are 5.1×10^{13}, 1.2×10^{14} and 1.0×10^{15} states/m^2, respectively. If it assumes that one monolayer corresponds to 10^{19} states/m^2, 1.0×10^{15} states/ma^2 does to 10^{-4} monolayer when the height of surface barrier is comparable to kT at 473 K. Therefore the adsorption of oxygen on ZnO is controlled by the surface barrier even very low coverage of oxygen species. The rate constant of desorption C is very small compared to that of adsorption A and the adsorption process can be believed as an irreversible one.

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Mechanism for the Reaction of Substituted Phenacyl Arenesulfonates with Substituted Pyridines under High Pressures

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The rates for the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines in acetone were measured by an electrical conductivity method at 1-2000 bars and 45 °C. The magnitudes of the Hammett reaction constants, ρ_X, ρ_Y and ρ_Z, represent the degree of Nu-C bond formation and that of C-L 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, $|\rho_Y|$ and ρ_Z are increased, but correlation interaction coefficient, $|\rho_{XZ}|$ and ρ_{YZ}, are decreased. The results indicate that the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines probably moves from an associative S_N2 to late-type S_N2 mechanism by increasing pressure.

Introduction

Menschutkin reactions of alkyl halides with tertiary amine forming quarternary ammonium salts have been widely investigated under various pressures.[1~5] The study of substituent and pressure effect provides one of the most powerful tools for probing the structure of transition state. The reaction mechanism for the nucleophilic substitution reaction of substituted phenacyl benzenesulfonates with substituted pyridines in acetonitrile has been investigated through multiple Hammett correlation under atmospheric condition.[6] In this connection, we have studied the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines in acetone in order to investigate the substituent and pressure effect. This yielded detailed information on the transition state. 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.[7~9] The Hammett coefficient 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.

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

The magnitudes of the ρ values in the nucleophile and leaving group can measure the degree of bond formation and bond breaking. 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.[10,11]

In previous work,[12] 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}. We report our results on the substituent and pressure effect for the reaction of substituted phenacyl benzenesulfonates with pyridines as shown in equation (2), respectively.

$$\text{(Z)-C}_6\text{H}_4\text{COCH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-(X)+(Y)-C}_5\text{H}_4\text{N} \rightarrow \text{(Z)-C}_6\text{H}_4\text{COCH}_2\text{-}^{+}\text{NC}_5\text{H}_4\text{-(Y)} \; {}^{-}\text{OSO}_2\text{C}_6\text{H}_4\text{-(X)} \qquad (2)$$

X=4-CH_3, H, 4-Br, 3-NO_2
Y=3,4-$(CH_3)_2$, 3-CH_3, H
Z=H, 4-Cl, 4-NO_2

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)-phenacyl (X)-benzenesulfonates with (Y)-pyridines in acetone at 45 °C. The second-order rate constants, k_2 for this reaction at respective pressures, are summarized in Tables 1 and 2.

Table 1. Second-order rate constants, 10^4 k_2, (1/mol·s), for the reactions of (Z)-phenacyl benzenesulfonate with (Y)-pyridines in acetone at 45 °C under respective pressures

Z	Pressure (bars)	Y		
		3,4-$(CH_3)_2$	3-CH_3	H
H	1	14.2	6.45	3.96
	500	21.0	8.91	5.58
	1000	28.8	12.5	7.36
	1500	37.7	15.5	9.08
	2000	49.4	20.1	11.5
4-Cl	1	15.2	7.15	4.40
	500	23.1	10.2	6.45
	1000	32.6	14.2	8.35
	1500	42.6	18.0	10.4
	2000	57.7	23.9	13.6
4-NO_2	1	17.2	8.36	5.31
	500	27.7	12.6	8.09
	1000	39.6	18.0	10.9
	1500	53.5	23.1	13.9
	2000	73.2	31.2	18.2

Table 2. Second-order rate constants, 10^4 k_2, (1/mol·s), for the reactions of (Z)-phenacyl (X)-benzenesulfonate with pyridine in acetone at 45 °C under respective pressures

Z	Pressure (bars)	X			
		4-CH_3	H	4-Br	3-NO_2
H	1	2.35	3.96	7.51	43.0
	500	3.06	5.58	10.1	64.8
	1000	3.87	7.36	16.0	90.3
	1500	5.30	9.08	20.6	136
	2000	6.93	11.5	28.1	219
4-Cl	1	2.91	4.40	8.51	45.1
	500	3.84	6.45	11.6	68.9
	1000	4.86	8.35	18.8	97.5
	1500	6.79	10.4	24.6	150
	2000	9.12	13.6	33.4	247
4-NO_2	1	4.10	5.31	10.5	49.0
	500	5.45	8.09	14.8	78.2
	1000	7.13	10.9	24.6	114
	1500	9.98	13.9	32.7	180
	2000	13.5	18.2	45.8	301

There is an enhancement in the rate of nucleophilic substitution for a given leaving group when electron-donating substituents are present in the nucleophile, and for a given nucleophile when electron-withdrawing substituents are present in the leaving group. The rate was increased by electron-donating substituents on pyridine, which acts as a nucleophile. With increasing leaving ability and electron-withdrawing ability in substrate, the rate was increased. The change of rate constants is more sensitive to the variation of substituents in the phenacyl substrate than to that of phenylethyl one because of -CO- group replacing for -CH_2- group. 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 sign of ρ_Y is negative and the magnitudes of $|\rho_Y|$ values are large, which indicates that the bonding action of the nitrogen atom in pyridine with the carbon center of substrate is progressed enough. In Tables 3 and 4, the magnitudes of $|\rho_Y|$ and ρ_X are decreased with a more electron-withdrawing substituent in the substrate, which suggests the degree of bond formation and bond breaking on reaction center is low. The variation of substituent in the substrate from Z=H to Z=p-NO_2 results in a similar decrease in $|\rho_Y|$ and in ρ_X. The sign of ρ_Z is positive in Tables 5 and 6, which indicates reaction center of substrate develops negative charge. That means the degree of bond-formation is greater than that of bond-breaking in the TS for the reaction series. 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

Table 3. Reaction constants[a] (ρ_Y) and correlation interaction coefficients (ρ_{YZ}) for the reactions of (Z)-phenacyl benzenesulfonate with (Y)-pyridines in acetone at 45 °C under respective pressures

Z	ρ_Y				
	1	500	1000	1500	2000 bars
H	−2.26	−2.36	−2.41	−2.52	−2.57
4-Cl	−2.18	−2.27	−2.40	−2.49	−2.55
4-NO_2	−2.07	−2.19	−2.27	−2.38	−2.46
ρ_{YZ}	0.24	0.20	0.19	0.18	0.15

[a] Correlation coefficients > 0.994

Table 4. Reaction constants[a] (ρ_X) and correlation interaction coefficients (ρ_{XZ}) for the reactions of (Z)-phenacyl (X)-benzenesulfonate with pyridine in acetone at 45 °C under respective pressures

Z	ρ_X				
	1	500	1000	1500	2000 bars
H	1.44	1.50	1.56	1.61	1.70
4-Cl	1.37	1.42	1.49	1.54	1.63
4-NO_2	1.24	1.31	1.38	1.44	1.53
ρ_{XZ}	−0.25	−0.24	−0.23	−0.21	−0.21

[a] Correlation coefficients > 0.996

Table 5. Reaction constantsa) (ρ_Z) and correlation interaction coefficients (ρ_{ZY}) for the reactions of (Z)-phenacyl benzenesulfonate with (Y)-pyridines in acetone at 45 °C under respective pressures

Y	ρ_Z				
	1	500	1000	1500	2000 bars
3,4-$(CH_3)_2$	0.105	0.152	0.173	0.192	0.213
3-CH_3	0.141	0.188	0.200	0.218	0.239
H	0.161	0.202	0.218	0.236	0.251
ρ_{ZY}	0.23	0.21	0.18	0.18	0.16

[a] Correlation coefficients > 0.995

Table 6. Reaction constants[a] (ρ_Z) and correlation interaction coefficients (ρ_{ZX}) for the reactions of (Z)-phenacyl (X)-benzenesulfonate with pyridine in acetone at 45 °C under respective pressures

X	ρ_Z				
	1	500	1000	1500	2000 bars
4-CH_3	0.303	0.313	0.333	0.344	0.360
H	0.255	0.267	0.284	0.314	0.332
4-Br	0.183	0.209	0.235	0.251	0.268
3-NO_2	0.0714	0.104	0.129	0.154	0.173
ρ_{ZX}	−0.26	−0.24	−0.23	−0.22	−0.22

[a] Correlation coefficients > 0.995

fission and Nu-C bond formation, respectively. 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 in the leaving group, nucleophile and substrate, respectively. The magnitude of ρ_{YZ} obtained from the plot of ρ_Y with σ_Z is smaller than that of $|\rho_{XZ}|$. The formation of the Nu-C bond in the TS is slightly more enhanced than that of the breaking of the C-L bond. As the substituent of substrate changes from Z=H to Z=p-NO_2, the decrease in the formation of the Nu-C bond is similar to that of the C-L bond breaking in the TS. Thus, from the sign of ρ_Z and the comparison of ρ_{ij} ($\rho_{XZ}>\rho_{YZ}$), this reaction is led to an associative S_N2 mechanism.[12a]

Effect of Pressure. The activation volumes obtained from equation (5) are shown in Tables 7 and 8.

$$(\partial \ln k_2/\partial P)_T=-\Delta V^{\neq}/RT \tag{5}$$

If $\Delta V^{\neq}$ is independent of pressure, equation (5) can be rewritten as follows

$$k_2=k_0 \exp(-P\Delta V^{\neq}/RT) \tag{6}$$

, where k_0 is the rate constant under 1 atm. From Table 7, we can see that the activation volumes $\Delta V^{\neq}$ are all negative. These results are valuable in considering the physical meaning involved in each item for the reaction mechanism.

Table 7. Activation volume ($-\Delta V^{\neq}$) for the reaction of (Z)-phenacyl benzenesulfonates with (Y)-pyridines in acetone at 45 °C under respective pressures

Y	Z		
	H	4-Cl	4-NO_2
3,4$(CH_3)_2$	13.6	14.4	15.7
3-CH_3	14.9	15.7	17.0
H	16.2	17.2	18.5

Table 8. Activation volume ($-\Delta V^{\neq}$) for the reaction of (Z)-phenacyl (X)-benzenesulfonate with pyridine in acetone at 45 °C under respective pressures

X	Z		
	H	4-Cl	4-NO_2
4-CH_3	14.1	14.9	15.7
H	15.7	16.4	17.5
4-Br	17.5	18.3	19.6
3-NO_2	20.9	21.9	23.2

The $\Delta V^{\neq}$ is equal to $V^{\neq}$-V_0, where $V^{\neq}$ is the volume of the activated complex and V_0 is the volume of reactants, and is composed of the substrate V_m (phenacyl benzenesulfonate), the nucleophile V_n (pyridine) and the solvent $V_s^{\neq}$, (acetone). But the apparent volume of the activated complex ($V^{\neq}$) is the sum of the volume of the complex ($V_a^{\neq}$) and the solvent $V_s^{\neq}$ (acetone). In particular, $V_s^{\neq}$ is different from V_s. We can assume that the sum of V_m and V_n of reactants is similar to that of activated complex $V_a^{\neq}$, even though the complex is somewhat electronically distorted. But the volume of solvents $V_s^{\neq}$ (acetone) is much different from that of the initial state because the charged complex causes more electrostriction than the reactants. As mentioned above, if the complex is more charged than the reactants, it is reasonable that the activation volume ($\Delta V^{\neq}$) is negative. From equation (6), we could know that k_2 increased with increasing pressure because of this negative $\Delta V^{\neq}$ value. Generally, a negative $\Delta V^{\neq}$ would be expected for S_N2 reactions, since two molecules are brought together in the transition state. The $\Delta V^{\neq}$ of S_N2 reaction of benzyl benzenesulfonate with pyridine in acetone at 40 °C under high pressure was reported to be -13.0 cm^{3}mol^{-1}.[13] There is resemblance with other S_N2 reaction (*e.g.*, Menschutkin reaction). For example, in the reactions of EtI with pyridine[14] and phenacyl bromide with pyridine[15] in acetone, the value of $\Delta V^{\neq}$ is reported to be -15~-20 cm^{3}mol^{-1} in both cases. In Tables 7 and 8, the $\Delta V^{\neq}$ values of this reaction are in a range of $-13.6\sim-23.2$ cm^{3}mol^{-1}. Thus, this reaction probably obeys an S_N2 mechanism.

In Tables 3 and 4, the magnitudes of the $|\rho_Y|$ and ρ_X values are increased as the pressure is increased, suggesting that the degree of bond formation and breaking are increased. Changing of the pressure from 1 to 2,000 bars seems to cause more increase in $|\rho_Y|$ compared with that in ρ_X because the magnitudes of the $|\rho_Z|$ values are increased with increasing pressure. That indicates the degree of bond formation is more than that of bond breaking in the TS for this reaction series. Therefore, effect of pressure for this reaction leads to the formation of late TS.

These results accord with the comparison of ρ_{ij}. In comparison with ρ_{YZ} and $|\rho_{XZ}|$, the magnitude of ρ_{YZ} is smaller than that of ρ_{XZ} at low pressure, since the degree of the Nu-C bond formation is more enhanced than that of the C-L bond breaking in the TS. As the pressure is increased, the formation of the Nu-C bond is increased more than the breaking of the C-L bond in the TS, because the variation degree of ρ_{YZ} is larger than that of $|\rho_{XZ}|$ with increasing the pressure. That indicates that the leaving moiety is less away from the reaction center of the substrate. Thus, the variation degree of the distance from the reaction center becomes small but bond formation of nucleophile is increased largely, hence the TS moves from associative S_N2 to a tighter associative S_N2 with increasing pressure. This result accords with the sign and variation of ρ_Z values, and ρ_Z values is increased with increasing pressure. The sign of the product $\rho_{XZ}\cdot\rho_{YZ}$ can predict the movement of TS.[12b] 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 $\rho_{XZ}\cdot\rho_{YZ}$ permits the TS to move according to the Hammond effect.

In conclusion, the Hammett ρ values for the nucleophile, leaving group and substrate can estimate the structure of the TS. The magnitude of ρ_{ij} can be a useful tool to determine the structure of TS. In particular, the comparison of ρ_{YZ} with $|\rho_{XZ}|$ and the sign of ρ_Z can indicate the type of S_N reaction. The ρ_Z value at low pressure, is smaller than that at high pressure. That ρ_{YZ} value is smaller than $|\rho_{XZ}|$ value at low pressure indicates that this reaction series proceeds *via* an associative S_N2 mechanism. But at high pressure, ρ_{YZ} value is smaller than $|\rho_{XZ}|$, *i.e.*, the value of $\rho_{YZ}/|\rho_{XZ}|$ becomes small with increasing pressure, which indicates that this reaction series moves from an associative S_N2 mechanism to a tighter and late-type S_N2 mechanism with increasing pressure.

Experimental

Instruments. The conductivity meter is TOA 60-V equipped with a FISHER 9010 circulator. The conductivity cell is composed of two parts, a glass cylinder of 5 cm^3 in which two Pt circular plate electrodes are sealed, and one-branched teflon tube with 8 cm long and 1 cm in diameter. The former acts as a conducting cell and the latter acts as a pressure conductor. The cell is set in the pressure vessel.

Materials. All materials were purchased from Wako (Japan) or Merck (Germany). 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 ampoules under a nitrogen atmosphere.

The preparation of the substrate and the product analysis were as described previously.[16]

Kinetics. The reaction of phenacyl benzenesulfonate with pyridine at respective pressures was measured through 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 pyridine and phenacyl benzenesulfonate under condition that the former is over 100 times as concentrated as the latter. 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

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

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