagent:

$$k_{obs} = k_2[\mathrm{Nu}]$$

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