vents could exhibit a nonmonotonic FRS decay profile. Consideration of permanent dipole moments and the polarity of the solvent provides a qualitative explanation for this observation although a more systematic study appears to be necessary to understand the behavior in detail. We also confirmed experimentally that the extraction of two individual diffusivities from DGD type FRS decay profiles is very troublesome. Nonetheless, we can measure the mean diffusivity quite reliably, and we can at least infer a range for τ_1 and τ_2 individually from the q^2 dependence of the τ's. Difficulty in deducing individual τ's from nonmonotonic FRS decay signals seems to be inherent to FRS method, which evidently mandates independent measurements of the amplitudes A_1 and A_2.

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Structure-Reactivity Relationship of Substituted Phenylethyl Arenesulfonates with Substituted Pyridines under High Pressure

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Nucleophilic substitution reactions of (Z)-phenylethyl (X)-benzenesulfonates with (Y)-pyridines were investigated in acetonitrile at 60 °C under respective pressures. The magnitudes of the Hammett reaction constants, ρ_X, ρ_Y and ρ_Z indicate that a stronger nucleophile leads to a greater degree of bond formation of C-N and a better leaving group is accompanied by a less degree of bond breaking. The magnitude of correlation interaction term, ρ_{ij} can be used to determine the structure of the transition state (TS) for the S_N reaction. As the pressure is increased, the Hammett reaction constants, ρ_X and $|\rho_Y|$, are decreased, but correlation interaction coefficient, ρ_{XZ} and $|\rho_{YZ}|$, are increased. The results indicate that the reaction of (Z)-phenylethyl (X)-benzenesulfonates with (Y)-pyridines probably moves from a dissociative S_N2 to early-type concerted S_N2 mechanism by increasing pressure. This result shows that the correlation interaction term ρ_{ij} can be useful tool to determine the structure of TS, and also the sign of the product $\rho_{XZ} \cdot \rho_{YZ}$ can be predict the movement of the TS.

Introduction

One of the linear free energy relationships (LFER), the notable Hammett equation, has been used as an empirical means of characterizing transition-state (TS) structures.[1-3] The Hammett ρ is first derivative of log k as shown in

equation (1) and reflects TS structures involved in a series of reactions with structural changes affecting the reaction center.

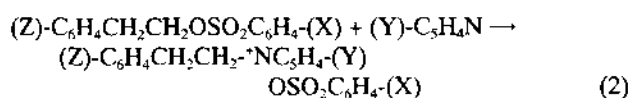$$\rho = \log k / \partial \sigma \qquad (1)$$

The magnitudes of the ρ values in the nucleophile and

leaving group can estimate the degree of bond formation and bond dissociation. However, it has occasionally been suggested that the ρ value cannot be used as a measure of TS structure, since the efficiency of charge transmission for different reactions series may differ.[4,5]

In previous work,[6] we proposed that the TS structure in nucleophilic substitution (S_N) reactions can be predicted by the sign and absolute values of ρ_Z and comparison of the relative value of the correlation interaction coefficient, ρ_{XZ} with ρ_{YZ}.

Menschutkin reactions – typical S_N2 reactions of alkyl halides with tertiary amine to form quaternary ammonium salts – have been widely investigated for the effects of pressure.[7,8] Recently kinetic studies of Menschutkin type reactions of benzyl benzenesulfonate with pyridines in acetone were carried out by the electric conductivity method under 1 to 2,000 bars at 20-40 °C.[9] From the enthalpy, entropy, and volume of activation, it was found that this reaction proceeds via the S_N2 reaction mechanism in which the rate of the reaction was determined by C-N bond formation in the transition state. In this connection, we studied on pressure dependence of the reaction rate of phenylethyl arenesulfonate with pyridines to get some detailed information about the transition state which is expected to be more typical S_N2 under high pressure at 60 °C in acetonitrile. Under atmospheric condition, the substituent effect in substrate of phenylethyl system was not so significant as expected, but still the electron-donating substituents showed the slight acceleration to give a small negative ρ value and Hammett plot slightly curvatures on the acting substituents, even though it is not so remarkable as that of benzyl system.[10] These results represented a little bit favorable bond-breaking at the transition state by the electron-donating substituents.

In this paper, we report the results of the relationship of the effect of substituent on the substrate(Z), nucleophile(Y), and leaving group(X) by the Hammett reaction constants, ρ_X, ρ_Y and ρ_Z, and correlation interaction coefficients, ρ_{XZ} and ρ_{YZ}, on the reaction between (Z)-phenylethyl (X)-benzenesulfonates with (Y)-pyridines in acetonitrile under respective pressures as shown in equation (2).

$$(Z)\text{-}C_6H_4CH_2CH_2OSO_2C_6H_4\text{-}(X) + (Y)\text{-}C_5H_4N \longrightarrow$$
$$(Z)\text{-}C_6H_4CH_2CH_2\text{-}^+NC_5H_4\text{-}(Y)$$
$$OSO_2C_6H_4\text{-}(X) \tag{2}$$

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

Results and Discussion

Effect of Substituent. The reaction rates were determined by monitoring the changes in the electrical conductance on formation of the salt from the reaction of substituted (Z)-phenylethyl (X)-benzenesulfonates with substituted (Y)-pyridines in acetonitrile. The second-order rate constants, k_2 for this reaction at respective pressures, are summarized in Tables 1 and 2.

The rate was increased by electron-donating substituent on pyridine nucleophile, which is expected for nucleophile as nucleophilic attack of nitrogen in the pyridine on the carbon atom. With increasing leaving ability and electron-

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

Z	Y bar	3,4-(CH$_3$)$_2$	3-CH$_3$	H	3-Cl
4-CH$_3$	1	2.931	1.541	0.911	0.188
	1000	3.921	2.219	1.345	0.274
	2000	6.221	3.721	2.454	0.501
H	1	2.793	1.462	0.851	0.171
	1000	3.809	2.130	1.273	0.250
	2000	6.071	3.630	2.353	0.461
4-Cl	1	2.641	1.355	0.790	0.152
	1000	3.633	1.998	1.191	0.226
	2000	5.916	3.466	2.234	0.421

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

Z	X bar	H	4-Br	3-NO$_2$
4-CH$_3$	1	0.409	0.911	4.640
	1000	0.598	1.345	6.165
	2000	0.993	2.454	9.234
H	1	0.382	0.851	4.361
	1000	0.557	1.273	5.890
	2000	0.933	2.353	8.934
4-Cl	1	0.349	0.790	4.075
	1000	0.516	1.191	5.582
	2000	0.874	2.234	8.656

donating ability in substrate, the rate was increased. The change of rate constants is less sensitive to the variation of substituents in the phenylethyl substrate than to that of benzyl one because of the intervention of the more -CH$_2$- group. Thus the magnitude of ρ_Z values for the substrate is smaller than ρ_Y and ρ_X. The Hammett plots are generally good linear correlations and the ρ_X, ρ_Y, and ρ_Z values are listed in Tables 3-6.

In Table 3, the signs of ρ_Y are negative and the magnitudes of $|\rho_Y|$ values are fairly large, that the nucloephilic nitrogen atom locates in the aromatic ring. The magnitudes of $|\rho_Y|$ and ρ_X are increased with a more electron-withdrawing substituent in the substrate, which suggests the degree of bond formation on reaction center is high. The vari-

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 under respective pressures

Z	ρ_Y		
	1 bar	1000 bars	2000 bars
4-CH$_3$	− 1.940	− 1.892	− 1.799
H	− 1.975	− 1.937	− 1.843
4-Cl	− 2.017	− 1.974	− 1.888
ρ_{YZ}	− 0.192	− 0.202	− 0.221

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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 under respective pressures

Z	ρ_X		
	1 bar	1000 bars	2000 bars
4-CH$_3$	1.484	1.420	1.339
H	1.488	1.434	1.355
4-Cl	1.500	1.448	1.376
ρ_{XZ}	0.041	0.069	0.092

ation of substituent in the substrate from Z=p-CH$_3$ to Z=p-Cl cause a larger increase in $|\rho_Y|$ than in ρ_X. The value of ρ_X is decreased with a more electron-donating substituent in the substrate in Table 4, which means a less degree of bond breaking. Thus a stronger nucleophile is accompanied by a greater degree of bond formation and a better leaving group is accompanied by a less degree of bond breaking, *i.e.*, a stronger nucleophile and/or better leaving group lead to formation of early TS. The sign of ρ_Z is negative in Tables 5 and 6, which indicates reaction center of substrate has developed positive charge, and that means degree of bond-breaking is greater than that of bond-formation on the TS for the reaction series. The change of bond formation is more than that of bond breaking with a more electron-withdrawing substituent in the substrate. This is reasonable explain since bond breaking has already progressed much further than bond formation in the TS. These results will affect the correlation interaction term ρ_{ij} values. The ρ_{ij} (ρ_{XZ} or ρ_{YZ}) is dependent on the change of distance between the reaction centers of *i* and *j* which can express the sensitivity of $\rho_i\sigma_j$ (or $\rho_j\sigma_i$). In other words, ρ_{XZ} and ρ_{YZ} indicate the degree of C-L bond fission and Nu-C bond formation, respec-

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 under respective pressures

Y	ρ_Z		
	1 bar	1000 bars	2000 bars
3,4-(CH$_3$)$_2$	− 0.113	− 0.083	− 0.054
3-CH$_3$	− 0.140	0.114	− 0.078
H	− 0.154	− 0.132	− 0.102
3-Cl	− 0.230	− 0.208	− 0.188
ρ_{ZY}	− 0.191	− 0.202	− 0.222

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 under respective pressures

X	ρ_Z		
	1 bar	1000 bars	2000 bars
H	− 0.172	− 0.159	− 0.138
4-Br	− 0.154	− 0.132	− 0.102
3-NO$_2$	− 0.140	− 0.108	− 0.070
ρ_{ZX}	0.042	0.069	0.091

tively. The ρ_{ij} derived from Taylor series expansion is log $(k_{ij}/k_{00}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j$ and therefore ρ_{XZ} (ρ_{ZX}) and ρ_{YZ} (ρ_{ZY}) are represented by the equations (3) and (4)

$$\log(k_{XZ}/k_{00}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \tag{3}$$

$$\log(k_{YZ}/k_{00}) = \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{YZ}\sigma_Y\sigma_Z \tag{4}$$

, where X, Y and Z are the substituents of the leaving group, nucleophile and substrate, respectively. The magnitude of $|\rho_{YZ}|$ obtained by the plot of ρ_Y with σ_Z is larger than that of ρ_{XZ}. The length of the C-L bond in the TS stays the same or become slightly longer than that of the Nu-C bond when the substituent of substrate is p-CH$_3$. As the substituent of substrate is changed from Z=p-CH$_3$ to Z= p-Cl, the formation of the Nu-C bond increase largely, but the breaking of the C-L bond increase slightly in the TS. That the magnitude of ρ_{XZ} is smaller than that of $|\rho_{YZ}|$ on the change of substituent of substrate indicates that leaving moiety already is away from the reaction center of substrate, so the variation degree of distance from the reaction center is small in the case of ρ_{XZ}, but is large in the case of $|\rho_{YZ}|$. Thus, from the sign of ρ_Z and the comparison of ρ_{ij} ($|\rho_{YZ}|>$ ρ_{XZ}), this reaction is led to a dissociative S_N2 mechanism.[6b]

Effect of Pressure. In Table 3, the magnitudes of the $|\rho_Y|$ and ρ_X values are decreased when the pressure is increased, which suggests that degree of bond formation and breaking are decreased. The change of the pressure from 1 to 2,000 bars seems to cause less decrease in $|\rho_Y|$ compared with that in ρ_X because the magnitudes of the $|\rho_Z|$ values decrease with increasing pressure, which indicates degree of bond breaking is less than bond formation on the TS for this reaction series. Therefore, effect of pressure for this reaction leads to the formation of an early TS and more similar to concerted S_N2-type reaction pathway.

These results accord with the comparison of ρ_{ij}; the magnitude of $|\rho_{YZ}|$ is larger than that of ρ_{XZ} at low pressure, since the degree of the C-L bond cleavage is enhanced and the Nu-C bond formation has poor develops in the TS. When the pressure is increased, the formation of the Nu-C bond decreases less than the breaking of the C-L bond in the TS, because the variation degree of ρ_{XZ} is larger than that of $|\rho_{YZ}|$ with increasing the pressure. It indicates that the leaving moiety is less away from the reaction center of the substrate, so the variation degree of the distance from the reaction center becomes large but bond formation of nucleophile decreases slightly, hence the TS moves from dissociative S_N2 to more concerted S_N2 type with increasing pressure. This result accords with the sign and variation of $|\rho_Z|$ values, in which $|\rho_Z|$ values decrease with increasing pressure. In the cases of Menschutkin type reaction, concerted S_N2 reaction has smaller negative ρ_Z value than that of dissociative S_N2. The sign of the product $\rho_{XZ}\cdot\rho_{YZ}$ can predict the movement of TS.[6b] In other words, if the sign of the product $\rho_{XZ}\cdot\rho_{YZ}$ is positive, the TS movement accords with the Thornton effect, but if it is negative, the TS movement obeys the Hammond effect. In the case of these reaction series, a negative sign of $\rho_{XZ}\cdot\rho_{YZ}$ would permit the TS to move according to the Hammond effect.

In conclusion, the Hammett ρ values of the nucleophile, leaving group and substrate can estimate the structure of the TS. The magnitude of ρ_{ij} can be useful tool to determine the structure of TS. In particular, the comparison of ρ_{XZ}

with $|\rho_{YZ}|$ and the sign of ρ_Z can indicate the type of S_N reaction. The $|\rho_Z|$ value at low pressure, is slightly larger than that of high pressure. That at low pressure, $|\rho_{YZ}|$ value is greater than ρ_{XZ} indicate that this reaction series proceeds via dissociative S_N2 process. But at high pressure, $|\rho_{YZ}|$ value is slightly larger than ρ_{XZ}, which indicates that this reaction series move from dissociative S_N2 process to early-type concerted S_N2 process with increasing pressure, and a negative sign of $\rho_{XZ} \cdot \rho_{YZ}$ permits the TS to move according to the Hammond effect.

Experimental

Instruments. The conductivity meter is TOA 60-V equipped with FISHER 9010 circulator. The conductivity cell is composed of two parts, a glass cylinder of 5 cm³ in which two Pt circular plate electrodes are sealed, and one-branched teflon tube of 8 cm long and 1 cm in diameter. The former acts as a conducting cell and the latter acts as a pressure conductor by pressing. The cell is set in the pressure vessel.

Materials. All materials were purchased from Wako (Japan) or Merck (Germany). Acetonitrile was purified by distillation after putting anhydrous potassium carbonate in it for three days at room temperature. Pyridine was commercial and was purified by several distillations through potassium hydroxide. Other liquid pyridines were used without further purification, but solids were recrystallized before use. All purified pyridines were stored in brown ampules under nitrogen atmosphere.

The preparation of the substrate and the product analysis were as described previously.[11] 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 mL) 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%, mp 57 °C (recrystallized from n-hexane) (lit., 58-59 °C).

N-Phenylethylpyridinium p-bromobenzenesulfonate; Pyridine (0.554 g, 0.007 mol) was added to a solution of phenylethyl p-bromobenzenesulfonate (2.387 g, 0.007 mol) in anhydrous acetonitrile (80 mL). 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 ether, crystalline (45%), mp 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%); δ (DMSO) 3.2 (2H, t, β-H), 4.7 (2H, t, α-H), 8.7 (2H, d, α-H of pyridine), 8.2 (2H, t, β-H of pyridine), and 7.5 (9H, m, phenyl).

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

The reproducibility of the data (λ_∞ and λ_0) was difficult to confirm, so all kinetic data were carried out under pseudo-first-order conditions, with a molar concentration of pyridine over 100 times that of phenylethyl brosylate. Guggenheim plots were used for determining the pseudo-first-order rate constant, from which the second-order rate constants were calculated. Rate constants were accurate to ±5% at 1-2000 bars. The rate constants, k_{obs} are linearly correlated with the nucleophile concentration, which indicates that the reaction is second order. The pseudo-first-order with respect to each reagent is the following rate law

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

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